Semiconductor Nanowire Field-Effect Transistors: Exploring Cation Exchange Mechanisms and Electrical Transport Properties

DISSERTATION

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Abstract

Nanowires represent a promising system as they bridge the microscopic and nanoscopic worlds, rendering them well-suited for optoelectronic applications, for example in light harvesting, sensing or photocatalysis. Cation exchange facilitates the tailoring of material composition, and consequently, the material properties post-synthetically; thus, expanding the available synthesis options and yielding heterostructures that would otherwise be inaccessible. A comprehensive understanding of the cation exchange reaction is essential for precise adjustment of nanostructures for various applications. Conventional characterization methods primarily rely on harmful electron or X-ray radiation, which can alter the nanostructures; thereby limiting access to relevant information required for elucidating the cation-exchange reaction. To address this issue, nondestructive methods based on the optoelectronic characterization of nanowire-based field-effect transistors were developed in this work. Well-characterized cadmium sulfide nanowires served as a model system to study the cation exchange with silver. Initially, nanowire field-effect transistors have been optimized to obtain devices that yield reliable data. Analysis of the nanowire surface revealed that the surface of the native cadmium sulfide nanowires is oxidized to certain extent, which limits device performance. Several chemical and physical methods were presented that enhance the device fabrication process. The optimized nanowire-based devices exhibited low electrical conductivities in the range of 10⁻⁶ S/m under ambient dark conditions. Upon illumination, changes in the chemical environment, or heating, a significant increase in electrical conductivity – by approximately four orders of magnitude – was observed, primarily attributed to drastic changes in electron concentration. This pronounced response to external stimuli demonstrates their potential for sensing applications. After cation exchange of the nanowires to silver sulfide, enhanced electrical conductivities in the range of 10^{-2} S/m were recorded even under dark ambient conditions. The transport characteristics indicate nontrivial transport phenomena that must be considered during measurement and analysis. Monitoring the cation exchange using confocal fluorescence spectroscopy was unfeasible since no signals corresponding to silver sulfide were detected, and nanowire degradation was observed. The combination of atomic force microscopy and Kelvin probe force microscopy ultimately enabled nondestructive monitoring of the cation exchange reaction, providing insights into topographical and surface potential changes. Significant differences were observed in the response of the similar systems of cadmium sulfide and cadmium selenide nanowires to cation exchange with silver. To gain further insights into the complex nature of charge transport in silver sulfide nanowires, additional transport measurements could be performed in future research based on the optimized devices, while accounting for the sensitivity of the material. The results presented contribute to a deeper understanding of the complex fabrication and optimization of nanowire-based devices and demonstrate the potential of transport measurements on nanowire field-effect transistors to nondestructively monitor of the cation exchange reaction.

Kurzfassung

Nanodrähte repräsentieren ein vielversprechendes System, da sie die mikroskopische mit der nanoskopischen Welt verbinden, wodurch sie sich hervorragend für die optoelektronische Anwendung eignen, wie beispielsweise in der Stromerzeugung, Detektion oder Fotokatalyse. Der Kationenaustausch ermöglicht die Anpassung der Materialzusammensetzung und somit auch der Materialeigenschaften nach der eigentlichen Synthese, wodurch die synthetischen Möglichkeiten erweitert und Heterostrukturen hergestellt werden können, die auf andere Weise nicht zugänglich wären. Ein tiefgehendes Verständnis der Kationenaustauschreaktion ist essenziell, um die Nanostrukturen gezielt für unterschiedlichste Anwendungen zu modifizieren. Konventionelle Methoden basieren häufig auf der Verwendung schädlicher Elektronen- oder Röntgenstrahlung, die die Nanostrukturen beeinflussen können; dementsprechend ist der Zugang zu relevanten Informationen zur Aufklärung der Kationenaustauschreaktion limitiert. Zur Lösung dieses Problems wurden in der vorliegenden Arbeit nicht zerstörerische Methoden entwickelt, die auf der optoelektronischen Charakterisierung von Nanodraht-basierter Feldeffekttransistoren basieren. Die gut charakterisierten Cadmiumsulfid Nanodrähte dienten hierbei als Modelsystem, um den Kationenaustausch mit Silber zu untersuchen. Zunächst wurden die Nanodraht-Feldeffekttransistoren optimiert, um Bauteile zu erhalten, welche zuverlässige Daten liefern. Die Analyse der Nanodrahtoberfläche ergab, dass die Oberfläche der nativen Cadmiumsulfid-Nanodrähten zu einem gewissen Grad oxidiert ist, was die Leistung der Transistoren beschränkt. Es wurden mehrere chemische und physikalische Methoden vorgestellt, die die Bauteilherstellung verbessern. Die optimierten Nanodraht-Feldeffekttransistoren wiesen bei dunklen Umgebungsbedingungen eine geringe elektrische Leitfähigkeit im Bereich von 10-6 S/m auf. Bei Beleuchtung, veränderter chemischer Umgebung oder erhöhter Temperatur wurde ein signifikanter Anstieg der elektrischen Leitfähigkeit um ungefähr vier Größenordnungen beobachtet, welcher primär auf eine stark erhöhte Elektronenkonzentration zurückgeführt wird. Diese ausgeprägte Reaktion auf externe Veränderungen verdeutlicht das Potential für Sensoranwendungen. Nach dem Kationenaustausch der Nanodrähte zu Silbersulfid wurde selbst unter dunklen Umgebungsbedingungen eine erhöhte elektrische Leitfähigkeit im Bereich von 10⁻² S/m gemessen. Die Transportcharakteristiken deuten auf nicht-triviale Transportphänomene hin, die bei den Messungen und der Auswertung berücksichtigt werden müssen. Das Nachverfolgen des Kationenaustauschs mittels konfokaler Fluoreszenzspektroskopie war nicht umsetzbar, da keine dem Silbersulfid zugeordneten Signale detektiert werden konnten und eine Zersetzung der Nanodrähte festgestellt wurde. Die Kombination aus Rasterkraftmikroskopie mit Raster-Kelvin-Mikroskopie ermöglichte schlussendlich die nicht-zerstörerische Nachverfolgung der Kationenaustauschreaktion, welche Einblicke in die Veränderung der Topografie und Oberflächenpotentiale bot. Signifikante Unterschiede in der Reaktion auf den Kationenaustausch mit Silber wurden für die ähnlichen Systeme Cadmiumsulfid und Cadmiumselenid beobachtet. Um tiefere Einblicke in die komplexe Natur des Ladungstransports in Silbersulfid zu gewinnen, könnten in zukünftigen Forschungen weitere Transportmessungen an den optimierten Feldeffekttransistoren durchgeführt werden, wobei die Sensitivität des Materials berücksichtigt werden muss. Die präsentierten Ergebnisse tragen zu einem tieferen Verständnis der komplexen Herstellung und Optimierung von Nanodraht-basierter Feldeffekttransistoren bei und demonstrieren das Potential von Transportmessungen an Nanodraht-Feldeffekttransistoren um die Kationenaustauschreaktion nicht-zerstörerisch nachzuverfolgen.

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List of Abbreviations

0D/	Zero dimensional/		
1D	One dimensional		
AFM	Atomic force microscopy		
APD	Avalanche photodiode		
CE	Cation exchange		
СВ	Conduction band		
DUV	Deep ultraviolet		
EDX	Energy dispersive X-ray spectroscopy		
EFM	Electrostatic force microscopy		
ЕМ	Electron microscopy		
EUV	Extreme ultraviolet		
FE	field emission		
HRTEM	High-resolution transmission electron microscopy		
KPFM	Kelvin probe force microscopy		
NB	Nanobelt		
NIR	Near infrared		
NP	Nanoparticle		
NR	Nanorod		
NW	Nanowire		
NWFET	Nanowire field-effect transistor		
ОМ	Optical microscopy		
PDI	Paul-Drude-Institut für Festkörperelektronik		
PEB	Post-exposure bake		
PL	Photoluminescence		
PVD	Physical vapor deposition		
QD	Quantum dot		
RE	Reflection (scan)		
SEM	Scanning electron microscopy		
SLS	Solution-Liquid-Solid		
SPM	Scanning probe microscopy		

STEM	Scanning transmission electron microscopy		
ТЕ	Thermionic emission		
ТЕМ	Transmission electron microscopy		
TFE	Thermionic field emission		
UHH	University of Hamburg		
UV	Ultraviolet		
VB	Valence band		
Vis	Visible		
VLS	Vapor-Liquid-Solid		
XPS	X-ray photoelectron spectroscopy		
XRD	X-ray diffraction		
XRF	X-ray fluorescence		

1. Introduction

Recent global developments, including the rise of artificial intelligence and the ongoing increase in computational cost, demand for ever more powerful and efficient computer chips.¹⁻⁴ The semiconductor industry has emerged as one of the most crucial sectors in the advancement of new technologies, driven by the miniaturization of devices.⁴⁻⁸ In 1965, Moore postulated that the number of components per integrated circuit would double approximately every year.⁹ Moore revised that prediction in 1975 to doubling every two years.^{10,11} Nearly six decades later, in 2023 Moore's Law remains relevant, as the first next-generation extreme ultra-violet lithography system was delivered, allowing for production of devices with a resolution down to 8 nm.^{6,7} The semiconductor industry is gradually entering the nanoscopic regime, where quantum effects, such as size quantization and quantized transport, are becoming increasingly relevant.^{12,13} These effects have been the subject of study within the nanoscience community for over 20 years;^{14,15} consequently, the semiconductor industry and nanoscience are becoming closely interconnected.

In nanoscience, particularly within the colloidal-nanocrystal community, bottom-up approaches are employed to synthesize nanostructures, contrasting with the semiconductor industry, which predominantly utilizes lithography, a process that can be classified as top-down approach.^{12,16,17} Bottom-up approaches facilitate a broad range of synthetic variations, yielding a large structural diversity and a variety of material compositions.¹⁶⁻¹⁸ Particularly one-dimensional (1D) nanostructures, such as nanowires (NWs), proved to be exceptionally well-suited for application in semiconductor devices.^{17,19-21} Nanowires effectively bridge the microscopic and nanoscopic worlds, given their lengths in the micrometer range while exhibiting diameters in the nanometer scale.^{17,19} This unique geometry and size lead to an enormous surface-to-volume ratio, which is essential for optoelectronic applications,^{17,19} including solar cells,^{22,23} sensors,^{18,21,24} photocatalysis,^{25,26} where a reaction or photon absorption occur primarily at the surface. The microscopic length of NWs facilitates efficient charge transport along their elongated axis, enhances crucial charge-carrier separation, and simplifies device integration.^{20,26}

Semiconductor NWs can be fabricated using various synthesis strategies based on different mechanisms,¹⁹ including a liquid-solid interface,^{27,28} templated or kinetically controlled growth,^{29,30} and oriented attachment.^{31,32} While a wide variety of NWs, exhibiting diverse lengths, diameters, crystal structures, and compositions, can be synthesized using these methods, not all desirable nanostructures are available through direct synthesis due to thermodynamic or kinetic constrains, or both.^{19,33} In recent years, cation exchange (CE) has emerged as an elegant method to address this limitation.^{33–35} CE allows to exchange cations in an existing nanostructure, thereby enabling the post-synthetic modification of material composition.^{33–35} During CE the nanostructure geometry and crystal structure is preserved, granting access to various nanostructures that were previously inaccessible.^{33–36} Additionally, partial CE can yield homogenous or heterogenous nanomaterial compositions, further expanding the synthetic palette of nanostructure composition.^{33,34,37}

Common characterization methods for nanostructures are primarily based on electron or on X-ray techniques.^{19,34} However, these methods can induce reactions or even destroy the nanostructures,^{38,39} limiting their applicability to the final characterization step. Monitoring the progress of the CE reaction or the formation of intermediates can only be carried out using aliquots,³⁷ which inhibits the ability to obtain detailed information regarding the reaction pathway of individual nanostructures. Such information is often essential for elucidating the CE mechanism

and understanding the formation of intermediates. Furthermore, it is challenging to extract the influence of the geometry – such as NW diameter – from these measurements.

The objective of this works is to address this issue by employing a method that allows for the nondestructive tracking of the CE reaction on the same individual NWs throughout the entire reaction. In a previous work from Schwarz,⁴⁰ the CE reaction from CdSe to Ag₂Se was studied by recording the transport properties of individual nanowire field-effect transistors (NWFETs). In this work, this method should be refined and then transferred to a similar CE reaction, specifically the CE from CdS to Ag₂S, which is expected to exhibit different exchange characteristics. To perform such a study, the fabrication of high-quality NWFETs is essential. High electrical conductivities, linear transport characteristics indicating ohmic contacts, low contact resistances, and high yields of responsive NWs are desired. The quality of the measured data and results obtained is strongly dependent on the quality of the device; consequently, the fabrication process should be optimized.

This work is organized as follows: In chapter 2, the theoretical foundation for this work is presented, including the fundamentals of semiconductors, the relevant chemical aspects, and the principles of lithography. In the semiconductor theory section, emphasis is placed on the system studied and resulting characteristics. The chemical aspects of this work include the synthesis of NWs, the modification of their surface and the CE reaction. In chapter 3, the working principles behind the employed characterization methods are reviewed to facilitate understanding of the measurements and to identify the limitations of each method. In chapter 4, the results obtained are presented and discussed. This chapter is divided into three main sections: first, the fabrication and optimization of NWFETs are demonstrated; second, the electrical transport properties of the CdS NWFETs are studied by measuring current-voltage and transfer characterized using various methods. In chapter 5, the key findings are subsequently summarized. In chapter 6, the experimental details – including synthesis, treatments, fabrication, CE, and measurements – are presented to conduct this work.

2. Theoretical Background

This chapter provides the theoretical foundation to comprehend the analysis in the chapter 4. Results and Discussion. The focus is placed on the material system being studied and special features are pointed out. Basic concepts are assumed to be known and will be mentioned only briefly, to keep this chapter informative and condensed. First, the electrical properties of semiconductors with a focus on nanostructured devices are recapitulated to explain the resulting transport properties. Second, the chemical aspects of this work, such as the synthesis of NWs and the CE reaction, are elucidated. Third, a compressive guide to optical lithography is given to understand the complex fabrication process and to be able to reproduce the shown nanostructured devices.

2.1. Electrical Transport in Nanodevices

To understand the transport of charge carriers in nanostructured semiconductor devices, basic concepts such as the band gap or the Fermi level and their influence on the electrical transport are briefly reviewed. To access the transport properties of any material an electrical contact has to be established. Based on the work functions and the resulting band alignment, either ohmic or Schottky contacts are obtained, which will be explained in detail. Next, the possible charge-transport mechanisms are presented, and only the relevant mechanism is discussed in more detail.

2.1.1. Electronic Properties of Semiconductors

The electronic properties of a semiconductor are significantly influenced by the band gap energy E_g and the relative position of the Fermi level E_F . The band gap energy E_g is defined as the energy difference between the conduction band edge, denoted E_C , and the valence band edge, denoted E_V , as illustrated in Figure 2.1 (a). For an ideal semiconductor, E_F is typically located in the middle of E_g . Figure 2.1 (a1) and (a2) provide schematic illustrations of the band positions for an ideal semiconductor and for CdS, respectively. To accurately understand the position of E_F , first the occupation of states must be accessed.^{41,42}

For comprehensiveness the following discussion will primarily focus on the electrons. The states that can potentially be occupied in the conduction band by electrons are determined by the density of states $D_{\rm C}$ of the conduction band (CB), which can be described by:

$$D_{\rm C}(E) = \frac{1}{2\pi^2} \left(\frac{m_{\rm e}^*}{\hbar^2}\right)^{\frac{3}{2}} \cdot \sqrt{E - E_{\rm C}} , \qquad (2.1)$$

where m_e^* is the effective mass of the electron and \hbar is the reduced Planck constant.^{41,42} The occupancy *F* of these states is described by the Fermi-Dirac distribution function as:

$$F(E) = \frac{1}{1 + e^{\frac{E - E_F}{k_B T}}},$$
(2.2)

with the Boltzmann constant k_B and the temperature $T.^{41,42}$ For metals, E_F can be approximated to equal the electrochemical potential $\bar{\mu}$ at very low temperatures and under equilibrium conditions. As a result, it is common practice to replace $\bar{\mu}$ with E_F in the Fermi-Dirac distribution function. This simplification makes it easier to describe the behavior of electrons in metals, and it can also help with the description of semiconductors, where applying the concept of $\bar{\mu}$ is more complex. In general, the Fermi level for semiconductors is defined as the energy at which the probability of occupation by an electron is 50%, which means that F(E) = 1/2. Under the assumption that E_F is significantly lower than E_C ($|E_C - E_F| \gg k_B T$), F(E) can be simplified to the exponential term. The electron concentration n_e can then be derived from the integral:

$$n_{\rm e} = \int_{E_{\rm C}}^{\infty} D_{\rm C}(E) F(E) \, dE \approx 2 \left(\frac{m_{\rm e}^* k_{\rm B} T}{2\pi\hbar^2}\right)^{\frac{3}{2}} {\rm e}^{-\frac{(E_{\rm C} - E_{\rm F})}{k_{\rm B} T}} \approx N_{\rm C} \cdot {\rm e}^{-\frac{(E_{\rm C} - E_{\rm F})}{k_{\rm B} T}},$$
(2.3)

where $N_{\rm C}$ is the effective density of states for the CB.^{41,42}

While the Fermi level influences the concentrations of charge carriers, it does not affect their product, which follows from the mass action law ($n_e n_h = const.$). Assuming charge neutrality in an intrinsic semiconductor ($n_e = n_h$), E_F can be expressed as:^{41,42}

$$E_{\rm F} = \frac{E_{\rm C} + E_{\rm V}}{2} + \frac{3}{4} k_{\rm B} T \cdot \ln\left(\frac{m_{\rm h}^*}{m_{\rm e}^*}\right). \tag{2.4}$$

From equation 2.4 it follows that if the effective masses of both charge carriers are equal, E_F will be positioned at the center of the band gap and will remain temperature independent. In contrast, if the effective masses differ, E_F will be temperature dependent and will be at the center of the band gap only at 0 K. The density of states *D*, the occupancy *F* and the resulting charge carrier concentrations n_e , n_h are illustrated in the top panel of Figure 2.1 for an ideal semiconductor.



Figure 2.1: Schematic illustration of the band structure and underlying functions for semiconductors. (1, 2) The case for (1) an ideal semiconductor and (2) a *n*-type semiconductor: CdS. (a) Band structure depicting important energy states and the charge-carrier distributions. (b-d) Plot of (b) the density of states function *D*, (c) the Fermi-Dirac distribution function *F* and (d) the resulting product. Dashed and dotted lines are provided as a guide to the eye for important energy levels. Figure adapted from Ref. 41.

For an ideal semiconductor, where electrons and holes have the same effective mass, E_F is therefore exactly at the center of the band gap and the density of states for conduction D_C and valence band D_V are symmetric, as depicted in Figure 2.1 (b1). Figure 2.1 (c1) shows the occupancy F, as it is usually presented in textbooks.^{41,42} However, such a representation is either only schematically correct or for very high temperatures, for example, the F shown in (c1) was

obtained for T = 6000 K and $E_g = 1$ eV. The resulting n_e and n_h , shown in (d1), are as expected equal and represent the intrinsic concentrations $n_{e,i}/n_{h,i}$.

In reality, ideal intrinsic semiconductors do not exist; even for silicon, different effective charge-carrier masses are reported, and even the purest modifications still contain impurities.⁴¹ CdS is known to be an intrinsically doped *n*-type semiconductor, resulting from sulfur vacancies (*V*_S) which act as donor states $N_{\rm D}$.⁴³⁻⁴⁵ In particular, for nanostructures where the surface-volume ratio is high and a Cd-rich surface is expected, *V*_S must be considered.^{43,44} The energetic positions of the donor states $E_{\rm D}$ of the *V*_S are 0.03 eV and 0.7 eV below the CB, for the first $V_{\rm S}^-$ and the second ionized sulfur vacancy $V_{\rm S}^{2-}$, respectively.⁴³⁻⁴⁵ At room temperature (rt), where $k_{\rm B}T \approx 26$ meV, it can be assumed that the first electron is transferred into the CB while the second remains localized in the vacancy. The density of states *D* for CdS can be calculated using the quantities $E_{\rm g} = 2.49$ eV, $m_{\rm e}^* = 0.2 m_0$ and $m_{\rm h}^* = 0.7 m_0.^{41}$ The schematic band structure of CdS and the corresponding calculated *D* are shown in Figure 2.1 (a2) and (b2), respectively. The differing effective masses ($m_{\rm e}^* \neq m_{\rm h}^*$) result in distinct curvatures for $D_{\rm C}$ and $D_{\rm V}$.

Since CdS is intrinsically doped, the assumption $n_e n_h = n_{e,i}^2$ is no longer valid; hence the donor concentration n_D must also be considered in order to accurately determine F. Nevertheless, the mass action law ($n_e n_h = const.$) remains valid. Assuming that the acceptor concentration n_A is negligible and at room temperature $k_B T \approx E_D$, it can be inferred that $n \approx n_D$, leading to an estimation of E_F given by:^{41,42}

$$E_{\rm F} \approx E_{\rm C} - k_{\rm B}T \cdot \ln\left(\frac{N_{\rm C}}{n_{\rm D}}\right).$$
 (2.5)

The calculated *F* and the resulting *n* for CdS are shown in Figure 2.1 (c2) and (d2), respectively. It is evident that E_F is no longer in the center of the band gap but is instead positioned close to the CB. Given that n_e significantly exceeds n_h , the transport properties in CdS can be effectively described by considering primarily the electrons. This conclusion is crucial for the later determination of transport properties.

It must be noted that the calculation of $E_{\rm F}$ required an estimation of $n_{\rm D}$. Accurately determining $n_{\rm D}$, in particular for nanostructures is challenging. In addition, $E_{\rm F}$ is not only influenced by vacancies and temperature but also by surface states and other effects, such as oxygen adsorption.^{41,46-48} Therefore, the precise assignment of $E_{\rm F}$ poses a significant challenge.

2.1.2. Contacts to Semiconductors

For charge transport through a semiconductor, contacts are necessary, which are typically realized by metals due to their high electrical conductivity. Therefore, it is essential to understand the effects resulting from a direct contact between metal and semiconductor. A crucial quantity determining the type of contact is the work function ϕ , defined as the energy required to remove an electron from the material into the vacuum level.^{42,49} ϕ can be expressed as the difference in energy between the vacuum level E_{Vac} (free electron) and the energy of E_F , described by the following equations:^{41,42}

$$\phi = E_{Vac} - E_{F},$$

$$\phi_{m} = E_{Vac} - E_{F,m},$$

$$\phi_{s} = E_{Vac} - E_{F,s} = E_{Vac} - (\chi + \Delta E_{F,C}).$$
(2.6)

In these equations ϕ_m represents the work function of a metal, $E_{F,m}$ is the energy of the Fermi level of a metal, ϕ_s represents the work function of a semiconductor, $E_{F,s}$ is the energy of the Fermi level

of a semiconductor, χ is the electron affinity and $\Delta E_{\rm F,C}$ energy difference between E_C and $E_{\rm F,s}$. Since $E_{\rm F,m}$ is within a band, $\phi_{\rm m}$ can be directly measured. Conversely, determining $E_{\rm F,s}$ for semiconductors requires to calculate the sum of χ and $\Delta E_{\rm F,C}$, which can be readily determined. The electron affinity represents the energy released when an electron from the vacuum is added to the semiconductor CB edge, defined as $\chi = E_{\rm vac} - E_{\rm C}$, which differs from the work function ($\phi = E_{\rm Vac} - E_{\rm F}$). These quantities and their relation are visualized in Figure 2.2 (a).^{41,42,49}



Figure 2.2: Schematic representation of the formation of (1) a Schottky contact and (2) an ohmic contact. (a-c) Band alignment of the metal and semiconductor when they are (a) separated, (b) connected in a system but separated by a gap ($\delta \neq 0$) and (c) when an intimate contact ($\delta = 0$) is established. (d) The resulting IV-characteristic, along with the corresponding band diagrams under the biased conditions. Figure adapted from Ref. 41.

Depending on the work functions of the metal and the semiconductor, two distinct contact configurations are possible: Schottky or ohmic contact. Figure 2.2 shows the formation of (1) a Schottky contact and (2) an ohmic contact. When the metal and the semiconductor are brought into close proximity forming one system but are separated by a gap distance (δ), charge transfer can occur and the potential changes until the Fermi levels are equalized, as shown in Figure 2.2 (b). Given that the metal typically has a substantially higher concentration of free charge carriers than the semiconductor, $E_{\rm F,m}$ remains unchanged when transferring charge carriers to the semiconductor. In contrast, $E_{\rm F,s}$ significantly changes as charge carriers are transferred. Consequently, equilibrium is achieved as $E_{\rm F,s}$ adjusts to approach $E_{\rm F,m}$, representing charge balance between metal and semiconductor. For an n-type semiconductor, when $\phi_{\rm m} > \phi_{\rm s}$, the semiconductor donates electrons to the metal, resulting in the formation of a Schottky contact. Conversely, if $\phi_{\rm m} < \phi_{\rm s}$, the semiconductor accepts electrons from the metal, leading to the formation of an ohmic contact.^{41,42,49}

Considering the Schottky contact, electrons are withdrawn from the semiconductor until equilibrium is achieved, leaving immobile positive donors behind to maintain charge neutrality. The region from which mobile charge carriers are depleted in the semiconductor is called depletion zone, characterized by its width *W*. This separation of charge carriers generates an intrinsic electric field that repels additional electrons from entering the depletion zone. Therefore, to transfer into the metal, electrons must overcome the so-called Schottky barrier. As δ between

metal and semiconductor is decreased until intimate contact is established, the exchange of charge carriers increases, as depicted in Figure 2.2 (c). 41,42

In the Schottky contact configuration, *W* increases as more electrons are transferred into the metal, leaving fewer electrons in the semiconductor at metal-semiconductor interface. This increase in *W* results in a higher Schottky barrier height ϕ_{Bn} , as illustrated in (c1). Once an intimate contact is achieved, ϕ_{Bn} can be described by the equation:

$$\phi_{\rm Bn} = \phi_{\rm m} - \chi \tag{2.7}$$

and thus, is solely dependent on material parameters of both, the metal and the semiconductor.⁴¹ However, *W* is also influenced by external conditions, such as applied bias or temperature, which affect the electron concentration. In contrast, for an ohmic contact, where electrons are injected into the semiconductor, a depletion zone and barrier do not form (in the CB) as shown in (c2), and thus electrons can freely exchange between metal and semiconductor.^{41,42} However, analogous definitions for holes can still be applied, which would lead to a Schottky barrier for holes.^{41,42}

In ohmic configuration, electrons freely transfer between metal and semiconductor, even when a bias is applied, resulting in a linear current-voltage characteristic, as illustrated in Figure 2.2 (d2), which also includes the corresponding band scheme. Conversely, for the Schottky contact configuration, electron transport is hindered by the Schottky barrier, which prevents electrons from passing through, depicted in Figure 2.2 (d1). When positive voltages are applied to the metal – representing the forward direction – $E_{\rm F,m}$ is lowered by the applied voltage $V_{\rm F}$. This decrease reduces the energy required for electrons to transfer into the metal $\Psi_{\rm bi}$ – V, which is composed of the built-in potential $\Psi_{\rm bi}$ and voltage V, resulting in an exponential increase in current. At high voltages, the barrier is overcome, leading to a linear increase in current, similar to an ohmic contact. When negative voltages are applied to the metal – representing the reverse direction – the $E_{\rm F,m}$ is raised by applied voltage $V_{\rm R}$, resulting in an increased energy required to overcome the barrier and thereby yielding only negligible leakage currents.^{41,42}

In this work, the objective is to obtain ohmic contacts, as the CE should be studied by electrical transport. Changes in ϕ_{Bn} would affect the measured current, complicating the interpretation of the resistance since it would be no longer a function of the semiconductor. Based on the model presented, an ohmic contact to CdS can be achieved with metals exhibiting a ϕ_m less than 5.0 eV⁵⁰ ($\phi_s = \chi + \Delta E_{F,C} = 4.8 \text{ eV} + 0.2 \text{ eV}$)⁵⁰. Titanium, often used as a contact material, has a ϕ_m of 4.33 eV,⁵¹ suggesting that using Ti should result in an ohmic contact to CdS, as depicted in Figure 2.3 (a). However, nonlinear current-voltage (*IV*) characteristic have been observed for the Ti-CdS system. Often the experimentally determined ϕ_{Bn} does not agree with the theory.⁴¹ Several factors contribute to this discrepancy: the material ϕ are highly sensitive to surface contamination, establishing intimate contact without an interfacial layer is unattainable ($\delta \neq 0$), and surface states at the interface can influence the electrical transport. Therefore, both the surface and interface states have to be considered as well.⁴¹

It is assumed that the thickness of the interfacial layer δ is on the order of one to two monolayers (a few nm), allowing electrons to transfer while permitting a potential to develop. Additionally, it is presumed that the interface states at the surface are characteristic of the semiconductor and independent of the contact metal. The density of these interface traps D_{it} influences the position of $E_{\rm F}$ at the surface, thereby affecting $\phi_{\rm Bn}$. The surface properties can be approximately described by the constant $c_2 \equiv \varepsilon_i/(\varepsilon_i + q^2 \delta D_{it})$, where ε_i is the permittivity of the interfacial layer ($\varepsilon_i \approx \varepsilon_0$). The constant c_2 then can be used to calculate $\phi_{\rm Bn}$ by:

$$\phi_{\rm Bn} = c_2(\phi_{\rm m} - \chi) + (1 - c_2)(E_{\rm g} - \phi_0) \equiv c_2\phi_{\rm m} + c_3, \qquad (2.8)$$

where ϕ_0 is the neutral energy level of the interface states.⁴¹ The coefficients c_2 and c_3 can be obtained experimentally through linear regression by measuring the barrier height for various metals. If no interface traps are present ($D_{it} = 0$), c_2 becomes one and the former equation 2.7 remains valid.⁴¹

$$\phi_{\rm Bn} = \phi_{\rm m} - \chi \tag{2.7}$$

However, if interface traps become dominant and approach infinity ($D_{it} = \infty$), c_2 becomes zero, rendering the barrier height independent of the metal, as indicated in equation 2.9.⁴¹

$$\phi_{\rm Bn} = E_{\rm g} - \phi_0 \tag{2.9}$$

In this case, the interface states are filled up to ϕ_0 , effectively pinning E_F at this level and resulting in a constant barrier height. Notably, $E_{F,m}$ and $E_{F,s}$ must still equilibrate when in contact, with the potential difference Δ being compensated by the interface layer. The band scheme for the case of complete pinning for the Ti-CdS system is shown in Figure 2.3 (b).⁴¹



Figure 2.3: Schematic visualization of the phenomena of Fermi-level pinning at the metal-semiconductor interface. (a-c) Band diagrams for (a) an ideal contact, (b) a contact with complete pinning of $E_{\rm F}$, and (c) a realistic contact exhibiting moderate pinning. Figure adapted and values taken from Ref. 41.

In practice, there are neither ideal conditions nor a fully pinned $E_{\rm F}$. Instead, some degree of pinning $E_{\rm F}$ is observed, with the extent of pinning being influenced by the semiconductor type and the surface condition. Generally, more ionic semiconductors such as CdS, exhibit a higher dependence on $\phi_{\rm m}$ and are less prone to pinning than more covalent semiconductors such as InP, in which pronounced pinning is observed. For bulk CdS, the coefficients c_2 and c_3 have been determined to be 0.38 and -1.17, respectively. Using equation 2.8, a $\phi_{\rm Bn}$ of 0.5 eV is calculated, and the resulting band diagram is shown in Figure 2.3 (c). Since an exchange between semiconductor and metal is possible in this case, the interface states are filled by the metal above ϕ_0 , which is described by the charge of the interface trap states $Q_{\rm t}$. The excess potential Δ is compensated by the interfacial layer.⁴¹

According to Equation 2.8 and the values obtained for c_2 and c_3 , for CdS, ϕ_m must be below 3.1 eV to give an ohmic contact to CdS. However, most commonly used and suitable metals possess ϕ_m above 4 eV.⁴¹ Consequently, modifications to the interfacial layer or semiconductor surface are necessary to obtain ohmic contacts. Methods to alter the surface properties are discussed in Section 2.2.2 (Surface Treatments). It is important to note that the model presented for the barrier formation and barrier height remains idealized and additional factors, such as image-force lowering, must be included for a more comprehensive and accurate model.

2.1.3. Transport in Nanostructured Devices

Electrical transport within semiconductor devices can be examined from two distinct perspectives. From the semiconductor perspective, the electrical conductivity is treated as nearly constant under ambient conditions, governing charge transport through the semiconductor. In contrast, from the device perspective, the measured current depends not only on the intrinsic properties of the material but also on the device geometry and the nature of the contacts. Both perspectives are dependent on external influences such as the temperature.^{41,42}

The electrical conductivity σ for a semiconductor can be generally described by:

$$\sigma = e(n_{\rm e}\mu_{\rm e} + n_{\rm h}\mu_{\rm h}), \qquad (2.10)$$

with the elemental charge e, the charge-carrier concentration for electrons $n_{\rm e}$ and holes $n_{\rm h}$ and their corresponding mobility $\mu_{\rm e}$ and $\mu_{\rm h}$.^{41,42} Both, the charge-carrier concentrations and mobilities are material-specific and significantly influenced by various external influences. The charge-carrier concentration was already introduced and described by equation 2.3 in Section 2.1.1. Since CdS is an n-type semiconductor where $n_{\rm e} \gg n_{\rm h}$ applies (see Figure 2.1 (d)), σ can be adequately represented by only considering the contribution of electrons, giving $\sigma = en_{\rm e}\mu_{\rm e}$. The electron mobility $\mu_{\rm e}$ can be calculated using the relation:

$$\mu_{\rm e} = \frac{e\tau}{m^*},\tag{2.11}$$

where τ is the mean free time, indicating the average time an electron travels before being scattered.^{41,42} Instead of τ , the mean free path λ is sometimes used, representing the average distance an electron travels before scattering. Both parameters can be used interchangeably and are related by $\tau = \lambda/v_{\text{th}}$, where v_{th} is the thermal velocity, which can be expressed as $v_{\text{th}} = \sqrt{3k_{\text{B}}T/m^*}$. Besides being directly influenced by temperature (over the thermal velocity v_{th}), both τ and λ are additionally influenced by the scattering probability. At low temperatures (T < 50 K) impurity scattering (and the concentration of these impurities n_{sc}) dominates, leading to an electron mobility that is proportional to the temperature following $\mu \propto T^{3/2}$. At higher temperatures (T > 50 K) phonon scattering becomes the dominant mechanism, resulting in electron mobility that follows $\mu \propto T^{-3/2}$. Since both n and μ_{e} are affected by the temperature through different mechanisms, they contribute to the complexity of charge transport processes, making them challenging to describe comprehensively.^{41,42}

When not only the semiconductor is considered but the entire device, the system becomes more complex due to influence of contacts. In the presence of ohmic contacts (which exhibit negligible barrier effects), the previous equations adequately describe the electrical transport. However, for devices with Schottky contacts, the barrier height significantly influences the transport properties, as depicted in Figure 2.4.

2 Theoretical Background



Figure 2.4: Schematic illustration of transport mechanisms with a Schottky Barrier present. (a-c) Band schemes for (a) reverse bias, (b) no bias, and (c) forward bias applied. The possible transport pathways – thermionic emission (TE), thermionic field emission (TFE) and field emission (FE, = tunneling) – are indicated with dark blue arrows. Figure adapted from Ref. 41.

In general, electrons can pass through the barrier by three principal mechanisms: thermionic emission (TE), field emission (FE) and thermionic field emission (TFE). The dominant mechanism depends on *T* and n_D of the semiconductor. At room temperature and moderate doping concentrations ($n_D \approx 10^{17}$ cm⁻³)⁴¹ TE is the primary transport mechanism, whereby electrons with sufficient energy overcome the Schottky barrier. At low temperatures or at high n_D , FE becomes dominant, allowing electrons to quantum mechanically tunnel through the Schottky barrier. TFE represents a combination of both TE and FE, wherein electrons tunnel through the Schottky barrier at higher energies than the Fermi level, where the barrier is thinner. A schematic illustration of these three transport mechanisms is provided in Figure 2.4⁴¹

Given that thermionic emission is the dominant transport mechanism in the system studied in this work, this mechanism is briefly outlined. The model assumes that the barrier height ϕ_{Bn} is significantly greater than k_BT , that thermal equilibrium is established, and that the equilibrium is unaffected by the current flow between semiconductor and the metal. The resulting current density *J* then can be described by:

$$J = A^* T^2 e^{\frac{e\phi_{Bn}}{k_B T}} \left[e^{\frac{eV}{k_B T}} - 1 \right] = J_0 \left[e^{\frac{eV}{k_B T}} - 1 \right],$$
 (2.12)

where A^* is the so-called effective Richardson constant and J_0 is the current density at equilibrium (V = 0 V).⁴¹ A^* can be calculated using:

$$A^* = \frac{4\pi e m_{\rm e}^* k_{\rm B}^2}{h^3}.$$
 (2.13)

The Richardson constant A^* is a material constant that is dependent solely on the effective electron mass m_e^* . Using equation 2.12, ϕ_{Bn} can then be determined from the measured current.⁴¹

The concepts introduced in the theory so far are all universally applicable and not specifically adjusted for nanostructured semiconductors. Since the diameters of the NWs studied in this work are rather large, in the range of 20 - 50 nm, and no effects suggesting quantized transport were observed, it can be assumed that the transport properties of the NWs are adequately described by the presented classical models and equations. The increasing contribution of the surface properties of nanostructures, such as defects or adsorbates, can be accounted for by the classical equations, by adjusting parameters like the doping concentration or charge-carrier mobility. Due

to their large surface-to-volume ratio, nanostructures and especially NWs, are highly sensitive to surface processes. This sensitivity can be advantageous for sensing applications, including gas detector⁵² or photodetectors,²¹ in addition to application in light harvesting²³ or catalysis reactions.²⁵

Since this work involves measurements conducted often under ambient conditions with illumination, the effect of illumination is shortly discussed. The electrical conductivity is strongly dependent on the charge-carrier concentrations, see equation 2.10. When a semiconductor is irradiated and absorbs light that has sufficient energy to transfer an electron from the VB into the CB, then both n_e and n_h increase. Doping can affect the charge-carrier concentration, while maintaining neutrality so that $n_e n_h = n_{e,i}^2$ is valid. However, under illumination, both concentrations increase, leading to a situation where $n_e n_h$ exceeds $n_{e,i}^2$. In order to express the increased n in the system, E_F would have to shift closer to the CB. However, this shift would decrease n_h , contradicting the observed increase in n_h . Shifting E_F closer to the VB would have the opposite effect as electrons would be underrepresented. To resolve this discrepancy, the electron and hole distributions can be represented by separate quasi-Fermi levels: the quasi-Fermi level for holes $E_{F,h}$. Therefore, the increase in σ under illumination for CdS is primarily attributed to the enhancement of both n_e and n_h . Recent results briefly outlined in Section 4.2.2 (Charge-Carrier Distribution of Locally Illuminated CdS Nanowires) may underline this picture.^{41,42,49}

2.2. Chemistry of Nanostructures

In this chapter the chemical background relevant for this work is presented. First, general synthesis strategies in order to obtain one dimensional nanostructures such as nanowires are introduced. Second, options for the necessary surface treatment are given. Third, the cation exchange reaction is presented, with details on the requirements, the potential and the limitations of this reaction.

2.2.1. Synthesis of Nanowires

Nanostructures with at least one dimension below 100 nm,¹⁷ can be synthesized through either top-down or bottom-up approaches.¹⁶⁻¹⁸ Top-down approaches yield nanostructures by reducing the size of the bulk starting material, often using physical techniques.^{16,18} The advantages of this approach are high yields and relatively simple processes, making it optimal for cost-efficient large-scale production.^{16,18} However, controlling the morphology becomes increasingly difficult as the particle size decreases, complicating access to anisotropic nanostructures with precisely controlled dimensions.^{16,18} Conversely, bottom-up approaches involve the assembly of nanostructures from molecular precursors.¹⁶⁻¹⁸ By carefully selecting the precursors and adjusting the synthesis conditions, the growth of the nanostructures can be tailored, providing access to a wide variety of nanostructures with different sizes and shapes.¹⁶⁻¹⁹ Nevertheless, yields tend to be lower in comparison to top-down methods, and up-scaling remains challenging, rendering large-scale production problematic.¹⁶⁻¹⁸ Given that large-scale production is often secondary for fundamental research, while precise morphology control is crucial, bottom-up methods are discussed in detail below.

To synthesize 1D nanostructures such as nanowires, nanobelts and nanorods (NRs), it is necessary to introduce anisotropy into the growth process. A selection of common methods for achieving anisotropic growth is briefly presented and schematically illustrated in Figure 2.5 (a). One widely used method for inducing 1D growth involves the introduction of a liquid-solid interface *via* a

catalyst particle. Alternatively, templates can be employed to restrict available growth directions, thus confining growth to a single axis. These templates may consist of features on a solid substrate, channels in porous materials, self-assembled molecular structures (such as micelles) or pre-existing nanostructures. Another strategy involves the kinetic control of growth through the use of ligands that specifically passivate certain facets, allowing growth to occur only on the exposed facets. Lastly, 1D nanostructures can be obtained by self-assembly of zero dimensional (0D) nanostructures such as quantum dots (QDs).^{17,19}

For this work, nanowires were obtained using the solution-liquid-solid (SLS) method, which is based on catalyzed growth,^{17,27,28} and the solvothermal method, which combines templated and kinetically controlled growth mechanisms.^{17,29} The mechanisms for both, the SLS and solvothermal method, are schematically illustrated in Figure 2.5 (b) and (c), respectively.



Figure 2.5: Schematic illustration of synthesis strategies for 1D nanostructures. (a) Overview of synthesis methods for anisotropic growth based on different mechanisms. (b, c) Growth mechanisms for (b) the SLS method and (c) the solvothermal method. M and E are elements typical for II-VI semiconductors. Figure adapted from Ref. 17, Ref. 27 and Ref. 29.

The SLS method is closely related to the vapor-liquid-solution (VLS) method, sharing numerous similarities.^{17,27,28} In general, for both methods, the reaction can be divided into three distinct phases. The precursors are dissolved in solution for SLS, while in the VLS process, they are present in the gas phase.^{27,28} Under reaction conditions, the precursors decompose at the solution-liquid interface on the metal-catalyst particle, resulting in the formation of an alloy and byproducts. This process imposes two requirements on the metallic catalyst particle: First, the metal must have a low melting point to melt at the reaction temperature below the boiling point of the solvent; second, the metal must be capable of forming an alloy with the desired elements. Once the critical contraction of the elements (M, E) within the liquid droplet is reached, the solid semiconductor (ME) nucleates and grows from the liquid-solid-interface.^{27,28} The size of the reaction zone, and consequently the resulting NW diameter is determined by the catalyst particle size. The growth of NWs can be controlled by the selection of precursors, ligands, catalyst particles and their size.^{17,27,28} Furthermore, the SLS method can be performed on substrates where the catalyst area is lithographically defined, from which catalyst particles are formed upon melting at reaction temperature, leading to the formation of NWs anchored at specific locations on the substrate.^{53,54}

In addition to the SLS method, the solvothermal method has also been used to grow NWs.¹⁷ In solvothermal reactions, the solvent is pressurized and heated above its critical point, typically within an autoclave. Performing a reaction above the critical point can have several advantages, including enhanced precursor solubility, increased reaction rate, or improved product crystallinity.¹⁷ However, solvothermal reactions are limited by few adjustable parameters, making the control over morphology and crystallinity challenging. Furthermore, the autoclave required to reach high pressures is often incompatible with most *in-situ* techniques, hindering the elucidation of the growth mechanism.^{17,29,30} Nonetheless, once optimal reaction parameters are identified, the solvothermal method can yield highly crystalline NWs on a large scale.

To obtain NWs by the solvothermal method, a reagent that can control and template the growth reaction is required.^{17,29,30} In this work, ethylenediamine (en) is used as the solvent and also functions as a coordinating template.²⁹ The NW growth can be described by the solvent coordination molecular template (SCMT) mechanism proposed by Deng *et al.*²⁹ In this mechanism, en forms a layered structure that allows the precursor to gradually decompose, forming a semiconductor layer. The en layer thereby stabilizes the formed semiconductor layer. As en is depleted from the edges of the layers due to reaction dynamics, the semiconductor layer becomes destabilized and can rapture along the c-axis. These layers can fuse together to form NRs seeds, which are again stabilized by en. Subsequently, these NRs seeds can grow along the c-axis into NWs. More detailed theoretical background on the used precursor, the role of en, and reaction control can be found in previous work.⁵³

2.2.2. Surface Treatments

As introduced in Section 2.1.2 (Contacts to Semiconductors), achieving ohmic contacts to CdS is not solely a matter of selecting a metal with a low work function ϕ_m ; the surface must also be considered, as it can lead to phenomena such as Fermi-level pinning (shown in Figure 2.3). Obtaining ohmic contacts to CdS has been a challenge for researchers already for more than 70 years.^{47,55-57} In 1954, Buttler and Muscheid proposed that it is possible to obtain ohmic contacts to CdS with any metal, regardless of ϕ_m , by bombarding the CdS surface with electrons.^{55,56} A year later, Smith reported that ohmic behavior was observed with In and Ga contacts without any surface treatment.⁵⁷ In contrast, Kröger *et al.* (1956) argued that bombardment is essential, even for In and Ga contacts.⁴⁷ These contradicting reports illustrate the complexities involved in achieving ohmic contacts and suggest that different approaches may yield success.

For bulk CdS (single) crystals, a common preparation step involved mechanically treating the surface to obtain a clean and flat surface, for example by polishing with Al_2O_3 abrasives or lapping with SiC.^{48,58,59} Another mechanical approach involves cleaving the crystals in ultra-high vacuum.^{60,61} However due to the reduced dimension of NWs, mechanical treatments are not feasible for this work.

Mechanical treatments were frequently followed by chemical treatments such as etching, predominantly using HCl.^{46,48,58,59} Wet-chemical etching is utilized to not only remove surface contaminations but also to remove a few layers of the crystal, resulting in a clean surface.^{46,58} It is reported that HCl can dissolve an insulating oxide layer on the surface.^{46,62} Wet-chemical etching can be controlled by the concentration (pH) and treatment duration. Nevertheless, this method may not be compatible with all fabrication protocols due to unwanted side reactions and can lack uniformity and reproducibility.

When chemical treatments are incompatible or do not lead to the desired results, physical treatments – such as plasma cleaning or bombardment – are used.^{47,48,55,62–64} Most physical

methods are compatible with standard device fabrication, facilitating seamless integration into the fabrication protocol. An additional advantage of physical treatments is the high degree of control, resulting in a uniform cleaning (ablation) with limited side reactions. Plasma cleaning is a gentle technique commonly used to remove residues such as ligands, solvents and photoresist residues. The plasma process can be adjusted flexibly by varying the gas, power, pressure and duty-cycle. For instance, using Ar plasma at high power levels can remove residues and also modify the crystal surface.⁶² If Ar plasma is insufficient, the crystal can be subjected to bombarded with Ar ions.^{48,63} Cambell and Farnsworth reported that polishing (mechanical), etching (chemical), and annealing (physical) did not yield maximum surface crystallinity; rather optimal results were achieved following Ar-ion bombardment.⁴⁸ Similar to plasma, bombardment can be adjusted by process parameters such as power and time to control the depth of ablation. Besides bombardment with ions, it is also possible to use electrons. The reports from Buttler⁵⁵ and Kröger⁴⁷ emphasized that electron bombardment is necessary to obtain ohmic contacts to CdS. All of these bombardment techniques are known to alter the surface and can introduce lattice defects.⁶²⁻⁶⁴ Look studied the effect of electron bombardment and proposed that such treatments primarily lead to the formation of S vacancies $V_{\rm S}$, thereby increasing the charge-carrier concentration.⁶⁴ Furthermore, Gu *et al.* reported that Ar-ion bombardment can also generate $V_{\rm S}$, which narrow the Schottky barrier and lead to ohmic contacts with Ti.63

Aside from modifying the metal-semiconductor-interface prior to metal deposition, the interface characteristics can also be modified through annealing after metal deposition.^{58,65} Stewart⁶⁵ and Yamaguchi⁵⁸ observed that ohmic contacts to CdS can be obtained with In contacts subsequent to annealing, attributing this effect to the interdiffusion of In into CdS.

Lastly, the role of oxygen during fabrication should be considered. Oxygen can significantly influence the surface properties and increase the work function of CdS by 1 eV.^{46,48,60} The change in work function due to oxygen adsorption directly affects the choice of the contact metal and the formation of a Schottky barrier. The time elapsed between surface treatment and metal deposition is critical; exposure of the freshly cleaned surface to oxygen during this interval may nullify the benefits of previous surface treatments due to oxidation. In addition, annealing in the presence of oxygen poses the risk of undesirable oxidation processes. Yamaguchi noted that the diffusion of In into CdS is inhibited when In is oxidized.⁵⁸

2.2.3. Cation Exchange Reaction

In cation exchange reactions, the cations of an ionic crystal are replaced by other cations while the anion lattice remains intact. Given that material properties are highly dependent on material composition, CE allows for the adjustment of properties even post-synthesis, facilitating optimization. However, CE reactions in bulk crystals have not been extensively studied because of slow reaction rates, even at elevated temperatures. The limiting factor is the diffusion of cations, which diminishes with increasing penetration depth, resulting in only superficial CE in bulk crystals. In contrast, nanostructures exhibit a high surface-to-volume ratio, enabling rapid cation diffusion under ambient conditions, which leads to a quick and complete transformation. Short reaction times, relatively mild reaction conditions and a broad range of applications have generated considerable interest in CE in nanocrystals in recent years. Notably, the preservation of the anion host lattice is crucial, which is the case when the crystallite size is larger than the reaction zone (≈ 5 nm),³⁶ as CE can yield nanostructures that are unattainable through direct synthesis. Depending on the materials involved, either homogenous CE resulting in doped or alloyed nanostructures, or a heterogenous CE resulting in core-shell or segmented nanostructures, can be observed.³³⁻³⁵

To assess the feasibility of a CE reaction and predict the resulting structure, an understanding of the thermodynamics and kinetics of the reaction is essential. A CE reaction occurs spontaneously when thermodynamically favored; that is, when the product exhibits greater stability or is energetically more favorable. Nonetheless, it is the kinetics rather than the thermodynamics that dictate the reaction pathway and possible intermediates. The kinetics are governed by the activation energies of the sub-reactions as well as by factors such as crystal structure and mobility of cations.³³⁻³⁵

First the thermodynamics of the CE are considered. The simplest reaction model is that the cation (A⁺) of the crystal (AX) is replaced by another cation (B⁺) to form the crystal (BX), as shown in equation 2.14.^{33–35} Additionally, the reaction equation for the studied system, CdS/Ag₂S, is provided along with the standard Gibbs free energy ΔG^0 in kJ/mol. Note that CE is an equilibrium reaction, capable of proceeding in both forward and backward direction.^{33–35} If the standard Gibbs free energy of the reaction ΔG_R^0 is negative, as it is the case for CdS/Ag₂S, the forward reaction is thermodynamically favored.^{33,66} To determine ΔG_R^0 and to describe the CE, the reaction can be divided into four sub-reactions: the dissociation of AX (eq. 2.15), the desolvation of B⁺ (eq. 2.16), the association of BX (eq. 2.17) and the solvation of A⁺ (eq. 2.18). ^{33–35}

	$AX + B^+ \rightleftharpoons BX + A^+$	$CdS + 2Ag^+ \rightleftharpoons Ag_2S + Cd^{2+}$	$\Delta G_{\rm R}^0 = -116.2$	(2.14)
(I)	$AX \rightleftharpoons A^0 + X^0$	$CdS \rightleftharpoons Cd^0 + S^0$	$-\Delta G_{\rm f}^{0} = 156.6$	(2.15)
(II)	$B^+ + e^- \rightleftharpoons B^0$	$2 \text{ Ag}^+ + 2 \text{ e}^- \rightleftharpoons 2 \text{ Ag}^0$	$-\Delta G_{\rm r}^0 = -154.3$	(2.16)
(III)	$B^0 + X^0 \rightleftharpoons BX$	$2 \operatorname{Ag}^0 + \operatorname{S}^0 \rightleftharpoons \operatorname{Ag}_2 \operatorname{S}$	$\Delta G_{\rm f}^{0} = -40.7$	(2.17)
(IV)	$A^0 \rightleftharpoons A^+ + e^-$	$Cd^0 \rightleftharpoons Cd^{2+} + 2e^-$	$\Delta G_{\rm r}^0 = -77.8$	(2.18)

The desolvation energy of CdS into Cd⁰ and S⁰ is equal to the negative value of the standard Gibbs free energy of formation ΔG_f^0 of CdS, see equation 2.15 and Table 2.1.^{33,66} The negative value of the standard Gibs free energy of reduction ΔG_r^0 , which describes the desolvation of Ag⁺ to Ag⁰ (eq. 2.16), can be calculated using the relationship:

$$\Delta G_{\rm r}^0 = nFE^0 \tag{2.19}$$

where *n* is the number of transferred electrons, *F* is the Faraday constant and E^0 is the standard reduction potential (see Table 2.1).^{33,66} The association of Ag₂S (eq. 2.17) is described by $\Delta G_{\rm f}^0$ and the desolvation leading to Cd²⁺ (eq. 2.18) is described by $\Delta G_{\rm r}^0$.^{33,66} By summing ΔG^0 of the four sub-reactions $\Delta G_{\rm R}^0$ can be obtained, as shown in equation 2.20.^{33,66}

$$\Delta G_{\rm R}^{0} = \left(\Delta G_{\rm f}^{0}\right)_{\rm B} + \left(-\Delta G_{\rm f}^{0}\right)_{\rm A} + \left(\Delta G_{\rm r}^{0}\right)_{\rm B} + \left(-\Delta G_{\rm r}^{0}\right)_{\rm A}$$
(2.20)

Based on the values provided in Table 2.1 and the equations (2.19, 2.20), for equation 2.14 a value of -116.2 kJ/mol was calculated for $\Delta G_{\rm R}^0$, indicating that the forward reaction is thermodynamically favored.

Another measure for determining whether a reaction is thermodynamically feasible involves comparing the solubility product constants K_{SP} of the reactant and product.³⁴ The material with the smaller K_{SP} is thermodynamically more stable, and therefore, less likely to dissolve, thereby shifting the equilibrium of the reaction to that side.³⁴ For CdS the K_{SP} is $8 \cdot 10^{-27}$, while for Ag₂S it is $6 \cdot 10^{-50}$, indicating that Ag₂S is more stable and less likely to redissolve once formed.³⁴ A summary of relevant thermodynamic quantities for the studied systems CdS/Ag₂S and CdSe/Ag₂Se is provided in Table 2.1. It should be noted that the values provided were determined for bulk

crystals and may be different for nanocrystals, as factors such as nanocrystal size and shape, solvents, and ligands can have a significant effect.

Table 2.1: Thermodynamic parameters for the CE of CdS/Ag₂S and CdSe/Ag₂Se. The standard Gibbs free energy of formation $\Delta G_{\rm f}^0$ and standard reduction potential E^0 were taken from Ref. 67 for CdS/Ag₂S and from Ref. 68 for CdSe/Ag₂Se. The standard Gibbs free energy of the reaction $\Delta G_{\rm R}^0$ was calculated using the listed values and equations 2.19 and 2.20. The solubility-product constant $K_{\rm SP}$ were taken from Ref. 34.

Material	$\Delta G_{ m f}^0$	E 0	$\Delta G_{ m R}^0$	K _{SP}
	(kJ/mol)	(V)	(kJ/mol)	(a. u.)
CdS	-156.5	-0.4030	116.2	8.10-27
Ag_2S	-40.7	0.7996	-116.2	6·10 ⁻⁵⁰
CdSe	-140.9	-0.4030	138.1	4·10 ⁻³⁵
Ag ₂ Se	-46.9	0.7996	-138.1	3.10-54

Particularly, solvents and ligands can be used to modify the thermodynamics of the reaction and favor the equilibrium toward either the product or reactant side.^{33,34} According to the hard and soft acids and bases (HSAB) theory, hard Lewis acids bind preferentially to hard Lewis bases and *vice versa*.^{33,34,69} Thus, the solvation of the leaving cation can be enhanced by using a solvent that corresponds with the hardness η of the cation.^{33,34} Cd²⁺ is a relatively hard Lewis acid with a η of 10.29 eV while Ag⁺ is a softer Lewis acid with a η of 6.96 eV.^{34,69} Therefore, to extract Cd from the lattice, a hard Lewis base, such as methanol ($\eta = 6.67 \text{ eV}$)⁷⁰ or water ($\eta = 9.5 \text{ eV}$)⁶⁹ is favored.^{34,69} Conversely, for the extraction of Ag, soft Lewis bases such as alkyl phosphines would be preferred.^{33,34} In addition to the solvent, ligands can further stabilize or destabilize the product. Ligands can also stabilize the leaving cation by forming a metal-ligand complex; for soft Lewis acids, alkyl phosphines are appropriate, while amines such as oleylamine can stabilize hard Lewis acids.^{33,34}

Even when a CE reaction is thermodynamically favored, the kinetics must also be taken into consideration, as reactions are seldomly performed under thermodynamic equilibrium.³³⁻³⁵ Based on the ion diffusion pathways, crystal structures and their miscibility, lattice parameters and volume changes, CE can lead to either homogeneous or heterogeneous intermediate phases.³³⁻³⁵ In general, the cations can diffuse into the lattice either *via* vacancies or interstitial sites.³⁴ For vacancy-controlled diffusion, either sufficient vacancies are already present at the surface or formed by the dissociation of the host lattice.³⁴ In contrast, diffusion *via* interstitials requires the desolvation of the incoming cation prior to dissociation.³⁴ For the CE from CdSe to Ag₂Se, Ott *et al.* reported that Ag⁺ first occupies interstitial sites and subsequently replaces surface Cd²⁺ though a kick-out mechanism.⁷¹ The high diffusion rate of monovalent cations, such as Ag⁺ or Cu⁺ within CdE (E = S, Se, Te) lattices, is advantageous for a fast and complete CE.³³⁻³⁵ Besides the diffusion of cations, determining the reaction mechanism and pathway, the crystal structure is important for the formation of intermediate phases.³³⁻³⁵

The crystal structures for CdS and CdSe are quite similar, but the CE mechanism differs due to the crystal structures of the resulting products Ag₂S and Ag₂Se.³³⁻³⁵ For the selenide, both lattices (CdSe and Ag₂Se) possess similar lattice constants, resulting in minimal volume change, and subsequently no strain effects are observed or reported.^{33,36} Furthermore, there are no reports of immiscibility between the two phases, suggesting a homogeneous CE over a doped and later alloyed intermediate.^{33,37} Conversely, for the sulfide, considerable lattices mismatch leads to notable volume changes and strain effects.^{37,72} Given that the CdS phase is also immiscible with

the Ag₂S phase, heterogeneous intermediates are observed during CE.^{33,37,72} The negative chemical formation energy for the CdS-Ag₂S interface and the lattice-mismatch induced strain thereby lead to a special exchange mechanism.^{37,72} Robinson *et al.* demonstrated that randomly distributed Ag₂S domains initially form on CdS NRs due to the negative interface energy.^{37,72} As CE progresses, the domains coalesce, forming a stripped phase to minimize the lattice strain.^{37,72} Due to the high mobility of Ag⁺ in the CdS lattice, these stripes can order themselves regularly to further minimize the lattice strain.^{33,37,72} These Ag₂S segments continue to growth as CE proceeds until complete exchange is achieved.^{37,72}

From the thermodynamic and kinetic consideration, the following predictions may be made regarding CE reactions. CE is likely if the crystal structures of the reactant and product are similar, with an acceptable mismatch of approximately 15 %. The equilibrium thereby is on the product side if the resulting crystal is more stable (low ΔG_R^0) and less soluble (low K_{SP}). Furthermore, the reaction can be driven toward the product side by using an excess of the incoming cation and a solvent (and adding a ligand) that preferentially dissolves the outgoing cation (matching η). This requires that both cations are mobile in the host lattice and soluble in the solvent.^{33–35}

2.3. Lithography

In lithography, a pattern is transferred onto a substrate, typically silicon wafers, by selectively exposing a photoresist on its surface. In the modern semiconductor industry, nearly all devices and components, including diodes, transistors, and integrated circuits are manufactured using photolithography. A variety of illumination sources, techniques, resists, and processing steps are available for lithography; these are summarized in the following sections to provide a condensed guide for fabricating nanostructured devices.^{73–75}

Lithography is commonly categorized based on the irradiation source used for exposure: photolithography (or optical lithography), which utilizes photons (light), and electron beam (e-beam) lithography, which uses electrons. In industry, photolithography is preferred due to its cost-effectiveness and efficiency. Conversely, in academia, e-beam lithography remains prevalent for fabricating of high-resolution structures where high throughput is less critical.

Coupled with the illumination source is the illumination technique. In photolithography, patterns can be transferred using a photomask (employed in mask aligners or steppers) or with a focused laser (used in maskless aligners or laser writers). Exposure with a photomask allows for rapid and straightforward exposure, thus facilitating high throughput, but achieving high resolution can be challenging and the flexibility is limited. In contrast, patterning with a focused laser offers significant flexibility by directly writing the desired pattern directly into the photoresist (and therefore also called direct writing), but at the cost of longer exposure times. Similarly, focused electron beam exposure is a slow process but yields higher resolution. Consequently, maskless and e-beam lithography are generally employed for structures that are subjected to frequent changes or for fabricating photomasks.⁷³⁻⁷⁵

The choice of resist must align with the selected illumination source, as resists are sensitive to specific irradiation types. For e-beam lithography, resists sensitive to electron exposure are utilized, while for photolithography resists that are sensitive to light of a certain wavelength are used. Hg lamps, frequently used in photolithography, generate spectral lines at 435 nm (g-line), 405 nm (h-line), and 365 nm (i-line). Consequently, photoresists are categorized based on their sensitivity to these wavelengths; for example, an i-line photoresist must be exposed to 365 nm light. Furthermore, resists are classified as positive or negative, based on their reaction to exposure. Diazonaphthoquinone-based (DNQ) photoresists, for instance, react with light in the

presence of water to form an indene carboxylic acid, releasing N_2 in the process. Positive photoresists become soluble in the developer post-exposure, while unexposed areas remain insoluble; the reverse is true for negative photoresists. The choice between positive or negative photoresists is guided by the specific area requiring structuring and the details of the fabrication process.⁷³⁻⁷⁵

The following guide serves to assist in selecting the optimal lithography process. The initial step involves the design and evaluation of the intended structure (e.g. resolution requirement). For standard device structure that will be frequently replicated or remain unmodified, exposure through a photomask is beneficial. In contrast, for structures less frequently utilized or subjected to continuous modification, maskless lithography is more appropriate. The next consideration is the selection of illumination source, which should be based on the required resolution of the desired structure. In mask lithography, high resolution can be achieved with deep ultraviolet (DUV, for features \geq 20 nm) or extreme ultraviolet (EUV, for features < 20 nm) light, while lower resolution (features \geq 500 nm) is possible with traditional UV light such as the i-line. In maskless lithography, an e-beam can yield high resolution (feature \geq 50 nm), while a focused laser is sufficient for low resolution (features \geq 500 nm). After determining the exposure, the resist must be selected accordingly, considering the acid and base stability of the device. Pure silicon wafers are typically acid-stable, allowing for metal film deposition prior to photoresist application and subsequent etching to remove excess metal. For devices that are unstable in acidic conditions – such as pre-patterned devices - bases may be employed, and the metal film is deposited after the photoresist. The timing of the metal deposited relative to photoresist application must be considered in the resist choice. When a pattern covers a large area of the device, a positive photoresist is advantageous, as the exposed regions will dissolve in the developer and be subsequently etched away. Conversely, for smaller areas requiring patterning, a negative photoresist is more beneficial. When the metal film is deposited after the photoresist the recommendation reverses; a positive photoresist should be used for a large area pattern, while a negative photoresist is preferable for a smaller pattern. This distinction is important because the metal film will only remain in areas that are directly in contact with the wafer, while the overlying metal (on the resist) will be removed during lift-off. A schematic overview of this selection guide is presented in Figure 2.6, along with two examples relevant to this work: fabricating a basic device structure with markers and contacting nanowires.73,74



Figure 2.6: Illustration of the selection of suitable lithography techniques and photoresist. The categories are listed at the top, while the choices for two examples are presented at the bottom.

In the first example, the basic device structure, including contact pads and small markers with relatively low resolution, should be written on several blank wafers. Given that this structure

remains constant, is utilized frequently, and only covers a relatively small area, mask lithography employing UV light in combination with a negative photoresist emerges as an appropriate choice. In the second example, leads and contacts to nanowires should be defined. Due to the variability in the positions of the nanowires, only maskless lithography is feasible for this application. In this case, UV illumination is favored over e-beam exposure to avoid concerns regarding radiation damage. Although the area to be patterned remains small, the NWs preclude the use of acids (which could dissolve them); thus, bases are used, making a positive photoresist advantageous. Note that this brief guide serves as a general orientation based on personal experience; other factors may also influence the choice of the lithography process. Additionally, personal preference plays a role in the choice between acids or bases, with both approaches yielding comparable results.

In the following the lithography process steps are explained according to the standard workflow used in this work to fabricate basic devices, including contact pads and markers. This workflow is schematically illustrated in Figure 2.7. Silicon wafers are typically sold and shipped with common diameters of 6, 8, or 12 inches (150, 200 or 300 mm), and must first be cut to a practical size.⁷³ Following the cutting process, the wafers undergo a cleaning procedure using organic solvents and deionized water to eliminate dust and residues from processing and storage. Prior to the photoresist deposition, the wafer may be dehydrated to remove any adsorbed moisture or subjected to plasma cleaning, both of which enhances resist adhesion.^{73–75}



Figure 2.7: Schematic visualization of the steps involved in photolithography. The workflow depicted is for the fabrication of basic devices using UV exposure and a positive photoresist.

The photoresist is typically applied through spin coating where acceleration, rotation speed, and duration determine the resulting resist thickness. To ensure the complete drying of the photoresist and the removal of residual solvents, a so-called soft-bake is performed at a precise temperature and time. This step is crucial because it enhances the overall quality of the resulting structure by improving the resist adhesion, suppressing blistering, increasing the softening temperature (important for following metal deposition), and reduces the removal rate of unexposed resist.^{73–75}

The desired pattern is then transferred to the photoresist through selective exposure. To achieve reliable and reproducible results, it is essential to determine the appropriate exposure dose

beforehand, ideally through a dose-focus test. An insufficient dose (indicating underexposure) may result in incomplete reaction of the resist, leading to incomplete removal and resulting in no pattern on the wafer. Conversely, a dose that is too high (indicating overexposure) can cause unintended reactions in adjacent areas, leading to broader and blurred patterns. To avoid the risk of failing to transfer a structure due to process deviations, a slightly higher dose than technically necessary is often selected. Following exposure, certain resists may require a post-exposure bake (PEB) to complete the photoreaction initiated by exposure. PEB can also further enhance the thermal stability of the resist, which can be crucial for the subsequent metal deposition.⁷³⁻⁷⁵

The developer then dissolves the exposed regions of the resist (for a positive photoresist), revealing the transferred pattern. The removal rate is closely linked to the baking temperature and time, which dictate the extent of cross-linkage. As with the previous steps, precise timing is critical for a robust process. Development times that are too brief can result in incomplete removal, similar to the issues associated with an underexposed resist. Conversely, prolonged development times can lead to removal beyond the exposed areas, resembling results associated with overexposure. Developers are usually based on dilute sodium (or potassium) hydroxide, but if metal ions must be avoided due to subsequent sensitive processes or electrical measurements, metal ion-free (MIF) developers based on tetramethylammonium hydroxide (TMAH) are recommended.⁷³⁻⁷⁵

A plasma cleaning step can be inserted between development and metal deposition if required. Plasma cleaning, prior to spin coating, can enhance metal adhesion and remove resist residues. Additionally, surface modifications may be performed prior to metal deposition that should be limited to a specific area. In this work, the contact area of the nanowire surface is treated immediately before metal deposition to improve the metal-semiconductor interface.

Metal deposition is typically accomplished *via* sputtering or physical vapor deposition (PVD), depending on the film quality requirements. Generally, PVD is more directional than sputtering, which is critical when depositing thick metal films or when pronounced fencing is observed after lift-off. Since PVD relies on the thermal evaporation of the desired metal, high temperatures can be reached during deposition, potentially altering the properties of the photoresist. Therefore, a thermally stable resist may be selected, or sputtering may be used as an alternative.⁷³

Following metal deposition, the metal that is not in direct contact with the wafer is removed during lift-off. For the lift-off, the wafer is immersed in a solvent capable of dissolving the photoresist, regardless of whether it is exposed or unexposed. Typically, organic solvents such as acetone or isopropanol are used, but in certain circumstances, specialized removers or strippers are necessary to ensure complete resist removal. If the flanks of the resist were also covered during the deposition and a continuous metal film was formed, the metal film may detach and tear at random position, leading to a phenomena known as fencing, where the metal film bends upward at the edges of the desired structure – resembling a fence. This can also result in difficulties to remove the metal film between closely spaced structures. To avoid such issues, a lift-off resist (LOR) can be spin-coated before the photoresist. While the LOR is not photosensitive, it dissolves faster than the photoresist, creating a small so-called undercut during development that prevents the formation of a continuous metal film and improves the lift-off process. If additional structures need to be transferred to the wafer, then the lithography cycle can be repeated starting from the spin coating step.⁷³

3. Characterization Methods

This chapter provides the theoretical basis for the characterization methods used in this work. The theory is intended to facilitate an understanding of the measurement results, the associated uncertainties, and the limitations of the used methods. First, the basics of electrical transport measurements are introduced by extending and applying the concepts presented in 2.1 Electrical Transport in Nanodevices. Second, imaging methods based on optical, electron and scanning-force microscopy are briefly explained. Third, spectroscopic methods using photons and X-rays are briefly discussed.

3.1. Electrical Transport

To determine the electrical transport properties of a material, it is essential for the current to pass through the material. However, conventional direct measurements using probes are not feasible due to the small size of nanostructures. Consequently, devices based on the nanostructure must be fabricated and subsequently characterized. As introduced in Section 2.1.2 (Contacts to Semiconductors), obtaining a good contact to semiconductor nanostructures, especially with CdS, can be challenging and these contacts can substantially influence the measurements.⁴¹ Lithographic techniques are used to fabricate nanowire-based field-effect transistors in order to investigate the electrical transport properties of CdS NWs. A schematic representation of the device and its characterization is shown in Figure 3.1.



Figure 3.1: Schematic illustration of the measurement of a nanowire field-effect transistor. The electrical circuit is included to highlight the components relevant to the transport.

For the measurements, two probe needles are positioned on contact pads that are connected to the nanowire via leads. By applying a bias voltage (V_{sd}) to the source contact (left) and measuring the resulting current (I_{sd}) at the drain contact (right), the total system resistance R_{Total} is determined. R_{Total} is the sum of all resistances:

$$R_{\rm Total} = 2R_{\rm S} + 2R_{\rm L} + 2R_{\rm C} + R_{\rm NW}$$
(3.1)

where R_S is the system resistance, R_L is the metal lead resistance, R_C is the contact resistance, and R_{NW} is the nanowire resistance. R_S combines all device-independent resistances in the system, such as the probe needles, cables and instruments. R_L represents the resistance of the metal leads, which depends on the electrical resistivity ρ of the metals used, film quality, and geometric factors, such as lead length and cross-sectional area. Both R_S and R_L are independent of the nanostructure and typically have a small influence, with $R_S \approx 60 \ \Omega$ and $R_L \approx 1 \ k\Omega - 1 \ M\Omega$. R_C reflects the resistance encountered by charge carriers when crossing the metal-semiconductor interface (see Section 2.1.2). For ohmic contacts, charge carriers face no or a very minimal barrier, rendering R_C negligible. In contrast, for Schottky contacts, the Schottky-barrier height ϕ_{Bn} significantly affects

the charge-carrier transport (see Section 2.1.3), making $R_{\rm C}$ non-negligible. The nanowire resistance $R_{\rm NW}$ is highly dependent on the material composition (represented in ρ), as well as geometric factors such as the diameter d (or radius r) and length L. Given that the NW is a semiconductor, $R_{\rm NW}$ may also be affected by external influences such as surface properties, illumination, temperature, and the chemical environment (see Section 2.1.1). In the studied system, $R_{\rm C}$ is anticipated to be approximately 1 G Ω , while $R_{\rm NW}$ is expected to be in the range of 10 G Ω .⁶³ Given that $R_{\rm S} \ll R_{\rm L} \ll R_{\rm C} < R_{\rm NW}$, equation 3.1 can be simplified to

$$R_{\text{Total}} \approx R_{\text{NW}}.$$
 (3.2)

Minimizing $R_{\rm C}$ to the lowest possible value is advantageous to ensure equation 3.2 remains valid, as the focus of this work involves studying the CE. Under these conditions, the change in $R_{\rm Total}$ (= $R_{\rm NW}$) is ideally a function of material composition, assuming similar measurement conditions, due to the topotaxial nature of CE. $R_{\rm Total}$ can be determined by applying a linear fit to the measured *IV*-curve and using:

$$R_{\rm Total} = \frac{\mathrm{d}V_{\rm sd}}{\mathrm{d}I_{\rm sd}} \tag{3.3}$$

Since R_{Total} is still geometry dependent, converting it to ρ or σ allows for the comparison of values across multiple devices. In this work, σ is used to evaluate the transport properties of the NWs and is calculated as follows:⁴¹

$$\sigma = \frac{1}{\rho} = \frac{L}{R_{\text{Total}}A} = \frac{\mathrm{d}I_{\text{sd}}}{\mathrm{d}V_{\text{sd}}} \cdot \frac{L}{\pi r^2}.$$
(3.4)

To gain further insight into the transport properties, a transistor characterization must be conducted. For this purpose, a bias voltage $V_{\rm g}$ is applied to the conducting silicon wafer, which serves as the back-gate, as depicted in Figure 3.1. When a positive bias is applied, negative charges are induced in the semiconductor, and conversely, when a negative bias is applied, positive charge are induced.⁴¹ For n-type semiconductors, where the electrical transport is predominantly governed by the electrons, an increased current is measured for $0 < V_{\rm g}$, while conversely a decreased current is measured for $0 > V_{\rm g}$. The susceptibility of a semiconductor to an external electric field is reflected by the transconductance $g_{\rm m}$, which can be determined from:

$$g_{\rm m} = \frac{\mathrm{d}I_{\rm sd}}{\mathrm{d}V_{\rm g}},\tag{3.5}$$

by applying a linear fit to the measured transfer curve.^{76,77} Using $g_{\rm m}$, $\mu_{\rm e}$ can be calculated by:

$$\mu_{\rm e} = \frac{g_{\rm m}L^2}{V_{\rm sd}C},\tag{3.6}$$

where *C* is the capacitance, which depends on the dielectric constant of the insulating layer and geometric factors such as the insulating layer thickness and NW diameter.^{76,77} To accurately determine *C*, which sensitively dependents on device geometry, *C* was determined through finite element simulations using COMSOL Multiphysics[®].^{76,78} With μ_e , n_e can be determined by:

$$n_{\rm e} = \frac{\sigma}{e\mu_{\rm e}},\tag{3.7}$$

which involves modifying equation 2.10 accordingly for an n-type semiconductor.^{76,77} With σ , μ_{e} , and n_{e} , the electrical transport properties of a semiconductor can be adequately described.
It should be noted that the values obtained with the presented equations and methods are subject to various assumptions, which may lead to significant deviations between theoretical and experimental results.^{79,80} In particular, the contact resistance can alter σ , and gate coupling can strongly influence $g_{\rm m}$ and the resulting quantities.

3.2. Microscopy

In this work, nanostructured devices with features in both the micrometer (μ m) and nanometer (nm) regimes are studied. Since, the human eye is incapable of resolving such small features, microscopy methods must be used to make these features visible.^{81–83} In microscopy different methods based on photon, electrons, X-rays or probes are available, each with its own operating range,^{81–83} as illustrated in Figure 3.2.



Figure 3.2: Schematic representation of the operating ranges for various microscopy techniques. The sizes of selected objects related to this work are presented below.

Figure 3.2 shows that the typical characteristics of the studied system span several orders of magnitude, and not all parameters can be accessed using one method. Optical microscopy (OM) is used to locate NWs and to monitor the device fabrication steps. Relevant features, such as the contact distance, can be obtained from OM, but Scanning probe microscopy (SPM) is preferred due to its superior resolution. SPM also allows for the determination of the NW diameter, enabling the extraction of quantities necessary for calculating the conductivity with minimal error. Although electron microscopy (EM) could theoretically be utilized to determine these values, irradiation damage from the electron beam would render the device unusable. Consequently, EM is used to gather information about the device properties after transport measurements have been completed, particularly regarding crystal structure, where standard SPM reaches its limitations. The theoretical foundations of these microscopy techniques are presented below.

3.2.1. Optical Microscopy

In OM, light in the visible range (380 – 750 nm)⁸³ is utilized to obtain a magnified image of the desired structure.⁸¹ For this purpose, light is directed through an objective lens, which creates an enlarged intermediate image of the structure within the intermediate-image plane. This intermediate image is then collected by the ocular lens, which enlarges the image again to produce the final magnified image. Both the objective and the ocular lenses are usually made of glass and are capable of controlling light based on their shape and refractive index.^{81,83}

Fundamentally, the enlarged image is produced through diffraction of the light at the structure, resulting in interference within in the intermediate-image plane.⁸¹ In order to observe an image, at least a second-diffraction order must be captured by the objective, otherwise no interference is possible.⁸¹ Consequently, the resolution of an optical contingent upon on capturing the

interference image at the intermediate-image plane and can be approximately described by the diffraction at a grating.⁸¹ Considering the refractive index (*n*) and the half angular aperture (α), the numerical aperture *NA* is defined as $NA = n \cdot \sin(\alpha)$.⁸¹ The resolution limit *d* of an optical microscope, according to Abbe, can be expressed as

$$d = \frac{\lambda}{2NA'}$$
(3.8)

where λ is the wavelength of the light.⁸¹ The resolution limit is defined as the minimum distance between two objects, where both still can be distinguished from another.⁸¹ Since typical values for *NA* are in the proximity of one, the resolution limit is frequently simplified to $d = \lambda/2$. From equation 3.8, it follows that resolution can be enhanced either by decreasing λ or increasing *NA*. For an optical microscope utilizing white light with an average λ of approximately 550 nm and exhibiting a high *NA* of 1.4, the resolution is limited to 200 nm.⁸¹ To achieve higher resolution, it is essential to reduce λ , as *NA* is mechanically (and physically) limited and cannot be significantly increased. Since the human eye cannot perceive light below 380 nm, alternative techniques must be employed to image smaller structures.^{81,83}

In general, optical microscopes can be categorized into transmitted light microscopes and reflected light microscopes, based on the position of the lamp and the ocular. In transmitted light microscopes, light is typically sourced from below the sample, passes through the sample, and is subsequently collected by the ocular. Conversely, in reflected light microscopes, light is sourced from above the sample, reflects on the sample, and is then collected by ocular. Therefore, the microscope configuration must be selected based on the transparency of the sample. Given that the devices studied in this work are mainly based on non-transparent silicon wafers, reflected light microscopes must be used.⁸¹

The intensity of the reflected light is influenced by several factors, including the wavelength, angle of incidence, the refractive index of the structure, and its thickness.⁸³ Additional phenomena such as absorption or scattering, resulting from a rough surface, also affect the reflection. In the case of the substrate, which is a silicon wafer coated with a 300 nm thick SiO₂ layer, a dark blue or violet color is typically observed. Pure silicon exhibits a metallic gray color, while SiO₂ is transparent; therefore, the observed color cannot be attributed solely to a mixture of the two materials. In fact, the color of coated Si/SiO_2 wafers contingent upon the SiO_2 thickness, varying from dark blue, to yellow, green and red.⁸⁴ The reason for this observation is the reflection and interference of light at the thin insulating layer.^{83,84} Light may be reflected at the surface of the thin film, or it may be transmitted into the thin film, subsequently reflecting or transmitting at the film-substrate interface. The reflected light may then again reflect or transmit at the surface of the thin film. Depending on the thickness and angle of incidence, certain wavelengths of the reflected light will interfere constructively, while others will interfere destructively, leading to the mitigation of specific wavelengths and resulting in the perception of the complementary color^{83,84} This phenomena similarly applies to other thin structures, such as metal films or the nanowires. Relatively thin metal films and the nanowires are frequently perceived as exhibiting a turquoise color in the light microscopy images.

A specialized optical microscopy technique, confocal fluorescence microscopy, was additionally used in this work. In confocal microscopy, the light is focused onto the sample as a localized spot and the image is generated by scanning in the x and y directions.⁸³ A pinhole is implemented at the detection plane, enabling the detection of only the light that is in focus.⁸³ This approach enhances spatial resolution and minimizes interference from stray light originating from out-of-focus planes.⁸³

When illuminated, a sample can interact with the light in different ways; in addition to scattering, the sample can also absorb the light.⁸³ When a semiconductor is illuminated with light of higher energy than its band gap, the light may be absorbed, facilitating the excitation of an electron from the VB into the CB.⁸³ Following excitation, non-radiative processes lower the energy of the excited electron until the vibrational ground state of the exited state is reached.⁸³ The excess energy is then released through the emission of a photon, referred to as fluorescence, which is again followed by non-radiative processes.⁸³ Consequently, the emitted photon possesses a lower energy than the absorbed photon due to the non-radiative processes.⁸³ By incorporating a filter that eliminates excitation light, only the fluorescence can be measured.⁸³

In a confocal fluorescence microscope, the confocal geometry is used to image the fluorescence of a system. In this work, confocal fluorescence microscopy is used to detect and to image the differently emitting domains of the NWs.

3.2.2. Electron Microscopy

As described in the previous sections, electron microscopy is employed to image structures that cannot be resolved by optical microscopy. Given that the resolution of the OM and EM is constrained by the wavelength utilized (see eq. 3.8), it is advantageous to use electrons or X-rays, as their λ fall within the range of a few of picometers (pm). For electrons, λ can be described using the de-Broglie relation, which relates momentum p to λ . The momentum p is dependent on the electron mass m_0 and the corrected applied acceleration voltage E^* , adjusted for relativistic effects. Consequently, while it is possible to reduce λ based on E^* , the resolution cannot be enhanced proportionally to the decreased λ due to relativistic effects, lens defects and imaging errors, ultimately reaching a limit of approximately 0.1 nm.^{81,82}

Similar to LM, EM can be categorized into two techniques: transmission electron microscopy (TEM) and scanning electron microscopy (SEM), based on the detected electrons (transmitted vs. secondary and backscattered). A transmission electron microscope operates similarly to a transmitted light microscope: the sample is fully illuminated, and the transmitted light is detected. In a transmission electron microscope, the transmitted electrons are detected. Conversely, a scanning electron microscope is more similar to a confocal microscope, as the electron beam is focused onto the sample surface. The electron beam is scanned over the sample and the secondary and backscattered electrons are detected to obtain an image. In TEM, since the transmitted electrons are detected, only very thin samples (< 1 µm) are compatible; typically, thin copper grids with a thin graphene layer are utilized for sample deposition. Thus, TEM is suitable for studying NWs and exchange processes in solution, but it is ineligible for investigating NWs incorporated into a device. For resolving the lattice to study different material compositions or defects such as stacking faults, high-resolution TEM (HRTEM) is utilized. To study the fabricated devices, SEM must be used. Therefore, the following discussion of EM will be based on a scanning electron microscope, although most concepts remain similar and applicable to a transmission electron microscope.81,82

A schematic cross-section of a scanning electron microscope is shown in Figure 3.3 (a), illustrating the electron beam path and the components involved. The electron beam is generated in the electron gun, which consists of a cathode, a Wehnelt cylinder and an anode. For thermal emitters, the cathode is heated in an ultra-high vacuum to facilitate electron emission. The electrons emitted from the cathode are then accelerated by the anode, with the acceleration dependent on the applied bias, thereby controlling λ (or *E*) and the penetration depth of the electrons. Since conventional optical elements are typically made from glass, and the electrons do

not interact with the glass, the electron beam must be manipulated differently. The counterpart to glass lenses (in OM) are electromagnetic coils (in EM). By passing a current through these coils, an electromagnetic field is generated that interacts with the electrons. The electron beam is then focused by the condenser lenses, while the spray blends remove the unfocused fraction of the beam. Furthermore, the spray blends protect the condensers from irradiation, which could comprise both their resolution and longevity. The aperture blend, positioned just before the objective, controls the beam diameter. Within the objective, additional coils are present; the deflection coils determine the final spot size and deflect the electron beam to allow scanning over the sample. The electron beam ultimately strikes the sample on the stage, and the scattered electrons can be detected by the detectors. Possible interactions between the electron beam and the sample are depicted in Figure 3.3 (b, c).^{81,82,85}



Figure 3.3: Schematic cross-section of a scanning electron microscope and the interaction of electrons with the sample. (a) Electron beam path of a scanning electron microscope and the components controlling the beam. (b) Scheme illustrating the various interaction possibilities between the sample and the electron beam. (c)Schematic illustration of the processes that occur during electron irradiation: (1) no scattering and elastic scattering of electrons, (2) inelastic scattering and backscattering of electrons, and (3) X-ray emission resulting from the relaxation of an electron. Figure adapted from Ref. 81 and Ref. 85.

The simplest interactions involved, are no scattering or elastic scattering (c1), where in both cases, no energy is transferred, limiting the information that can be obtained about the sample. In the case of inelastic scattering (c2), the electron collides with an electron in the sample, resulting is deflection and the transfer of energy (ΔE) to the other electron. If sufficient energy is transferred to the electrons in the sample by inelastic scattering, an electron can be ejected from its shell; these ejected electrons are referred to as secondary electrons. In TEM, both elastic and inelastic scattered electrons contribute to imaging through the superposition of images formed by unscattered and scattered electrons. Additionally, primary electrons may be deflected by the core to an extent that they exit the sample in the same direction from which they entered; these are referred to as backscattered electrons. In SEM, backscattered and secondary electrons are collected at each spot, and the resulting image is generated by scanning the sample. In a subsequent relaxation step, an electron from a higher energy shell may fill the vacancy left by an ejected electron, resulting in the emission of X-rays (c3). This process can yield valuable information about the sample and is further discussed in Section 3.3.2.^{81,85}

3.2.3. Scanning Probe Microscopy

In this work, the geometric dimensions of the devices are accessed using atomic force microscopy (AFM), to avoid radiation damage associated with EM. AFM is categorized as one of the SPM techniques. Generally, SPM methods rely on the interaction between the sample and a probe. By scanning over the sample and recording the influence on the probe, an image is generated based on this interaction. Since no photons or electrons are used for imaging, the resolution is no longer constrained by the Abbe-limit but is instead determined by the probe dimension and scanning precision.^{82,85,86}

In conventional atomic force microscopes, the topography is recorded by scanning over the sample, while measuring the deflection of the probe, as illustrated in Figure 3.4 (a). The probe is typically a silicon chip, featuring an elongated cantilever with a very fine tip. The resolution and potential interactions with the sample are primarily influenced by the tip size, angle and composition. In the simplest measurement mode, known as the contact mode, the tip makes direct contact with the sample upon approaching, maintaining intimate contact throughout scanning. To measure changes of tip and cantilever position while scanning, a detection laser in conjunction with a quadrant photodiode is utilized. The detection laser is directed onto the cantilever, reflects off its backside – which is coated with a reflective material to enhance reflectivity – and then lands on the quadrant photodiode. Any changes in height result in corresponding changes in deflection, which subsequently alters the position of the laser spot on the quadrant photodiode, thus allowing to record the topography. For precise scanning, the cantilever is moved in the x-y plane using piezoelectric motors. Due to the measurement technique, the resolution of an AFM is highest in the vertical direction (z-axis), whereas the lateral resolution (x- and y-axis) is diminished by the tip diameter and precision of the piezoelectric motors.^{85,86}



Figure 3.4: Schematic illustration of the imaging with a scanning probe and associated measurements modes. (a) Typical measurement setup for a contacted nanowire sample utilizing a scanning probe microscope. The feedback loop and the potential loop are indicated by a red and a green line, respectively. (b) Illustration of the three common measurement modes: contact, tapping and non-contact mode. (c) Schematic scans that would result from the sample shown in (a).

While the contact mode is the simplest measurement mode with the highest sample interaction, it is seldomly utilized due to rapid degradation of the tip (particularly with solid samples) and the high force applied on to the sample, which may cause damages. Consequently, measurements are commonly performed in either the tapping (intermittent contact) mode or non-contact mode, as depicted in Figure 3.4 (b). In both modes, the cantilever is resonantly excited along the z-axis by a piezoelectric actuator, and the oscillation is detected by the photodiode, as indicated in (a) as the feedback loop. The oscillation can be characterized by its frequency, amplitude, and phase, all of which changes as the tip interacts with the sample. In AFM, the height is determined by changes in frequency, while variations in amplitude and phase provide mechanical information about the

sample. In tapping mode, the tip is oscillated near the sample surface, resulting in contact with sample only at the apex of oscillation. This approach reduces tip degradation and limits the potential damage to the sample while maintaining the high resolution due to the close interaction with the sample. The non-contact mode is similar to the tapping mode, differing primarily in that the oscillation occurs further away from the sample surface, preventing any direct contact between the tip and the sample. While this mode is even more gentle on both the sample and tip, it compromises resolution. As discussed previously, resolution is determined by the tip and its interaction with the sample; the further the tip from the sample, the weaker the interaction becomes, leading to overlapping long-ranged interaction and resulting in rather blurry images. In this work, tapping mode is primarily used, as high resolution is necessary, and this mode is sufficiently gentle to avoid damaging the NWs.^{85,86}

As introduced before, in addition to the topography, several other properties can be accessed by SPM based on the interaction between tip and sample. For example, techniques such as conductive atomic force microscopy (CAFM), electrostatic force microscopy (EFM), or kelvin probe force microscopy (KPFM) can be performed with an electrically conductive tip, while magnetic force microscopy (MFM) can be performed using a magnetic tip. Since KPFM was utilized in this work to acquire additional electrical information about the NWs, a brief introduced to KPFM is provided below.^{85,86}

In KPFM, an electrically conductive tip is brought in contact with the sample, resulting in a situation similar to that described in Section 2.1.2 (Contacts to Semiconductors). The Fermi levels of the tip and the sample, which is represented by their work functions ϕ_{tip} and ϕ_{sample} , will equilibrate upon contact. The difference in work functions is expressed by the contact potential difference (CPD), defined as $V_{CPD} = (\phi_{tip} - \phi_{sample})/-e)$. This charging is compensated by applying a potential to the tip during KPFM measurements, ensuring that no potential difference exists between tip and sample. By scanning the tip across the sample and recording the potential necessary to compensate for the CPD at each recorded point, the KPFM scan is generated. Since V_{CPD} is primarily dependent on ϕ_{sample} , the work function can be readily determined using KPFM. In practice, however, as previously discussed, various effects affect the charge-carrier concentration on the surface, and consequently $E_{\rm F}$ and ϕ , leading to challenges in obtaining reliable values. To account for these uncertainties, the surface potential, rather than the CPD, is used.^{85,87,88}

Figure 3.4 (c) shows a schematic representation of the scans anticipated from AFM and KPFM measurements of the sample depicted in (a). In AFM, the color scale is based on height values, with lower values depicted in dark blue and higher values in bright yellow. The AFM scan allows the height of the contacts, the nanowire and the patch to be determined. Note that the two different heights of the contacts can be distinguished. In contrast, the KPFM scan color scale is based on the surface potential, with small or negative values presented in dark petrol and large or positive values in bright green. The KPFM scan allows for the determination of the surface potential of the elements on the sample. In the specific example discussed, a positive bias was applied to the contact; hence, varying surface potentials are observed for the gold patch and the gold contact. The surface potential of the patch is primarily corresponding to the ϕ of gold, while the applied bias results in a shift of the observed surface potential at the contact by this amount relative to ϕ . Note that the two different metals are indistinguishable, as intimate contact and the applied potential have altered the ϕ . Additionally, the charge transport through the NW can be observed in the KPFM scan *via* the potential gradient along the NW.

3.3. Spectroscopy

Spectroscopy is the study of the interaction between electromagnetic radiation and a sample. Information about the sample can be obtained based on the radiation source, the sample, and the nature of their interaction. Due to the wide range of the electromagnetic spectrum and the resulting diversity of spectroscopic methods, only a limited selection relevant to this work will be presented in the following sections.⁸⁹ In this work, methods utilizing photons, electrons and X-rays were used primarily to access the composition of the NWs. Given that the interaction and mechanism are strongly influenced by the radiation source, a separate discussion of each methods will follow, beginning with photoluminescence spectroscopy.

3.3.1. Photoluminescence Spectroscopy

Photoluminescence (PL) spectroscopy is a photon-based spectroscopy method that, as implied by its name, is based on the process of luminescence. Luminesce is a relaxation process involving the radiative decay of photons, which is categorized into phosphorescence and fluorescence. Furthermore, luminescence is distinguished by the nature of excitation: if an electron is excited by a photon *via* absorption, this process is termed photoluminescence (PL), whereas electrical excitation of electrons is referred to as electroluminescence (EL). In this work, the fluorescence of the NWs was primarily investigated after optical excitation, therefore the terms fluorescence and PL are used synonymously.^{83,89}

As introduced in Section 3.2.1 (Optical Microscopy), a confocal microscope can be utilized to spatially resolve the fluorescence, yielding images, maps or so-called PL scans that reveal fluorescent domains. Nonetheless, these PL scans do not provide information concerning the emitted wavelength $\lambda_{\rm em}$, beyond the fact that $\lambda_{\rm em}$ exceeds the excitation wavelength $\lambda_{\rm ex}$ ($\lambda_{\rm ex} < \lambda_{\rm em}$). Since the PL predominantly occurs at the band edges, the $\lambda_{\rm em}$ can give information about the bandgap. As the bandgap is specific to each semiconductor and its composition, alterations in composition – such as those induced by CE – should be reflected in the PL, thus making it a promising technique for monitoring CE alongside transport measurements. Furthermore, if defects or dopants – commonly referred to as traps – are present exhibiting states energetically positioned within the bandgap, they may also affect the PL. Therefore, $\lambda_{\rm em}$ can also contain information about the presence and relative position of these traps.^{43,89}

To retrieve λ_{em} from the PL scan, the detected polychromatic emission must be decomposed into its individual components. This process is facilitated by a spectrograph, whose main component is the monochromator, which is based on either a prism or a grating. A prism decomposes light based on the different dispersion characteristics of various λ within it, while a grating separates λ through diffraction. Generally, gratings are preferred due to the higher resolution resulting from the easier fabrication of high-quality gratings compared to prisms. In both cases, the polychromatic light is spatially decomposed, allowing for the determination of λ . Depending on the design of the spectrograph, the separated light may either be directly detected or a specific λ may be selected through mirrors. A charge-coupled device (CCD) camera is required to directly detect the separated light, featuring a pixel array for photon detection. Calibration is necessary to correlate the detected light on the pixels to the corresponding λ . Consequently, the PL spectrum is obtained through the decomposition of light *via* a grating and subsequent detection using a CCD camera.⁸⁹

3.3.2. Energy Dispersive Spectroscopy

Energy dispersive spectroscopy (EDS), also referred to as energy dispersive X-ray spectroscopy (EDX), is based on the process outlined in Section 3.2.2 (Electron Microscopy) and illustrated Figure 3.3. When the sample is irradiated with electrons, inelastic scattering may occur, leading to the ejection of secondary electrons. This created vacancy is energetically unfavorable, and an electron from a higher shell will occupy it, resulting in the emission of an X-ray, as depicted in Figure 3.3 (c2 and c3). X-rays are a form electromagnetic radiation with λ ranging from 0.01 nm to 10 nm (50 keV – 100 eV).⁹⁰ Therefore, EDX is an electron-based method that detects X-rays.^{81,85,90}

This X-ray radiation resulting from the relaxation of electrons transitioning from a higher energy shell to a vacancy in a lower shell is referred to as characteristic X-ray lines. These lines are specific to certain elements because the energy levels of the electron shells and their energy difference are unique to each element. Consequently, recording characteristic X-ray lines yields valuable information regarding the sample composition. The nomenclature of such lines is based on shells and states involved in the transition; for example, $L\alpha_1$ or $L\beta_2$ lines were observed in this work. The first letter indicates the shell in which the initial ionization occurred – in these cases, the L-shell. The second letter corresponds to the source of the electron filling the vacancy; if it comes from the energetically next higher shell, it is classified as α , while an electron from the next higher shell is designated β . The index number denotes the subshell from which the electron from the M_5 state to the L_3 state, while $L\beta_2$ corresponds to the relaxation of electron from the N_5 state to the L_3 state.^{85,90}

Depending on the electron microscope used, either a specific region is irradiated, resulting in the acquisition of an EDX spectrum, or each spot is irradiated individually, resulting in an EDX map composed of EDX spectra for each pixel. EDX maps are particularly valuable for revealing domains of different composition, which is essential for investigating the CE.

3.3.3. X-ray Photoelectron Spectroscopy

X-ray photoelectron spectroscopy (XPS) can be distantly regarded as reverse EDX process, wherein X-rays are utilized to emit electrons that are subsequently detected. In XPS, the sample is irradiated with X-rays, typically with an energy E_X of 1.25 keV (Mg K α), which can lead to the emission of so-called photoelectrons. Due to the limited penetration depth of the X-rays and the requirement that generated photoelectrons must be emitted from the sample, XPS is classified as a surface-sensitive technique.^{82,91}

Electrons are bound in their core levels prior to excitation, which is described by their binding energy $E_{\rm B}$ depending on the orbitals involved. For an electron to be released, at least $E_{\rm B}$ must be overcome; therefore, the resulting kinetic energy $E_{\rm K}$ of the photoelectron can be described by $E_{\rm K} = E_{\rm X} - E_{\rm B}$. Similar to EDX, each elements possesses specific binding energies that correspond to its orbitals, thereby allowing for the determination of the elemental composition of the sample through XPS. However, in contrast to characteristic lines in EDX, the binding energy in XPS is influenced not only by the host element but also by the chemical environment. This indicates that binding partners or adsorbates can shift $E_{\rm B}$, enabling the distinction between different modifications, such as CdS from CdO. For all orbitals (expect for the s orbitals), the observed signals split into two signal due to spin-orbit splitting, with a distinct intensity ratio determined by the involved orbital.^{82,91}

4. Results and Discussion

In this chapter, the concepts introduced in the previous chapters are utilized to the analyze, interpret, and discuss the results obtained. The objective of this work is to investigate the CE dynamics in individual nanowires, ideally in a non-destructive manner. To achieve this, nanowire field-effect transistors (NWFETs) are fabricated and analyzed. This chapter is organized into three subchapters: First, the contact materials and device fabrication for CdSe and CdS nanowires are studied in detail to obtain optimal devices for subsequent investigations (4.1 Contacts to Individual Nanowires). Second, the general transport properties of CdS NWFETs and the charge-carrier distribution under local illumination are analyzed (4.2 Electrical Properties of CdS Nanowire-based Devices). Third, the CE is investigated. In the case of CdSe-Ag₂Se NWFETs, the exchange tracking is briefly presented alongside the transport characteristics under cryogenic conditions. Additionally, the CE from CdS to Ag₂S is studied using electrical, spectroscopic and microscopic methods (4.3 Cation Exchange in Nanowire-based Devices).

4.1. Contacts to Individual Nanowires

For the fabrication of high-quality samples and devices, establishing a reliable electrical contact between the metal and semiconductor is essential. This aspect often poses significant challenges when studying a new material system, as only a limited amount of previous experience can be transferred. The metal-semiconductor interface between metal contact and nanowire surface, is critical. In principle, certain criteria must be satisfied to obtain a good ohmic contact, as already explained in the theory section (see Section 2.1.2 Contacts to Semiconductors). Specifically, the work function ϕ of the metal should ideally be lower than that of the n-type semiconductor nanowires. This requirement can be achieved either by selecting a suitable metal (see Section: Contact material) or by modifying the semiconductor surface (see Section: CdS nanowire surface and following), both of which will be addressed in detail in later sections.

Besides the work function, several other factors influence the choice of the contact metal and the resulting device quality. High electrical conductivity is essential, to minimize the metal lead resistance R_L (see eq. 3.1), ensuring equation 3.2 remains valid. Moreover, ensuring adequate adhesion to the substrate surface is critical; a lack of adhesion would prevent the formation of a stable contact. Devices should ideally demonstrate stability over extended periods of time and under varying operational conditions; accordingly, the contact metal should also be stable, especially against oxidation and temperature. Lastly, the film of the deposited metal should be smooth and uniform (referred to as film quality), as inhomogeneities may hinder the electrical transport. Table 4.1 lists these criteria, provides values or ratings for the criteria, and compares the properties of the metals with those of the semiconductors studied.

The table indicates that the metals positioned above the semiconductors represent suboptimal choices for ohmic contacts due to their high work function, whereas the metals below may facilitate an ohmic contact (neglecting surface effects). Nevertheless, additional criteria must also be considered when selecting the ideal contact metal. For example, Ti can be a good choice due to its good adhesion to the Si/SiO₂ wafer, high film quality and thermal stability, but potential oxidation processes must be considered. An alternative strategy is to combine two metals to benefit from their respective advantages, while mitigating their disadvantages. For instance, In can be combined with Au; In provides a matching work function along with good substrate adhesion, while Au provides a smooth film that is stable against oxidation. Therefore, no metal contact is

suitable for all applications, and careful consideration must be given to choice of the contact material to ensure the production of high-quality devices.

Table 4.1: Comparison of various metals with CdSe/CdS in terms of their suitability as contact material. The parameters considered include work function ϕ , electrical conductivity σ , adhesion to the substrate, observed stability against oxidation and temperature, and the resulting film quality. The values for the metal ϕ were obtained from Ref. 51, while the σ was calculated from the electrical resistivity ρ (at 273 K) as reported in Ref. 67. For the semiconductor ϕ and electron affinity χ values were obtained from Ref. 50 and σ from Ref. 18.

Material	φ	χ	σ	Adhesion to	Stability		Film
	(eV)	(eV)	(S/m)·10 ⁶	Si/SiO ₂ Wafer	Oxidation	Thermal	Quality
Pt	5.65	-	10.4	Good	Good	Good	Good
Au	5.10	-	48.8	Poor	Good	Good	Good
CdSe	5.22	4.95	10-6	-	-	-	-
CdS	5.01	4.79	10-7	-	-	-	-
Ti	4.33	-	2.56	Good	Poor	Good	Good
Ag	4.26	-	68.2	Poor	Good	Poor	Good
In	4.12	-	12.5	Good	Poor	Good	Poor
Mg	3.66	-	24.7	Good	Poor	Good	Good

4.1.1. Contacts to CdSe Nanowires

The previous section and Table 4.1 demonstrate that Ti/Au may represent an appropriate choice for making an ohmic contact with CdSe. Ti possesses a suitable ϕ that facilitates an ohmic contact and provides adequate adhesion to the substrate, while the Au layer on top prevents oxidation and enhances the conductivity. However, prior research conducted by Maximilian Schwarz indicated that the use of Ti/Au can lead to various fabrication challenges, frequently resulting in the formation of Schottky contacts.⁴⁰ Direct contact between gold and the nanowire which may lead to the formation of a depletion layer is difficult to prevent. There it was concluded that 75 nm Ti contacts are ideal for making a contact with CdSe.⁴⁰ Figure 4.1 illustrates the fabrication process of CdSe devices, accompanied by light microscopy images and a scheme representation of the surface conditions of the nanowire.

The device fabrication process comprises more steps than lithography and metal deposition, as illustrated in Figure 4.1. These additional steps have been implemented to improve the metal-semiconductor interface, thereby improving reproducibility and resulting in higher quality devices, reflected in increased conductivity and higher yield (fewer non-conductive NWs per device). Initially, after nanowire synthesis on the substrate, the nanowires must be localized (Figure 4.1 (1)). At this stage, the nanowire surface is passivated with ligands. Following lithography (2), two distinct areas are formed: one that is free of photoresist, referred to as the contact area (outlined in blue), and one that is covered with photoresist, referred to as the free area (outlined in green).



Figure 4.1: Schematic summary of the processes involved in fabricating contacts to nanowires. (a) Light microscopy images showing the fabrication steps from localization on the substrate to the final device. (b, c) Scheme illustrating the (surface) conditions of the nanowire depicted in cross-sectional view at the shown steps above for the (b) contact area and the (c) free area. The contact area and free area are marked in last panel with a blue and green box, respectively.

Prior to metal deposition, the first treatment step is performed (3) to remove not only the ligands from the synthesis but also photoresist residues and other contaminations in the contact area. This treatment must be carefully designed to ensure cleaning of the nanowire surface (contact area) from contaminants while preserving the integrity of the photoresist (free area). For this purpose, a mild air plasma cleaning (P = 7 W, p = 0.3 mbar, t = 30 s) is utilized. Following this cleaning, the metal is deposited onto the treated surface, and any excess metal is subsequently removed (4).

To further improve the metal-semiconductor interface, a second treatment is performed to smooth the interface between the metal and the nanowire (contact area) and to remove any residues and ligands in the free area (5). This is achieved by irradiating the device with UV-light for 20 min, followed by annealing under vacuum (30 min at 150 °C, 30 min at 300 °C). The device-fabrication protocol presented (taken from Schwarz⁴⁰) served as starting point for this work to produce ohmic contacts to CdS nanowires. The following subchapter presents the optimal fabrication protocol for CdS, beginning with the selection of the ideal contact material.

4.1.2. Contacts to CdS Nanowires

Contact material

For CdS, Ti, along with the previously described protocol, represents the most intuitive option for a contact material. This option has been studied in precedent work with moderate success.⁵³ Similar to CdSe, metals with a lower ϕ than that of CdS (listed in Table 4.1), are viable candidates to obtain ohmic contacts to CdS. Among the four metals, Ti and In were tested as pure contacts, while pure Ag and Mg were excluded due to concerns about low adhesion and oxidation. The devices fabricated using Ti and In, along with their transport properties, are shown in Figure 4.2 (a).



Figure 4.2: Measured current-voltage characteristics (*IV*-curves) for various contact metals. (a, b) *IV*-curves for (a) pure metal and (b) metal combination contacts. The standard measurement conditions are: room temperature, under air and illumination (USB camera) which is referred to as "Bright"; in absence of illumination it is referred to as "Dark" (shown in a lighter color). Light microscope images of the corresponding devices to the *IV*-curves are shown in the insets with matching outline colors. The scale bar for each image is 5 µm.

The fabrication process for the Ti contacts was straight forward and resulted in a typical device (see Figure 4.2 (a1) inset). However, the device did not display any current in the dark or under illuminated conditions. In contrast, the fabrication of the In device was more difficult. Although In demonstrates good adhesion to the substrate, it often undergoes dewetting, leading to rough, poor-quality films (see (a2) inset). Such behavior has also been reported for Ag metal films.⁹²⁻⁹⁴ The In device showed no current in the dark, analogous to the Ti device, but when illuminated, it showed nearly linear and symmetric responses, suggesting its potential as a promising contact material. Note that the measured current varied significantly for different NWs, as can be seen in Figure 4.2 (a2).

To enhance device performance, contact metals were combined to mitigate their respective disadvantages. The combination thereby is the sequential deposition of two contact metals, denoted by the nomenclature "first metal/ second metal", for example Ti/Au. The devices fabricated using a combination of contact metals are depicted in Figure 4.2 (b). For Ti, combinations with Ag and In are studied. Surface effects, such as Fermi-level pinning may hinder the formation of an ohmic contact with Ti (see Figure 2.3). Therefore, the use of metals with a lower ϕ in combination with Ti may address this issue. Additionally, depositing Ag on top of Ti could enhance device performance by increasing the conductivity and the chemical stability.

Indeed, the Ti/Ag contacts demonstrate higher currents even at lower applied biases. However, the obtained *IV*-curves exhibit neither linearity nor symmetry (see Figure 4.2 (b1)), indicating the existence of asymmetric barriers. An interesting observation is the sudden increase and decreases in current, which is surprisingly even more pronounced in dark conditions. Given the unexpected dark current, the observed peak in current, and its shift, a Ag migration from the contacts into the

NW seems likely (discussed in detail in Section 4.3.2).^{95,96} This issue not only leads to non-reproducible device performance, but also results in an unknown composition of the nanowire. Silver migration from the contacts into the NW poses a serious problem when studying the CE with silver, as the composition cannot be controlled, and the contributions cannot be distinctly identified.

An improved response was also recorded for device using Ti/In contacts, showing linear and symmetrical *IV*-curves, although no dark current was observed. A correlation was observed between the symmetry of the *IV*-curves and contact quality. When the In layer was not centered – resulting in a lack of direct contact with the nanowire on both sides – the current measured for that contact was lower, yielding linear but asymmetric *IV*-curves. The contact area of In with the NW can be seen in the inset ((b1) left), indicated by the light green edge around the contact, demonstrating a well-centered layer in this case.

Indium was combined with Au to improve the contact by filling the rough resistive In film with a smooth, conductive Au layer. This approach yielded partial success, as the contacts shown in the inset (in (b2)) appear smoother. However, similar to the challenges encountered with Ti/Au contacts, it remains difficult to prevent Au from establishing contact to the NWs and forming a Schottky contact. The absence of a light green halo around the contact in the inset suggest that not only In is in contact to the NW. This assumption is further supported by the *IV*-curves, which demonstrate that no current can be measured under illumination.

This first study indicates that In represents a promising contact material, and with further optimization – such as more precise deposition of the Au layer – improved contacts may be achievable. The device using Ti contacts surprisingly show no current, while the device using a combination with Ag indicates Ag migration. Theoretically (assuming ideal contacts), Ti should give an ohmic contact if the ϕ of the studied CdS NWs aligns with literature values. The work function ϕ of a system is highly dependent on the surface conditions and can be significantly influenced by factors such as synthesis conditions, storage, passivation and treatments.^{46,48} To elucidate the reasons why Ti does not facilitate an ohmic contact the surface of the nanowires will be studied in the following section.

CdS nanowire surface

To gain a closer insight into the surface of the CdS nanowires, a surface-sensitive method, specifically X-ray photoelectron spectroscopy (XPS), was utilized. XPS provides information regarding the atoms present at the surface, typically few nm deep, as well as their chemical environment (see Section 3.3.3).^{91,97} For this study, a silicon wafer was coated with a thick film (> 100 µm) of NWs and subsequently annealed under vacuum to ensure the complete removal of the solvent. The XPS experiments were performed under high vacuum conditions, and to obtain a clean surface of the analyte, samples were sputtered using Ar^+ ions.^{91,97} In order to acquire information about deeper layers of the NW and to compare them with the surface, XPS measurements were performed before and after sputtering for a specific duration. The XPS measurements and following peak fitting were conducted by Dr. Heshmat Noei (Group of Prof. Andreas Stierle, DESY NanoLab)⁹⁸. The results of the XPS study, including the survey spectra and the element core level spectra, are presented in Figure 4.3.



Figure 4.3: Deconvoluted XP spectra of a CdS NW thin film deposited on a silicon wafer, measured before and after sputtering with Ar⁺ ions. (a) Survey spectra prior to (0 min) and following 50 and 140 mins of sputtering. Colored boxes behind the data indicate the measurement range of the detail spectra of the Cd 3d, S 2p, O 1s, and C 1s core levels shown in (c). (b) Evolution of the measured intensities of the various elements with ongoing sputtering. Each intensity is normalized by its values at 0 min, resulting in starting value of 1 for all element. The boxes behind the data indicate to the survey spectra with specific sputtering time. (c) Detail spectra of the core levels of Cd 3d, S 2p, O 1s, and C 1s for the corresponding sputtering time. The raw data is depicted as a gray line, the fits as filled curves and the envelope of the fits as a red line. The background was subtracted for every curve and fit. All peaks were assigned according to the Handbook of X-ray photoelectron spectroscopy.⁹¹

From the survey spectra (Figure 4.3 (a)) it can be concluded that CdS is present, along with oxygen and carbon species. The observation of oxygen and carbon species is common and likely originates from solvents, ligands, and the atmosphere. No significant changes in the survey spectra can be observed with ongoing sputtering; therefore, core level spectra for specific elements were recorded and are presented in Figure 4.3 (c).

Before sputtering, the characteristic 3d peak for Cd is observed, splitting into j = 5/2 and j = 3/2, which can be attributed to Cd²⁺ bound to S. For S, two broader peaks are observed: one peak with a substantial shoulder around 160 eV and a broad peak around 166 eV. The first peak is typical for S²⁻ 2p splitting into j = 3/2 and j = 1/2, which is assigned to S²⁻ binding to Cd.⁹¹ The second peak is particularly interesting as it corresponds to an oxidized S species, either SO₂ or SO₄^{2-.91} The

interpretation of the oxygen peak is often challenging, particularly when attempting to assign it to a specific species, due to its broadness and the large number of potential sources. It is assumed that the peak contains components from hydroxyl groups from water (-OH) and ethanol (-OH, -OC, solvent), and a species that is bound to S (-OS) in some form. Similar challenges apply to the interpretation of the carbon peak. The peak at 283 eV is attributed to carbon bound to the nanowire surface (-CS), originating from carbon-containing ligands. The small peak at 286 eV is assigned to carbon bound to oxygen (-CO), as found in the solvent. Peak assignment was performed using the Handbook of X-ray photoelectron spectroscopy.⁹¹

Investigating the evolution of these peaks with progressing sputtering time is particularly interesting, as this can provide insights into the "pristine" state of nanowire. The first observation after 50 min of sputtering is that the intensity of the Cd and S signals significantly increased, while the signals of 0 and C decreased. This strongly suggest the removal of surface contamination, such as ligands and solvent residues. Additionally, the small carbon peak disappeared, further indicating the removal of residual solvent. The intensity of the peak assigned to oxidized S has also diminished, indicating that a fraction of the potentially oxidized surface has been removed through sputtering. After further sputtering (140 min), the Cd and S signal have increased in intensity, while the 0 and C continued to decrease in intensity. The peak corresponding to oxidized S at 166 eV has become barely visible.

The evolution of the XPS peaks can be more clearly observed in Figure 4.3 (b), where the peak intensity of the elements is plotted against the sputtering time. For comparative purposes, the intensities were normalized by dividing the intensities after sputtering by the intensity measured before sputtering, resulting in all elements to start at a value of 1. Figure 4.3 (b) shows that the intensities of the Cd 3d and S 2p peaks increase at a faster rate than observed in (c); within 20 min, the intensity has increased by nearly 70 %. Conversely, the peak intensities of 0 1s and C 1s decrease more rapidly than observed in (c), with only 60 % of the original peak intensity remaining after 20 min of sputtering. After 140 min, it can be observed that the C 1s signal decreased more than the 0 1s signal, which may indicate that the removal of surface contamination (*e.g.* from ligands and solvents) is easier than the removal of the oxidized surface. Moreover, the intensities appear to saturate, indicating that complete removal of contamination or oxidation may not be possible. This observation might be explained by the sample topography. For the XPS study, a thick NW film was deposited by drop casting, resulting in an inhomogeneous film with non-uniform thickness. Therefore, it is likely that even after sputtering, there are regions that remained unaffected or less affected by sputtering.

In summary, the XPS study demonstrates that surface contamination is indeed present and can be removed through sputtering. Particular noteworthy is the observation of an oxidized sulfur species, most likely SO_4^{2-} , which suggest the occurrence of oxidation processes at the surface of the NWs. This shows that the nanowire surface and surface treatments should be taken into account. Therefore, the following sections will focus on various surface treatments, beginning with methods applied prior to metal deposition.

Plasma cleaning

One method commonly employed for cleaning surfaces in device fabrication is plasma cleaning. This technique utilizes plasma is to remove surface contamination, such as ligands, without harming the device. A significant advantage of plasma cleaning is its compatibility with solid samples and availability of numerous designated devices, which makes it user-friendly. Consequently, plasma cleaning can be conveniently integrated into the device fabrication protocol.

Moreover, plasma process parameters, such as power, pressure, and treatment duration, can be flexibly adjusted, facilitating tailored treatments.

For plasma cleaning air plasma is most frequently utilized due to its widespread availability and its effectiveness in gently removing contaminants. Initially, a mild air plasma treatment (P = 7 W, p = 0.3 mbar, t = 30 s, continuous) was performed for Ti and In contacts to assess whether there are improvements compared to previous measurements without cleaning. The results of the measurements, along with images taken during the plasma cleaning process, are shown in Figure 4.4.



Figure 4.4: Influence of air and argon plasma on the transport in NWs. (a, b) *IV*-curves of devices subjected to a treatment in (a) air plasma and (b) an argon plasma. The standard measurement conditions are: room temperature, under air and illumination (USB camera) which is referred to as "Bright"; in absence of illumination it is referred to as "Dark" (shown in a lighter color). Light microscope images of the corresponding devices to the *IV*-curves are shown in the insets with matching outline colors. The scale bar for each image is 5 μ m. (c, d) Photos of the sample chamber taken during the treatment in (c) air (*P* = 7 W, *p* = 0.3 mbar, *t* = 30 s, continuous) and (d) argon plasma (*P* = 200 W, *p* = 0.4 mbar, *t* = 2 min, *f* = 27.12 MHz, pulse = 100 ms at 50% duty cycle) of the devices.

It can be observed that the plasma treatment had no significant influence on the device or the metal adhesion, both devices appear similar to those without cleaning (compare with Figure 4.2 (a)). However, a difference is evident in the electrical transport properties. For Ti contacts, a slight improvement was measured for most NWs, with the NW shown exhibiting the best improvement, but the *IV*-curves remain asymmetric, indicating incomplete or inhomogeneous removal of residues. For In contacts, only minor changes were measured, with most NWs still demonstrating almost linear and symmetric *IV*-curves (blue curve). In a few cases (red curve), a higher current was observed; however, asymmetry was also observed. It remains unclear whether this asymmetry originates from inhomogeneous cleaning of the contacts based

on the sample position in the plasma chamber (see (c)). However, the distance between the contacts is relatively small compared to the device and chamber size, making this explanation unlikely.

To investigated whether the cleaning was incomplete and if air plasma might induce further oxidation of the NWs, argon plasma was also studied. Ar plasma is less commonly used, since a constant supply of Ar and conditioning of the chamber is required. For these experiments, the former plasma-enhanced chemical-vapor-deposition (PECVD) setup from Charlotte Ruhmlieb was utilized.⁹⁹ This setup does not only provide the necessary equipment but also allows for much higher power levels as compared to the air plasma cleaner. This capability allows to go beyond cleaning and attempt to remove several layers from the NW surface, which may aid in removing the oxide layer. For this purpose, two power levels were tested for Ti: 50 W for surface cleaning and 200 W for layer removal, with p = 0.4 mbar, t = 2 min, f = 27.12 MHz, pulse = 100 ms at 50% duty cycle. The results are illustrated in Figure 4.4 (b). At 50 W, no changes in fabrication were encountered, and no current was measured. Similarly, at 200 W, no current was recorded, but difficulties arose during for the lift-off. It is likely that the high plasma power caused the photoresist to crosslink to an extent that made it more difficult to being removed. Unfortunately, neither the mild nor harsh Ar plasma treatments led to any improvement in device performance. Multiple factors could explain this observation; perhaps the Ar plasma is either too weak or too aggressive, possibly leading to surface reactions or decomposition. Additionally, the plasma may cause significant charging or even damage to the device, although none of these hypotheses can be verified.

From the plasma cleaning study, the following conclusions can be drawn: A mild air plasma can help to slightly enhance device performance by removing residues from the surface. However, harsher conditions using Ar plasma do not yield improvements; rather, the opposite effect was observed. An efficient removal of any potential surface oxide layer could not be achieved by any plasma treatment. A possible solution to address this issue of an insulating oxide layer could involve a wet-chemical approach, such as etching with acids.

Wet-chemical etching

The simplest method, closely aligned to existing procedures (see Section 2.2.2), would be to dip the substrate into a HCl solution prior to metal deposition. The HCl would, depending on exposure time and concentration, etch away a fraction of the NW, resulting in a clean surface for contact formation. Such treatments, were utilized on bulk CdS single crystals to obtain ohmic contacts.⁵⁸ Initial experiments conducted with the assistance of Christian von Bredow (student apprentice) demonstrated that HCl could indeed etch the surface of NWs. AFM measurement indicated a reduction in NW diameter following HCl treatment. However, several problems were encountered with this treatment. First, there was no control over the etching rate or depth through the adjustment of etching time or concentration (pH). In fact, longer etching times and lower pH values resulted in generally faster and deeper etching, yet the variance across different NWs was too vast to allow for precise adjustment of the etching rate. Second, etching the entire device led to issues with the photoresist and contact quality. The photoresist detached from the substrate in certain areas, resulting in either shifts in contact position or complete removal of the photoresist. Third, the etching process was performed in solution, requiring subsequent drying of the device; this step often resulted in residues drying on the substrate, which impaired the overall device quality. For these reasons, this approach was not pursued further.

Instead of etching the entire device, a more elaborate and complex approach involves etching the NWs in solution prior to their deposition on the substrate. This method would mitigate the issues

encountered, while ensuring a homogeneous reaction across all NWs. Dufaux *et al.*⁶² have presented a fabrication protocol to obtain ohmic contacts for similar CdS NWs grown *via* a solvothermal method (see Section 6.2). A schematic illustration of the procedure and the surface conditions of the NW, based on the work of Dufaux *et al.*⁶², is shown in Figure 4.5 (a).



Figure 4.5: Influence of the procedure proposed by Dufaux *et al.*⁶² on NWs. (a) Schematic cross-sectional view illustrating the NW surface condition throughout the surface treatment, based on Dufaux. (b) *IV*-curves of devices after different steps of the surface treatment. The standard measurement conditions are: room temperature, under air and illumination. Light microscope images of the corresponding devices to the *IV*-curves are shown in the insets with matching outline colors. The scale bar for each image is 5 μ m. Additionally, images of sample vials containing the NW solution are presented following treatment with HCl and ligands.

They attribute weak device performance to an insufficient contact with the CdS NWs, claiming that an CdO layer is present, while we suspect that CdSO₄ may be present at the surface. Nonetheless, the first step in this protocol is to remove the oxide layer by etching with HCl. The etched surface is then stabilized and protected by adding a covalently binding thiol ligand (thioglycerol), with excess ligands being removed through washing steps. After the deposition of the NWs onto the substrate, the ligands are removed by annealing under argon atmosphere at 350 °C, yielding NWs with a clean surface. Dufaux *et al.*⁶²also note that this process alone is insufficient to achieve an ohmic contact to Ti, indicating that an additional Ar plasma treatment is necessary prior to metal deposition.

In this work, the proposed procedure was evaluated by performing measurements after each step. The first device was fabricated using NWs etched with HCl, the second device incorporated ligands, and so forth. This investigation was conducted with the assistance of Brian Jessen (student apprentice). Unfortunately, the Ar plasma step has not been adequately described in the literature, so a suitable parameter set had to be estimated. The same conditions established in the previous chapter (PECVD setup: P = 200 W, p = 0.4 mbar, t = 2 min, f = 27.12 MHz, pulse = 100 ms at 50% duty cycle) have been chosen for application to all devices. The transport properties of these devices are presented in Figure 4.5 (b).

The first observation was that the NWs treated with HCl exhibited reduced colloidal stability, as shown in the top left corner of the first plot Figure 4.5 (b). For the device fabrication, similar issues arose as previously experienced with the Ar plasma treatment. Residues of photoresist are visible around the contact in the inset. In electrical transport measurements, NWs treated with HCl did not show any current. Upon addition of the ligand thioglycerol, the NWs immediately regained their colloidal stability (see inset second plot). Furthermore, the transport properties improved significantly, as linear and symmetric IV-curves were recorded, despite challenges encountered during the metal deposition. Unfortunately, the deposition chamber overheated during the deposition process, leading to an unknow extent of oxidation of the contacts upon venting, as evidenced by the dark color of the contacts (see the device inset). For the NWs which were annealed after deposition, no current was recorded. These devices encountered the same issue as the previous device, since the metal was deposited in the same batch. The complete procedure was repeated and tested for In/Au contacts as well. These NWs demonstrated similarly good transport properties as the Ti contacts without heating. Again, a familiar dependence on the alignment of the second deposited film was observed, similar to the Ti/In combination. If both layers are not properly aligned, and Au contacts the NW on one side, that contact becomes less conductive, resulting in asymmetric *IV*-curves.

In conclusion, the procedure proposed by Dufaux *et al.*⁶² can successfully produce devices with ohmic contacts under certain conditions. The removal of ligands through annealing resulted in a complete loss of conductivity for Ti contacts, which could be compensated by In/Au contacts. Given that the Ar plasma treatment was applied to all devices, it is assumed that the plasma alone is not effectively removing the oxide layer, but it can enhance the transport properties when paired with wet-chemical etching.

Another proposed surface treatment for bulk CdS single crystals to obtain ohmic contacts with any metal involves bombarding the sample with electrons prior to metal deposition (see Section 2.2.2).⁵⁶ Dufaux *et al.* referenced this report to prove the necessity of an Ar plasma treatment after the wet-chemical etching. Consequently, electron bombardment was investigated as an alternative to Ar plasma. Due to the lack of specific definition and experimental parameters in the literature, suitable parameters had to be estimated. A scanning electron microscope was utilized as electron source, operating at an acceleration voltage of 20 kV, and the devices were irradiated for 2 min before metal deposition. For Ti contacts, no current was measured. For In contacts, a small current was recorded, but this response was inferior compared to that of other In contacts. For this reason, electron bombardment was not studied further.

One crucial aspect that has been overlooked thus far is the tendency of the nanowire surface to oxidize, as indicated by the XPS study, which suggest that $CdSO_4$ is present (see Section CdS nanowire surface). Additionally, numerous reports in the literature document the oxidation of $CdS_{100-102}$ Therefore, the time interval between the surface treatment and metal deposition is critical. In all previously presented cases, the treatment was performed in a separate setup, and the samples had to be transferred to the physical vapor deposition (PVD) chamber for deposition. Although efforts were made to minimize this transfer time, the minimum interval between treatment and vacuum in the PVD chamber is approximately 2 min. This duration provides the freshly cleaned, potentially more reactive, nanowire surface sufficient time to oxidize again, thereby negating the effect of the preceding treatments. To address this issue, either a transport chamber with conditioning should be utilized or, ideally, treatment and deposition should occur within the same device. Unfortunately, access to such options is limited in the institute. Currently, the only available option is the sputtering system, which employs Ar ions for etching and sputtering.

Combining surface treatment with direct metal deposition

The sputtering system is utilized to directly deposit the metal following the surface treatment. The system operates using Ar ion guns, which emit Ar ions that may be accelerated toward either the sample or metal targets. When the etching gun is used, Ar ions are directed onto the sample or substrate, where they initially collide with and then remove surface atoms. This process results om a slow and homogenous removal of the sample surface. This type of etching is termed Ar etching and is classified as physical etching, as it does not occur in solution and does not involve chemicals, in contrast to etching with HCl. During his internship, Christian von Bredow investigated the removal rates using AFM for both HCl and Ar etching. A more uniform, controllable, and clean etching process was observed for Ar etching compared to HCl, demonstrating its potential as a promising treatment method.

In addition to the etching gun, the sputtering system is equipped with two sputter guns that direct Ar ions at a metal target. This results in the removal of metal atoms that then condense on the substrate. This process enables rapid deposition of metal films. Although, the resulting metal films are not as smooth and uniform as those deposited using PVD.

To prevent oxidation of the treated NW surface, the sputtering system is utilized without breaking the vacuum in between. Initially, a few nanometers of the surface are removed through Ar etching, followed directly by the deposition of a metal film through sputtering. The conditions of Ar etching were optimized to remove approximately 2 nm of material. Titanium, In and Mg were evaluated as contact metals for this surface treatment, and the resulting devices, along with their *IV*-curves, are presented in Figure 4.6.



Figure 4.6: *IV*-curves of NWs after argon etching and direct deposition of various contact metals. The standard measurement conditions are: room temperature, under air and illumination. Light microscope images of the corresponding devices to the *IV*-curves are shown in the insets with matching outline colors. The scale bar for each image is 5 μ m.

The first Ti contacts fabricated (gray curve) demonstrate a linear and symmetrical *IV*-curve while exhibiting a good metal film quality. The parameters used for Ar etching were E = 1.7 keV, $I = 10 \ \mu$ A, t = 20 s. To explore whether a reduction in beam energy could yield comparable results, the Ar etching was repeated with 1.4 keV. Furthermore, an alternative photoresist was used due to complication with encountered during the lift-off with the previous photoresist after Ar etching, potentially resulting from crosslinking of the photoresist, similar to the issue observed with Ar plasma. The device fabricated using this modified procedure, along with the corresponding *IV*-curve, is depicted in red in Figure 4.6. Unfortunately, no improvements were observed; no current was measured and the metal film exhibited significant roughness accompanied by

significant fencing. For In contacts, the initial parameters were again applied, with a beam energy of 1.7 keV. This device did not show any response and displayed insulating contacts, as confirmed by KPFM. Indium deposition presents intrinsic challenges due to the dewetting (see previous Section: Contact material). Despite the film appearing smoother in comparison to that shown in Figure 4.2 (a), it still exhibited very fine grains. Significant voltage drops at these grains were detected using KPFM, resulting in insufficient bias reaching the NWs. Consequently, due to insulating contacts, the effectiveness of the treatment could not be evaluated for In. Lastly, Mg was studied in conjunction with Ar etching, despite the concerns regarding oxidation of Mg afterwards. Linear and symmetric *IV*-curves were again recorded, with acceptable currents obtained at increased electrode distances (> 6 μ m). The resulting metal films are comparably smooth (as achievable with sputtering), and the lift-off was comparable to the Ti device. This finding indicates that Mg presents a viable option as contact metal.

In summary, Ar etching has proven to be a reliable and controllable method to remove not only contaminants but also several nm of the NW surface, if correct parameters are selected. Therefore, direct metal deposition *via* sputtering may effectively mitigate or prevent reoxidation of the NW surface, thereby enabling ohmic contacts with Ti and Mg. Conversely, sputtering of In proves unfeasible due to the resulting insulting contacts. Additionally, the challenges related to lift-off must be considered for all metals.

Splitting In/Au deposition into two steps

Before transitioning from treatments conducted prior to metal deposition to those performed afterward, an intermediate process is briefly introduced. As previously demonstrated, the combination of In with Au is very promising but presents the challenge of asymmetric transport when Au is in contact with the NW. This issue can be effectively addressed by dividing the fabrication into two steps: first, a broader contact is defined lithographically, followed by the deposition of In. Second, the lithography is repeated with a thinner contact, followed by Au deposition. This two-step approach ensures adequate separation between Au and the NW, when careful aligned is maintained. Note that this procedure increases complexity due to the additional processing step, but it also presents another advantage. As the photoresists are baked at elevated temperatures, and substrate holder heats during Au deposition, diffusion of In into the NW surface becomes feasible possible. This interdiffusion can have similar effects as doping and lead to a reduction of a potential Schottky barrier (see Section 2.1.2 and 2.2.2).^{47,58,65,103} In fact, devices with In/Au contacts that were deposited separately have shown ohmic transport properties, as detailed in the Chapter 4.2.2 Charge-Carrier Distribution of Locally Illuminated CdS Nanowires.

Annealing

As previously mentioned, the influence of treatments performed after metal deposition is now studied. Similar to CdSe (compare with Section 4.1.1), the annealing process is anticipated to smooth the metal-semiconductor interface and remove residues from lithography (see Figure 4.1).Moreover, annealing may promote interdiffusion of the metal, resulting in doping of the interface and a decrease in the contact resistance.^{47,58,65,103} The effect of annealing was investigated for most contacts (including various treatments); in this case, comparisons are made with the first devices that underwent no treatment (with exception of Ti (red), In and Mg). The devices and their respective transport properties before and after annealing are illustrated in Figure 4.7.

The Ti devices were annealed in a custom-build annealing oven under vacuum conditions (30 min at 150 °C + 30 min at 300 °C). The untreated Ti contacts (depicted in grey) exhibited no charge

transport neither prior to annealing nor afterward. The Ti device treated with Ar etching (red) displayed high currents before annealing, which nearly vanish afterward (1 h at 300 °C). No changes in topography were observed for the Ti contacts; thus, the loss of conductivity cannot be attributed to alterations in the contact metal and likely originates from changes in the NWs.

Similarly, the In device (shown in purple) demonstrated some conductivity prior to annealing, which was lost afterward. The In device was annealed in the PECVD setup under vacuum for 30 min at 150 °C and for 30 min at 325 °C. In contrast to Ti, a significant change in topography was observed for In. The contacts became flatter, and a diffusion into the Au contact pads was noticed. It is possible that the high temperature induced some form of alloy formation between the two metals.¹⁰⁴



Figure 4.7: Measured *IV*-curves of NWs before and after annealing. Annealing was performed differently for the devices. The Ti devices were annealed in annealing oven at 300 °C und vacuum, the In device was annealed in the PECVD setup at 325 °C under vacuum, the other devices were annealed in the Linkam stage at 150 °C/ 300 °C under nitrogen atmosphere. The measured current is represented in saturated colors prior to annealing and in darker colors after annealing. The standard measurement conditions are: room temperature, under air and illumination. Light microscope images of the corresponding devices to the *IV*-curves are shown in the insets with matching outline colors. The scale bar for each image is 5 μ m.

For the Mg device (illustrated in turquoise), the annealing was conducted in a probe stage that allows control over the environment and temperature (referred to as Linkam stage). The significant advantage of using the Linkam stage for annealing is the capability to monitor the current throughout the heating process. The device was annealed under nitrogen atmosphere for 30 min at 150 °C and for 1 min at 300 °C. During the heating to 150 °C, an increase in current was observed, which can be attributed to thermal excitation and a subsequent increase in excited charge carriers – a phenomenon that will be elaborated further in the next section (see

Section 4.2.1). However, upon further heating to 300 °C, just prior to reaching 300 °C, the current abruptly dropped to zero. Consequently, the annealing process was stopped immediately, explaining the short annealing duration of 1 min at 300 °C. No topographic changes were observed for the Mg contacts.

Given that all devices subjected to annealing at 300 °C or higher lost their electrical conductivity, it is likely that a reaction is induced within the NWs. Reports suggest that accelerated oxidation and other decomposition reactions of CdS may occur at elevated temperatures.¹⁰⁰⁻¹⁰² Although efforts have been made to minimize oxygen exposure by conditioning the chambers – alternating several times between vacuum and inert gas – complete exclusion of oxygen, and thus oxidation, could not be guaranteed. Therefore, all subsequent annealing procedures were performed at 150 °C.

For the metal combinations Ti/Ag (blue), Ti/In (green) and In/Au (dark yellow), annealing was performed in the Linkam stage under nitrogen flow for 30 min at 150 °C, while simultaneously monitoring the current. In the case of Ti/Ag, only a few NWs were measured due to decomposition of the metal contacts was observed. The Ag layer started to show dewetting after annealing, indicating instability at elevated temperatures. Chi *et* al. have also observed dewetting of Ag films upon annealing.⁹⁴ The measured NW displays a asymmetric and nonlinear *IV*-curve before and after annealing that, as previously suggested, is a result of the asymmetry of the silver interface. The inversion of the *IV*-curves can be explained by a change in the source and drain configuration of the contacts between measurements.

The only device to show consistent improvement with annealing was the Ti/In device. For nearly all measured NWs, conductivity increased following annealing, likely due to successful interdiffusion of In into the metal-semiconductor interface, as the temperature of 150 °C is insufficient to induce unwanted reactions in the NW or between In and Au (contact pads). This observation is further confirmed by the In/Au device, where no changes in topography or reactions with the Au contact pads were observed after annealing, while the measured current increased. It is important to note that the *IV*-curve presented is not completely comparable with the others, as it was recorded immediately after annealing. It has been observed (also for other devices) that thermal excitation decays slowly, resulting in considerably higher currents immediately after annealing compared to measurements taken, for instance, 10 min later (see Figure 4.10). Unfortunately, no further measurements were conducted with the In/Au device, as only one NW showed any response prior to annealing. The asymmetry of the *IV*-curve in this case can again be explained by the asymmetry of the contact interface (Au vs. In in contact to the NW). In summary, annealing above 300 °C should be avoided, as it negatively impacts device performance. The observed loss in electrical conductivity can likely be attributed to oxidation and other decomposition reactions at elevated temperatures. Conversely, annealing at lower temperatures, such as 150 °C, may yield slight improvements in device performance. Notably, these enhancements have been exclusively observed in contacts containing In, suggesting that interdiffusion of In into the interface may reduce the contact resistance. Special care must be taken when annealing contacts containing In and Ag, as their mobility can lead to dewetting and diffusion into the Au contact pad, resulting in non-conducting metal contacts.

Evaluation of all treatments and contact metals

After presenting the various metals used for contact and surface treatments applied before and after metal deposition, it remains unclear which procedure yields the most optimal contact. As previously indicated, no contact is universally suitable for all applications. Therefore, the specific requirements for the application and operating conditions must be considered when determining

the optimal contact. In this work, an ohmic contact characterized by high electrical conductivity σ , stability against chemical reactions, and reproducible fabrication is required for effectively monitoring the CE reaction from CdS to Ag₂S.

Given that high σ is essential, the contacts (devices) are compared based on their respective σ . A direct comparison using *IV*-curves is impractical; improvements in device fabrication have allowed, for example, for larger electrode distances, which leads to variations in devices geometry that hinder direct comparison. To facilitate a more precise evaluation of the devices, the σ is calculated from all measured IV-curves (see Section 3.1). Since the surface treatments were studied and no modification to the NW composition or measurement conditions were introduced, the nanowire resistance R_{NW} is expected to remain constant. Consequently, variations in the total resistant R_{Total} should primarily result from changes in contact resistance R_{C} . Furthermore, it was frequently observed that only a few NWs formed a good contact, while the majority displayed insulting behavior. Although comparing solely the best NWs can yield values that closely align with the intrinsic properties of the NWs – especially when $R_{\rm C}$ approaches negligible values resulting in $R_{\text{Total}} \approx R_{\text{NW}}$ – this does not provide insights into reproducibility or yield. This can be addressed by considering all NWs and calculating the average and median σ along with the standard deviation. Given that the obtained values vary across multiple orders of magnitude, the statistical calculations were performed using the logarithmic values. In cases of negative σ , likely caused by leakage currents or other charging effects, the value is set to $1\cdot 10^{-6}$ S/m, representing the lowest measurable σ . Figure 4.8 presents the results of this analysis for all studied contact types before and after annealing.



Figure 4.8: Comparison of all presented contact types and devices based on their electrical conductivity. Given the extensive range of conductivities, the logarithmic values are plotted. The obtained electrical conductivity for every NW is depicted as a small symbol (data), and from these data, the mean value with a standard deviation was calculated, represented as a box with the mean indicated as a center line. Furthermore, the median was calculated and is displayed as a large symbol. To facilitate the comparison of devices before and after annealing, they were plotted in the same column, following the style of the previous figure, with the data represented in bright colors before annealing and in darker colors afterward. A gray box indicating the resolution limit of the setup (corresponding to $R > 10 \text{ T}\Omega$) is positioned behind the data to enable direct identification of insulating devices.

The discussion begins with Ti devices, as the majority of treatments were applied to them. Among the nine contact types presented, only two procedures consistently yielded ohmic contacts with moderate σ , as evidenced by the median (depicted as corresponding large symbol) being positioned above the gray box, which indicates the resolution limit of the measurement setup. Other contact types may have exhibited one or two NWs showing a response, but these were frequently nonlinear and asymmetric. For the Ti contacts, the best average and median σ were achieved through the ligand treatment followed by Ar etching. With σ in the range of 2.66·10⁻² S/m, these measurements are slightly below literature values for bulk CdS (3.37·10⁻¹ S/m,⁵⁸ and see Table 4.2) and comparable to other CdS NWs (1.92·10⁻¹ S/m^[105] – 1·10⁻⁴ S/m^[106]). Devices that underwent annealing consistently exhibited poorer responses afterward, indicating that annealing is inadvisable for Ti devices.

The combination of Ti with Ag or In yielded conductive devices even without surface treatments. However, the *IV*-curves measured for Ti/Ag were all nonlinear and showed evidence of electromigration. Furthermore, during annealing process, dewetting and Ag diffusion (see Figure 4.16) was observed, rendering Ti/Ag contacts unsuitable for CE experiments. In contrast, Ti/In contacts demonstrated reliably linear and symmetric *IV*-curves, which could be slightly improved through annealing. A median σ of 1.68·10⁻² S/m was determined, which is marginally lower than that of Ti contacts with ligand treatment.

In contrast to the Ti devices, almost all In devices exhibited ohmic behavior. Only the Ar etching produced non-conductive devices, attributed to poor films resulting from sputtering rather than the treatment itself. The highest median σ (1.78·10⁻² S/m) was obtained for the devices with pure In contacts without any surface treatment, placing it between the Ti and Ti/In devices. After annealing at 300 °C, all devices experienced a significant decrease of σ , and diffusion into the Au contact pads/ alloy formation were noted. Unfortunately, no experiments were conducted at lower annealing temperatures (150 °C), even though experiments with Ti/In and In/Au showed promising improvements. Therefore, no definitive recommendation for annealing of In devices can be given.

Combining In with Au may help to mitigate issues related to resistive In films (due to dewetting), provided the alignment of the Au layer is executed correctly. However, during initial fabrication, achieving this alignment proved challenging (one-step deposition), resulting in many insulating contacts. As a consequence, the obtained median σ of devices with pure In/Au contacts is as low as $1.00 \cdot 10^{-4}$ S/m, approaching the insulating range. With more experience and implementation of the ligand treatment (labeled with heat), it became possible to reliably obtain ohmic contacts with a median σ of $1.08 \cdot 10^{-2}$ S/m. Notably, the smaller standard deviation compared to other devices with In contacts indicates a more robust fabrication process. Annealing was performed with only one device, and measurements were conducted immediately afterward, distorting the results due to thermal excitation. Consistent with the later fabricated two-step In/Au contacts, a mild annealing below 200 °C is considered to be beneficial.

Lastly, the device with Mg contacts (Ar etched) demonstrated the highest overall median σ of 5.55·10⁻² S/m, accompanied by a very narrow standard deviation, making them a promising candidate for further studies. As with the other devices, annealing at 300 °C resulted in significant decrease in σ ; the effect of a low temperatures annealing is hard to estimate.

In summary, it is feasible to obtain ohmic contacts with three contact metals: Ti, In and Mg. Depending on the age of the NWs and the extent of surface oxidation, certain surface treatments are necessary. In this regard, wet-chemical etching (ligand treatment) and physical Ar etching yielded the highest median σ with a narrow standard deviation. For further investigation in this work, devices with Ti/In, In/Au and Mg contacts were used.

4.2. Electrical Properties of CdS Nanowire-based Devices

In this chapter, a selection of previously presented devices is utilized to demonstrate the optoelectronic properties of the NWFETs. First, a fundamental characterization of the NWFETs is

performed to identify essential parameters, including the electrical conductivity σ , charge-carrier mobility μ and concentration n. Furthermore, the response of the NWFETs to environmental changes, such as illumination, chemical environment and temperature, are investigated. In the second part, the charge-carrier distribution under local illumination is briefly highlighted, with primary focus on the device design and fabrication to facilitate such complex measurements.

4.2.1. Electrical Transport in CdS Nanowire Field-Effect Transistors

Transistor characterization

The theory background has provided the essential concepts necessary to understand and explain the electrical transport in nanostructured semiconductor devices (see Section 2.1.3 and 3.1). In the previous chapter, the electrical transport through the devices was utilized as a basis for evaluating the different contact materials and treatments. In this section, a concise overview of the retrieval of the transport properties is presented and compared to similar devices in literature. For this investigation, the device using Mg contacts is studied. The measured *IV*- and back-gate sweeps are illustrated in Figure 4.9.



Figure 4.9: *IV*- and transfer characteristic of a NWFET with magnesium contacts. (a) *IV*-curve and (b) back-gate sweep of the NWFET. The standard measurement conditions are at room temperature, in air and under illumination (bright, saturated color; if not illuminated dark, lighter color). The applied linear fit for calculations is shown in red. A light microscope image of the corresponding device to the measurements is shown in the inset. The scale bar is set to 5 µm.

As demonstrated in previous figures, essentially no current is observed under dark conditions; only upon illumination is a symmetrical and linear *IV*-curve recorded (Figure 4.9 (a)). By applying a linear fit and considering the device geometry, σ was calculated (see Section 3.1Electrical Transport). The determined σ is $8.59 \cdot 10^{-6}$ S/m in the dark and $6.38 \cdot 10^{-2}$ S/m under illumination. The back-gate sweeps show an increase in current with increasing gate bias, indicating n-type character of the NW, consistent with the expectation from the literature.^{24,41,107} Notably, even without illumination, a current could be measured at higher gate voltages. Both curves exhibit a significant hysteresis when transitioning from increasing to decreasing bias. Hysteresis in transfer curves is not uncommon for NWFETs and is often attributed to the charging of the surface or trap states.^{108,109} Although the measured transfer curves are not strictly linear, a linear fit was applied to the linear region to estimate μ_e and n_e . With the common assumption for n-type semiconductors, that $n_e \gg n_h$ (see Section 3.1), an μ_e of 9.32·10⁻³ cm²/Vs and an n_e of 4.27·10¹⁷ cm⁻³ were determined under illumination. Interestingly, in the dark, a lower yet comparable μ_e of 5.99·10⁻³ cm²/Vs was determined, whereas n_e with 8.95·10¹³ cm⁻³ is four order of magnitudes lower. This observation is consistent with earlier explanations stating that σ

increases due to an increase in available charge carriers. The obtained values are compared in Table 4.2 to literature values reported for similar devices.

Table 4.2: Comparison of calculated electrical conductivity σ , electron mobility μ_e , and electron concentration n_e , under consideration of the contact metal and a potential treatment, with literature reports. To ensure comparability, the listed values were obtained from measurements under ambient conditions (air, rt, illumination, unless otherwise noted). In cases where measurement conditions are not detailed, ambient conditions are assumed.

System	Metal	Treatment	σ	$\mu_{\rm e}$	n _e	Notes
			(S/m)	(cm ² /Vs)	(cm ⁻³)	
		-		3.50·10 ²		Ref. 41
Bulk	-			3.16·10 ²	2.9·10 ¹⁶	Ref. 110
			$1.10^{-5} - 1.10^{-3}$			Ref. 48
Thin Film ¹⁰⁰	-	-	4.10·10 ⁻²	3.16.100	2.48·10 ¹⁵	
Nanobelt ⁷⁷	In/Au	None	(3.6-5.4)·10 ⁻¹	(2.3-3.2)·10 ²	(3.8-8.2)·10 ¹⁶	
Nanowire	М	Are stales d	8.59·10 ⁻⁶	5.99·10 ⁻³	8.95·10 ¹³	Dark
(This work)	Mg	Ar etched	6.38·10 ⁻²	9.32·10 ⁻³	4.27·10 ¹⁷	Bright
Nanowire ¹¹¹	In/Au	None	5·10 ⁻⁷ – 5·10 ⁻⁶			Dark
			3.7·10 ⁻³			Bright
	In/Au	Cl doping	1·10 -5 - 5·10 -1	(1.8·10 ⁰)	1.4·10 ¹⁴	Dark
			$1.10^{\circ} - 6.10^{1}$	$1.8 \cdot 10^{0}$	1.1·10 ¹⁸	Bright

In the literature, the values reported for the transport properties of CdS stray enormously, heavily influenced by factors such as the sample preparation (*e.g.* synthesis, device fabrication) and measurement conditions. In particular, the significant effects of air and light on these measurements are frequently highlighted.^{52,107,111} To ensure comparability, only results obtained under ambient conditions (in air, at room temperature and illumination by room light or sunlight) were included in the table and discussion. For single crystal CdS (bulk), σ of up to 10^{-3} S/m,⁴⁸ μ_e in the range of 10^2 cm²/Vs,^{41,110} and n_e around 10^{16} cm^{-3[110]} have been reported. When the dimensions are reduced, σ tends to decrease, accompanied by a reduction in μ_e , while n_e appears to remain relatively constant (see Table 4.2). Nanoscopic devices under illumination exhibit conductivities comparable to macroscopic devices, although significantly lower conductivities are observed under dark conditions, with reported dark-to-photocurrent ratios ranging from 10^3 to $10^{5,52,110}$

For nanobelts, μ_e comparable to those of bulk CdS have been reported, whereas lower values have been determined for nanowires, which align more closely to those of thin films. In contrast, NWs present higher n_e , in some cases even exceeding bulk values. It is important to note that these elevated values for μ_e and n_e for NWs compared to those found in this study, likely arise from the Cl-Doping, as the undoped NWs exhibit similar conductivities. Unfortunately, data regarding μ_e and n_e for the undoped NWs have not been reported. Additionally, Wu *et al.*¹¹¹ assumed that μ_e remains constant for the NWs, using this assumption to derive n_e under dark conditions. Overall, the values determined for the NWs presented in this work appear to be within a reasonable range for CdS NWFETs, with a lower mobility μ_e but higher carrier concentration n_e .

A final remark must be made regarding the extraction of the values presented in Table 4.2. The obtained values dependent not only on the measurement condition but also on the measurement

type (*e.g.*, hall-bar, van-der-Pauw, or FET) and the various device configuration used. Wu *et al.*⁷⁷ compared back-gate and top-gate configuration, finding that top-gate nanobelt FETs exhibited a higher transconductance and lower hysteresis. Furthermore, Schwarz demonstrated that the gate coupling in NWs is relatively weak due to the limited interface with the substrate compared to a surrounding gate.⁴⁰ This factor must be considered when calculating the capacitance, as it subsequently effects the values obtained for μ_e and n_e . To properly estimate the device capacitance, finite element simulations based on the method from Schwarz⁴⁰ were utilized, while literature reports typical used the common approximations for FET devices,^{77,111} inevitably leading to deviations.

The observed low overall σ and even lower dark σ , coupled with a pronounced response to external excitation, such as illumination, can be attributed to the intrinsic properties of the used CdS NWFETs. First, CdS has a large band gap of 2.5 eV,⁴¹ and in combination with the synthesis yielding highly crystalline NWs with minimal stacking faults, there are few mid-gap states available. Second, a spectroscopic study conducted on the NWs in previous work⁵³ revealed only weak trap band fluorescence, indicating a low trap state concentration.⁴³ These defects can function as donor states, donating electrons and thus enhancing σ .^{43,77,107} It should be noted that several resistances were neglected in these calculations (see Section 3.1Electrical Transport). While these resistances may be significant in certain cases, they are expected to be several orders of magnitude smaller than the resistance of the NW ($R << R_{NW}$). Therefore, the values determined may be marginally lower than the actual values, but this discrepancy is negligible. The same consideration applies to the various assumptions made during analysis.

Given the strong response to external excitation, CdS nanostructures are extensively researched for a variety of optoelectronic applications, such as solar cells and photocatalysis.^{24,52} 1D-nanostructures, such as NWs, are particularly promising due to their high surface-to-volume ratio in combination with their macroscopic lengths, which facilitates straight forward device fabrication. Consequently, the following section demonstrates the sensory capabilities of the fabricated CdS NWFET.

CdS NWFET as sensor for light, oxygen and temperature

To demonstrate the sensory properties of the NWFETs, a device with Ti/In contacts was used, as the previous study have indicated their stability at elevated temperatures. The recorded *IV*-curves of this device under different conditions are presented in Figure 4.10. The influence of optical excitation has been demonstrated multiple throughout times in this work. Upon optical excitation, new free charge carriers are generated, which can subsequently contribute to charge transport.²⁴ Due to the limited availability of "free electrons" in large band-gap semiconductors, the response to light becomes significant.²⁴ Under illumination, both radiative and non-radiative processes compete with one another.⁵² Therefore, when utilizing charge transport, efficient charge-carrier separation is important. In previous work,⁵³ it has been shown that the fluorescence intensity of the CdS NWs is indeed decreased in NWFETs compared to isolated NWs. Here, it is demonstrated that the measured current consistently increases with increasing illumination intensity (see Figure 4.10 (a)). It should be emphasized that this finding primarily indicates the intensity dependence rather than being a sophisticated study, as the light source is just a white-light LED without further optical element. The brightness was adjusted using a control knob with the following settings: off (gray) – middle (red) – on (blue). For a clear intensity (power) dependence, a laser with a specific wavelength should be utilized, where the brightness is adjusted via a power controller and monitored by an external power meter. Such a study was conducted by Littig et *al*.¹¹² for an ensemble of CdSe NWs.



Figure 4.10: Measured IV-curves of a NWFET with Ti/In contacts under various environmental conditions. (a-c) All measurements are performed in the Linkam stage under varying (a) illumination, (b) atmosphere conditions, and (c) before and after heating. For reference and clarity, the curve with the same setting is transferred to the subsequent panel; for instance, the blue curve was taken under illumination and is transferred into the next panel, indicating that all curves in that panel were obtained under illumination as well. A light microscope image of the corresponding device to the IV-curves is shown in an inset. The scale bar is set to 5 µm.

In addition to the light response, the response to oxygen was investigated. In the Figure 4.10 (b) *IV*-curves under different environmental conditions are presented. These measurements were conducted using a probe stage (referred to as Linkam stage), allowing for the modification of the chamber environment. Under standard condition, measurements are performed in air, but the system can also be connected to a N₂-supply, enabling N₂ flow through the chamber. As oxygen is replaced by nitrogen (green curve), the measured current increases compared to the measurement conducted in air (blue curve). When the chamber is purged with fresh N₂ (directly sublimated form liquid N₂), the current increases further (violet curve). This observation indicates that the NWs are responsive to their chemical environment.

Multiple reports in literature describe 1D nanostructured semiconductor gas sensors based on such as CdS or ZnO.^{21,52} Often, the sensing mechanism is attributed to adsorption and desorption of oxygen from the NW surface, which extracts electrons from the NW.^{21,48,107} The CdS NW surface is generally expected to be Cd-terminated, exhibiting a significant number of S-vacancies (V_S), which are anticipated to donate electrons (see Section 2.1.1).^{77,107} When oxygen adsorbs on to the NW surface and withdraws these electrons, the overall number of free electrons decreases, resulting in a reduced σ . Conversely, when the adsorbed oxygen is removed, the number of free electrons increases, leading to a rise in σ , which aligns well with the observations made. The removal of oxygen can be accelerated through conditioning (cycles of vacuum and inert gas) or by simultaneously applying heat and purging, which facilitates faster oxygen desorption and increases the availability of free electrons.^{21,48,107} An interesting experiment would involve flowing pure oxygen through the Linkam stage and examine whether the conductivity decreases compared to that measured in air. However, this experiment was not conducted due to the already low currents observed in air and the safety risk associated with handling pure oxygen in conjunction with electrical or heating experiments.

The last excitation studied was thermal excitation. Semiconductors are generally characterized by an increasing conductivity upon heating, transitioning from practically insulating state to a conducting state. Unlike optical excitation, there is no direct excitation of charge carriers over the band gap; instead, the number of electrons in the CB increases due to thermal excitation, accompanied by a slight shift of Fermi level towards the CB (see Eq. 2.4). It should be noted that

these considerations and equations assume equilibrium conditions, which may not be directly transferable to explain results from the measurements due to factors such as illumination.

Figure 4.10 (c) shows that the measured current significantly increases; previously recorded currents were in the pA-regime (violet curve), while after heating the current falls within the nA-regime (golden curve), representing an increase of almost three order of magnitude. Given that the measurements were performed before and after heating, rather than during, the observed increase in current may be attribute to multiple contributing factors. First, as mentioned earlier, heating and purging with an inert gas leads to the removal of adsorbed oxygen, which accounts for part of the increased current. Second, consideration must be given to the timescale of thermal excitation, as evidenced by the decrease in current for the turquoise curve, which was recorded 10 min after the golden curve. The substantial increase in current following heating can be explained by combined effects of oxygen removal and the gradual decay of thermal excitation.

To acquire further insight into the increasing current resulting from thermal excitation, continuous monitoring during the heating would be desirable. In fact, such measurements were performed between the previously discussed measurements (violet and golden curve). For this study, the source-drain voltage was pulsed, and the current was recorded at a set plateau bias. The pulse parameters – including ramping and plateau duration, voltage step size and maximum voltage – were carefully chosen to ensure rapid pulsing without causing sudden bias jumps that could potentially damage the device or interfere with the measurement. In this works, such pulsed measurements are referred to as current-tracks.

Simultaneously with current monitoring, the temperature of the ceramic plate (on which the substrate is placed) was controlled. Again, the settings, including heating and cooling rates and plateau temperature, were chosen to ensure reliable data collection. Accordingly, the heating and cooling rates were set to 10 °C/min, ensuring sufficient time for proper heating and cooling of the stage. For the first heating measurement, which can also be interpreted as annealing (see previous Section Annealing), a plateau temperature of 150 °C was selected. This temperature was maintained for 30 min, in accordance with the other annealing protocols, before the stage was gradually cooled down. The measured current-track is shown in Figure 4.11 (a), with the current depicted gray and the temperature indicated in red.

The first observation regarding the current-track is that the current appears to respond more slowly than the temperature rises. The current exhibits an exponentially increase after approximately 20 min, at which point the maximum temperature has already been reached. Once the maximum current is reached, it remains relatively constant. Upon cooling, the current decreases exponentially, although at a slower rate. Indeed, when the same data is presented using a logarithmic y-axis, the current response of the NW to heating and cooling appears linear, but with different slopes. It is also noteworthy that the current increases immediately upon heating, but this increase – similar to the starting current – falls within the pA scale, explaining the apparent delayed current response on a linear y-axis. Notably, the current after heating does not return to the starting value, a trend that is also reflected in the previous Figure 4.10 and discussed above.



Figure 4.11: Current-tracks (current versus time) for the same NWFET as in the previous figure (Ti/In contacts) under varying temperature. All measurements were performed in the Linkam stage under illumination and under nitrogen atmosphere (if not indicated otherwise). The current-tracks were recorded by pulsing the source-drain voltage (V_{sd}) and recording the current at V_{sd} = 1 V. The temperature of the Linkam stage is depicted in red on the second y-axis. (a) Current-track where the temperature of the Linkam stage is increased to 150 °C, held for 30 min and then cooled down to room temperature. (b) Similar current-track where the temperature was maintained at 160 °C; during this period, illumination was blocked (indicated by gray boxes), and this section is shown in detail in (d), the yellow panel. At the end the stage is vented, this section is shown in detail (e), the blue panel. (c-d) Current-tracks where the illumination is blocked (c) at room temperature and (d) at 160 °C. (e) Current-track at room temperature where nitrogen flow is stopped (blue box) and the stage is vented with air.

To determine whether the difference in timescales (slopes) for increasing and decreasing current are solely attributable to thermal excitation and decay, the current-track was repeated (with a slightly higher plateau temperature of 160 °C) without venting the chamber in between, as shown in (b). It should be noted that the second current-track was measured the following day (with N₂ running), which explains the slightly lower starting current in comparison to the final current presented in Figure 4.11(a). Moreover, Figure 4.10already indicated that the current decay was not complete after the previous current-track. Additionally, during this current-track (Figure 4.11 (b)), illumination was discontinued at the plateau temperature to facilitate a comparison of the response to optical excitation at room temperature (Figure 4.11 (c)); further details regarding the influence of optical excitation will be provided in Section 4.2.2 (Charge-Carrier Distribution of Locally Illuminated CdS Nanowires). For the second current-track, a more rapid increase in current was observed, accompanied by a similar decrease. This finding clearly indicates that during the initial heating, not only thermal excitation but also removal of oxygen influenced the charge transport. Furthermore, since the current-track was recorded for a substantially longer duration after heating, it can be observed that the current decreases over a period of approximately two hours.

To differentiate between the timescales of optical and thermal excitation, similar current-tracks were recorded in which the illumination is cycled between on and off. The results of these measurements are present in Figure 4.11 (c) and (d). It is evident that the current immediately decreases significantly when the illumination is stopped. Upon illumination, the current quickly recovers and even increases slightly with each cycle, which may indicate that switching occurred too rapidly. A similar response to light is observed at elevated temperatures; however, this response appears to occur more slowly.

To quantitatively analyze these observations, the response time t was calculated, also specified as time constant τ , when considering the response time for 63 % of the maximum response.¹¹³ τ were derived by applying an exponential decay fit to both the decay and rise in current, yielding the decay time constant τ_{decay} and the rise time constant τ_{rise} . At rt, average values for τ_{decay} of 0.867 s and for τ_{rise} of 1.37 s were obtained, indicating that τ_{rise} is approximately 60 % slower than τ_{decay} . This observation may suggest a faster decay of excited charge carriers compared to their generation. At 160 °C, average values for τ_{decay} of 25.8 s and for τ_{rise} of 14.2 s were obtained. In relation to τ_{decay} at rt, this represents an increase by roughly a factor of 30, and a factor of 10 for τ_{rise} . This clearly demonstrates that the response to optical excitation is slower at elevated temperatures, as previously estimated qualitatively. Another interesting finding is that at higher temperatures, τ_{decay} becomes smaller than τ_{rise} , exhibiting an opposite trend compared to that at rt. It is possible that thermal excitation may blocked or saturated relaxation pathways, which may be available at rt.

Another relevant quantity often determined for sensors is the sensitivity, which corresponds to the response to a stimulus and is represented by the slope of response curve (signal *vs.* stimulus intensity).¹¹³ Here, the sensitivity can be estimated by the ratio of the photocurrent (light on) to the dark current (light off), denoted as I_{on}/I_{off} . For both decays, a 60 % to 70 % lower I_{on}/I_{off} was calculated (68.0 at rt and 14.0 at160 °C) compared to the rises (117 at rt and 19.4 at 160 °C). Thus, I_{on}/I_{off} at rt is roughly five times higher than at 160 °C. This further supports the hypothesis that the thermal excitation slows or blocks relaxation pathways that are available at room temperature.

Lastly, the timescale of the influence of oxygen was studied. To this end, a current-track was recorded while venting of the Linkam stage with air (by stopping N₂ flow and opening the chamber); the resulting response is enlarged and presented in Figure 4.11 (e). As expected, the current decreased instantaneously upon venting but exhibits a much slower τ_{decay} of 139 s. This can be attributed to the more complex nature of the reaction, as oxygen must first diffuse to the NW surface, subsequently adsorb to it, and finally extract electrons. Unfortunately, no further switching experiments were conducted with the N₂ and air.

To conclude the sensor section, the CdS NWFET investigated in this work is compared to similar nanostructured photodetectors in Table 4.3. The criteria used to evaluate the photodetector performance include τ_{decay} and τ_{rise} , along with I_{on}/I_{off} . To ensure good comparability, only devices with individually contacted nanostructures were selected. It is important to acknowledge that the values reported in the literature may have been calculated differently than those presented here. However, it is reasonable to assume that the values are comparable.

Table 4.3: Comparison of various nanostructured CdS photodetectors based on their decay time constant τ_{decay} , rise time constant τ_{rise} and photocurrent-to-dark current ratio I_{on}/I_{off} . Furthermore, the contact material and light source (OM = optical microscope) are given for comparability. The values were obtained under ambient conditions unless otherwise specified.

System	Contact	Light source	τ_{decay}	τ_{rise}	I_{on}/I_{off}	Notes
			(\$)	(3)	(a. u.)	
Nanowire	Ti /In	White light LED	0.867	1.37	117	rt
This Work	11/111	White light LED	25.8	14.2	19.4	160 °C
Nanobelt ¹¹⁴	Silver paste	Green Laser	0.846	0.91	105	
Nanowire ¹¹¹	In/Au	White light (OM)	< 1	< 1	10 ³	
Nanowire ¹¹⁵	Pt	White light (OM)	0.320		104	Schottky
	Pt:Ga	White light (OM)	0.572	-	17.55	ohmic

The comparison shows that the literature reports similar or slightly lower τ_{decay} and τ_{rise} . In contrast, significantly higher sensitivities, reaching up to 10^5 have been achieved in other studies.¹¹⁴ These observations can be attributed to the optimization of those devices specifically for the photodetector application, whereas the device presented here was not optimized for that purpose. For example, Wei *et al.*¹¹⁵ have demonstrated that device performance improves when the nanowire is contacted using Schottky contacts. They attribute this enhancement to the formation of Schottky barrier, which results in a low dark current and, upon illumination, yields high currents due to charge accumulation near the contacts.¹¹⁵ These results suggest that nanostructured CdS devices are promising candidates for optoelectronic application.^{24,52}

4.2.2. Charge-Carrier Distribution of Locally Illuminated CdS Nanowires

This chapter outlines the collaborative project conducted in partnership with Moritz Wehrmeister and Carlo Höhmann. The primary objective of this project is to investigate the impact of local illumination on CdS NWFETs under operational (biased) conditions. This project is organized into three sections: device fabrication (Lengle), measurements (Wehrmeister) and simulations (Höhmann). A detailed discussed of the fabrication process is provided, while the contributions of Wehrmeister and Höhmann are summarized concisely.

Combining local illumination with KPFM and simulations

Thus far, the samples have always been illuminated using a white light LED, which illuminates the entire NW. The complete illumination of the NW is defined here as "global illumination". Nevertheless, illuminating the nanostructure with a focused laser beam can provide further insights into device performance and charge-charrier dynamics. Given that the spot diameter is approximately 300 nm, only a fraction of the NW is illuminated; thus, this laser illumination is referred to as "local illumination". In a prior study conducted by the Lauhon group, local illumination was utilized on CdS NW devices to determine the mobility-lifetime product and to demonstrate the different photocurrent responses, based on the metal contacts.⁶³ Schäfer *et al.*¹¹⁶ have taken an alternative approach, by combining local illumination with an EFM study. They demonstrated that in CdSe NWs charges accumulate in distinct regions upon illumination, due to differing mobilities of electrons and holes.¹¹⁶ This result demonstrates the effectiveness of these

measurements for analyzing optoelectronic devices and for revealing potential bottlenecks that may limit the charge transport.

Wehrmeister has enhanced the spatial resolution of the KPFM setup, facilitating a more precise localization of charges within the sample. As introduced in the method chapter (see Section 3.2.3), KFPM enables the direct measurement of surface potential, which is composed of material work functions, applied biases and further charges (for example, originating from excess charge carriers). Theoretically, if the nanostructure is illuminated locally, the excited charge carriers generate an internal electric field that can be mapped directly using KPFM. The amplitude of the charging and its spatial expansion can reveal crucial parameters of the charge-carrier dynamics in the nanostructure.

While these measurements are powerful, they are not without limitations and do not provide all the desired information. The spatial resolution is restricted by the tip dimension and laser spot size. The pyramid-shaped geometry and tip size facilitate a spatial resolution down to a few tens of nanometers. The laser spot size is diffraction limited to roughly half of the laser wavelength (λ = 488 nm). Furthermore, charges originating from other sources than bias or illumination may distort the measurements. These experimental limitations and uncertainties do not apply to simulations. Höhmann models the fabricated devices and simulates their response to local illumination in his thesis, using the software COMSOL Multiphysics[®].⁷⁸ These simulations give access to information that cannot be measured directly, such as the band structure throughout the entire nanostructure along with the corresponding quasi-Fermi levels. While surface conditions, such as ligands or contamination, can be neglected, significant imperfections, such as vacancies or dangling bonds, can be implemented to enhance the model accuracy. Once a reliable and robust simulation is established, it can be adjusted flexibly, enabling configurations that are experimentally tedious or even impossible. For instance, the laser spot size can be reduced below the diffraction limit if desired. Moreover, modifications to the metal contact can be made with a few adjustments, whereas the process of fabricating and measuring a new device with different contacts is notably time-consuming. In summary, simulations are a vital and advantageous addition to the experimental measurements.

Device design and fabrication

In the context of this collaborative project, the fabrication and optimization of the devices are fundamental for conducting this study. Special requirements are placed onto the device to facilitate the combined KPFM and local illumination measurements. To combine KPFM with local illumination, a transparent substrate is essential, as the illumination originates from the opposite direction as the tip. Furthermore, this transparent substrate must also be conductive to enable KFPM measurements, as it needs to be grounded to remove residual charges that may interfere with the measurement. To prevent the applied bias to transferring directly into the grounded substrate, an insulating layer must be deposited on top. In light of these constraints, transparent glass substrates featuring a conductive indium tin oxide (ITO) layer and an insulating silicon dioxide (SiO₂) layer were selected. Detailed information regarding the fabrication of these substrates can be found in the experimental chapter (see Section 6.3). With such a substrate, the NWs can be illuminated from below while the tip can scan from above, allowing for the recording of AFM and KPFM data. Figure 4.12 (a) provides a schematic illustration of the measurement setup, emphasizing illumination from below while scanning with the tip. Additionally, the electrical circuits for the transport and KPFM measurements are depicted in blue and green, respectively.



Figure 4.12: The KPFM setup, the device layout, and light microscopy images of different contact types. (a) Schematic representation of the setup that combines an optical confocal setup with a KPFM setup. The regular circuit (source-drain) is indicated by blue lines, while the KPFM circuit is represented by green lines. (b) Schematic illustration of the device geometry optimized for these measurements, providing a detailed look at the device center and a single NW. (c) Light microscopy images of devices with different contact types fabricated. The contact type is given above the image and the metals used are indicated with arrows.

Combining local illumination with KPFM requires more than just modifying the substrate; it requires the design of a completely new device layout. Generally, it is advantageous to have multiple NWs contacted per substrate to provide sufficient statistics and account for faulty contacts. However, an excessive number of contacted NWs complicates the design and extends fabrication time. Given that the movement of the tip and laser is constrained by the stages, it is preferable to contact NWs as closely as possible to one another and to the center of the substrate. Additionally, the bonds made between the substrate and the chip carrier must be considered. If these bonds situated directly at the center, near the NWs, the AFM head may damage them, resulting in a loss of electrical connection to the substrate. To mitigate this risk, the contacts to the NWs are separated in two areas. First, contacts are established with the NWs in the center and the center field. Second this center field is then connected *via* thin leads to contact pads positioned near the edges of the substrate. Considering the minimum required size of the contact pads for reliable bonding, a maximum number of 16 NWs can be contacted. To prevent defects in the insulating layer from creating a short circuit to the back-gate, the overall dimensions of the contact pads, leads, center field and NW contacts had to be minimized. To ensure a reliable connection to the back-gate for grounding, the insulating layer had to be removed at the corners and large contact pads were added. Taking all the aforementioned factors into consideration, the final layout was obtained, depicted in Figure 4.12 (b) along with a magnification of the center field and a contact to a NW.

As extensively demonstrated in Section 4.1.2 (Contacts to CdS), and reported by Gu *et al.*,⁶³ the type of contacts significantly influence the device performance. To investigate the effect of the

contact type under local illumination using KPFM, three different contact configurations were fabricated: Schottky-Schottky, ohmic-Schottky and ohmic-ohmic. Given that Schottky contacts to CdS can be readily obtained, the double-Schottky configuration can be achieved using nearly any metal. For the formation of a reliable Schottky contact with a high barrier, Pt was selected as contact metal due to its high work function (see Table 4.1). For the double-ohmic configuration In/Au contacts, fabricated using the two-step fabrication, were chosen based on insights derived from the previous Section (Splitting In/Au deposition into two steps). Previous experiments with misaligned In/Au contacts have revealed ohmic-Schottky behavior (see section Contact material and Annealing). This behavior has been attributed to one contact forming a Schottky contact due to a direct contact of Au and NW forming a depletion zone, while the other contact forms an ohmic contact due to direct contact of In and NW. This observation enables the control of the contact type (ohmic vs. Schottky) based on the relative positioning of the Au and In layer, thus circumventing the need for an additional metal deposition step. Consequently, In/Au contacts with a relative offset of In and Au were chosen for Schottky-ohmic configuration. To ensure direct contact of Au on one side and In on the other, the second lithographic step was adjusted to be intentionally offset by 1 µm. An exemplary NW contacted for all three contact configurations is presented in Figure 4.12 (c).

The optimized devices, now fulfilling the requirements for locally illuminated KPFM measurements, can be used for measurements, and the obtained results can be utilized as input for simulations. Given that the KPFM investigation of these devices is a central theme of Wehrmeister's thesis and that the simulations represent a significant part of Höhmann's thesis, the discussion here will be concise, focusing exclusively on the ohmic-ohmic configuration. The following section is intended to provide a preview of our collaborative work and forthcoming publication, as well as for their theses.

Local illumination of NWs with ohmic contacts

First, it is essential to verify whether ohmic contacts to the NW have indeed been established. To this end, *IV*-curves were measured in the KPFM setup under conditions analogous to those in the electrical setup. In the KPFM setup, the measurements were conducted under air atmosphere. As expected, no current was measured under dark conditions. For global illumination, the laser beam was defocused, resulting in a spot size of approximately 6 μ m (\approx NW length), with the power set to 3.48 μ W, yielding a power density of 1.23 \cdot 10⁵ W/m². A linear and symmetric *IV*-curve was recorded, thereby confirming the ohmic nature of both contacts. These measurements are illustrated in Figure 4.13 (a) in the top panel. For local illumination, the laser beam was focused to a spot size of approximately 300 nm, and the power was reduced to 8.7 nW, maintaining the same the power density. In contrast to global illumination, local illumination of the NW near the source or drain contact resulted in IV-curves that did not exhibit strict linearity. These IV-curves are depicted in the bottom panel of (a) and reveal three interesting features: First, the IV-curves displayed different slopes for negative and positive biases. Second, the absolute measured current reaches its maximum at negative bias for source illumination and at positive bias for drain illumination. These features suggest a difference in mobilities for electrons and holes, which aligns with previous observations by Schäfer *et al.*¹¹⁶ and reported bulk values for CdS.⁴¹ Third, both *IV*-curves are asymmetrical with respect to one another, indicating a disparity between the two contacts. Coincidently to the optoelectrical characterization, KPFM data were recorded and are presented in Figure 4.13 (b).


Figure 4.13: Results of the KPFM Investigation of the ohmic device. (a) Measured *IV*-curves of the NWFET under varying illumination conditions. These *IV*-measurements were performed in the KPFM setup under ambient conditions. The illumination source was a 488 nm laser with 8.7 nW of power; for global illumination, the laser was defocused, and the power was increased to $3.48 \,\mu$ W (maintaining the power density). A light microscope image of the corresponding device is shown in the inset with a 5 μ m scale bar. (b) AFM and KPFM scans under varying illumination and bias conditions. All scans are scaled individually to ensure maximum visibility of the features. (c) Profiles of the surface potential extracted from line profiles along the nanowire in the KPFM scans depicted in (b). The line color of the profiles matches the outline color of the scans it was taken from. For the biased case (lower panel), simulations were performed and are indicated in the corresponding color with a dotted line. For clarity, the source and drain contact are indicated by yellow boxes, while the point of illumination is indicated by correspondingly colored arrows.

The AFM scan (b, top) illustrates the dimensions of the investigated NW device, featuring an electrode gap of approximately 6 µm and a NW diameter of 34 nm. Below this, KPFM scans conducted under various illumination and bias conditions are presented. These scans indicate that the NW charges locally positive upon illumination, with the spatial distribution correlating to the laser spot size. When a bias is applied, a gradient from source to drain is observed, as expected for an ohmic device. In the illuminated regions, positive charging is again observed, further confirming the generation of free charge carriers and highlighting differences in their mobilities, which is consistent with the earlier conclusions drawn from the IV-curves. To facilitate a more quantitative discussion of these scans, extracting surface-potential profiles across the nanowire proves beneficial. These profiles, illustrated in Figure 4.13 (c), provide a clearer representation of the previous observations and can be used for the simulation. In the bottom panel of (c), simulation results are shown as dashed lines with the corresponding colors to the measurements. The simulation was optimized to produce results closely aligned with the blue curve (drain illumination at 2 V). By fitting to one measurement (blue), further measurements (black and red) can be predicted when the parameters are carefully chosen. The output of the simulation (dashed black and red curve) aligns well with the measurements, thereby validating the feasibility of this approach. This simulation model facilitates the extraction of critical transport properties, such as electron and hole mobility.

In the forthcoming publication, additional details will be presented regarding the KPFM measurements performed, the data obtained, the development of the simulation model, and the change of transport properties under local illumination. The transport properties of Schottky-Schottky and ohmic-Schottky devices are likely be included in the thesis of Wehrmeister. A comprehensive step-by-step guide on developing a valid simulation model, along with the effects of various parameters, will presumably be addressed in another publication and in the thesis of Höhmann.

4.3. Cation Exchange in Nanowire-based Devices

In this chapter, CE in NWs is investigated using various methods. The first section discusses the CE from CdSe to Ag₂Se. Highlights from the recent publication are presented to demonstrate the potential of tracking the CE using NWFETs. Additionally, the transport properties of completely exchanged Ag₂Se NWs at both elevated and cryogenic temperatures are analyzed. The second part presents the CE from CdS to Ag₂S. Initially, the electrical transport properties of completely exchanged Ag₂S NWs are characterized. The optical properties of these NWs are investigated using confocal microscopy. Furthermore, a novel approach employing KPFM has been developed to monitor the CE reaction in the NWFETs. The results obtained are correlated and validated through a HRTEM study.

4.3.1. Cation Exchange of the CdSe/Ag₂Se System

Tracking the cation exchange with NWFETs

As introduced in Section 2.2.3, CE is a powerful and versatile tool for modifying the composition of nanostructures. One of the earliest reports on the CE for the CdSe/Ag₂Se system was presented by Son *et al.*³⁶ in 2004, where they demonstrated the successful transformation from CdSe to Ag₂Se and subsequently back to CdSe. They also observed that the shape and morphology of the nanostructure remain unchanged when the dimension of the nanostructure exceeds the reaction zone (\approx 5 nm). Since CdSe is a semiconductor with a band gap of 1.7 eV and a low electrical conductivity (below 10^{-3} S/m), while Ag₂Se has a band gap of 0.1 eV and a high electrical conductivity (up to 10⁵ S/m), significant changes in electrical properties are expected during the CE.^{76,117} Dorn *et al.*¹¹⁷ utilized the shape preservation and the drastic change in electrical conductivity to *in-situ* monitor the CE in NW films by measuring the current throughout the entire exchange reaction. Building upon this approach, Schwarz further investigated the CE in individual NWs demonstrating the fabrication of CdSe NWFETs, the CE in such devices, and the superionic phase transition of Ag₂Se NWs.⁴⁰ Based on the results of the exchange tracking from Schwarz and the methodology developed by Dorn, an article promoting a method to monitor CE in NWs through transistor characterization was collaboratively published.⁷⁶ The following sections will highlight certain key findings from the publication.

Most importantly, a method is presented that enables the non-destructive monitoring of the CE at the single-particle level. In contrast to other commonly used electron or X-ray based methods,^{33,34} probing the electrical transport with small bias do not harm the NWs, thus allowing for the investigation of the same nanostructures over the course of the complete reaction. This approach not only reduces uncertainties originating from variations among different nanostructures or different batches but also facilitates morphology- or size-dependent studies, such as the correlation between exchange rate and NW diameter. By performing the CE on devices with multiple NWFETs per device after fabrication, uncertainties arising from device fabrication and slightly varying CE conditions can be minimized. Variations between devices remain unresolved

by this approach, but this issue is diminished due to the reduced number of devices required. Given that CE can be easily performed on existing devices, device characteristics can be modified even after fabrication, making this method perfectly suited for tailoring optoelectronic properties post-synthetically. The potential applications of this method are vast and spans over various material systems with different exchange mechanisms, as illustrated in Figure 4.14.



Figure 4.14: Schematic illustration of the use of single nanowire field-effect transistors in combination with cation exchange to investigate nanowires with various material compositions and properties. Reprinted with permission from *ACS Nano* **2024**, 18, 27, 18036–18045. Copyright 2024 The Authors.⁷⁶

For systems in which CE proceeds homogenously, for instance through doping or alloying, a continuous increase or decrease in current is expected to until complete exchange is achieved. In contrast, for systems exhibiting heterogeneous CE, for instance through a segmented intermediate, distinct features – such as stairs or a sudden transition – are expected in the measured current. The CE in the system $CdSe/Ag_2Se$ is expected to be homogenous (see Section 2.2.3), thus leading to a continuous increase in current.

To monitor the CE in the NWFETs, an *IV*-curve and a back-gate sweep are recorded at every exchange step. As demonstrated in Section 3.1 (Electrical Transport), these data facilitate the retrieval of the electrical conductivity σ , the electron mobility μ_e and the electron concentration n_e , which characterize the electrical transport properties. The *IV*-curves measured after certain exchange steps are shown in Figure 4.15 (a). A clearly increasing current is observed with the progression of exchange time, exhibiting linear behavior. The back-gate sweeps, presented in Figure 4.15 (b), demonstrate a similar trend, with increasing currents. However, the gate response is initially rather weak and improves with ongoing CE. The transistor characterization was conducted for all measured exchange steps, and the resulting σ , μ_e , and n_e are depicted in Figure 4.15 (c). Notably, σ increases continuously over 8 orders of magnitude, consistent with the previous expectations. As μ_e also increases, the increasing σ can be primarily attributed to the increasing μ_e . The most significant changes occur within the first 300 s of CE, while values comparable to bulk Ag₂Se being reached after approximately one hour.

These results not only confirm the feasibility of the proposed approach but also indicate that the cations are mobile enough to diffuse in and out beneath the metal contacts to facilitate exchange. Since exchange below the contacts is crucial for the monitoring the process *via* transistor characterization, a X-ray fluorescence (XRF) study was conducted to confirm CE below contacts. The XRF maps demonstrate the successfully removal of Cd and the presence of Ag beneath the metal contacts (see fig. 4 ref.⁷⁶), thereby validating the assumption of highly mobile Ag ions within the host lattice.



Figure 4.15: (a) *IV* curves and (b) transfer characteristics of a nanowire with a diameter of 50 nm after 20, 400, and 3000 s of cation exchange. All measurements were performed under ambient conditions in the dark. (c) Evolution of the specific conductivity σ , charge-carrier mobility μ_e , and charge-carrier concentration n_e as a function of cation-exchange time from CdSe (0 s) to Ag₂Se (3600 s) for three different nanowires with diameters of 50, 65, and 83 nm. The inset in the top panel shows a magnification of the first 300 s. Reprinted with permission from *ACS Nano* **2024**, 18, 27, 18036–18045. Copyright 2024 The Authors.⁷⁶

Another important factor is the time scale of the CE, as the conductivity significantly changes in the first 300 s, with bulk values being reached only after approximately 3000 s. In contrast, EDX experiments suggest a much faster CE rate. This discrepancy most likely arises from differences in accessibility for the cations – specifically, free surface compared to the buried interface. Coupled with the weak device response observed in the first several hundred seconds, a more detailed analysis of the *IV*-curves was performed. The analysis revealed the presence of a Schottky barrier, which decreases gradually with CE time and disappears after 300 s (see Figure 5 in Reference⁷⁶). This finding, consistent with the XRF results, indicates that CE is feasible beneath the metal contacts; however, the exchange is slower for the buried interface compared to the free surface.

To address the delayed response of the transport properties in the initial stage of CE (< 300 s), the contacts must be optimized. As a reminder, Ti contacts are used in the standard fabrication protocol for CdSe NWs (see Section 4.1.1) and were also utilized in this publication.⁷⁶ The slower response of the current is attributed to the sluggish diffusion of Ag beneath the contacts; therefore, introducing Ag into the metal-semiconductor interface prior to CE should accelerate the device response.

The proposed approach to resolve this issue involves incorporate Ag into the contacts, similar to the Ti/Ag contacts (see Section Contact material). Narrower Ti contacts are deposited as the first layer, followed by wider Ag contacts in the second layer. The thin Ti layer ensures necessary

substrate adhesion, as Ag films do not adhere well to the substrate (see Table 4.1). The wider Ag contacts form the direct contact to the NWs, improving σ and preventing the oxidation of Ti. According to the work functions presented in Table 4.1, this configuration is expected to yield ohmic contacts. In Figure 4.16 (a), the fabricated Ti/Ag contacts are presented alongside a schematic illustrating the contact configuration.



Figure 4.16: (a) SEM image of a device fabricated with Ti/Ag (10/50) nm contacts. The dashed line indicates the regions where both metals are present and where only silver is left. The inset schematically shows the metal contact profile (b-c) Higher magnification SEM images of the NWs. EDX was performed on this fraction of the NW and the determined cadmium and silver content is noted. Additionally, the diameter measured by AFM is given. (d) Current-voltage curves of the two devices shown. (e) The obtained conductivity of these devices (No. 4 and 5) is compared to the devices in the manuscript (No. 1–3) after complete cation exchange with Ti 75 nm contacts. Reprinted with permission from *ACS Nano* **2024**, 18, 27, 18036–18045. Copyright 2024 The Authors.⁷⁶

Figure 4.16 (b) and (c) display higher magnification of the NWs. These devices were characterized immediately after fabrication, prior to the standard post-processing steps of annealing and UV treatment (see Section 4.1.1), to also study the influence of annealing. The obtained *IV*-curves, shown in Figure 4.16 (d), exhibit linear behavior with unusually high currents. A comparison of the σ of these devices (No. 4-5) with those after CE (No. 1-3), presented in Figure 4.16 (e), suggests a complete transformation of the NWs even before CE was performed in solution. EDX analysis (with Ag and Cd contents indicated in Figure 4.16 (b) and (c)) reveals that the NWs are indeed fully exchanged, as their composition is Ag₂Se, with no Cd detected. This transformation is likely attributed to the high mobility of Ag ions within the NW lattice, combined with the elevated temperature during metal deposition, which facilitated the exchange. The complete transformation of the NWs prior to the CE experiments renders this approach and contact configuration impractical.

In addition the previously presented approach, which has been published,⁷⁶ further experiments were conducted to enhance the device response to CE. Attempts were made to control the Ag diffusion from the contacts by reducing the Ag layer thickness in conjunction with subsequent annealing at varying temperatures and durations. Another strategy involved incorporating Ag into the surface of the contact area of the NWs through a brief CE during lithography, just prior to metal deposition. However, the CE could not be confined to the contact area, and the photoresist film was negatively affected by the solvents employed, resulting in poor contact quality. Additional experiments aimed to facilitate cation diffusion during the CE by implementing annealing after

each exchange step. Unfortunately, none of these approaches yielded the desired improvements. These experiments underscore the complexity and challenges inherent in the field of contact engineering.

Transport properties of Ag₂Se NWs

In addition to tracking the CE, transistor characterization can also be used to investigate the transport properties of fully exchanged devices across various aspects. In his thesis, Schwarz conducted a detailed study on the transport properties of Ag₂Se NWFETs, analyzing both the diameter dependence and the influence of temperature.⁴⁰ Furthermore, another publication resulted from the investigation of transport properties upon heating.⁵⁴ The work from Schwarz *et al.*^{40,54} is briefly summarized, to facilitate comparability between transport at cryogenic (studied in this work) and at elevated temperatures.

It was demonstrated that upon heating to approximately 80 °C, the σ of the Ag₂Se NWs exhibits a slight decrease, which underscores the metallic character of the Ag₂Se NWs.⁵⁴ The metallic transport behavior was attributed to the small band gap of 0.1 eV in combination with a high Ag doping concentration resulting from the CE, thereby positioning the Fermi level within the CB.⁴⁰ Upon further heating, a sudden increase in σ is observed between 80 to 100 °C. This phenomenon is attributed to the superionic phase transition of silver chalcogenides from β to α phase,⁵⁴ consistent with a prior report by Junod *et al.*¹¹⁸ for bulk crystals. At elevated temperatures (> 100 °C), the conductivity decreases again, aligning with the metallic nature observed. Upon cooling back to rt, reverse observations are noted, with a transition back to the β phase. A reproducible switching behavior is observed after the first cycle.⁵⁴ Transistor characterization revealed that the increase in σ is accompanied by an increase in n_e and a decrease in μ_e . While the increase in $n_{\rm e}$ can be attributed to thermal excitation and the phase transition, the decrease in $\mu_{\rm e}$ is ascribed to enhanced electron-phonon scattering.⁵⁴ Upon decreasing the temperature to below rt, the measured resistance R decreased with decreasing temperatures.⁴⁰ The decrease in R is primarily attributed to the observed increasing mobility μ_{e} , likely resulting from a reduction in electron-phonon scattering.⁴⁰

As part of the work presented here, transport measurements at cryogenic temperatures were performed in collaboration with the *Paul-Drude-Institut für Festkörperelektronik* (PDI). With the assistance of PD Dr. Stefan Ludwig and Serkan Sirt, transport measurements at cryogenic temperatures were successfully conducted. The cryostat used for these measurements was cooled by liquid helium, allowing for temperatures as low as 4.2 K (-269 °C). The obtained measurement data are presented in Figure 4.17.

To compare the results under cryogenic temperatures, standard measurements (under dark condition) were first performed at the University of Hamburg (UHH). The typical behavior was observed, characterized by a linear *IV*-curve and a transfer curve exhibiting a positive slope with small hysteresis (see Figure 4.17 (a-b) light gray curve). For the σ , μ_e and n_e values of 7.74·10⁴ S/m, 36.4 cm²/Vs and 1.33·10²⁰ cm⁻³ were obtained, respectively. It is important to note that these measurements were conducted with the device inside the chip-carrier (necessary for the following measurements), and a higher σ (1.05·10⁵ S/m) was measured directly after device fabrication (outside the chip-carrier). The slightly lower conductivity observed could be attributed to an increased resistance of the overall system due to the chip-carrier, minor degradation of the NWs during prolonged exposure to air, or a combination of both factors. The *IV*-curve shown in Figure 4.17 (a) in dark gray, recorded at the PDI before the entire system was cooled, demonstrates linear behavior with slightly lower currents, resulting in a slightly lower σ

of $6.72 \cdot 10^4$ S/m. Again, this decrease in σ can be ascribed to either an increase in system resistance, degradation of the NW, or both.



Figure 4.17: Device characteristics of an Ag₂Se NWFET under cryogenic conditions. All measurements were performed at the PDI, except those labeled with UHH. (a) Comparison of *IV*-Curves under standard conditions (at UHH) with those measurements performed at 4.2 K (at PDI, liquid helium cooled) and with an external magnetic field. (b) Transfer characteristics recorded both under standard conditions and cryogenic conditions. A light microscope image of the device is shown in the inset with a 5 µm scale bar. (c) Magnetoresistance measurements performed with varying applied back-gate voltages. All measurements were performed under exclusion of light.

After cooling to 4.2 K, linear behavior is still observed, with an increased current that yields a σ of 7.31·10⁴ S/m (blue curve), which is comparable to the initial measurement at rt at UHH (light gray curve). The increasing σ is consistent with previous observations, further demonstrating the metallic transport behavior of the Ag₂Se NWs. With a magnetic field of -12 T applied (green curve), also linear behavior was observed, but the current decreased to levels even lower than those recorded at rt (dark gray curve), resulting in a σ of 6.68·10⁴ S/m. This indicates that the transport properties of the NWs are sensitive to a magnetic field.

The transfer characteristics, shown in Figure 4.17 (b), recorded at 4 K and at -12 T, differ significantly from those observed at rt. The measured current is more sensitive to the applied back-gate voltage, and notably, the current cannot be suppressed at higher negative voltages, suggesting a high carrier concentration. Additionally, the curves reveal a fluctuating current that recurs in both sweep directions. These fluctuations may be indicative of universal conductance fluctuations (UCF), which originate from disorder (such as grain boundaries or stacking faults) and impurities,¹¹⁹ both of which are very likely present in the NWs. By applying a linear fit to these transfer curves, μ_e was estimated to be 240 cm²/Vs at 4 K and 216 cm²/Vs at -12 T. Both measurements reveal a similar high n_e of $1.90 \cdot 10^{19}$ cm⁻³ (at 4 K) and $1.93 \cdot 10^{19}$ cm⁻³ (at -12 T). Therefore, the increase in σ at cryogenic temperatures can, as previously observed, be attributed to an increase in μ_e while the n_e decreases, reducing the overall increase in σ .

To further investigated the influence of the magnetic field on the transport properties of the NWs, magnetoresistance measurements were performed while sweeping the magnetic field, with the source-drain and gate voltage maintained constant. The resulting curves, shown in Figure 4.17 (c), demonstrate that the current is maximal when no magnetic field is applied. With positive back-gate voltages, the current shifts to higher currents in accordance with the transfer curves presented in (b), approaching saturation above $20 V_g$. Upon application of a magnetic field, the current decreases in both directions (positive and negative) while displaying distinct features or fluctuations. When considering the absolute magnetic field |B|, the features exhibit limited symmetry. These observations further confirm the sensibility of the Ag₂Se NW to a magnetic field.

Kim *et al.*¹²⁰ have reported similar fluctuations in their magnetoresistance measurements, attributing them to Shubnikov–de Haas (SdH) and Aharonov–Bohm (AB) oscillations, which arise from conducting surface states. However, given the limited data available and uncontrolled orientation of the NW in the magnetic field, it is not possible to definitively assign the fluctuations observed in this study to either SdH or AB oscillations. Further investigations are necessary, involving a larger number of NWs and multiple cycles of magnetic field sweeps. It is particularly important to precisely orient the measured NW in the magnetic field in order to draw sound conclusions.

To summarize this chapter, it has been demonstrated that transistor characterization can provide essential transport properties, such as σ , μ_e and n_e , for CdSe/Ag₂SE-NWFETs under various experimental conditions, including temperature and magnetic field. This technique can be utilized to monitor CE reactions, determine the causes of conductivity changes, and verify whether metallic or semiconducting properties are predominant. The field of contact engineering has once again proven to be relevant and challenging. Based on the various experiments conducted at elevated and cryogenic temperatures, the metallic transport behavior of Ag₂Se NW has been further confirmed. Initial magnetoresistance measurement revealed interesting features that require a more sophisticated study. The established transistor characterization method and the experience gained in this investigation will be applied to study CE in the CdS/Ag₂S system.

4.3.2. Cation Exchange of the CdS/Ag₂S System

To study the CE for CdS/Ag₂S, electrical, optical and microscopic methods are employed. In this chapter, first the transistor characterization is utilized to determine the transport properties of Ag₂S NWs. Fluorescence is monitored using a confocal fluorescence microscope, which provides information regarding visible (Vis) and near infrared (NIR) emission. SPM methods are used to investigate laser-induced degradation. Furthermore, SPM is utilized to monitor the CE reaction for both systems: CdS/Ag₂S and CdSe/Ag₂Se; demonstrating either homogenous or heterogenous CE. The obtained results and corresponding conclusions are validated and supported by a HRTEM study.

In contrast to the CdSe/Ag₂Se system, the CE for CdS/Ag₂S is anticipated to be heterogeneous, involving multiple intermediate phases, as introduced in the Section 2.2.3 (Cation Exchange Reaction). Robinson *et al.*³⁷ demonstrated that, in CdS NRs, that an intermediate domain phase is formed initially. As CE progresses, these domains coalesce to form a regularly spaced striped intermediate.^{37,72} These stripes subsequently grow until complete CE is achieved. Not only does the exchange mechanism differ from that of the selenide system, but the electronic transition also exhibits noticeable distinctions. Since both CdS and Ag₂S are semiconductors with band gaps of 2.5 eV⁴¹ and 1.0 eV,¹²¹ respectively, the change in transport properties is expected to be less drastic. This characteristic is advantageous when monitoring the CE with optical methods. The successful transformation of CdS to Ag₂S NWs *via* CE has been demonstrated in a previous work and verified through EDX.⁵³

Transport properties of Ag₂S NWs

First, the transport properties of fully exchanged Ag_2S NW are studied. For this purpose, devices with In contacts were utilized. The *IV*-curves of these devices are presented in Figure 4.18 (a), with the insets displaying the complete sweep range for the measurements conducted prior to CE.



Figure 4.18: Measured transport of NWFETs before and after CE. (a) *IV*-curves before and after CE. The inset shows a larger bias range with a more sensitive y-axis. Light microscope images of the corresponding devices are shown in the inset, with a 5 μ m scale bar. (b) Evolution on the *IV*-response over time and after multiple sweeps. The standard measurement conditions are at room temperature, under air and illumination. Measurements before CE were performed under illumination, while those after CE, were conducted without. For clarity, arrows were added to indicate the sweep direction.

Before CE, both NWs exhibit a weak response with small currents and nearly linear behavior. Electrical conductivities σ of 1.86·10⁻³ S/m and 9.72·10⁻³ S/m were obtained for the NWs depicted in the top and bottom panel, respectively. The electrical conductivity σ are relatively low in comparison to the best-performing Mg and In devices ($\sigma \approx 10^{-2}$ S/m) but remain within the range of untreated In devices (see Figure 4.8). After CE, both NWs demonstrate an enhanced response, displaying two distinct *IV*-curves. The *IV*-curve for the devices depicted in the top panel (referred to as top device) resembles that of a device exhibiting two different Schottky barrier heights. In contrast, the *IV*-curve for the devices shown in the bottom panel (referred to as bottom device) is linear around $V_{sd} = 0$ mV and saturates at $V_{sd} > 100$ mV. To further investigate these two differing responses, the sweep voltage was increased, and multiple sweeps were conducted to assess the reproducibility. The recorded *IV*-curves are shown in Figure 4.18 (b).

Beginning with the top device, the second *IV*-curve (denoted as 02, which is the first measurement with higher V_{sd}) exhibits a significant increase in current above 300 mV, followed by a steep decay occurring above 450 mV (see inset). When the voltage is decreased from 500 mV back to 0 mV, relatively small currents are recorded, showing a hysteresis. Upon reversing the sweep direction to negative bias, the current rises again, this time occurring earlier at approximately -90 mV, peaking at -165 mV, followed by a sharp decline. As the bias is further increased, the current rises once more, but a decrease is observed after -430 mV. The subsequent measurements (denoted as 03, 04) demonstrate a similar behavior, although with a less pronounced hysteresis, and the peaks are now reproducible at ±170 mV. It is noteworthy that the behavior around 0 mV has transitioned from insulating to linear increasing, reminiscent of the behavior of the bottom device.

In contrast to the top device, the bottom device exhibited a positive slope around 0 mV in the first *IV*-curve. This response was also observed in subsequent sweeps. At higher applied voltages, the saturated current was surpassed, continuing to increase up to 450 mV, at which point the current decreased (similar to the behavior of the top device). As the voltage was reduced, the current continued to decline, remaining slightly above the previous plateau and decreasing linearly near 0 mV. At negative bias, a similar saturation was observed, which was overcome at higher voltages. The subsequent measurements demonstrated almost the same behavior, but with a decreasing hysteresis.

The distinct behavior exhibited in the first *IV*-curves, particularly the more pronounced hysteresis, suggests that an initial transformation has occurred in the NWs. This behavior is reminiscent of the shift in the superionic phase transition temperature observed after the first cycle by Schwarz.⁴⁰ The changing response was attributed to an initial recrystallization process.

The nonlinear and complex *IV*-curves suggest that the electrical transport in the Ag₂S NWs cannot described solely in terms of electron transport. As early as 1952, Hebb demonstrated that σ in Ag_2S is composed of both an electronic and an ionic fraction.¹²² Liao *et al.* observed that for Ag_2S NWs, at higher voltages (> 2 V), there is a significant increase in current, indicating a transition from an "off-state" to an "on-state".⁹⁶ Once switched to this on-state, the NW maintains this state, with the current being considerably higher even at lower voltages than in the previous off-state.^{95,96} In a subsequent study, Liao *et al.* found that if the voltage is kept constant, switching still occurs even at lower voltages (100 mV). At 10 K ,the switching is reversible over time; however, at rt, the on-state is reached only once, after which the device remains in the off-state.95 Liao et al. attribute this switching behavior to the migration of silver ions within the Ag₂S NW, leading to the formation of a conducting filament that switches the NW "on".^{95,96} Prolonged applied bias results in joule heating, which leads to the rupture of this filament, thereby switching the NW "off".^{95,96} A similar resistive switching behavior was observed in Ag₂Se NBs obtained via CE by Guo et al.¹²³ They noted that, similar to the top device, the Ag₂Se NBs exhibited initially a Schottky-like behavior, which changed upon application of the higher voltages.¹²³ For the Ag₂Se, both the high mobility of Ag ions in the lattice and the formation of a metallic filament are considered to contribute to this behavior.¹²³ Terabe *et al.* utilized resistive switching based on the electromigration of Ag in Ag₂S NWs to operate a "quantized conductance atomic switch", demonstrating distinct logic gate funtionalities.¹²⁴ An *in-situ* HRTEM study on Ag₂S NWs conducted by Xu et al. indicated that the resistive switching phenomenon originates from a transformation of the acanthite (α -phase dominant at low temperature)¹¹⁸ to the argentite (β -phase dominant at higher temperatures)¹¹⁸ crystal structure, in combination with the formation of a metallic Ag filament.38

The difference in transport characteristics between the top and bottom device is surprising, given that they were fabricated nominally the same, as they were on the same wafer. The only distinction lies in the distance *L* between the contacts, which is 0.67 µm for the top device and 1.32 µm for the bottom device. This difference may account for the varying responses observed. In fact, the resistive switching has been predominantly observed in devices with L < 1 µm. For larger *L*, either switching occurred at higher biases or was not observed at all. This may indicate that the observed behavior is dependent on the formation of an argentite, a metallic phase, or both, bridging the contacts, which occurs more rapidly or at lower voltages for shorter *L*. Due to challenges associated with detecting such phenomena using HRTEM or other methods for the fabricated NWFETs, it can only be assumed that the reported mechanism of resistive switching also applies to the NWs studied here.

To determine if another "step" occurs in the bottom device, further measurements were performed at higher voltages. Additionally, transfer characteristics were recorded to access further transport properties. Both the *IV*-curves and the transfer characteristics are shown in Figure 4.19.



Figure 4.19: Transport characteristics of an Ag₂S NWFETs. (a) Evolution of the *IV*-curves over time and at higher applied voltages. Dotted lines have been added at the plateau-region for visibility, with colors corresponding to the respective bias range. (b) Back-gate response over multiple sweeps with different set source-drain voltages. All measurements were taken at room temperature, under air and without illumination.

Figure 4.19 (a) shows that as the voltage range is further increased, no additional steps appear; instead, the current decreases, even falling below the plateau current (sweep $\pm 1 V_{sd}$). Furthermore, higher biases result in a more pronounced hysteresis and reduction of the plateau current. The dashed lines in Figure 4.19 (a), which mark the plateau current, clearly indicate that after each sweep, the plateau current decreases, ultimately approaching 1 pA. This observation suggests an irreversible degradation of the NWs at higher voltages. Degradation was also observed in the back-gate sweeps shown in Figure 4.19 (b). The first sweep at V_{sd} = 200 mV (dark blue) exhibits a small positive slope, indicating n-type behavior. Subsequent measurements at $V_{\rm sd}$ = 400 mV (light blue), consistent with the *IV*-curves, show an overall higher current but lack clear gate dependence; instead, the current gradually decreases. Upon repeating the measurements at V_{sd} = 200 mV (turquoise), the overall current is lower than before, and the gate response has vanished. This further confirms the instability of these Ag₂S NWs under applied biases. It should be noted that for each voltage, two sweeps were performed: one sweeping first to positive gate voltages and one first sweeping to negative voltages. The resulting curves were identical, indicating no significant hysteresis, apart from the measurements in the V_{sd} = 400 mV case. The difference for the 400 mV sweeps most likely originates from the degradation occurring at the applied voltage.

The transistor characterization of the bottom device revealed a σ of 4.39·10⁻¹ S/m, determined by applying a linear fit to the region between -100 mV and 100 mV in the *IV*-curve. Compared to the σ of 9.72·10⁻³ S/m, measured under Illumination prior to the CE, this represents an increase by a factor of 45. To evaluate the contributions of μ_e and n_e , a linear fit was applied to the transfer curve (dark blue). An μ_e of 1.87·10⁻⁴ cm²/Vs and an n_e of 1.39·10²⁰ cm⁻³ were estimated. Since no transfer characteristic were recorded for this NW prior to CE, values obtained for the Mg device are used for comparison. The increase in σ after CE is even more pronounced when compared to measurements of CdS under dark conditions (8.59·10⁻⁶ S/m), representing an increase by almost five orders of magnitude. This drastic increase in σ is attributed to the increase in n_e , which increases by approximately six orders of magnitude (Mg: $n_e = 8.95 \cdot 10^{13}$ cm⁻³), while the

 $\mu_{\rm e}$ decreases slightly (Mg: $\mu_{\rm e} = 5.99 \cdot 10^{-3} \,{\rm cm}^2/{\rm Vs}$). This observation contrasts with the behavior seen for the CE of CdSe/Ag₂Se, where $\mu_{\rm e}$ increases by six orders, while $n_{\rm e}$ remains relatively constant. It should be noted that for CdSe, already high $n_{\rm e}$ of > 10¹⁹ cm⁻³ were observed. The determined σ for Ag₂S ($\sigma = 4.39 \cdot 10^{-1} \,{\rm S/m}$) is in good agreement with values reported in literature of 2.5 $\cdot 10^{-1} \,{\rm S/m}$ for acanthite.^{38,118} For comparison, these findings are summarized in Table 4.4.

Table 4.4: Summary of the determined transport properties, including the electrical conductivity σ , electron mobility μ_e , and electron concentration n_e , for the exchanged Ag₂S NWFET, and comparison to determined values before CE and literature.

System	Metal	σ	$\mu_{ m e}$	n _e	Notes
		(S/m)	(cm ² /Vs)	(cm ⁻³)	
CdS	Mg	8.59·10 ⁻⁶	5.99·10 ⁻³	8.95·10 ¹³	Dark
		6.38·10 ⁻²	9.32·10 ⁻³	4.27·10 ¹⁷	Bright
CdS	In	9.72·10 ⁻³	-	-	Bright
Ag ₂ S	In	4.39·10 ⁻¹	1.87.10-4	1.39.1020	Dark
Ag_2S	W-Tip	2.5·10 ⁻¹	-	-	Ref. 38

The nonlinear transport behavior hinders the extraction of transport properties, allowing only for rough estimation. The complex nature of the electrical transport, consisting of both electric and ionic components, further complicates the retrieval of accurate transport properties. Additionally, the transistor characterization reveals irreversible changes after several measurements, indicating an interference with the NW structure. Together, these factors render tracking the entire CE reaction through *transistor* characterization particularly challenging.

Optical Properties of Ag₂S NWs

Since the CdS NWs show fluorescence, an alternative approach, pursued in previous work,⁵³ involves investigating the CE by monitoring the PL of the NWs (see Section 3.2.1 and 3.3.1). It has been demonstrated that the PL corresponding to the near-band edge (NBE) emission of CdS decreases as the CE progresses and becomes undetectable after 30 s.⁵³ Additionally, the Raman signals attributed to CdS also diminished during the CE, while new peaks indicating the presence of Ag₂S were observed.⁵³ However, the PL of Ag₂S could not be detected due to unavailability of the experimental equipment necessary for recording the fluorescence in the near-infrared (NIR) region.⁵³ While investigating the CE in CdS NRs, Peng *et al.*¹²⁵ also observed immediate PL quenching and Robinson *et al.*³⁷ observed a quantized emission of Ag₂S, originating from small domains.³⁷ With ongoing CE, a redshift in the emission was recorded, indicating the growth of these domains until complete CE was achieved, at which point the emission fell within the range of bulk Ag₂S (1.0 eV \triangleq 1240 nm).^{37,118} In order to observe such behavior in our larger nanostructures, the setup was improved and extended.

The new setup is capable of simultaneously detecting fluorescence in both the visible (VIS) and NIR region. This is accomplished by incorporating a dichroic mirror into the detection beam path, which reflects light with $\lambda > 950$ nm to the NIR avalanche photodiode (APD) while allowing shorter λ light to pass through and be directed to the VIS APD. Consequently, emission resulting from CdS should be observable in VIS PL scans, while Ag₂S emission should be detected in the NIR PL scans. Spectral information can be gained if the emission is directed to the spectrograph. Although the VIS and NIR fluorescence can be detected simultaneously with the APDs, it is not feasible to record the spectra simultaneously due to various experimental and technical limitations, such as overlapping of diffraction orders, low intensities, and long integration times.

In the visible channel, the CdS NBE emission (at $\lambda \approx 500 \text{ nm}$)⁴³ and trap band emission ($\lambda \approx 700 \text{ nm}$)⁴³ should be detected. To mitigate issues related to the second-order of the NBE emission, a 532 nm long-pass (LP) filter was used in most measurements to filter it out. In the NIR channel, the Ag₂S band edge emission from potential domains ($\lambda \approx 900 - 1000 \text{ nm}$)³⁷ and the entire nanostructure (at $\lambda \approx 1200 \text{ nm}$)^{37,118} should be detected.

Before starting the CE tracking, fully exchanged NWs were studied to verify whether the setup can detect the emission of the Ag₂S NWs. This study was conducted with the assistance of Isa Moch (student apprentice). For this purpose, a standard CdS NWFET device (In/Au contacts) was subjected to CE for 5 min, which is expected to correspond to complete CE. The results of this study are presented in Figure 4.20. For orientation and localization, reflection (RE) scans, as shown in Figure 4.20 (a), were recorded first. Regions in the scan with high intensity predominantly reflect the incident light effectively, which is typical for metals (contacts) and the substrate (background). In contrast, regions of low intensity indicate poor reflection of the incident light, primarily due to scattering, absorption processes, or both. Typically, light is scattered at the edges of the metal contacts, resulting in low reflection intensity, as evidenced in Figure 4.20 (a). The NW also exhibits a low intensity, which can be attributed to either scattering (due to the geometry) or absorption of the light; it is likely that both processes are occurring. By comparing the RE scan with the light microscope image of the device shown in Figure 4.20 (d), the aforementioned assignments can be validated.



Figure 4.20: Spectroscopic investigation of an Ag₂S NWFET. (a) Reflection (RE) scan of the device (shown in (d)). The scan was taken with a wavelength of 660 nm and a power below 1 nW. (b-c) Photoluminescence (PL) scan of the device in the (b) visible (Vis) and (c) near-infrared (NIR) region. These scans were taken with a wavelength of 488 nm and a power of 475 nW. The white circles highlight the locations from which the spectra in (e-f) were obtained. (d) Light microscopy image of the investigated device. (e-f) Photoluminescence spectra in the (e) visible and (f) IR region of the NW, taken in the indicated position in the scans (a-c). Spectra were taken with an excitation power of 31.5 μ W at a wavelength of 488 nm.

In the PL scans, areas of high intensity correspond to regions that emit light, while areas of low intensity indicate the absence of emission. In the VIS PL scan shown in Figure 4.20 (b), it is evident

that the NW is not visible, confirming that no CdS emission is present. This observation indicates successful conversion to Ag₂S or potential fluorescence quenching. The scan also reveals that the wafer background has a higher intensity than the metal contacts, which is attributed to band edge emission from Si, as Si has an indirect band gap of 1.12 eV^{41} ($\triangleq 1100 \text{ nm}$), along with potential defect emission from the Si wafer (see spectra e, f). The metal contacts typically do not fluoresce, causing them to appear as low-intensity regions. In the NIR PL scan, shown in Figure 4.20 (c), the NW is also indistinguishable from the background, indicating that no Ag₂S emission is detected. Unlike the VIS PL scan, the NIR PL scan show that the contacts unusually exhibit a higher intensity than the wafer background. It is possible that the indium layer has oxidized to a certain extent at the surface; this indium oxide or associated defects could result in a weak fluorescence in the NIR regime.

To gain spectral information about the NWs, spectra were collected at the positions marked by circles in the PL scans. Figure 4.20 (e) displays the spectra in the visible range, while (f) presents the NIR spectra. Both the VIS and NIR spectra exhibit a pronounced background, primarily attributed to the wafer background. All spectra in the visible region display a broad peak ranging from 800 nm to 1000 nm, which can be assigned to fluorescence of the wafer. Only spectrum 3 shows a broader peak starting at 600 nm, which may be associated with trap band fluorescence of CdS, indicating incomplete CE near the metal contact. No peaks other than the wafer background were observed in the NIR spectra. These results demonstrate that the setup is capable of detecting NIR emission; however, measuring emission from the NWs was not possible and presents significant challenges. The signal intensity was rather low, requiring long integration times (> 5 s per spectra). Additionally, higher laser powers were not feasible, as NW degradation was observed in previous work.⁵³ These measurements suggest that conducting optical CE tracking on typically fabricated NWFETs is impractical due to the substrate background, thereby hindering the parallel investigation of optical and electrical properties.

Prior to optical investigation, the device was studied using SPM both before and after CE with the assistance of Wehrmeister. The AFM scan shown in Figure 4.21 (a) reveals a straight and uniform NW with a height of 34.5 nm, corresponding to the diameter, prior to CE. Figure 4.21 (b) presents the KPFM scan, which indicates a homogenous surface potential along the NW. After CE, significant changes were observed for the NW. The AFM scan shown in Figure 4.21 (c) exhibits three distinct regions: areas with a uniform surface (indicated by blue boxes), areas with a rough surface, and areas with nanoparticles (NPs) attached to the NW (indicated by red circles). The uniform regions, exhibiting a NW diameter of 33.6 nm, indicate that the height has remained nearly constant, thereby demonstrating shape preservation after CE. In contrast, the height in the rough regions has decreased by 12.2 nm, resulting in a diameter of 22.3 nm, while the newly formed NPs show heights of 103 nm and 76.9 nm. This suggests that these NPs have grown under the consumption of the surrounding domains. A bias of +10 V was applied to the left contact for the KPFM scan displayed in Figure 4.21 (d). The KPFM scan reveals a sharp drops in surface potential at the grain boundaries observed in the AFM scan. This observation suggests the presence of a potential barrier between these domains that inhibits charge equalization. These findings demonstrate that SPM can be a promising method for monitoring the CE.



Figure 4.21: Nanowire topography before, after CE and following spectroscopy. (a, c) AFM scan of the nanowire: (a) prior to and (c) subsequent to CE. (b, d) KPFM scan of the nanowire: (b) prior to and (d) subsequent to CE. All scans were scaled individually to maximize visibility of features. (e) Scanning microscopy image of the NW after the spectroscopic investigation (show in the previous figure). Red circles and blue boxes have been added (in c and e) as a guide to the eye for identifying existing and newly formed particles, respectively.

Following the SPM measurements, the previously described optical investigation was performed. To verify the complete CE, the NW composition was analyzed using SEM-EDX. The EDX spectra recorded at various positions confirm that the transformation to Ag₂S was successful. Nevertheless, Cd was still detected near the contacts, which accounts for the observed trap band emission in spectrum 3 (see Figure 4.20 (e)). The recorded SEM image of the NW, depicted in Figure 4.21 (e), reveals that another morphologic transformation has occurred after the spectroscopic measurements. The uniform domains (blue boxes) have undergone changes, resulting in the formation of particles and a decrease in diameter. The previously observed NPs (indicated by red circles) remained unchanged. The EDX spectra of the NPs reveal an increased Ag content (up to 90%), suggesting that these NPs consist predominantly of elemental Ag. Given that these Ag NPs were also present prior to the spectroscopic investigation, they may have contributed to the quenching of the fluorescence of the NW, thereby explaining the lack of detectable emission. To address this issue, two approaches were studied: enhancing fluorescence through ligands and preventing the formation of Ag NPs.

Further studies were conducted to enhance the fluorescence of Ag₂S NWs to a level that is detectable by the setup. Pan *et al.* demonstrated that the PL and quantum yield (QY) of Ag₂S quantum dots (QDs) can be significantly increased through a ligand exchange process involving chlorine ligands.¹²⁶ Vivien Lizinski, in her bachelor thesis, attempted to achieve a similar PL enhancement by testing various ligands with different treatments.¹²⁷ In summary, neither performing CE and ligand exchange in solution nor on the substrate yielded the desired improvement in optical properties.¹²⁷ Lizinski also observed a notable instability of the exchanged NWs, particularly under light exposure, following ligand exchange experiments, despite most of the reactions being conducted in the absence of light.¹²⁷ Recorded SEM images once again revealed the presence of Ag NPs, even before any optical experiments, suggesting that these NPs may form either during CE, during storage, or both.¹²⁷ Given that no Ag₂S emission could be detected in conjunction with Ag NP formation, it is most likely that the fluorescence is quenched by these NPs. It is widely accepted that metal nanoparticles can diminish the emission of semiconductor nanostructures.^{128,129}

To prevent the formation of Ag NPs on the NWs and thus enhance the optical properties, Yuan Wei investigated the formation process of the NPs in her master thesis.¹³⁰ By conducting the spectroscopic investigation on SiO₂ membranes, a correlation between laser illumination and structural changes was estabilished.¹³⁰ Generally, it was observed that a higher irradiation dose – mainly determined by the laser wavelength λ , laser power *P* and illumination duration *t* – results

in a larger area containing Ag NPs.¹³⁰ This suggests that the energy is absorbed by the NW, facilitating a reaction on the NW surface. With the assistance of Wehrmeister, an "*in-situ*" study on the formation of the Ag NPs was conducted using the SPM setup (presented in Section 4.2.2). It was observed that Ag NP formation occurs rapidly at the position of illumination.¹³⁰ With continuous irradiation, the NP increase in height, apparently consuming the adjacent NW, which decreases in height.¹³⁰ It is noteworthy that no new NPs were formed after initial laser irradiation; instead, if NPs were already present in the surrounding area of irradiation ($r \approx 1 \mu m$) before laser irradiation, grow of these NPs was observed rather than new NP formation.¹³⁰ Furthermore, Wei was also unable to measure any emission corresponding to Ag₂S, and no combination of illumination parameters could prevent the radiation damage leading to NP formation.¹³⁰ These results demonstrate that the Ag₂S NWs obtained through CE are highly sensitive to light, readily facilitate Ag NPs formation, and do not emit NIR light.

Currently, further studies are being conducted within the research group to observe the Ag NP formation *in-situ* using SEM. Since parallel optical and electrical investigation is not feasible, the emission from Ag_2S is undetectable, and the NWs degrade under illumination, optical characterization is considered as impractical for monitoring the CE on the same NW.

Monitoring the Cation Exchange by Scanning Probe Microscopy

Monitoring the CE *via* transistor characterization presented several challenges. First, making reliable ohmic contacts to CdS NWs proved to be complex and laborious (see Section 4.1.2). Second, transport measurements had to be performed carefully to prevent alterations to the NW composition and the Ag distribution (see Section Transport properties of Ag2S NWs). Optical tracking was found to be impractical, as the exchanged NWs exhibited no emission and demonstrated high sensitivity to irradiation. Consequently, an alternative tracking method had to be developed. Previously, SPM has been utilized to investigate the formation of Ag NPs and proved to be a promising method. AFM provides detailed information regarding morphological changes, while KPFM yields insight into the electrical properties. Since SPM data is obtained through the interaction of the tip with the sample, and no energy is transferred to the NW, for instance, through biasing or illumination, interference with the CE reaction should be minimal. This SPM study was conducted with the assistance of Wehrmeister, who performed the SPM measurements.

To obtain comparable and reliable SPM data, especially for KPFM, a specialized device structure is required. The device layout introduced in Section 4.2.2 (Device design and fabrication) was selected for this study due to the aforementioned advantages. The standard wafer (Si/SiO₂) was used, in contrast to ITO, because no optical excitation is necessary, and the overall stability is enhanced. Given that KPFM is sensitive to all charges, for instance those arising from electrostatic charging, such charges can influence the measured surface potential. Therefore, a metal with a known and constant work function, such as gold, is utilized as a reference to calibrate the scale of the measured surface potential. In this context, metal contacts were chosen to consist of Au on top, ensuring that the reference is consistently represent in the scans. It is important to note that this configuration rendered parallel transport measurements impossible due to the formation of a Schottky barrier between the contacts and the NW. Based on previous results,⁵³ the study was conducted until 100 s of CE, corresponding to complete CE (in the free area).In Figure 4.22, the measured AFM and KPFM scans are presented, along with the profiles extracted along the nanowire surface.



Figure 4.22: Investigation of the CE from CdS to Ag₂S with AFM and KPFM. (a, c, e) AFM scan of the nanowire: (a) before, (c) after 20 s, and (e) after 100 s of CE. (b, d, f) KPFM scan of the nanowire: (b) before, (d) after 20 s, and (f) after 100 s of CE. All scans were uniformly scaled for improved comparability. (g) Extracted height (blue) and surface potential (green) profiles along the nanowire from the corresponding scans. All measurements were performed under exclusion of light and under a nitrogen atmosphere.

The AFM scan (a) displays a straight and uniform NW prior to CE, with a diameter of 37 nm and a distance of 7.2 µm between the contacts. The corresponding KPFM scan (b) reveals the same structure, exhibiting different surface potentials for the contacts, wafer, and NW. The scale of the surface potential has been adjusted so that the left contact has a value of 0.2 V, which represents the work function difference between Au ($\Phi_{Au} = 5.1 \text{ eV}$)⁵¹ and the PtIr tip ($\Phi_{Tip} = 5.3 \text{ eV}$)¹³¹. The surface potential of the wafer ranges from 0.3 V to 0.4 V, while the average surface potential for the NW is 0.28 V. Theoretically, a surface potential of -0.1 V is anticipated for the wafer, assuming that the Fermi level is positioned in the center of the band gap ($\Phi_{SiO_2} = 5.4 \text{ eV}$, $\chi = 0.9 \text{ eV}$, $E_g = 9 \text{ eV}$).⁴¹ Furthermore, a surface potential of 0.3 V is expected for the CdS NW ($\Phi_{CdS} = 5.0 \text{ eV}$).⁵⁰ Unlike for metals, the measured surface potential for semiconductors and insulators does not directly correspond to the work function difference between the tip and the material. The measured surface potential is significantly influenced by factors such as adsorbed oxygen, which can shift Φ_{CdS} by up to 1 eV,⁴⁸ the presence of a water film (if present), and electrostatic charges. Additionally, intrinsic surface effects of the semiconductor, such as Fermi level-pinning or surface defects, may cause deviations between the expected and measured surface potential.

Consequently, the absolute values of the measured surface potential are considered less meaningful, and relative changes will be emphasized in the subsequent discussion.

From both the AFM and KPFM scans, a profile along the nanowire is extracted and presented in (g). These AFM profiles can be divided into two distinct regions: the first ($x < 0 \mu m$ and $x > 7.2 \mu m$) is attributed to the contacts, exhibiting heights of approximately 87 nm, corresponding to the sum of the metal contact (10/40 nm Ti/Au) and the NW (37 nm) height. The second region ($0 \mu m < x < 7.2 \mu m$) corresponds to the NW itself, with a consistent height of 37 nm. The height profile in NW region prior to CE is smooth, further demonstrating the uniformity of the CdS NW. The surface potential profile shows a sharp increase of approximately 0.2 V when transitioning from contact to NW and *vice versa* on the opposing side, thereby demonstrating good alignment of AFM and KPFM data. The surface potential in the NW region appears relatively rough, whereas it is smooth in the contact region, suggesting semiconducting and metallic behavior, respectively.

In Figure 4.22 (c, d) the SPM scans are presented after 20 s of CE. The data after 20 s serves as an exemplary representation for the partial CE, while the data for the entire exchange series is illustrated in Figure 4.23. To prevent irradiation damage, which could lead to NP formation, light exposure was minimized. Both the CE reactions and the measurements were conducted in the dark. In the AFM scan after 20 s, depicted in Figure 4.22 (c), the NW remained straight and uniform, but small inhomogeneities along with several large NPs were observed. The measured diameter has decreased slightly to 35 nm, possibly due to minor shifts in the background height resulting from line levelling. The nearly constant height, combined with the relatively uniform NW surface, indicates the expected shape preservation. The formed NPs exhibit heights ranging from 50 nm to 90 nm. The KPFM scan (d) indicates that the left half of the NW has positively charged, with a sharp decrease in surface potential in the middle region. Additionally, in the areas where the NPs are located, the surface potential is negatively charged compared to the surrounding NW. These observations are more apparent in the corresponding SPM profiles shown in (g). The surface potential decreases sharply, where the height peaks, corresponding to the position of the NPs. This behavior suggests that the NPs either they possess a different work function, or electrons are extracted from the NW and concentrated in the NPs, or both, indicating metallic behavior consistent with previous EDX results (see Section Optical Properties of Ag₂S NWs). This phenomenon also explains the fluorescence quenching induced by the NPs. The drop in surface potential in the middle of the NW does not align with a significant feature in height, which may indicate a boundary between the CdS and Ag₂S phases in the NW, where the charge cannot freely equalize. This would represent the first evidence of the heterogenous CE, as reported by Robinson et al.37

The measured SPM data after 100 s are presented in Figure 4.22 (e, f). The AFM scan (e) reveals that the NW remained straight, but the surface has become rougher, while the NPs size has decreased. The average NW diameter was determined to be 37 nm, confirming the shape preservation. The height of all NPs is now below 60 nm, demonstrating their reduction in size. In the KPFM scan (f), similar to the situation prior to CE, only features corresponding to the different materials are observable. It is noteworthy that the right contact is slightly negatively charged, which accounts for the observed difference in surface potential between both contacts. The AFM profile corresponding to 100 s of CE, shown in (g), illustrates that the inhomogeneity of the NW surface has increased, while the NPs heights has decreased more distinctly. In contrast to the height profile, the surface potential profile of the NW, shown in (f), has become smoother, with an average value of 0.18 V. The smoother surface potential on the NW surface could indicate an increased metallic character of the Ag₂S compared to CdS. Unlike for semiconductors, charges in

metals are less likely to accumulate or become trapped, leading to a more uniform distribution of charges.

To present the results of the entire CE reaction series in a single comprehensive figure, the extracted profiles, shown in Figure 4.22 (g), were plotted as a bar, where the color represents the height or surface potential in Figure 4.23, similar to the original SPM scans. The advantages of using the profiles instead of cropped scans include better readability due to larger lines, a linear representation of the curved NWs that saves space, enhanced alignment, and collective color scaling. It is important to note that the profile heights have been aligned based on the average height of the NW to correct for errors originating from scan processing, such as plane leveling and line alignment. The KPFM profiles were not aligned, as the KPFM scans had already been adjusted to the reference (left Au contact). Additionally, the x-axis (position) is slightly distorted due to the increased line thickness, which has been enhanced for better visibility. First, the CE process for the CdS/Ag₂S system is discussed, with the corresponding AFM and KPFM profiles presented in Figure 4.23 (a, b).



Figure 4.23: AFM and KPFM profiles for the complete CE reaction. (a, b) Profiles of the CdS-Ag₂S nanowire surface extracted from (a) AFM and (b) KPFM (as seen in the previous figure), plotted as bars where the height and surface potential are illustrated as a color map, consistent with the AFM and KPFM scans. (c, d) Profiles of the CdSe-Ag₂Se nanowire surface extracted from (c) AFM and (d) KPFM. All measurements were performed under exclusion of light and under a nitrogen atmosphere.

During the initial seconds of CE, the topography remains largely unchanged. After 20 s of CE, the first significant difference in height is observed, with NPs formed at $x \approx 0 \ \mu m$ and $x \approx 6 \ \mu m$, as previously shown in Figure 4.22 (c). Near the left contact, a second NP has formed after 30 s, while the other has decreases in height. In contrast, the NPs at $x \approx 6 \ \mu m$ have fused together and increased in size, as has the NP at $x \approx 7 \ \mu m$. Additionally, the overall NW surface has become rougher. After 40 s of CE, all formed NPs have significantly decreased in height, and as CE progresses, the NPs continue to shrink until some become indistinguishable. Moreover, the uniformity of the NW decreases, as previously observed in Figure 4.22 (e).

In contrast to the AFM profiles, the KPFM profiles already exhibit a different surface potential after just 1 s of CE. A positive charge was observed in the left half of the NW, decaying along the NW, while still displaying pronounced surface potential fluctuations. As the CE progresses, the positive charge decreases, resulting in the typical rough surface potential. After 20 s of CE, the previously discussed surface potential profile again reveals a sharp decay in the center, with a reduced surface potential at positions coinciding with the NPs. In the subsequent scan after 30 s of CE, the positive charge has mostly diminished. After 40 s, the surface potential becomes smoother, and the NPs are no longer negatively charged. The observation that a sudden charging occurred twice on the NW, which decayed by the subsequent CE step, suggest that this charging is not a result of CE itself but rather reflects electrostatic effect. However, this electrostatic charging can assist in identifying areas where the charges cannot equalize, as seen in the 20 s scan.

From the SPM study on CdS/Ag₂S system, the following conclusions can be drawn: The CE is most likely heterogeneous, as the nanowire becomes rougher during CE, and Ag NPs form on the NW surface. Concurrently, the surface potential becomes smoother, indicating an increasingly metallic behavior. Initially, the formed NPs are large and exhibit a significant negative charge, suggesting that they either possess a different work function, attract electrons from the NW, or both, which is typical metallic behavior. As CE progresses, both the size and the negative charge of the NPs decreases, indicating some form of ion migration and charge equalization. This leads to the hypothesis that these NPs are metallic Ag NPs formed during the CE reaction in solution and attached to the NW. This hypothesis is supported by the observation that the NW diameter did not decrease near the NPs, unlike the behavior observed during laser-induced Ag NP formation. The attached Ag NP could then serve as an additional Ag source for the CE, donating Ag and thereby explaining the observed decrease in NP size.

To evaluate the results obtained for CdS/Ag₂S, a second system that is expected to undergo a homogenous CE was studied next (see Section 2.2.3).^{33,36} The CdSe/Ag₂Se system was chosen due to its similarity to the CdS/Ag₂S system and the existing experience with it. For this study, the same device layout used for CdS was utilized. Since the CdSe NWs used in this work are grown directly on the substrate through a SLS approach, the markers and patches were coated with Bi for the synthesis. Aside from that, the fabrication process and contacts are similar, and the CE was performed under the same conditions.

In Figure 4.23 (c, d) the SPM profiles for CdSe/Ag₂Se are presented. The AFM profiles indicate that the as-synthesized CdSe NWs are significantly rougher, an observation made previously in TEM studies, which is likely attributed to defects such as stacking faults.^{40,76} With progressing CE, the topography remains unchanged, and no NP formation can be observed. The KPFM profile of CdSe is smoother than that of CdS, potentially due to the smaller band gap of CdSe, which may represent a more metallic character. Alternatively, surface effects that trap charges may be less pronounced for CdSe. Again, similar to the topography, no significant changes in the surface potential are detected as CE progresses. Only in the scan at 60 s is a sharp positive feature observed near the

right contact, most likely caused by positively charged particles that have attached to the contact (more clearly visible in the original scan). By calculating the standard deviation along the NW surface, a smaller standard deviation is determined for the 100 s profile, indicating an increasing metallic character, although not as pronounced as that for Ag₂S. Since no significant changes in topography or surface potential are noted, the CE is assumed to be homogenous for CdSe. These observations clearly demonstrate that the CE with Ag differs between CdS and CdSe. To further validate the results obtained from the KPFM study, a HRTEM study was performed, specifically to confirm the heterogenous nature of the CE.

HRTEM Investigation of the CdS/Ag₂S Cation Exchange

As demonstrated by Robinson *et al.*³⁷ for CdS NRs and indicated by the SPM study, the CE should occur heterogeneously in 4 stages: First, prior to the CE, pristine CdS is present. Second, after a few seconds of CE, Ag₂S domains form on the surface of the CdS host lattice. Third, after prolonged CE, the Ag₂S domains expand to stripes and grown into the CdS lattice, resulting in regular spacing due to lattice strain and electrostatic repulsion.^{37,72} Fourth, after complete CE, the Ag₂S striped phases further expanded and fused together, leading to the complete transformation.

To verify whether such stages also exist in larger nanostructures, this HRTEM study was performed. For comparison, the NRs used by Robinson *et al.*³⁷ had diameters of 4.6 nm and lengths of 64 nm, resulting in an aspect ratio of approximately 14, while the NWs used in this work typically have diameters around 30 nm and length exceeding 10 μ m, resulting in an aspect ratio of approximately 330. To ensure comparability between the HRTEM and SPM study, the NWs were deposited on a TEM grid by spin coating prior to CE, resulting in reliably separated and individual NWs. They were then subjected to CE on the grid for 1, 10 and 100 s under the same CE conditions. It is important to note that for each exchange step, a new sample was used due to electron beam induced damage to the sample.

The obtained scanning TEM (STEM) images and EDX maps are shown in Figure 4.24. TEM images of as-synthesized CdS NW can be found in previous work for comparision.⁵³ The STEM images for 1, 10 and 100 s of CE, shown in (a), reveal three different stages: After 1 s of CE, small brighter and darker domains (10 - 20 nm) on the surface can be observed. In theory, areas of higher density that interact more strongly with the electron beam should appear darker in conventional TEM and brighter in STEM images. Therefore, silver containing areas are expected appear brighter in the displayed images; however, due to the minimal density difference between CdS and Ag₂S, the contrast is relatively low. The brighter regions are assumed to be areas where both Cd and Ag are present, while the darker regions correspond to areas where the Cd has left the lattice but has not been completely replaced by Ag. CE can occur via several pathways (see Section 2.2.3),^{33,34} and it is most likely that both a kick-out and a solvation mechanism are involved here. After 10 s of CE, stripes (as bright areas) spanning the entire NW diameter, with widths of 10 to 20 nm can be observed. After 100 s of CE, stripes are no longer observed, and the entire NW appears uniform. A few dark spots can be observed, likely originating from density fluctuations due to electron beam irradiation. In general, the samples with a higher exchange degree, particularly after 100 s, displayed significant effects under irradiation. Reactions such as reduction or decomposition under TEM conditions are commonly reported for Ag-containing systems.^{38,39}

4 Results and Discussion



Figure 4.24: Scanning transmission electron microscopy (STEM) analysis for selected CE steps. (a) STEM images of the investigated nanowires exchanged for 1, 10 and 100 s. (b-d) Element-specific EDX maps of the nanowires (shown in (a), placed in the background) for (b) cadmium (blue), (c) silver (green), and (d) sulfur (yellow). (e) Summary energy dispersive X-ray spectroscopy (EDX) spectra of the images shown for 1, 10 and 100 s. Element specific transitions were assigned according to Deslattes *et al.*¹³²

To get information about the location of Ag and Cd, EDX maps of the images are presented in Figure 4.24 (b-d). The EDX maps with the elemental channels of Cd (b), Ag (c) and S (d) have been split into multiple images for improved visibility. The color scales have been adjusted for maximum visibility for each map individually. To facilitate the correlation of the regions, the images shown in (a) were placed in the background. The Cd map (b) after 1 s of CE indicated that Cd is predominantly present, with only a few regions at the edge lacking Cd. In contrast, the Ag (c) shows that Ag is primarily detected in regions close to the NW edge, forming small domains. Rarely Ag is found in the center of the NW. The S channel (d) shows an even distribution along the entire NW. The observed domains can be classified into two types, as described above: In bright domains, both Cd and Ag are detected, while in dark domains, Cd is predominantly absent, and Ag is only partially present. These observations indicate that, during the initial stage of CE, CdS remains the dominant phase, with small exchanged Ag₂S domains present on the surface.

After 10 s of CE, the Cd content has decreased significantly while the Ag content has increased. S remains evenly distributed along the NW. Both elements, Cd and Ag, are predominantly detected in the same area, more precisely in the bright stripes observed in the STEM image (a). This observation is likely the result of the following two factors: First, the separation of Cd and Ag signals in the EDX spectra can be challenging, particularly when approaching a 50:50 ratio, as the signals overlap considerably, which will be discussed in more detail later. Second, the overall signal intensity for this map is rather low, which is evident in the S map. Based on the EDX maps, the results suggest that the stripes are not alternating CdS/Ag₂S phases. Rather, they are alternating phases of a phase in which Cd is predominantly dissolved and a phase in which Cd is still present, but the Ag has occupied interstitial sites. However, it is unlikely that such large cation-free regions would be stable. It is more plausible that the low signal intensity, combined with the difficulty in separating the signals, leads to an under representation or overrepresentation of signals in these regions.

After 100 s of CE, complete CE is expected. In the Cd channel, Cd is detected evenly distributed along the entire NW. A similar observation is made for Ag and S, in their respective maps. Since no absence of elements is observed, the previously described dark spots are presumed to result from density fluctuations under irradiation. For complete CE, no Cd signals are anticipated; however, low intensities are recorded along the entire NW. This observation can be attributed to challenges in signal extraction. Given that the Ag intensity is significantly higher along the NW, it is reasonable to conclude complete CE, a conclusion that will be further validated by the following EDX sum spectra.

The EDX sum spectra of the maps are presented in Figure 4.24 (e). The EDX sum spectrum after 1 s of CE, shown in (e), displays a dominant peak at 2.31 keV, corresponding to the K α_1 transition of S.¹³² The peaks at 3.14, 3.33 and 3.54 keV can be attributed to the L α_1 , L β_1 and L β_2 transitions of Cd, respectively.¹³² The weak shoulder at 2.99 keV can be assigned to the L α_1 transition of Ag.¹³² The correct assignment of the peak at 3.14 keV is problematic, as both the L α_1 transition of Cd (Lit: 3.134 keV) and the L β_1 transition of Ag (Lit: 3.151 keV) are located in that region.¹³² Since the dominant peak for Ag (at 2.99 keV) is weakly pronounced, its contribution can be considered negligible, making it reasonable to assume that the above assignment is valid for the 1 s spectra.

In the 10 s spectrum, signals at 2.31, 2.99 and 3.14 keV are prominently observed. While the assignment of the peak at 2.31 keV to S and that at 2.99 keV to Ag is unambiguous, the assignment of the peak at 3.14 keV remains complicated. Previously the contribution of Ag could be assumed to be negligible, which clarified the distinction in the 1 s map. However, for the 10 s spectrum, this assumption is not applicable due to the significant Ag content, complimenting the accurate

determination of the Cd content. The challenges in signal determination also account for the observations made in the elemental maps.

The peaks observed in the spectrum obtained after 100 s of CE are similar to those in the previous spectrum but exhibit higher signal intensities for Ag compared to S. Given that the $L\alpha_1$ transition of Ag is dominant, the other peaks can be assumed to correspond to Ag, thereby confirming complete CE.

In addition to verifying the elemental composition *via* STEM, HRTEM was employed to investigate the preservation of morphology and crystallinity. The as-synthesized CdS NWs have been extensively studied in previous work⁵³; here, new images have been obtained using a similar sample preparation to that used for the exchanged NWs to facilitate comparison. For partial CE, the data was collected from the same sample as before (Figure 4.24), whereas for complete CE, the data was recorded from a sample that was underwent the same CE procedure (on TEM-grid) for 6 h. The acquired images, along with higher magnifications of those (shown in insets), are presented in Figure 4.25.

The HRTEM image of the pristine CdS NW, shown in Figure 4.25 (a), reveals a straight NW with high crystallinity. According to the synthesis literature^{30,133} and the previous results,⁵³ it is known that these CdS NWs exhibit the wurtzite (hexagonal) crystal structure with minimal defects. For the growth direction [001], a lattice spacing of 6.72 Å was measured (see inset), which corresponds to the reference value of 6.72 Å¹³⁴ for the (001) lattice plane spacing.

For Ag₂S, the monoclinic crystal structure (acanthite, α -phase) is expected to be most stable under ambient conditions.^{38,118} Ag₂S obtained through CE from CdS (wurtzite) has also been reported to exhibit the monoclinic (acanthite) structure, although with distortions.^{37,72} To illustrate the change in crystal structure, a model of both crystal structures based on Robinson *et al.*³⁷ is visualized in Figure 4.25 (b). One condition for successful CE is that the host anion lattice remains mostly intact; therefore, the acanthite lattice must adapt to the existing wurtzite lattice. This adaptation is achieved by a compression along the [100] direction by 4% (acanthite), which corresponds to the growth direction of the NW, identified as the [001] direction for wurtzite.^{37,72} In contrast, along the [010] direction, the wurtzite lattice is expanded by 15%.^{37,72} The [100] direction of wurtzite, which corresponds to the [001] direction acanthite (after CE), thereby remains unchanged (see smaller crystal structure).

After complete CE, no significant changes in morphology are observed in the HRTEM image, shown in (c), demonstrating the preservation of crystallinity, consistent with the previously mentioned adaptations. The measured lattice spacing of 2.56 Å can be attributed to the (022) planes $(2.58 \text{ Å}).^{135}$

In the case of partial CE, straight NWs are still observed, but with inhomogeneities in the crystal structure. The HRTEM image after 1 s of CE, shown in Figure 4.25 (d), displays a CdS NW with Ag₂S domains on the surface. Regions with a different crystal structure orientation are marked by dotted lines. The higher magnification of the region within the dashed box, shown in the inset, reveals a regular lattice spacing corresponding to the growth direction. The value of 3.35 Å, matches the reference for the (002) plane of CdS, which is 3.36 Å.¹³⁴ As CE progresses to 10 s, stripes can again be observed in (e), but this time the stripes are associated with different crystal structure orientations. The region, which is also magnified in the inset, exhibits a highly ordered structure. The measured lattice spacing of 6.61 Å can be assigned to the (001) planes of CdS.¹³⁴ After 100 s of CE, no inhomogeneities are visible in the HRTEM image presented in (f). Only the aforementioned density fluctuations can be identified as brighter spot. The lattice spacing shown

in the inset yields a value of 3.44 Å, which can be assigned to the (110) plane of Ag_2S (3.44 Å).¹³⁵ Since the lattice spacing can be attributed to acanthite and no other crystal structures are observed in HRTEM after 100 s, it can be concluded that the CE is complete.



Figure 4.25: Crystal structure analysis using HRTEM and XRD. (a, c) HRTEM image of a (a) CdS NW (before CE) and a (c) Ag₂S NW (after complete CE). (d-f) HRTEM images of nanowires after (d) 1 s, (e) 10 s and (f) 100 s of CE. Significant features, such as domains, are indicated a white dashed line for clarity. Higher magnification of the images (marked by dashed boxes) are shown in the insets showing the lattice spacing more clearly. (b) Model of both crystal structures, illustrating the orientation of the lattices, adapted fomr Robinson *et al.*³⁷ The lattices were constructed using crystal structure date provided by Sowa¹³⁴ for CdS and by Demchenko *et al.*⁷² for the Ag₂S. (g, h) XRD diffractograms of NWs: (g) before, and (h) after CE. Measurements were performed on NW films deposited on a silicon wafer. Reference data were taken from Sowa¹³⁴ (PDF No.: 01-074-9663) for CdS and from Blanton *et al.*¹³⁵ (PDF No.: 01-080-5476) for Ag₂S.

To confirm the crystal structures previously assumed, X-ray diffraction (XRD) was performed on NW films deposited on a silicon wafer. The obtained diffractogram for CdS is shown in (g) and that for Ag₂S is shown in (h). Both diffractograms display sharp reflexes, indicating large crystalline domains. This observation is consistent with the dimensions observed in TEM and suggest an absence of defects such as grain boundaries or stacking faults. Due to the large size of the NWs, they tend to lie flat on the substrate, causing a significant orientation effect. This orientation effect leads to an underrepresentation of reflexes in the growth direction and an overrepresentation of

reflexes parallel to the growth direction. The CdS diffractogram shows only a few reflexes, all of which can be assigned to the wurtzite crystal structure.¹³⁴ Due to the orientation of the NWs, the (002) reflex expected at 26.6° is not pronounced, while the (100) reflex at 24.9° and the (110) reflex at 43.7° are very pronounced.¹³⁴ Similarly, the (100) reflex corresponding to the growth direction in Ag₂S, which should appear at 22.4°, is not visible, while the reflex at 36.8° corresponding to the (12-2) planes is overly pronounced.¹³⁵ All appearing reflexes for Ag₂S can be attributed to the monoclinic acanthite structure.¹³⁵

In conclusion, HRTEM was used to verify the inhomogeneous CE for Ag₂S, as initially domains and with progressing CE, stripes were observed. Determining the content and precise localization of Cd and Ag was challenging due to overlapping signals; however, the expected trends were still noticeable. The EDX sum spectrum confirmed complete CE after 100 s. HRTEM images further validated the crystallinity of the NWs, both before and after CE. By analyzing the lattice spacings in conjunction with XRD diffractograms, the wurtzite structure was determined for CdS, while the acanthite structure was identified for Ag₂S. For partial CE, again domains and stripes with different crystal structures and orientations were again observed.

To summarize the entire chapter, tracking the CE from CdS to Ag₂S was not feasible by simply applying the transistor characterization method established for CdSe/Ag₂Se. The challenges encountered are diverse and can primarily be attributed to difficulties in retrieving a reliable signal in combination with a sensitive structure. Measuring transport was challenging due to the low currents in the pA-regime, while higher applied biases (> 200 mV) led to nonlinear transport characteristics. Additionally, degradation was observed during prolonged measurements. Therefore, while tracking via transistor characterization was demonstrated to be possible in principle, it must be performed carefully. In contrast, tracking by optical spectroscopy proved impractical due to the instability of Ag₂S under illumination, particularly with a focused laser beam. While no fluorescence was observed, the formation of Ag NPs was frequently noted under irradiation. Monitoring the CE using SPM was successful and enabled the nondestructive tracking of individual NWs throughout the entire CE reaction. This method revealed a significant difference in the exchange mechanism between CdS/Ag₂S and CdSe/Ag₂Se. The exchange for sulfide was found to be inhomogeneous, as demonstrated not only in topography but also in the evolution of the surface potential. In contrast, the CE for selenide was relatively featureless in both AFM and KPFM data, indicating a homogeneous CE. The inhomogeneous nature of the CE for CdS/Ag₂S was further confirmed by HRTEM, where Ag₂S domains and striped intermediate phases were observed for partial CE. Together with XRD, the crystal structure was determined to be wurtzite for CdS and acanthite for Ag₂S.

5. Summary

The objective of this work was to nondestructively investigate the CE on the same individual NWs throughout the entire reaction. For this study, the well-characterized CdS and CdSe NWs were exchanged with Ag. To achieve CE tracking, the transistor characterization developed for the CdSe/Ag₂Se system by Schwarz⁴⁰ should be refined and applied to the CdS/Ag₂S system.

Initially, NWFETs had to be fabricated for the transistor characterization. The existing NWFET fabrication protocol for CdSe NWs proved unsuitable for the studied CdS NWs. In particular, the formation of an ohmic contact with Ti to the CdS NW was found to be infeasible. Experiments with various metals demonstrated the difficulty in obtaining a satisfactory contact; only contacts containing In showed promising results. However, In contacts alone suffered from dewetting and oxidation, which resulted in rather insulating contacts. This issue was mitigated by the deposition of an Au layer on top of the In layer. It is essential that the Au layer is narrower than the In layer and well aligned to ensure that no direct contact between Au and NW is formed.

XPS measurements revealed that the S^{2-} on the NW surface is partially oxidized to SO_4^{2-} and that the surface is contaminated with organic residues. These findings explain the challenges encountered in obtaining an ohmic contact and demonstrate that the NW surface must be treated. Chemical treatments, particularly wet-chemical etching with HCl, followed by passivation with ligands and subsequent ligand removal through annealing prior to metal deposition, yielded promising results. Additionally, various physical treatments, including plasma cleaning, bombardment with electrons and Ar ions (Ar etching), and annealing were studied. It was observed that the time period between treatment and deposition is critical and should be minimized, as the surface readily re-oxidizes. The combination of Ar etching followed by the immediate deposition of Mg contacts through sputtering resulted in the highest conducting device. While both wet-chemical etching and physical-Ar etching are based on the removal of the oxidized surface to reliably obtain ohmic contacts, interdiffusion of In into the metal-semiconductor interface at elevated temperature, as occurring during annealing or in the two-step fabrication of In/Au contacts, also proved effective in achieving ohmic contacts. Annealing must be conducted with great care to avoid oxidation of the In contacts; thus the two-step fabrication is preferred. The best devices, demonstrating a high electrical conductivity, a high yield of responsive NWs, and chemical stability, were achieved with In/Au contacts produced through the two-step fabrication method. Ar-etched Mg device exhibited slightly better electrical performance but lacked chemical stability.

Prior to CE experiments, the fabricated CdS NWFETs were analyzed using current-voltage and transfer characteristics under various environmental conditions. Under dark ambient conditions, the NWs exhibited effectively insulating behavior, with a low electrical conductivity of $9 \cdot 10^{-6}$ S/m. This low electrical conductivity is attributed to a very low electron concentration of $9 \cdot 10^{13}$ cm⁻³, paired with a low electron mobility of $6 \cdot 10^{-3}$ cm²/Vs. Under illumination, the electrical conductivity significantly increased by four orders of magnitude, reaching up to $6 \cdot 10^{-2}$ S/m, primarily due to the generation of photoexcited charge carriers, as electron concentration increased to $4 \cdot 10^{17}$ cm⁻³, while electron mobility remained relatively constant, with values of $9 \cdot 10^{-3}$ cm²/Vs. Furthermore, it has been demonstrated that higher currents at a constant source-drain voltage can be observed at elevated temperatures and under nitrogen atmosphere, indicating the potential of the CdS NWFETs for sensor applications. By combining SPM techniques under local illumination with simulations, further insights into the charge-carrier distribution

could be gained. These results facilitate the retrieval of transport properties for both electrons and holes and reveal the contributions of drift and diffusion currents to the overall measured current.

CE tracking was demonstrated first on the CdSe/Ag₂Se system, thereby proving the potential of the method.⁷⁶ In addition, the transport properties of completely exchanged NWs under cryogenic conditions were studied, further validating the metallic transport behavior of Ag₂Se NWs. For the CdS/Ag₂S system, completely exchanged Ag₂S NWs were investigated using the transistor characterization. Nonlinear transport characteristics were observed, which impede the direct extraction of transport properties and suggest that both electric and ionic components influence charge transport. A rough estimation of the transport properties revealed a significant increase in electrical conductivity up to $4 \cdot 10^{-2}$ S/m, accompanied by a drastic increase in electron concentration to $1 \cdot 10^{20}$ cm⁻³ and a decrease in electron mobility to $2 \cdot 10^{-4}$ cm²/Vs, even under dark conditions. However, the retrieval of these parameters proved challenging, as the measured current was relatively low, and higher voltages induced irreversible transformations. Such observations have been reported in the literature under the term "resistive switching" and are attributed to the transformation of the crystal structure and the formation of a conducting Ag filament within the NW, which may also apply to the NWs studied in this work.

Due to the challenges encountered in employing transistor characterization to nondestructively monitor the CE, the optical properties were investigated through confocal fluorescence spectroscopy in an attempt to track CE *via* changes in fluorescence. However, fluorescence corresponding to Ag₂S could not be detected, and under illumination, the formation of Ag NPs was observed. Despite efforts to enhance the fluorescence intensity or to prevent the formation of Ag NP, these attempts were ultimately unsuccessful, rendering the tracking of CE through optical methods infeasible.

A novel approach involving SPM techniques, specifically AFM and KPFM, was successfully developed and implemented to nondestructively monitor the CE for both the CdS/Ag₂S and CdSe/Ag₂Se system. AFM facilitated the observation of alterations in topography, while KPFM provided insights into changes to the surface potential. The CE for the sulfide system was found to be inhomogeneous, as significant changes in both topography and surface potential were observed. In contrast, for the selenide system, no significant observations were noted, indicating a homogeneous CE. HRTEM further confirmed the inhomogeneous nature of the CE for CdS/Ag₂S, revealing the presence of domains and striped intermediate phases. Additionally, the preservation of shape and crystallinity was demonstrated. The crystal structure underwent considerable distortion from the wurtzite CdS host lattice to result in the acanthite Ag₂S lattice. The successful transformation and correct assignment of crystal structure were further verified using XRD.

Since the transport measurements on completely exchanged Ag_2S NWs were conducted using In contacts without any treatment, for future investigations the optimized device fabrication might be applied to study the transport properties more effectively. In particular, In/Au contacts fabricated in two steps, in which In interdiffusion likely occurs, represent a promising option. The diffusion of In into the NW and the resulting doping should be examined in greater detail to better understand the processes involved and to further optimize the contacts. It is conceivable that the fabrication of devices with four contacts on a single NW, in conjunction with four-point measurements, might enhance the measured device response. Additionally, further investigations into the nonlinear transport characteristics would help to unravel the contributions of electrons and ions to charge transport. Following the work of Junod *et al.*¹¹⁸ and Schwarz,⁵⁴ the superionic phase transition of Ag_2S might as well be promising to study using transistor characterization on the fully exchanged NWFETs.

6. Experimental Section

This chapter provides detailed information regarding the experiments and characterizations performed to obtain the results presented in the previous sections. Initially, a list of all used chemicals is provided to facilitate reproduction of the experiments. The protocol for the synthesis of CdSe and CdS NWs, along with the device fabrication that includes standard procedures and various surface treatments, is detailed. Subsequently, information regarding the CE reaction is provided. Finally, all characterization setups will be introduced, accompanied by the relevant measurement conditions.

6.1. Chemicals

All chemicals utilized in the experiments were used without further purification. Oxygen-sensitive compounds were stored under nitrogen atmosphere and photoresists were stored under exclusion of light in a refrigerator. The chemicals used, along with their formulas, purity, supplier and LOT-number are presented in Table 6.1.

Chemical	Formula	Supplier	Purity (%)	LOT-No.
Acetone	C_3H_6O	VWR Fischer Chemical	> 99.5 ≥ 99.8	-
Charcoal activated	С	Merck	-	K55605614347
Argon	Ar	SOL	99.996	-
Bismuth	Bi	chemPUR	99.999	Ch.160215
Cadmium diethyldithio- carbamate	$C_{10}H_{20}CdN_2S_4$	Self-synthesized	-	-
Cadmium avida	CdO	chemPUR	99.999	Ch.0290321
Caulifiulii oxide		Alfa Aesar	99.998	23972
Chrom etch	-	Self-synthesized	-	-
Developer AZ 726 MIF	-	MicroChemicals	-	DEAA510708
Developer Microposit MF-319	-	DOW	-	E751JB003
Diethyl ether	$C_{4}H_{10}O$	VWR	99	-
Ethanol	C_2H_6O	Fischer Chemical	99.8	-
Ethylenediamine	$C_2H_8N_2$	Acros Organics	99	A0307095
Gold	Au	Norddeutsche Edelmetall Schneideanstallt	99.99	-

 Table 6.1: Chemicals used for experiments including the formula, supplier, purity and LOT number.

Chemical	Formula	Supplier	Purity (%)	LOT-No.
Hexane	C_6H_{14}	Fischer Chemical	≥ 95	-
Hydrochloric acid	HCl	Fischer Chemical	~37	2229784
T 1.	In	ChemPUR	99.999	Ch.220317
Indium		ChemPUR	99.999	Ch.091123
Isopropanol	C_3H_8O	VWR	≥ 99.7	-
Lift Off Resist LOR 5A	-	KAYAKU	-	22050375
Magnesium	Mg	ChemPUR	99.98	Ch.904843
Mathanal	CH4O	Fischer Chemical	≥ 99.8	-
Methanoi		Grüssing GmbH	99.5	-
Octanoic acid	$C_8H_{16}O_2$	Sigma Aldrich	≥ 99	MKCG2986
Photoresist AZ ECI 3012	-	MicroChemicals	-	DEAA319379- 1RHN
Photoresist Microposit S1805	-	DOW	-	A016LBO010
Platinum	Pt	ChemPUR	99.9	Ch.100220
Remover Microposit 1165	-	DOW	-	E751JI005
Selenium	Se	Alfa Aesar	99.999 > 99.5	-
Silvor	٨a	Thermo Scientific	2)).5	A0433013
Silver	Ag	- Ciana Alduich	-	-
Silver nitrate	AgNO ₃	Sigma Aldrich	99.9999 99.9999	0000175935
Sulfur	S	Sigma Aldrich	99.99	MKCJ0986
Thioglycerol	$C_3H_8O_2S$	Sigma Aldrich	97	-
The second second		Alfa Aesar	99.995	61600846
litanium	11	ChemPUR	99.995	Ch.091123
Toluene	C_7H_8	Fischer Chemical	≥ 99.8	-
	$C_{24}H_{51}P$	ABCR	97	-
Trioctylphosphine		Cytec Inc.	97	-
		Strem Inc.	≥97	-
Trioctylphosphine oxide	$C_{24}H_{51}OP$	Sigma Aldrich	99	MKCW7577

Table 6.1 (Continuation): Chemicals used for experiments including the formula, supplier, purity and LOT number.

6.2. Nanowire Synthesis

In this work, two distinct types of NW syntheses were employed: the SLS synthesis of CdSe NWs and the solvothermal synthesis of CdS NWs. First, the synthesis of CdSe NWs, which includes the preparation of the precursors, is presented, followed by a detailed description of the synthesis of CdS NWs.

6.2.1. CdSe Nanowires

The synthesis of CdSe NWs was performed after the synthesis protocol of Schwarz *et al.*,⁵⁴ which was adapted from work of Littig *et al.*,¹¹² The synthesis requires cadmium and selenium precursors, which were synthesized in advance of the NW synthesis and were stored under a nitrogen atmosphere with continuous stirring. The synthesis of the NWs was carried out on pre-patterned substrates, with minor adjustments for synthesis, as described in Section 6.3.1.

Synthesis of the Cadmium-octanoate Precursor

In a three-neck flask equipped with a rubber septum, a thermocouple, a magnetic stirring bar, and a reflux condenser, 321 mg (2.5 mmol) CdO were dispersed in 2.5 mL (15.8 mmol) octanoic acid (OCA). The reaction mixture was conditioned at room temperature for at least 30 min by cycling between vacuum and nitrogen atmosphere three times. Subsequently, 2.5 mL (5.6 mmol) trioctylphosphine (TOP) were added to the reaction mixture, which was then gradually heated to 240 °C with a heating rate of 10 °C/min under nitrogen atmosphere. Upon reaching 240 °C, the reaction mixture underwent a transition from a turbid brownish dispersion to a clear colorless solution (with a slight yellowness), indicating the formation of the cadmium-octanoate $(Cd(OCA)_2)$ complex. Heating was discontinued upon reaching 240 °C, and the reaction mixture was allowed to cool slowly to room temperature. The resulting 0.5 M Cd(OCA)₂ precursor was transferred to a glass vial and stored in the glovebox under nitrogen atmosphere.

Synthesis of the Selenium Precursor

The selenium precursor was synthesized by dispersing 1.58 g (20 mmol) Se in 10.0 mL (22.4 mmol) trioctylphosphine (TOP) and stirring for at least 24 h at room temperature within the glovebox under nitrogen atmosphere. After 24 h, the reaction mixture transitioned from an initially turbid dark gray dispersion to a clear, slightly yellow solution, indicating the formation of the Se-TOP complex, resulting in the 2 M Se-TOP precursor.

Synthesis of the CdSe NWs on the substrate

Prior to synthesis, 20 nm of Bi were deposited onto the pre-patterned substrate (see Section 6.3.1). The excess metal was removed during lift-off in acetone, followed by rinsing in isopropanol and drying using nitrogen flow. The successful deposition of the Bi catalyst patches and complete lift-off were verified by optical microscopy.

In a four-neck flask equipped with a rubber septum, a thermocouple, a magnetic stirring bar, a substrate holder (clamp on a rod), and a reflux condenser, 20.0 g (51.7 mmol) trioctylphosphine oxide (TOPO) were weighted. The substrate was fixed on the substrate holder (above reaction volume), and the reaction volume was heated to 120 °C, with TOPO melting around 60 °C, allowing to stir the solution. The reaction solution was conditioned at 120 °C for at least 30 min by cycling between vacuum and nitrogen atmosphere three times. The reaction solution was gradually heated up to 255 °C with a heating rate of 10 °C/min under nitrogen atmosphere. Simultaneously, 300 μ L (0.15 mmol) 0.5 M Cd(OCA)₂ and 75 μ L (0.15 mmol) 2M Se-TOP were each diluted with TOP to a volume of 1 mL. Prior to lowing the substrate into the reaction solution, the rotation

speed of the stirrer was decreased to prevent damages to the substrate. Subsequently, the substrate was carefully lowered into the hot reaction solution, allowing the Bi patches to melt for 1 min before any precursor injection. The Cd(OCA)₂ was injected swiftly, and the reaction solution was allowed to restore the reaction temperature ($\approx 2 \text{ min}$). Next, the Se-TOP was added slowly over the course of 1 min, and the reaction was continued for an additional 10 min following the complete addition. The reaction was stopped by withdrawing the substrate from the reaction solution, allowing the reaction vessel to cool, and adding 20 mL of toluene at 100 °C. Subsequently, the substrate was removed, thoroughly rinsed with toluene, and then submerged in hexane for at least 30 min. The reaction solution, exhibiting a dark red-brown color upon successful reaction, was discard. Lastly, the substrate was rinsed with isopropanol and dried under nitrogen flow.

For reactions with only ¹/₄ Substrate, the reaction volume was reduced to 12.0 g (31.0 mmol) TOPO and the precursor amounts were adjusted to 200 μ L (0.10 mmol) 0.5 M Cd(OCA)₂ and 50 μ L (0.10 mmol) Se-TOP, both of which were diluted with TOP to a volume of 0.5 mL.

6.2.2. CdS Nanowires

The synthesis of CdS NWs was performed following a protocol reported by Böttcher,¹³³ which utilizes the single-source precursor cadmium diethyldithiocarbamate (Cd(DDTC)₂, referred to as cadmium thiocarbamate) in a solvothermal synthesis. The cadmium thiocarbamate was synthesized and extensively characterized in previous work.⁵³

For the solvothermal synthesis of CdS NWs, a commercially available autoclave with a Teflon inlay exhibiting a volume of 25 mL was used. 163.8 mg (0.4 mmol) Cd(DDTC)₂ were dissolved in 10 mL (0.15 mol) ethylenediamine (en) while stirring at ambient conditions for at least 20 min. The Teflon inlay was placed into the autoclave, which was then tightly closed, and the entire autoclave was placed in a box furnace. The furnace was programmed to gradually heat to 200 °C over the course of 2 h, maintain the reaction temperature for 60 h, and then turn off, allowing for slow cooling to room temperature over a period of 24 h (without opening the furnace). The autoclave was removed from the furnace and was allowed to cool further for 1.5 h before being carefully opened.

The reaction mixture was diluted with 10 mL ethanol and centrifuged for 10 min at 11 000 rpm at room temperature. The yellow precipitate, consisting of CdS NWs, was separated from the dark brown reaction solution, redispersed in 10 mL ethanol and then centrifuged again, while the reaction mixture was discarded. The centrifugation procedure was repeated under the same conditions using the following solvents in the order: deionized water, diluted (1 mM) hydrochloric acid, deionized water, and ethanol (four times). The CdS NW dispersion in ethanol was transferred into a flask, and the solvent was removed under vacuum. The CdS NW were once again redispersed in ethanol and dried under vacuum for one hour (reaching p = 0.07 mbar). Finally, the NWs were once more dispersed in 20 mL ethanol, transferred to a large Bottle (500 mL), diluted with ethanol to a total volume of 300 mL, and stored on an orbital shaker (Heidolph, Vibramax 100) at 200 rpm under ambient conditions.

For the deposition of individual CdS NWs, 5 mL of the bright yellow CdS NW stock solution were transferred in a smaller bottle (250 mL) and further diluted with 150 mL of ethanol, yielding a clear, slightly colored CdS NW deposition solution. The strong dilution, combined with storage on the orbital shaker, slows down NW aggregation and precipitation, which is crucial to enabling the deposition of individual NWs on the substrate in the following steps.

6.3. Device Fabrication

For the fabrication of NWFETs, various lithography techniques and resist systems (see Section 0) were employed, depending on the specific requirements. Positive photoresists were used for all lithography processes. All devices were fabricated on 500 µm thick Si wafers with a 300 nm thermally grown SiO₂ layer (Si-Tech Inc., N/As, $\rho < 0.005 \Omega$ cm, LOT-No. 10419), with the exception of devices designated for local illumination in combination with KPFM experiments (see Section 4.2.2), for which 175 µm thick 2x2 cm² ITO substrates (PGO, CEC020T, Borosilicate covered with ITO, $\rho \approx 20 \Omega/sq$) were used. First, the pre-patterning process for all substrate types is introduced. Second, the methodology for establishing contacts to NWs is presented. Third, the various surface treatments applied to CdS NW are described.

6.3.1. Pre-Patterning of Substrates

The pre-patterning of all substrates is similar, with variation primarily in the specific patterns transferred to each substrate. All device layouts, contacts, and other structures were designed using the software KLayout.¹³⁶ Depending on the quantity of substrates, the pattern was transferred either by using a mask and a mask aligner (Karl Suss, MJB3) or maskless aligner (Durham Magneto Optics, MicroWriter ML3).

Preparation of Si wafers

The Si wafers were initially cut into rectangles of approximately 2 cm by 2 cm by creating scars along the crystal axis using a diamond pen, followed by breaking the Si wafers along these scars with tweezers. The wafers were subsequently cleaned by submerging them in acetone and employing ultrasonication for at least 15 min. This cleaning procedure was then repeated using isopropanol and deionized water. After each cleaning step, the substrates were purged with nitrogen to prevent residues from drying onto the substrates.

Fabrication of a Mask

Patterning using the mask aligner requires a mask, fabricated from chrome blanks (Nanofilm, Soda Lime, AZ 1518 (0.53 μ m), B-3-08-18). The chrome blanks were pre-coated with the photoresist AZ 1518 and could directly be exposed using the MicroWriter with the following settings: For large structures (> 500 μ m, alignment windows and back-gate pads), the quality (Q) was set to "Normal", the resolution (R) to 2 μ m, the exposure dose (D) to 150 mJ/cm², and focus correction (F) to 0 μ m; for medium structures (> 50 μ m, contact pads and contact leads), R was set to 1 μ m, while all other parameters remained unchanged; for fine structures (< 50 μ m, marker and patches), the settings were adjusted by setting Q to "Super", R to 0.6 μ m, and D to 250 mJ/cm². The exposed chrome blank was developed in the developer AZ 726 MIF for 30 s, rinsed in deionized water for 60 s, and dried under nitrogen flow. The chrome layer was removed by submerging the blank in a chromium etchant until the structure became visible (≈ 3 min), followed by rinsing in deionized water for at least 60 s and drying under nitrogen flow. The photoresist was removed by submerging the mask in acetone for at least one hour, rinsing in isopropanol and deionized water, and drying under nitrogen flow. Persistent photoresist residues were gently removed using a soft, non-abrasive tissue soaked with acetone.

Patterning using the Mask Aligner

The cleaned $2x2 \text{ cm}^2$ substrates were placed onto the spin-coater (Süss MicroTec, Labspin6) and coated with photoresist by applying 150 μ L AZ ECI 3012 to the substrates, followed by spinning

using a defined program (5 s at 200 rpm/ 5 s acceleration to 4000 rpm/ 60 s at 4000 rpm). For the soft-bake, the substrates were placed onto a hot plate for 90 s at 90 $^{\circ}$ C.

Subsequently, the substrates were exposed for 16 s using the mask aligner, with the desired structure defined by the utilized mask. For the post-exposure bake (PEB), the substrates were again placed onto a hot plate for 90 s at 110 °C. The substrates were developed by immersing them in the the developer AZ 726 MIF for 60 s with gentle swiveling, followed by rinsing in deionized water and drying under nitrogen flow.

For the substrates intended for SLS synthesis, the patterning of the contact pads and patches is divided into two separate lithographic steps, requiring the following adjustments to the patterning. The contact pads are defined using the "structure mask" with an exposure duration of 8 s, while the patches are defined using the "patch mask" with an exposure duration of 16 s.

Patterning using the Maskless Aligner

The handling of the photoresist, including the spin coating and baking parameters, is identical for patterning using the MicroWriter. The substrates were placed in the MicroWriter, where the approximate height of the substrate ($\approx 500 \,\mu$ m) was set, and the auto focus was performed. Alignment was performed at the four corner of the substrate to correct for the offset and rotation. The desired pattern was loaded into the system, and the following parameter were set: for contact pads and contact leads, Q was set to "Normal", R to 1 μ m, D to 100 mJ/cm², and F to 0 μ m; for marker and patches, the parameters were adjusted by setting Q to "Super", R to 0.6 μ m, and D to 200 mJ/cm². Both the automatic focus lock (AFL) and the real-time focus correction (RTFC) were enabled.

For the substrates intended for SLS synthesis, the same parameters were utilized, but contact pads and patches were transferred in separate lithographic steps, as with the mask aligner. For the transparent ITO substrates, the RTFC option was disabled due to reduced reflectivity of the substrate, rendering the RTFC ineffective.

Metal Deposition and Lift-off

To enhance metal adhesion to the substrate, the substrates were placed in a plasma oven (Harrick Plasma, PDC-002) and treated with a mild air plasma (P = 7 W, p = 0.3 mbar) for 30 s prior metal deposition. Typically, for pre-patterning 10 nm Ti were deposited, followed by 40 or 50 nm Au, *via* physical vapor deposition (PVD) using a coating system (Oerlikon Leybold Vacuum, Univex 350G). The deposition was carried out within a pressure range of 10^{-7} to 10^{-6} mbar with slow deposition rates of 0.1 Å/s for the initial 5 nm, which was subsequently increased to 0.4 Å/s.

After metal deposition, excess metal was removed in the lift-off by submerging the substrates in acetone for at least 5 min. The lift-off process was completed by transferring the substrates into a fresh acetone solution and applying ultrasonication for a few seconds. Finally, the substrates were rinsed in isopropanol and dried under nitrogen flow. The substrates intended for CdS NWs were complete and stored until NW deposition.

For substrates intended for SLS synthesis of CdSe NWs, the lithography was repeated as described previously to deposit the patches. For these patches, only 5 nm Ti and 5 nm Au were deposited. For synthesis, 20 nm Bi were freshly deposited *via* PVD using a different coating system (Quorum, Q150T). The deposition was carried out at a pressure of $5 \cdot 10^{-4}$ mbar, with deposition rates of approximately 0.25 nm/s.

6.3.2. Contacts to Nanowires

Contacting the NWs is principally identical for both CdS and CdSe NWs, with the primary difference being the deposition of NWs. Since the synthesis of CdSe NWs was performed directly on the substrates (see Section 6.2.1), no further deposition was required, as in contrast for the CdS NWs.

Deposition of CdS NWs

For the deposition of CdS NWs, 1 mL was freshly taken from the CdS NW deposition solution (see Section 6.2.2) and subjected to ultrasonication for 5 min. In parallel, the substrate was fixed on a spin coater and rotated at approximately 3000 rpm. Subsequently, 40 μ L of the NW solution were deposited dropwise onto the spinning substrate. The concentration of individual NWs on the substrate was checked using an optical microscope. If the concentration of individual NWs was deemed insufficient, the NW solution was subjected to an additional minute of ultrasonication, followed by another dropwise deposition of 40 μ L. This procedure was repeated until a satisfactory concentration of individual NWs was achieved. Since prolonged ultrasonication may lead to fragmentation of the NWs, any remaining deposition solution (of the 1 mL) was discarded.

Defining Contacts using the Maskless Aligner

The substrates were quickly cleaned of potential dust under nitrogen flow and dehydrated on a hot plate for 5 min at 200 °C. 150 μ L of the lift-off resist LOR 5A were applied to the substrate by spin coating (5 s at 200 rpm/ 5 s acceleration to 3000 rpm/ 60 s at 3000 rpm). The substrates were then placed onto a hot plate and baked for 5 min at 180 °C. Subsequently, 150 μ L of the photoresist S1805 were applied by spin coating (5 s at 200 rpm/, 5 s acceleration to 4000 rpm/ 60 s at 4000 rpm), followed by a soft-bake for 60 s at 120 °C. To ascertain the optimal exposure dose, a 1x1 cm² Si-wafer was coated under the same condition in parallel.

The substrates were placed into the MicroWriter, the estimated height was set, and the auto focus was performed. Alignment was performed for the entire substrate based on the outer markers or patches to correct for offset, rotation, stretch and shear. To contact the NWs, the pattern to write was created using a self-written MATLAB¹³⁷ application, which utilized optical microscopy images to semi-automatically generate the required structure. The pattern to write was loaded into the MicroWriter, with Q set to "Super" and R to 0.6 μ m. The optimal values for D and F were derived from the dose-focus test; typical values for D ranged between 80 – 140 mJ/cm² and for F between -2 – +1 μ m. Additionally, both the AFL and RTFC were enabled for exposure (for ITO substrates only RTFC was disabled). In some cases, the AFL was also disabled and focus lock points were set to each individual NW to ensure correct and optimal exposure.

After exposure, no PEB was performed, as it is not required for this photoresist system. The substrates were directly developed for 90 s under gentle swiveling in the developer MF-319, followed by rising in deionized water for at least 60 s and drying under nitrogen flow. In some cases, prolonged development times up to 150 s were necessary to fully develop the resist, or the development time was intentionally increased to enhance the undercut formation. The rinsing time in water must be sufficient to ensure complete removal of the developer, as damage to thin NWs was observed when the rinsing time was too short. Prior further processing, the quality of the contacts was evaluated using light microscopy.

Treatments, Metallization and Lift-off

Prior to metal deposition, plasma cleaning was utilized, as for the pre-patterning, to enhance metal adhesion and to remove residues from the NW surface. For CdSe NWs, the same plasma cleaning

parameters (t = 30 s, P = 7 W, p = 0.3 mbar) used in the pre-patterning were applied. For CdS NWs on Si wafers , various treatments were utilized, which will be further explained in following section. For CdS NWs on ITO substrates, the same mild plasma cleaning for 30 s was employed.

For the CdSe NWs, Ti contacts with a typical thickness of 75 nm were deposited using the coating system from Pfeiffer (Classic Vacuum 250), due to the close position of the metal boat to the substrate in the chamber. For the deposition of various contact materials for CdS NWs, the deposition form Leybold (Univex 350G) was typically utilized. Commonly deposited materials included 75 nm Ti, 50/50 nm In/Au, or 10/50 Ti/Ag. For some devices, the metal was deposited *via* sputtering using the precision etching and coating system from Gatan (682 PECS), particularly for 50 nm Pt contacts or for metal deposition immediately following Ar etching (see Section 6.3.3). In all cases, the deposition process was conducted under similar conditions, with typical thicknesses ranging from 50 to 100 nm for the metal films.

After metal deposition, the lift-off was performed by submerging the substrates in the Remover 1165 for at least 1 h under constant stirring. Subsequently, the substrates were rinsed in acetone, isopropanol, and dried under nitrogen flow. For more complex contacts that were divided into two lithographic steps, the lithography was repeated using the same parameters, with only the transferred structure or deposited metal being changed.

The CdS-NW devices were typically studied directly after fabrication. In contrast, for the CdSe-NW devices, a post-processing, including an UV-treatment and annealing, was employed. For the UV-treatment, the substrates were placed in the mask aligner and irradiated for 20 min. Annealing was performed in the self-built annealing oven (by Jan Flügge) for 30 min at 150 °C and for 30 min at 300 °C in vacuum.

6.3.3. Surface Treatments

In this work, the effects of various surface treatments were studied, primarily prior to metal deposition, but in some cases, treatments were applied before lithography or after device fabrication.

Plasma Treatment

All plasma treatments were conducted immediately prior to metal deposition, and the duration between treatment and deposition was minimized as much as possible. For plasma treatments using air plasma, a commercially available plasma oven (Harrick Plasma, PDC-002) was utilized with the following settings: P = 7 W; p = 0.3 mbar; t = 30 s; pulse duration = continuous plasma. For plasma treatments using Ar plasma, the PECVD setup from Ruhmlieb was used.⁹⁹ The power of the plasma generator was set to 50 W for milder treatments and to 200 W for harsh treatments. The pressure was set to 0.4 mbar, and treatment duration was extended to 2 min. The Ar plasma was pulsed with a frequency of 27.12 MHz with a pulse duration of 100 ms at a 50% duty cycle.

Wet-chemical etching

The wet-chemical etching protocol using HCl and thiogly cerol was adapted from Dufaux et al.⁶²

10 mL of the CdS NW stock solution were taken and centrifuged for 20 min at 11 000 rpm. The precipitated CdS NWs were separated and redispersed in 10 mL diluted hydrochloric acid solution with a pH of 2. The dispersion was subjected to ultrasonication for 1 min and subsequently stirred for 20 min. The NWs exhibited limited stability in the hydrochloric acid solution, which was evident in strong aggregation and rapid precipitation when stirring was discontinued.
To the NW dispersion, $100 \ \mu$ L (1.16 mmol) thioglycerol were added and stirred for at least 1 h. Upon addition of thioglycerol, the colloidal stability of the NW dispersion was immediately regained, similar to that of the stock solution in ethanol. The dispersion was centrifuged for 15 min at 11 000 rpm, the supernatant was discarded, and the precipitated NWs were redispersed in 10 mL of ethanol. The NW suspension was again centrifuged under the same conditions and redispersed in ethanol. This washing with ethanol was repeated two times, and the final CdS NW solution stabilized with thioglycerol was stored on the orbital shaker at 200 rpm under ambient conditions.

Device fabrication was similar to that of other CdS NWs devices, with following treatments prior to metal deposition. Excess ligands were removed by annealing for 15 min at 350 °C under an argon atmosphere. Additionally, an Ar plasma treatment was performed using the previous settings at a power of 200 W.

Argon etching

Ar-etching was performed prior metal deposition using the precision etching and coating system from Gatan (682 PECS). First, the etching gun was allowed to warm up by operating at an energy (*E*) of 5 keV with a beam current (*I*) exceeding 100 μ A for 10 min. Subsequently, *E* and *I* were lowered to 1.7 keV and 10 μ A, respectively, and the etching gun was allowed to stabilize for an additional 5 min. For Ar etching, the shutter protecting the device was opened for the desired duration, typically 20 s, and then closed again.

Immediately following Ar etching, the desired metal was deposited *via* sputtering. For Ti, the following parameters were used for sputtering: E = 7 keV and $I = 360 \mu$ A, resulting in a deposition rate of approximately 0.8 Å/s. For In and Mg, the following parameters were employed: E = 5 keV and $I = 250 \mu$ A, leading to a deposition rate of approximately 1.0 Å/s. For both Ar etching and metal deposition, the rotation speed of the sample holder was set to 30 rpm to ensure homogenous removal and deposition.

Annealing

Annealing was carried out in various systems under differing conditions. In the self-built annealing oven, annealing was typically performed after conditioning the atmosphere by cycling three times between nitrogen and vacuum, for 30 min at 150 °C and for 30 min at 300 °C in vacuum. Similarly, annealing in the PECVD from Ruhmlieb was performed for 30 min at 150 °C and for 30 min at 325 °C in vacuum after conditioning with argon. In contrast, conditioning in the Linkam stage was achieved by purging the chamber with liquid nitrogen prior to heating (see Section 6.5.1). The annealing often was combined with transport measurements and was set up as follows: first the stage was heated to 150 °C with a heating rate of 10 °C/min. Upon reaching 150 °C, the temperature was maintained for 30 min, followed by gradually cooling the stage to room temperature with a rate of 10 °C/min. In a few instances, after holding 150 °C, the stage was heated to 300 °C at a rate of 10 °C/min, maintained at 300 °C for 30 min, and then cooled to room temperature at the same rate.

6.4. Cation Exchange

First, a 5 mM AgNO₃ stock solution was prepared by dissolving 8.5 mg (50 μ mol) AgNO₃ in 10 mL methanol under stirring for at least 20 min. Subsequently, 1 mL (5 μ mol) of the 5 mM stock AgNO₃ stock solution were diluted with 9 mL methanol to yield a 0.5 mM AgNO₃ stock solution. 80 μ L (40 nmol) of the 0.5 mM AgNO₃ stock solution were mixed with 8 mL methanol and 2 mL toluene

to yield the exchange solution. The stock solutions were used within 36 h, while the exchange solutions were freshly prepared for every exchange step and discarded afterward.

For CE, the substrates were first quickly submerged in methanol and then placed in exchange solution for the desired time (1 s - 24 h) under slow stirring (300 rpm). Depending on the reaction time, the substrate was either held by tweezers (t < 60 s) or by a clamp attached to the cap of the vial (t > 60 s). After CE, the substrate was removed, submerged in methanol for at least 2 min with gently swiveling, rinsed in isopropanol, and dried under nitrogen flow. All CE reaction were performed under ambient conditions at room temperature. Efforts were made to minimize exposure to light by performing the reactions in amber glass vials, covering the reaction vials during longer reaction times, and using minimal ambient light in the laboratory.

6.5. Characterization

The transport properties of the fabricated NWFETs were studied using a self-built transport measurements setup. All further characterization of the NWs and NWFETs regarding geometry, material composition or other properties, was performed using various methods.

6.5.1. Electrical Transport Measurements

The electrical transport measurements were typically performed using a self-built probe stage under ambient conductions. To study the response to changes in temperature or chemical environment, the setup was modified by changing the probe stage to a commercially available probe stage with environmental control (Linkam, LTS420E-P).

Ambient Measurements

For standard measurements, the devices were placed onto glass slide fixed to a sample stage (Thorlabs, XR25P-K1/M) with x and y-axis control, located within a grounded metal box. Electrical contact was established by placing gold-plated tungsten probe needles (Micromanipulator, 7B-10G) onto the contact pads using micromanipulators (Formfactor, DPP105). During device installation or positioning, all electrodes were grounded to prevent damage from electrostatic discharges. To assist in accurate positioning of the probe needles onto the contact pads, a USB digital microscope (Reflecta, DigiMicroscope Flex) equipped with a white light LED was used. All measurements were performed with the metal box closed. For measurements conducted in the dark (labeled as "Dark"), the white light LED was turned off, while for measurements under illumination (labeled as "Bright"), the LED remained on.

The drain and gate electrodes were connected to source units (Yokogawa, GS200) and the source electrode was connected to a multimeter (Keysight, 34465A) *via* a current-voltage amplifier (Femto, DLPCA-200). The gain was typically adjusted between 10⁶ to 10⁹ to ensure highest measurement precision. The source units and multimeter were controlled using a LabView¹³⁸ application. A 10 K Ω series resistance was installed between the gate electrode and source unit to protect the device in the event of failure of the insulating layer. The electrical transport measurement setup under illumination is schematically depicted in Figure 6.1.



Figure 6.1: Schematic illustration of the electrical transport measurement setup under illumination. Relevant components located inside the grounded metal box are annotated, while those outside are indicated by an arrow pointing outward.

The current-voltage characteristics were recorded by sweeping the applied bias to the drain electrode while recording current at the source electrode. The sweep range was chosen based on the device response. For practically insulting CdS NW devices, voltage sweeps up to \pm 5 V were performed with a sweep rate of 50 mV per 0.25 s, while for highly conductive Ag₂Se NW devices, voltage sweeps were limited to \pm 10 mV with a sweep rate of 250 μ V per 0.25 s. For all *IV* curves, the sweeps were performed first to positive voltages, then to negative voltages, and finally back to zero, while no gate voltage was applied (unless stated otherwise).

The transfer characteristics were recorded by sweeping the applied bias to the gate electrode while a constant source-drain bias was applied and recording the current at the source electrode. For typical gate sweeps, a potential range up to \pm 30 V was applied to the gate electrode with a sweep rate of 250 mV per 0.5 s. Similar to the *IV* curves, the transfer curves were recorded with positive gate voltages first, followed by negative voltages, expect for devices with a strongly pronounced hysteresis, where the sweep direction was reversed. The applied source-drain bias was selected based on the device response and ranged from 1 mV to 1 V.

The recorded measurements were semi-automatically evaluated using a self-written MATLAB¹³⁷ application. Linear fits were applied to the linear range of the recoded *IV* and transfer curves to obtain the electrical conductivity, charge-carrier and concentration (see Section 3.1)

Temperature- and Environmental-dependent Measurements

For transport measurement under elevated temperatures or in a nitrogen atmosphere, the devices, with a cover slip beneath, were placed on the heating plate of the probe stage (Linkam, LTS420E-P). The cables were disconnected from the metal box and connected to the Linkam stage. Electrical contact with the devices was established by placing gold-plated tungsten probe needles (Micromanipulator, 7B-10G) on the contact pads using specialized micromanipulators from the Linkam stage. Similar to the previous measurements, all electrodes were grounded during device installation, and a USB digital microscope (Reflecta, DigiMicroscope Flex) was utilized for precise

positioning of the devices. For most measurements, the white-light LED was kept on, whereas for measurements conducted under dark conditions, the LED was turned off, and the sample window was covered. Apart from the probe stage and microscope, all other components were identical to those used in the previous transport measurements.

For simple measurements under nitrogen atmosphere, the stage was flushed with nitrogen from the building's main line for at least 5 min before recording any current. For more sophisticated measurements or those conducted at elevated temperatures, the probe stage was purged for 10 min by connecting a dewer filled with liquid nitrogen to the pump and circulating nitrogen through the chamber while the stage was heated to 40 °C. After purging, again the building's main line was reconnected to maintain the nitrogen atmosphere during measurements.

IV-curves and transfer characteristics were recorded using similar sweep ranges and rated as those for ambient measurements. To record the temporal evolution of the current while heating, instead of measuring *IV* curves, the source-drain voltage was pulsed, and the current at the set plateau bias was recorded. Such pulsed measurements were referred to as "current-tracks" in this work. Typically, the pulse was constructed as follows: the plateau bias was set to 250 mV, the voltage ramp to 100 mV/s, the on-time to 1 s and the off-time to 2 s, allowing the current to be recorded every 8 s. Concurrently, the probe stage was heated to the desired temperature (often 150 °C) at a heating rate of 10 °C/min, maintained that temperature for a set time (often 30 min), and then cooled at a rate of 10 °C/min. The temperature of the Linkam stage was controlled using the corresponding software "Link" provided from the manufacturer.

Measurements at Cryogenic Temperatures

Transport measurements at cryogenic temperature were performed at the *Paul-Drude-Institut für Festkörperelektronik* (PDI) in Berlin with assistance from PD Dr. Stefan Ludwig and Serkan Sirt. The sample was cooled to 4.2 K using liquid helium. *IV* and transfer curves were recorded using measurements setting similar to those used for ambient measurement of Ag₂Se NWs. For magnetic sweeps, a constant source-drain and gate voltage were applied while the magnetic field was swept up to \pm 12 T, with sweep rates ranging from 0.03 T/min to 0.12 T/min.

6.5.2. Microscopy, Spectroscopy and Others

In addition to the electrical properties, the NWs were studied using various methods to obtain information about their geometry, material composition, and optical properties. The employed methods can be roughly divided into those utilizing light, electrons, a probe or X-rays to interact with the sample.

Optical Microscopy

Magnified images of the NWs for localization and of the NWFETs to monitor the fabrication process were acquired using an optical microscope (Olympus, BX51). The microscope objective and imaging mode were selected based on the structure and sample size.

Confocal Fluorescence Microscopy and Spectroscopy

To study the optical properties of the NWs, a self-built confocal fluorescence microscopy and spectroscopy setup (by Christian Strelow) was used. All measurements were performed under ambient condition at room temperature. The devices were placed on a piezo sample stage and exposed to a focused laser beam. The emission of the white-light laser (NKT Photonics, SuperK EXTREME, EXU-6) was filtered to a wavelength of 488 nm using a laser filter (NKT Photonics, Fianium LLTF Contrast, VIS HPs). For reflection scans, the laser power was set to a minimum (6%),

while for PL scans and spectra, the power was set to 20%, corresponding to a power of 31.5 μ W. The laser light was directed through an objective (Edmunds Optics, M-Plan APO-NIR HR 100x) onto the sample, and the reflected or emitted light was subsequently collected.

To record the scans, the light was directed through mirrors to the APDs, while a dichromic mirror separated the VIS and NIR light, allowing the VIS APD (Micro Photon Devices, PDM) to detect the visible fraction and the NIR APD (ID Quantique, ID230) to detect the NIR fraction of the light. To record PL spectra, the mirrors were flipped so that the light was directed into the spectrograph (Princeton Instruments, SpectraPro 2300i). For spectra in the visible region, the light was directed to the VIS CCD (Andor, iDus 420). For spectra in NIR region, the mirror in the spectrograph was flipped, directing the light to the NIR CCD (Teledyne, NIRvana 640 SWIR).

Transmission Electron Microscopy

Standard TEM images were taken by Stefan Werner using a JEOL JEM 1011. HRTEM and STEM images, as well as EDX maps, were obtained by Andrea Köppen using a JEOL JEM 2200 FS. To image individual CdS NWs, a two to three drops of the CdS NW deposition solution (see Section 6.2.2) were deposited on carbon-coated copper mesh grid, which was rotated with approximately 3000 rpm on a spin-coater. For images of the exchanged NWs, the NWs were deposited as previously described and subjected to CE, as introduced in Section 6.4, but without stirring the solution.

Scanning Electron Microscopy

SEM images of the NWs and NWFETs were acquired using a FEI Quanta 3D FEG with an acceleration voltage of 20 kV. Higher resolution SEM image acquisition and EDX analysis were performed by Robert Schön using a Zeiss LEO Gemini 1550, with acceleration voltages ranging from 5 – 20 kV.

Atomic Force Microscopy

The topography of the NWFETs was studied after device fabrication prior to CE, using an atomic force microscope (JPK, Nanowizard II). The obtained scans were processed with the software Gwyddion¹³⁹ using plane leveling, row alignment and scar correction. The electrode distance was determined using the ruler option, while the NW diameter was determined by taking 15 profiles across the NW. The profiles were processed in a self-written MATLAB application, subtracting the background and determining the peak height corresponding to the NW diameter. The averaged value from these 15 profiles was used as the final NW diameter.

Kelvin Probe Force Microscopy

The KPFM measurements were conducted by Moritz Wehrmeister using an atomic force microscope (Bruker, Nanowizard 4 XP) in conjunction with a lock-in amplifier (Zürich Instruments, HF2LI). The samples were placed onto a sample stage (JPK, Tip assisted optics module) mounted to an inverted microscope (Zeiss, Axiovert 200) located within an acoustically insulated chamber. The entire chamber was situated on an optical table to minimize vibration and facilitate integration into an optical setup. The environmental conditions within the chamber could be controlled by flushing it with nitrogen and drying the atmosphere.

To monitor the CE reaction, the devices were measured at room temperature under dry nitrogen atmosphere while excluding light. The NWs were grounded through direct contact to the back-gate.

For the local illumination experiments, the measurements were performed under air, utilizing a diode laser (Picoquant, LDH-D-C-488) with an excitation wavelength of 488 nm and a power of 8.7 nW. The devices were incorporated into a chip-carrier, and electrical connection was established through bonding. The device was biased using a source unit (Zürich Instruments, MFLI 5 MHz), and the current was amplified by a lock-in amplifier (Stanford Research Systems, SR570) and recorded by a multimeter (Zürich Instruments, MFLI 5 MHz). Simulation of these experiments were performed by Carlo Höhmann using COMSOL Multiphysics.⁷⁸

X-ray Photoelectron Spectroscopy

XPS measurements and peak fitting were conducted by Dr. Heshmat Noei at the DESY NanoLab.⁹⁸ For these measurements, a thick film (> 100 μ m) of the CdS NWs was deposited onto 1x1 cm² Si wafers *via* drop casting and annealed under vacuum to remove solvent residues.

X-ray Diffraction

X-ray diffraction patterns were recorded by Nina Schober using a Phillips X'pert Pro MPD from 5° to 60°. For these measurements, a thick film (> 100 μ m) of the CdS NWs was deposited onto 1x1 cm² Si wafers. For Ag₂S measurements, the substrate with the deposited CdS NW film was subjected to CE (see Section 6.4) for 24 h.

7. Safety Instructions and Disposal

The safety instructions with the corresponding GHS symbols, hazard and precautionary statements, and disposal information for the chemicals used in this work are listed in Table 7.1.

Chemical	GHS Symbol	Hazard Statements	Precautionary Statements	Disposal
Acetone	Danger	H225, H319, H336	P210, P233, P240, P241, P242, P305+P351+P338	А
Activated carbon	Not a	hazardous substan (Regulation (EG)	ace according to CLP 1272/2008)	В
Argon	\diamond	H280	P403	С
Bismuth	Warning Not a	hazardous substan (Regulation (EG)	ace according to CLP 1272/2008)	В
Cadmium diethyldithio- carbamate	Warning	H302, H315, H319	P280, P264, P270, P330, P301+P312, P302+P352, P332+P313, P305+P351+P338, P337+P313, P321, P362+P364, P501	D, E
Cadmium oxide		H330, H341, H350, H361fd, H372, H410	P202, P260, P264, P271, P273, P304+P340+P310	D, E
Cadmium selenide	Danger	H301+H331, H312, H373, H410	P201, P261, P273, P301+P310+P330, P308+P313, P403+P233	D, E
Cadmium sulfide	Danger	H302, H341, H350, H361fd, H372, H410	P201, P273, P301+P312+P330, P308+P313	D, E

Table 7.1: List of used chemicals with the corresponding safety and disposal instructions.^{140,141}

7 Safety Instructions and Disposal

Chemical	GHS	Hazard	Precautionary	Disposal
	Symbol	Statements	Statements	•
Chrom etch	Danger	H272, H290, 314, H317, H411	P210, P220, P273, P280 P303+P361+P353, P305+P351+P338	F
Developer AZ 726 MIF	Dangar	H290, 302+H312, H314, H371, H373	P260, P280, 308+P311, P362+P364.	G
Developer Microposit MF-319	Danger	H315, H319, H372	P260, P264, P270, P280, P302+P352, P305+P351+P338, P307+P311, P332+P313, P337+P313, P362+P363, P405, P501	G
Diethyl ether	Danger	H224, H302, H336, EUH019, EUH066	P210, P233, P240, P241, P301+P312, P403+P233	А
Ethanol	Danger	H225, H319	P210, P233, P240, P241, P242, P305+P351+P338:	А
Ethylenediamine	Danger	H226, H302+H332, H311, H314, H317, H334, H412	P210, P273, P280, P303+P361+P353, P304+P340+P310, P305+P351+P338	Е
Gold	Not a	hazardous substanc (Regulation (EG) 1	e according to CLP 272/2008)	В
Hexane		H225, H304, H315, H336, H361f, H373, H411	P202, P210, P273, P301+P310, P303+P361+P353, P331	Е
Hydrochloric acid	Danger Danger	H290, H314, H335	P234, P261, P271, P280, P303+P361+P353, P305+P351+P338	Н

 Table 7.1 (continuation): List of used chemicals, including safety instructions and disposal.^{140,141}

Chemical	GHS	Hazard	Precautionary	Disposal
	Symbol	Statements	Statements	-
Indium	Not a	hazardous substan (Regulation (EG)	ce according to CLP 1272/2008)	В
Isopropanol	Danger	H225, H319, H336	P210, P233, P240, P241, P242, P305+P351+P338:	А
Lift Off Resist LOR 5A	Warning	H225, H315, H319	P210, P260, P280, P233, P305+P351+P338, P312, P337+P313, P370+P378, P403+P235, P501.	А
Magnesium	Danger	H228, H252, H261	P210, P223, P280, P302+P335+P334, P370+P378, P402+P404	В
Methanol	Danger	H225, H301+H311+ H331, H370	P210, P233, P280, P301+P310, P303+P361+P353, P304+P340+P311	Ε
Octanoic acid	Danger	H314, H412	P280, P301+P330+P331 P305+P351+P338, P310, P303+P361+P353	А
Photoresist AZ ECI 3012	Danger	H226, H318, H335	P210, P261, P303+P361+P353, P304+P340+P312, P305+P351+P338+ P310, P370+P378	А
Photoresist Microposit 1805	Warning	H226	P210, P233, P240, P241, P242, P243, P280, P303+P361+P353, P370+P378, P403+P235, P501.	А
Platinum	Not a	hazardous substan (Regulation (EG)	ce according to CLP 1272/2008)	В

 Table 7.1 (continuation): List of used chemicals, including safety instructions and disposal.^{140,141}

7 Safety Instructions and Disposal

Chemical	GHS	Hazard	Precautionary	Disposal
	Symbol	Statements	Statements	•
Remover Microposit 1165	Danger	H227, H315, H319, H335, H360.	P201, P202, P210, P261, P264, P271, P280, P281, P302+P351, P304+P340+P312, P305+P351+P338, P308+P313, P332+P313, P337+P313, P362+P363, P370+P378, P403+P233, P403+P235, P405, P501.	E
Selenium	Danger	H301, H331, H373, H413	P260, P264, P273, P301+P310, P304+P340+P311, P314	D, E
Silver	Not a	hazardous substand (Regulation (EG) 1	ce according to CLP 1272/2008)	В
Silver nitrate	Danger	H272, H290, H314, H410	P210, P260, P273, P280, P303+P361+P353, P305+P351+P338, P308+P310	В
Sulfur	Warning	H315	P264, P280, P302+P352, P332+P313, P362+P364	В
Thioglycerol	Danger	H302, H311+H331, H315, H317	P261, P264, P280, P301+P312, P302+P352+P312, P304+P340+P311	Е
Titanium	Not a	hazardous substand (Regulation (EG) 1	ce according to CLP 1272/2008)	В
Toluene	Danger	H225, H315, H361d, H336, H373, H304, H412	P202, P210, P273, P301+P310, P303+P361+P353, P331	Е
Trioctylphosphine	Danger	H314	P280, P303+P361+P353, P304+P340+P310, P305+P351+P338, P363, P405	E

 Table 7.1 (continuation): List of used chemicals, including safety instructions and disposal.^{140,141}

 Table 7.1 (continuation): List of used chemicals, including safety instructions and disposal.^{140,141}

Chemical	GHS	Hazard	Precautionary	Disposal
	Symbol	Statements	Statements	
Trioctylphosphine oxide	Danger	H315, H318, H412	P264, P273, P280, P302+P352, P305+P351+P338,	D, E
			P332+P313	

Disposal Instructions:

- A Discard into the container for halogen-free organic solvents.
- B Discard into the container for contaminated solid waste.
- C Return gas cylinder to supplier.
- D Dissolve in suitable solvent.
- E Discard into the container for halogen-containing or toxic organic solvents.
- F Discard into the container for nitrate-containing inorganic acids.
- G Discard into the container for inorganic bases.
- H Discard into the container for nitrate-free inorganic acids.

List of Hazard Statements¹⁴²

H224	Extremely flammable liquid and vapor
H225	Highly flammable liquid and vapor
H226	Flammable liquid and vapor
H227	Combustible liquid
H228	Flammable solid
H252	Self-heating in large quantities; may catch fire
H261	In contact with water releases flammable gas
H272	May intensify fire; oxidizer
H280	Contains gas under pressure; may explode if heated
H290	May be corrosive to metals
H301	Toxic if swallowed
H301+H311+H331	Toxic if swallowed, in contact with skin or if inhaled
H302	Harmful if swallowed
H302+H312	Harmful if swallowed or in contact with skin
H302+H332	Harmful if swallowed or if inhaled
H304	May be fatal if swallowed and enters airways
H311	Toxic in contact with skin
H311+H331	Toxic in contact with skin or if inhaled
H314	Causes severe skin burns and eye damage
H315	Causes skin irritation
H317	May cause an allergic skin reaction
H318	Causes serious eye damage
H319	Causes serious eye irritation
H330	Fatal if inhaled
H331	Toxic if inhaled
H332	Harmful if inhaled
H334	May cause allergy or asthma symptoms or breathing difficulties if inhaled
H335	May cause respiratory irritation
H336	May cause drowsiness or dizziness
H341	Suspected of causing genetic defects
H350	May cause cancer
H360	May damage fertility or the unborn child
H361d	Suspected of damaging the unborn child

Suspected of damaging fertility
Suspected of damaging fertility. Suspected of damaging the unborn child.
Causes damage to organs
May cause damage to organs
Causes damage to organs through prolonged or repeated exposure
May cause damage to through prolonged or repeated exposure
Very toxic to aquatic life with long lasting effects
Toxic to aquatic life with long lasting effects
Harmful to aquatic life with long lasting effects
May cause long lasting harmful effects to aquatic life
May form explosive peroxides
Repeated exposure may cause skin dryness or cracking

List of Precautionary Statements¹⁴²

P201	Obtain special instructions before use.				
P202	Do not handle until all safety precautions have been read and understood.				
P210	Keep away from heat, hot surfaces, sparks, open flames and other ignition sources. No smoking.				
P220	Keep/Store away from clothing//combustible materials.				
P233	Keep container tightly closed.				
P234	Keep only in original container.				
P240	Ground and bond container and receiving equipment.				
P241	Use explosion-proof [electrical/ventilating/lighting/] equipment.				
P242	Use non-sparking tools.				
P243	Take precautionary measures against static discharge.				
P260	Do not breathe dust/fume/gas/mist/vapors/spray.				
P261	Avoid breathing dust/fume/gas/mist/vapors/spray.				
P264	Wash thoroughly after handling.				
P270	Do not eat, drink or smoke when using this product.				
P271	Use only outdoors or in a well-ventilated area.				
P273	Avoid release to the environment.				
P280	Wear protective gloves/protective clothing/eye protection/face protection.				
P281	Use personal protective equipment as required.				
P301+P310	IF SWALLOWED: Immediately call a POISON CENTER/doctor/				
P301+P312	IF SWALLOWED: Call a POISON CENTER/ doctor//if you feel unwell.				
P301+P330+P331	IF SWALLOWED: Rinse mouth. Do NOT induce vomiting.				
P302+P335+P334	F ON SKIN: Brush off loose particles from skin. Immerse in cool water.				
P302+P352	IF ON SKIN: Wash with plenty of water/				
P303+P361+P353	IF ON SKIN (or hair): Take off immediately all contaminated clothing. Rinse skin with water/shower.				
P304+P340+P310	IF INHALED: Remove person to fresh air and keep comfortable for breathing. Immediately call a POISON CENTER/ doctor.				
P304+P340+P311	IF INHALED: Remove person to fresh air and keep comfortable for breathing. Call a POISON CENTER or doctor/ physician.				
P304+P340+P312	IF INHALED: Remove person to fresh air and keep comfortable for breathing. Call a POISON CENTER or doctor/ physician if you feel unwell.				
P305+P351+P338	IF IN EYES: Rinse cautiously with water for several minutes. Remove contact lenses, if present and easy to do. Continue rinsing.				

P307+P311	IF exposed: call a POISON CENTER or doctor/physician.
P308+P310	IF exposed or concerned: Immediately call a POISON CENTER or doctor/physician.
P308+P311	IF exposed or concerned: Call a POISON CENTER/doctor/
P308+P313	IF exposed or concerned: Get medical advice/ attention.
P310	Immediately call a POISON CENTER/doctor/
P312	Call a POISON CENTER/doctor//if you feel unwell.
P314	Get medical advice/attention if you feel unwell.
P321	Specific treatment (see on this label).
P330	Rinse mouth.
P331	Do NOT induce vomiting.
P332+P313	If skin irritation occurs: Get medical advice/attention.
P337+P313	If eye irritation persists: Get medical advice/attention.
P362+P364	Take off contaminated clothing and wash it before reuse.
P363	Wash contaminated clothing before reuse.
P370+P378	In case of fire: Use to extinguish.
P402+P404	Store in a dry place. Store in a closed container.
P403	Store in a well-ventilated place.
P403+P233	Store in a well-ventilated place. Keep container tightly closed.
P403+P235	Store in a well-ventilated place. Keep cool.
P405	Store locked up.
P501	Dispose of contents/container to

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Use of Artificial Intelligence Assisted Tools

All artificial intelligence assisted tools were used in accordance with the good scientific practice and no output was directly copy pasted. If suggested changes were accepted the manuscript was corrected individually at the corresponding position.

DeepL Write was used to for language correction of individual sentences.¹⁴³

DeepL Translator was used to translate coherent German words or to the check whether a written sentence in English had the intended meaning by translating it into German.¹⁴⁴

UHHGPT GPT 4 omni mini was used for language correction of connected sentences or paragraphs. In addition, UHHGPT was used for simple search queries, such as the explanations of error messages. ¹⁴⁵

Appendix

A. Publications

Articles

Wehrmeister, M; **Lengle, D.**; Höhmann, C.; Mews, A.; Kipp, T. The Internal Electric Fields of Nanowires with Ohmic Contacts *in Operando*. Manuscript in preparation.

Lengle, D.; Schwarz, M.; Patjens, S.; Stuckelberger, M. E.; Ruhmlieb, C.; Mews, A.; Dorn, A. Tracking Cation Exchange in Individual Nanowires via Transistor Characterization. *ACS Nano* **2024**, *18*, 18036–18045.

Herber, M.; **Lengle, D.**; Valandro, S. R.; Wehrmeister, W.; Hill, E. H. Bubble Printing of Ti₃C₂T_x MXene for Patterning Conductive and Plasmonic Nanostructures. *Nano Lett.* **2023**, *23*, 6308–6134.

Conference Contributions

- 11/2024 821. WE-Heraeus-Seminar: Uniting Today's Nanotechnology for Advancing Tomorrow's Semiconductor Physics, Bad Honnef, Germany
 Talk: Tracking Cation Exchange in Individual Nanowires via Transistor Characterization
- 03/2024 87. *DPG Frühjahrtagung: Sektion Kondensierte Materie* (SKM), Berlin, Germany **Talk:** Monitoring Cation Exchange in Individual Semiconductor Nanowires via Transistor Characterization
- 08/2023 ACS Fall 2023: Harnessing the Power of Data, San Francisco, CA, USA **Talk:** Monitoring of the Cation Exchange on Individual Semiconductor Nanowires
- 06/2023 Bunsen-Tagung 2023 Physical Chemistry of the Energy Transition, Berlin, Germany Poster: Cation Exchange on Single Semiconductor Nanowires

10/2022 NANOHYBRID – Hamburg Conference on Complex Nanostructures, Hamburg, Germany **Poster:** Cation Exchange on Single Semiconductor Nanowires

- 09/2022 Bunsen-Tagung 2022 Understanding Dispersion Interactions in Molecular Chemistry, Giessen, Germany Poster: Cation Exchange on Single Semiconductor Nanowires
- 03/2022 763. WE-Heraeus-Seminar: Optoelectronic Processes at Nanostructured Interfaces, Bad Honnef, Germany **Poster:** Cation Exchange on Single Semiconductor Nanowires
- 07/2021 Bad Honnef Physics School Exciting nanostructures: Characterizing Advanced Confined Systems, Bad Honnef, Germany **Poster:** Cation Exchange on Single Semiconductor Nanowires

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C. Eidesstattliche Erklärung

"Hiermit versichere ich an Eides statt, die vorliegende Dissertationsschrift selbst verfasst und keine anderen als die angegebenen Quellen und Hilfsmittel benutzt zu haben. Sofern im Zuge der Erstellung der vorliegenden Dissertationsschrift generative Künstliche Intelligenz (gKI) basierte elektronische Hilfsmittel verwendet wurden, versichere ich, dass meine eigene Leistung im Vordergrund stand und dass eine vollständige Dokumentation aller verwendeten Hilfsmittel gemäß der Guten wissenschaftlichen Praxis vorliegt. Ich trage die Verantwortung für eventuell durch die gKI generierte fehlerhafte oder verzerrte Inhalte, fehlerhafte Referenzen, Verstöße gegen das Datenschutz- und Urheberrecht oder Plagiate."

Ort, Datum

Daniel Lengle