Novel absorber layer materials for thin film solar cells studied using transmission electron microscopy

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Abstract

The purpose of this thesis is to investigate an innovative and promising approach to increasing the efficiency of low-cost amorphous Si (a-Si:H) solar cells. In essence, the approach involves incorporating semiconducting nanoparticles (NP) in a-Si:H solar cells as absorbers, exploiting the high absorption coefficients of the nanoparticles and the low production costs of the a-Si:H solar cells, which are grown at low temperature. Producing NPs in a first step, and then embedding them in the solar cell in a second step, offers new degrees of freedom to optimize the nanoparticle absorbers. Promising NP material systems were investigated with respect to their composition, morphology and structural defects, in order to find NPs suitable for embedding. The FeSi$_2$ NPs investigated are the first pure $\beta$-phase NPs reported so far. A range of post-treatment methods were found for optimizing them in order to meet the requirements for NP absorbers. Suitable NPs of $\alpha$-Fe$_2$O$_3$, Cu$_2$O, CuO and Cu$_{31}$S$_{16}$ were embedded in a-Si:H solar cells to study the influence of the plasma-enhanced chemical vapor decomposition (PECVD) growth process on the NP absorbers and vice versa. The a-Si:H solar cells based on $\alpha$-Fe$_2$O$_3$ NPs reach efficiencies of 1.3%. This shows that it is possible to embed NPs in a working a-Si:H solar cell using PECVD. However, the $\alpha$-Fe$_2$O$_3$ NP-based solar cell was not superior to a reference a-Si:H solar cell. An SiO$_x$ shell was observed at the interface between the NPs and the a-Si:H solar cell. This shell is attributed to a chemical reduction of the NPs during embedding. It reduces carrier extraction and the contribution of the NPs to the solar cell efficiency. Studies of the embedding of the Cu$_2$O, CuO and Cu$_{31}$S$_{16}$ revealed that two different decomposition mechanisms take place during PECVD embedding: chemical reduction and diffusion of the NP elements. With the identification of these two decomposition mechanisms, it is now possible to select NPs that are stable during PECVD embedding. Such NP material systems are both oxygen-free and composed of materials with low mobilities in a-Si:H. Therefore, optimized $\beta$-FeSi$_2$ NPs or FeS$_2$ and ZrS$_2$ NPs are promising absorbers for the development of future NP-based solar cells.
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<tbody>
<tr>
<td>1/d</td>
<td>Reciprocal lattice distance</td>
</tr>
<tr>
<td>ADF</td>
<td>Annular Dark-Field</td>
</tr>
<tr>
<td>ADT</td>
<td>Automated Diffraction Tomography</td>
</tr>
<tr>
<td>BF</td>
<td>Bright Field</td>
</tr>
<tr>
<td>BG</td>
<td>Background</td>
</tr>
<tr>
<td>CCD</td>
<td>Charge-Coupled Device</td>
</tr>
<tr>
<td>DF</td>
<td>Dark Field</td>
</tr>
<tr>
<td>DFT</td>
<td>Density Functional Theory</td>
</tr>
<tr>
<td>EDX</td>
<td>Energy Dispersive X-ray Spectroscopy</td>
</tr>
<tr>
<td>ED</td>
<td>Electron Diffraction</td>
</tr>
<tr>
<td>EEL</td>
<td>Electron Energy-Loss</td>
</tr>
<tr>
<td>EELS</td>
<td>Electron Energy-Loss Spectroscopy</td>
</tr>
<tr>
<td>EFTEM</td>
<td>Energy-Filtered Transmission Electron Microscopy</td>
</tr>
<tr>
<td>ERDA</td>
<td>Elastic Recoil Detection Analysis</td>
</tr>
<tr>
<td>FEG</td>
<td>Field Emission Gun</td>
</tr>
<tr>
<td>FIB</td>
<td>Focused Ion Beam</td>
</tr>
<tr>
<td>FT</td>
<td>Fourier Transformation</td>
</tr>
<tr>
<td>FTIR</td>
<td>Fourier Transform Infra Red</td>
</tr>
<tr>
<td>FWHM</td>
<td>Full Width at Half Maximum</td>
</tr>
<tr>
<td>GGA</td>
<td>Generalized Gradient Approximation</td>
</tr>
<tr>
<td>HAADF</td>
<td>High Angle Annular Dark Field</td>
</tr>
<tr>
<td>HR</td>
<td>High Resolution</td>
</tr>
<tr>
<td>IV</td>
<td>Current-Voltage</td>
</tr>
<tr>
<td>NBED</td>
<td>Nano Beam Electron Diffraction</td>
</tr>
<tr>
<td>NP</td>
<td>Nanoparticle</td>
</tr>
<tr>
<td>PECVD</td>
<td>Plasma-Enhanced Chemical Vapor Decomposition</td>
</tr>
<tr>
<td>PDS</td>
<td>Photothermal Deflection Spectroscopy</td>
</tr>
<tr>
<td>SAED</td>
<td>Selected Area Electron Diffraction</td>
</tr>
<tr>
<td>STEM</td>
<td>Scanning Transmission Electron Microscopy</td>
</tr>
<tr>
<td>TEM</td>
<td>Transmission Electron Microscopy</td>
</tr>
<tr>
<td>XPS</td>
<td>X-Ray Photoelectron Spectroscopy</td>
</tr>
<tr>
<td>XRD</td>
<td>X-Ray Diffraction</td>
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<tr>
<td>ZLP</td>
<td>Zero Loss Peak</td>
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1. Introduction

Our environment is suffering because of our insatiable need for energy. The best way to produce the energy we need in an environmentally friendly manner is to reduce the costs per watt for renewable energy to a value below the costs per watt for coal, gas or nuclear energy. Renewable energies like solar power do not consume expensive resources, their energy production price is mostly determined by the cost of producing the solar cell. To optimize cost efficiency, future solar cells should fulfill the following criteria:

- The solar cell spectrum should be used efficiently for power generation.
- The raw materials should be abundant in nature, non-toxic and inexpensive.
- The energy demand and costs for producing them should be low.

Today, inorganic solar cells are based on silicon (Si), cadmium telluride (CdTe), gallium arsenide (GaAs) or copper indium gallium selenides (Cu(In,Ga)Se$_2$). Apart from Si, which is abundant in nature, Ga, Se, In and Te are of limited availability in the medium term [47, 52]. Solar cells from crystalline Si require a thick absorber layer due to the indirect band gap of silicon. High growth temperatures are required for production, which decrease the defect concentration and increase efficiency, but also raise production costs. Thin film solar cells of amorphous Si (a-Si:H) and micro-crystalline Si ($\mu$-Si:H) fulfill most of the criteria set forth above, but suffer low conversion efficiency [138]. Tandem cells containing a-Si:H (band gap of 1.8 eV) and $\mu$-Si:H (indirect band gap of 1.12 eV) allow efficient use of the solar spectrum, but the absorption coefficients and absorber layer thicknesses do not allow the light to be fully absorbed, even in combination with light trapping concepts. At present, conversion efficiencies of 12% [169] are achievable with a-Si:H/$\mu$-Si:H tandem cells.

New absorber materials with different band gaps and with higher absorption coefficients are needed to meet the requirements of future, cost-efficient solar cells.

In the past, various semiconductors were studied with a view to possible light harvesting applications, including silicides (e.g. $\beta$-FeSi$_2$), sulfides (e.g. Cu$_2$S) or oxides (e.g. $\alpha$-Fe$_2$O$_3$, Cu$_2$O,…). These materials are abundant in nature and do show appropriate properties such as suitable band gaps and high absorption coefficients above $10^5$ cm$^{-1}$ [17, 128, 68, 130, 98].

Until now, however, these materials have been considered unsuitable for crystalline thin film solar cells for the following reasons:

In the case of $\beta$-FeSi$_2$ thin film solar cells, conversion efficiencies are limited to less than 3.7% [90] due to high recombination rates and defect concentrations [147, 89]. Cu$_2$S
suffers from the high mobility of the copper atoms \[125\], which leads to degeneration of the solar cells\[124\]. Cu\(_2\)O tends to deoxidize \[57\] and \(\alpha\)-Fe\(_2\)O\(_3\) suffers from a low carrier diffusion length, less than 5 nm \[68, 10\].

However, these materials may still serve as advantageous solar cell absorbers if the paradigm of thin absorber layers is shifted towards nanoparticulate absorbers.

Recent advances in nanotechnology offer new low-cost processes for producing nanoparticles (NPs) in a narrow size distribution. The NPs can be dispersed on substrates using simple methods such as spin-coating or ink-jet printing. They can subsequently be embedded in a-Si:H by low temperature plasma-enhanced chemical vapor deposition (PEVCD).

The concept of an a-Si:H solar cell with a nanoparticulate absorber layer\(^1\) is investigated in this thesis. Figure 1.1 shows one possible design of a NP-based solar cell.

As with p-i-n junction a-Si:H solar cells, the electrical fields needed for carrier extraction can be introduced by n- and p-doped a-Si:H layers. The NPs can be embedded in a matrix of intrinsic a-Si:H layers, which is assumed to passivate interface defects. This design allows growth and optimization of the NP absorber material independently of the solar cell.

Therefore, it is expected that phase-pure and almost defect-free nanoparticulate absorbers can be developed from materials that would otherwise be unsuitable for crystalline thin film solar cells.

High-quality NPs fulfill the following criteria:

- Environmentally friendly material of the NPs is abundant in nature and possesses a suitable band gap in the range from 0.6 eV to 2.2 eV.

• The NPs should be good absorbers with absorption coefficients greater than $10^5 \text{ cm}^{-1}$, which allow them to absorb most of the light on a path of 100 nm. This absorption coefficient is sufficient for NPs with diameters larger than 10 nm, as light trapping by rough interfaces and back contact reflectors allows to increase the light path by a factor of 15 in an absorber layer [106].

• The size of the NPs should be suitable. The minimum size is governed by the material specific thermal de Broglie wavelength of the conduction band electrons (e.g. 15.6 nm in the case of $\beta$-FeSi$_2$ see chap. 3.6.2). Below this size, quantum confinement effects will occur and the band gap will depend to a significant degree on the NP size. The size distribution of the NPs will lead to a band gap distribution that is undesirable for possible future multijunction solar cells. The maximum size of the NPs is governed by the defect density and the associated carrier diffusion length. NPs that are significantly larger than the carrier diffusion length will absorb photons that do not contribute to carrier generation.

• The NPs should be dispensable in a liquid in order to allow spin coating or ink-jet printing. Aggregation or agglomeration of the NPs is undesirable. The aggregate or agglomerate size determines the minimum thickness of the intrinsic a-Si:H matrix in which the NPs are embedded. If this thickness approaches the carrier diffusion length of the a-Si:H, about 200 nm [154], charge carriers will recombine before extraction is possible.

The focus of this thesis is on the measurement of the shape, crystallographic phase, structural defects and local composition and binding states of pristine NPs and NPs embedded in a solar cell structure.

In particular, $\beta$-FeSi$_2$ NPs (see chap. 3), $\alpha$-Fe$_2$O$_3$ NPs (see chap. 4) and Cu-based NPs (see chap. 5) were investigated with respect to their suitability as absorber layers within amorphous Si thin film solar cells.

This study was conducted with several partners from: IEK-5 of FZ Jülich, PGI-1 of FZ Jülich, IVG of the U. of Duisburg-Essen, WSI of Tech. U. Munich, ACII of Ruhr-U.-Bochum and EVONIK GmbH as part of the BMBF project NADNuM (Neue Absorbermaterialien für Dünnschichtsolarzellen mit Nanopartikeln aus unbegrenzt verfügbaren Materialien).
2. Experimental fundamentals and details

The aim of this thesis is to study NPs on a local scale ranging from 0.1 nm to several hundred nm before and after they are embedded in solar cell structures. For this, various transmission electron microscopy (TEM) methods were applied: (scanning) TEM imaging, electron diffraction, energy dispersive X-ray spectroscopy and electron energy loss spectroscopy. These methods will be introduced in chapter 2.3 together with the TEM sample preparation methods.

In many cases, results from other non-local techniques are available, having been obtained from the same samples. Although the experiments were not performed by the author they are included in this thesis as they give additional information or proof. These techniques will be introduced in chapter 2.2.

Chapter 2.1 provides an introduction to the method used to embed NPs from different material systems in a solar cell structure. The synthesis of NPs depends to a large degree on the material system, and will be addressed in the following chapters.

2.1. Embedding NPs in a solar cell

NPs are embedded as an additional absorber layer in a p-i-n junction a-Si:H solar cell. The a-Si:H layers are deposited on the substrate using a low temperature plasma-enhanced chemical vapor deposition (PECVD) process.

For PECVD growth, the substrate is attached to the grounded anode. Radio frequency (RF) electrical fields are applied via the cathode to generate a plasma in the low pressure reactor chamber. Silane (SiH$_4$) gas is decomposed by the plasma electrons. As described in [131], neutral radicals such as SiH$_3$, SiH$_2$, SiH, Si and ions such as SiH$_x^+$ or H$_x^+$ are formed. These radicals diffuse into the growing film surface, where they react with the film surface to form hydrogen terminated a-Si:H films. The reaction can be described as follows:

\[
\text{SiH}_x(\text{plasma}) \rightleftharpoons \text{Si} \, (\text{solid}) + x\text{H}.
\]

The forward reaction represents the film deposition, whereas the reverse direction represents hydrogen etching on the growing film surface. As the reaction takes place in both directions, the growth rate and film quality are highly dependent on the exact PECVD parameters, such as deposition temperature, pressure, gas flow, plasma frequency and power.

Additional H$_2$ gases are provided to reduce the number of dangling bonds in the final a-Si:H film. Other gases, such as phosphine (PH$_3$) and trimethyl boron (B(CH$_3$)$_3$) allow
To embed NPs as an absorber layer in an a-Si:H solar cell structure (see draft in chapter 1), growth conditions similar to the growth of amorphous p-i-n-Si:H solar cells were chosen (13.56 MHz radio frequency and pressures of 3 torr [108]).

Corning glass covered with Al-doped ZnO was used as the substrate [106]. It also functions as a transparent contact for the solar cell structure. After introducing the substrate into the PECVD chamber it was heated in a vacuum for 1 h reaching a final temperature of \( \approx 150^\circ C \). SiH\(_4\) and H\(_2\) gases were used as a source for growing the various layers of a-Si:H at temperatures below 250 \(^\circ C\). The first 20 nm thick layer of p-doped a-Si:H was grown using B(CH\(_3\))\(_3\) in addition to SiH\(_4\) and H\(_2\). Also, CH\(_4\) was provided during the p-layer deposition as small amounts of C increase the transparency of the p-Si:H layer [108].

After deposition of the p-Si:H layer, the sample was transferred to the spin-coating system where the NP suspension was spin-coated onto the p-Si:H layer in an inert gas atmosphere. For further growth, the sample was transferred back to the PECVD chamber. The sample was transported between the PECVD chamber and the spin-coating system both with and without exposure to air. Back in the PECVD chamber, the sample was heated for 1 h, up to \( \approx 150^\circ C \) to remove residual water from the NP suspension. The intrinsic a-Si:H and the n-doped layers were grown using SiH\(_4\), H\(_2\) and phosphine for doping. The final ZnO:Al/Ag/ZnO:Al back contact was sputtered in an adjacent chamber.
2.2. Macroscopic investigation methods

In this chapter, non-local experimental methods are discussed. Also included is a brief introduction to the density functional theory used to calculate the formation energies and band gap structures associated with the observed crystallographic defects (see chap. 3.4.2).

2.2.1. X-ray diffraction

X-ray diffraction (XRD) was used as a complementary technique to determine the crystallographic phase of NPs by comparing with reference XRD data. Further capabilities of XRD, e.g., strain or average crystal size analysis are described in the review articles by Moram and Langford [104, 80].

The basic physical effect of diffraction is described by Bragg’s law

\[ n \lambda = 2d \sin(\theta). \]  

An electromagnetic wave having wavelength \( \lambda \) is diffracted by a crystal with lattice plane distances of \( d \), wherein \( n \) is the order of diffraction and \( \theta \) is the angle of diffraction relative to the lattice planes. Usually, Cu-K\( \alpha \) X-ray sources are employed as they emit light with a wavelength of about 0.154 nm which is in the order of typical lattice plane distances observed in metals or semiconductors.

The set of lattice plane distances obtained allows the crystallographic phase of the crystals to be identified. Homogeneous strain introduces a shift of the lattice planes. Randomly orientated crystalline NPs, as investigated in this thesis, yield powder diffraction pattern rings. The finite size of the single nanocrystal has the effect of broadening the Bragg diffracted beams.

XRD spectra were acquired in a PANalytical X’Pert PRO diffractometer with a Cu-K\( \alpha \) X-ray source operated at 40 kV and 40 mA. An X’Celerator Scientific detector equipped with a graphite monochromator was used. Scan ranges and steps of 20-80° and 0.0334° were used (for details see e.g. [22]). The spectra were evaluated by direct comparison with literature data or using the TOPAS V4 software package [20].
2.2.2. Photothermal deflection spectroscopy

Photothermal deflection spectroscopy (PDS) was used to investigate the optical absorption of the NPs. The ratio of the sub-band gap absorption compared to the band gap absorption was used to evaluate the crystalline quality of the NPs.

PDS enables the absorption properties to be determined indirectly in a wide dynamic range (see review articles [62, 13]). When a photon is absorbed by the sample it excites electrons, which can relax by transferring their energy to phonons. The generation of phonons leads to heat generation and a temperature change which can be detected. This relaxation path is considered to be dominant for ambient and high temperatures [13]. The excited sample may also relax by photon emission.

For PDS investigation, the sample is placed inside a quartz vessel and surrounded with CCl$_4$, a chemically inert liquid with a highly temperature-dependent diffraction index. When the sample absorbs light and generates heat, a temperature gradient evolves in the surrounding CCl$_4$. Increasing the temperature of CCl$_4$ has the effect of reducing its refractive index.

As outlined in figure 2.1 a second laser beam parallel to the sample surface is deflected by the change in the refraction index of the CCl$_4$. The deflection angle of the laser beam is proportional to the temperature gradient and to the absorption of the sample when the absorbed light is of low intensity. Changing the wavelength of the absorbed photons allows absorption spectroscopy.

![Figure 2.1: Principle setup of Photothermic Deflection Spectroscopy from [114].](image)

NPs for PDS were drop-coated on a quartz glass substrate for PDS measurements. Since
the thickness of the NP layer on the substrate is unknown, only relative changes in absorption can be determined.

The PDS spectra shown in this thesis were acquired in a homemade setup as illustrated in figure 2.1. A monochromator is used to excite the sample with specific energies. The laser beam deflection is measured using a four quadrant Si diode.

2.2.3. Fourier Transform Infrared Spectroscopy

Fourier transformed infrared (FTIR) spectroscopy was used to investigate the quantity of Si-O bonds present as a function of the exposure of NPs to air (see chap. 3.5.2).

In principle, infrared (IR) spectroscopy allows to characterize the vibrational modes of crystalline, amorphous material or molecules (see review article [9]). The vibrational modes of bonded atoms are discrete in energy and depend on the atomic distance, vibrating mass and bonding type (single, double, triple). Photons excite vibrational modes as a direct result of interaction with the dielectric dipole moment.

The IR spectra can be acquired using a Fourier transformed infrared (FTIR) spectrometer which consists of a polychromatic light source, a Michelson interferometer, a detector, and a computer to calculate the IR spectra from the detected signal using a Fourier transformation.

The experimental setup is depicted in figure 2.2. One half of the beam is deflected by a splitter to a fixed mirror and back through the beam splitter towards the detector. The other half travels through the beam splitter to a movable mirror and back to the beam splitter where it is deflected towards the detector. The recorded intensity depends on the position of the movable mirror and the phase difference of the two beams. Moving the mirror constantly allows the intensity to be measured as a function of the wave path difference $d$.

A Fourier transformation is used to obtain the IR spectrum of the sample placed in front of the detector. Vibrational modes of the sample change the spectrum and can be detected.

The FTIR spectra presented here were measured with a Bruker Vertex 70v Fourier-transform spectrometer, further experimental details are given in [2].
2.2 Macroscopic investigation methods

![Schematic diagram of a Fourier transform spectrometer from [9].](image)

2.2.4. Raman spectroscopy

Raman spectroscopy was used as a complementary technique to confirm the phases of the embedded Fe\(_2\)O\(_3\) NP (see chap. 4.6). Raman spectroscopy allows characterization of the vibrational modes of a molecule of crystal, which are excited by Raman scattering [141].

In the case of elastic Rayleigh scattering, the incoming photon excites the atom to a virtual state \(E^*\), which can relax back into the original state upon emission of a second phonon with the same energy.

In case of inelastic Raman scattering the atom relaxes to a vibration state upon emission of a photon with reduced energy, called the Stokes case. If the atom was already in a vibrational state before the photon excitation, it may relax to a lower vibrational state upon emission of a photon with increased energy, called the anti-Stokes case. Only vibrational states of changing polarizability of the molecule or crystal can be excited by Raman scattering.

To acquire the Raman spectra presented here, a homemade setup as described in [44] was used. The samples were excited using a Cobolt Samba laser with a wavelength of 532 nm. The spectra were acquired with a Si CCD (charged-coupled device) camera from the Photometrics Company in line with a Horiba iHR 320 grating monochromator.
2.2.5. X-ray photoelectron spectroscopy

X-ray photoelectron spectroscopy (XPS) was used to investigate the Si and Fe oxidation state at the \( \beta \)-FeSi\(_2\) NP surface. XPS reveals information about composition and bonding in the first few nm of the surface (see review article [38]). X-ray photons are used, e.g., emitted from an AlK\( \alpha \) cathode with an energy around 1487 eV to excite sample electrons. Due to the photo effect, the excited electron may leave the sample, depending on its energy state before excitation and the photon energy. The residual kinetic energy of the electrons is detected. This energy is specific to the element and oxidation state.

The technique is sensitive to the surface as the inelastic mean free path \( \Lambda_e \) of the excited electron inside the sample is in the order of 1 nm. \( \Lambda_e \) depends on the kinetic energy of the electron and the composition of the sample [38]. The number of electrons detected \( I \) decays exponentially with the escape depth \( z \) and the takeoff angle \( \theta \): \( I(z) = I_0 \exp\left(-z/\Lambda_e \sin \theta\right) \).

For XPS, a homemade ultrahigh vacuum setup equipped with an Al cathode [2] was used. The measured energies were compared with the literature to assign the bonding state.

2.2.6. Elastic recoil detection analysis

Elastic recoil detection analysis (ERDA) was used to determine the composition of \( \beta \)-FeSi\(_2\) NPs quantitatively (see chap. 3.3) as it allows standard-less quantification (see review article [137]). During the ERDA measurement, high energy iodine ions recoil sample atoms. The number of recoil atoms detected allows to determine the sample composition because the cross section for the Coulomb interaction of the incident iodine ion and the recoiled element can be calculated exactly. The Z number of the recoiled element was determined using a \( \Delta E \)-E detector containing an ionization chamber and a solid state energy detector. The stopping power of the recoiled atom in the ionization chamber leads to a \( \Delta E \) energy loss, which depends on \( Z \) and on the kinetic energy of the atom. The additional detection of the remaining recoiled atom energy using the solid state energy detector allows to determine the Z number.

The measurement was performed using 170 MeV iodine ions, which approach the sample surface at an incidence angle of 15°. An ionization chamber \( \Delta E \) and solid state E hybrid detector were used at a detection angle of 38°. The \( \beta \)-FeSi\(_2\) NPs were drop-coated from a 1% ethanol suspension onto a germanium substrate to prepare a suitable sample. Further experimental details are given in [12].
2.2 Macroscopic investigation methods

2.2.7. Density functional theory & generalized gradient approximation

The aim of density functional theory (DFT) is to determine the ground state energy of a many-electron system containing \( N_i \) atoms and \( N_j \) electrons.

This problem can be described with the following Schrödinger equation in a Born Oppenheimer approximation of static nuclei:

\[
\left( -\frac{\hbar^2}{2m} \sum_j \nabla_j^2 - \sum_{j,l} \frac{Z_le^2}{|\vec{r}_j - \vec{R}_l|} + \frac{1}{2} \sum_{j\neq j'} \frac{e^2}{|\vec{r}_j - \vec{r}_{j'}|} - E \right) \Psi(\vec{r}_1, \vec{r}_2, \ldots, \vec{r}_{N_j}) = 0;
\]

where \( \vec{r}_j, m \) and \( e \) are the positions, mass and charge of the electrons and \( \vec{R}_l \) are the positions of the nuclei approximated to be fixed. \( Z_l \) and \( \hbar \) denotes the atomic numbers of the nuclei and the reduced Planck constant, whereas \( E \) is the energy. The dimension of the wave function \( \Psi \) is \( 3N_j \). To store a numerical found solution for an \( N = 29 \) system such as a Cu atom using a grid of 10 points per coordinate and one byte accuracy would require \( 10^{88} \) bits. This number is rather large. For comparison, the number of electrons in the universe is estimated to be in the order of \( 10^{80} \). Therefore, solving the Schrödinger equation for a many-electron system is not feasible.

DFT offers a way to find a solution for the ground state energy of the system in a computationally feasible way.

The basic idea of DFT is that the ground state energy of a system of \( N_j \) interacting electrons can be described uniquely by the electron density \( n(\vec{r}) \) in the ground state. The problem of all electrons interacting with each other is reduced to the problem of one electron interacting with the surrounding electron density.

The effective potential \( V_{eff}(r_j) \) for each electron \( j \) is given by:

\[
V_{eff}(r_j) = -\sum_{l,j} \frac{Z_le^2}{|\vec{r}_j - \vec{R}_l|} + \int \frac{n(\vec{r}')}{|\vec{r}_j - \vec{r}'|} d^3r' + V_{XC},
\]

where the sum describes the external potential of the nuclei, the integral describes the classic Coulomb interaction with the potential from the surrounding electron density, and \( V_{XC} \) describes the quantum mechanical exchange-correlation potential.

Each electron obeys the one-electron Kohn-Sham equation:

\[
\left( -\frac{1}{2} \nabla^2 + V_{eff}(\vec{r}) - E_n \right) \phi_n(\vec{r}) = 0,
\]

where \( n \) denotes the quantum numbers of the energy state.
After an initial estimate of the electron density, the Kohn-Sham equation can be solved and the new electron density
\[ n(\vec{r}) = \sum_{n=1}^{N_n} |\phi_j(\vec{r})|^2 \]
can be calculated. An iterative process feeds back the new electron densities into the independent one-electron Kohn-Sham equations used to find the next iteration of ground state electron density. Summing up the energies \( E_n \) of all electrons in the system (occupying the lowest possible states) gives the ground state energy of the system \( E \). If the exchange-correlation potential \( V_{XC}(\vec{r}) \) were known, the DFT approach would lead to an exact solution. Unfortunately, \( V_{XC}(\vec{r}) \) is unknown. However, the exchange-correlation potential can be estimated to depend on the local electron density \( n(\vec{r}) \) and a functional \( f[n(\vec{r})] \) of the local electron density. In the case of local density approximation (LDA), the exchange correlation potential is estimated as:
\[ V_{XC}^{LDA}(\vec{r}) = \int f[n(\vec{r})]n(\vec{r})d\vec{r}. \]
An exchange-correlation functional in the form of the exchange-correlation function of a uniform electron gas is used.
In the case of the generalized gradient approximation (GGA), the functional \( f \) also depends on the derivative of the local electron density, giving:
\[ V_{XC}^{GGA}(\vec{r}) = \int f[n(\vec{r}), \nabla n(\vec{r})]n(\vec{r})d\vec{r} \]
For further insights into DFT, the reader is referred to the review article by W. Kohn [75]. The calculations were performed using the FLEUR code (www.flapw.de).
2.3. TEM-based investigation methods

In 1932, Max Knoll and Ernst Ruska discovered that magnetic fields of inductors and electric fields of specially shaped capacitors allow an electron beam to be focused similar to optical lenses for photons [70, 71]. This discovery paved the way for tremendous development in electron microscopes. Modern transmission electron microscopes (TEM) offer a wide variety of methods that allow imaging, diffraction analysis, compositional analysis on the atomic scale and the determination of electrical and magnetic fields. This chapter introduces the basic optical elements of the TEM, the sample preparation and different TEM methods used in this thesis.

2.3.1. Set-up of transmission electron microscopes and operational modes

Modern transmission electron microscopes are optical workbenches that contain a large number of optical elements. Figure 2.3 presents a highly simplified setup of a TEM highlighting the basic operating modes TEM and STEM.

In the following, the basic component groups will be introduced. Their influence on the beam path will be given for the example of a TEM in high resolution TEM mode (see fig. 2.3 a)). Deviations of this beam path for different operating modes will be given later.

- The electron gun is the uppermost element in the microscope column. Today’s field emission guns emit the electrons from a very fine tungsten tip with a radius at the tip in the order of 100 nm [31]. Due to this small radius, very strong electrical fields can be observed at the tip, which reduce the required extraction energy by the Schottky effect. The work function of the tip is further reduced with a zirconia coating. Therefore, tip temperatures of approximately 1500 °C [40] allow electron extraction.

- Two subsequent anodes provide the potentials for extracting the electrons from the tip and accelerating them to the desired energies, typically between 80 kV and 300 kV [162]. These energies are arrived at through a compromise between resolution, beam damage and acceptable sample thickness (see chap. 2.3.8 and 2.3.2).

- Several condenser lenses and condenser apertures (e.g. the C2 aperture) as well as the upper part of the objective lens are used to tune the illumination of the sample (parallel in TEM mode). Scanning coils in the condenser system allow the beam to be shifted with respect to the sample.
The sample itself is placed on a special holder. It allows the sample to be tilted in two perpendicular directions to orientate it with respect to the beam. The sample changes the transmitting electron beam by elastic (see chap. 2.3.3 and 2.3.4) and inelastic scattering (see chap 2.3.5 and 2.3.6). Differently elastically scattered beams are indicated in the figure 2.3 by blue, black and green lines, and by black dots.

The lower objective lens magnifies the sample by a factor of 20 to 50. Here, the scattered electrons show high angles with respect to the optical axis. As the aberrations scale with the angle of diffraction (see eq. 14 in chap. A), they are mainly introduced by the lower objective lens.

The objective aperture is placed in the focal plane of the objective lens. This plane is equal to the Fourier transform of the object exit wave or to the diffraction plane.
2.3 TEM-based investigation methods

In figure 2.3, the beams indicated with black dots are blocked by the objective aperture. Limiting the diffraction angles with the objective aperture enables the aberrations to be optimized. Selecting specific diffracted beams allows dark field and bright field TEM (see chap. 2.3.4).

- The selected area aperture is positioned in the first image of the lower objective lens. Electrons originating from specific parts of the sample can be selected, which is interesting for electron diffraction (see chap. 2.3.3).

- The projection lenses are used to further magnify the TEM image of the sample on a CCD camera, where it is recorded.

- The CCD camera used to record TEM images can be removed to allow the electron to enter the GIF (Gatan Imaging Filter), which consists of a magnetic prism, an energy selecting slit, further electron optics (not shown here) and a CCD camera. The magnetic prism disperses the electrons in energy as indicated by the red and purple beams in figure 2.3. A slit aperture in the energy dispersive plane allows recording of energy filtered TEM images for compositional analysis (see chap. 2.3.6). Electron energy loss spectra can be recorded by projecting the energy dispersive plane directly onto the CCD camera.

- Additionally, the energy dispersive X-ray detector (EDX) can be used to study the composition of the sample (see chap. 2.3.7).

In **diffraction mode**, the projection lenses project the diffraction plane of the objective aperture onto the TEM CCD. More details on the resulting electron diffraction pattern are given in chap. 2.3.3.

For **STEM mode** (see fig. 2.3 b)) the beam path in the microscope changes significantly. The condenser system and upper objective lens are used to focus the electron beam to a point, which is shifted across the sample using the scanning coils. The lower objective lens and projection system are used to simply project the electrons onto the high angle annular dark field (HAADF) detector according to their scattering angle. Scattering angles reaching the HAADF detector are colored red. Smaller scattering angles, which do not contribute to the HAADF signal, are color-coded in cyan (see fig. 2.3 b)). Electrons scattered at low angles can be collected with the GIF to acquire an electron energy spectrum in parallel. More details on STEM and electron energy loss spectroscopy (EELS) are described in chapters 2.3.5 and 2.3.6.
2.3.2. TEM specimen preparation techniques

For TEM investigation, samples with specific thicknesses are needed. The ideal sample thickness depends on the planned TEM investigation methods, which require different amounts of inelastic scattering.

The mean free path for inelastic electron scattering $\Lambda_e$ depends on the electron energy and the material. In the case of XPS, the energy of the detected electrons is around 1 kV, which corresponds to $\Lambda_e$ values in the order of a few nm (see chapter 2.2.5). In the case of TEM, $\Lambda_e$ is in the order of 150 nm for electrons accelerated by 200 kV. The specimen thicknesses needed vary from 5 nm up to 500 nm depending on the TEM technique applied.

In the following, the sample preparation methods used to prepare the pure NPs and cross sections of solar cell structures will be presented. The pure NPs have diameters suitable for TEM investigation, whereas cross sections of solar cell structures have to be thinned. In this thesis, three different techniques were used for NP sample preparation. For all three cases, the samples were prepared on Cu grids with a thin carbon layer containing a lot of holes, which will be referred to as "lacey" in the following. Before the NPs of interest are prepared, Au NPs with a size of approximately 15 nm were sputtered onto half of the Cu grid using a Cressington sputter coater at 30 mm sample distance, 15 mA current and 45 sec sputtering time as a reference for electron diffraction. (These Au NPs present on half of the grid may also help in aligning the probe corrector in STEM mode.)

The first method of NP preparation used is to dip the lacey carbon grid in the NP powder. Agglomerated NPs will not be dispersed during this preparation method. Large agglomerates of NPs can hang partly above a hole in the lacey carbon layer. At the rim, the large agglomerates of NPs can be observed with no lacey carbon layer underneath, which allows chemical and high resolution imaging without the influence of the supporting carbon layer.

To investigate the NP size distribution using TEM, the NP agglomerates have to be dispersed during preparation. Therefore, a second preparation method is used in which the NPs are dispersed in a liquid. The suspension is then dropped on a lacey carbon grid with a tissue underneath. For this method, a liquid has to be found that gives the best NP dispersion possible. A different liquid is appropriate for each NP material system and synthesis route.

Depending on the NPs and their surface chemistry, the suspension might only be stable over a timescale of a few minutes; therefore, additional mechanical forces are needed to separate agglomerated NPs in the liquid. The third method used to prepare NP samples involved a Branson Sonifier W250A ultrasonic resonator coupled to the suspension, which
applied these mechanical forces. The resonator induced pressure changes in the liquid below the limit of vaporization. A cloud of small bubbles forms which implodes during the high pressure phase. This mechanically very violent effect is called cavitation. During the implosion, pressures in the order of \(10^{10}\) bar and temperatures in the order of 5000 K can be observed in the very center of the implosion for fractions of a microsecond [18]. These high temperatures are indicated by the spectrum of light emitted during cavitation [63, 43]. For deeper insights into cavitation and bubble dynamics, the reader is referred to the monograph of C. E. Brennen [18].

The ultrasonic tip of the Sonifier was placed in a cone-shaped, 5 ml container with the NP suspension. An increase in temperature reduces the coupling between the tip and the water. Therefore, the container was cooled using a surrounding ice bath. The sonification was performed in pulses so that for 80\% of the 5 min treatment time the ultrasonic tip did not move, thus allowing heat dissipation. Liquids other than water can be used for the NP suspension but this is expected to reduce the cavitation as the resonator frequency is optimized for water.

After the NPs were dispersed, the suspension was dropped on a lacey carbon grid with a tissue underneath.

**Cross sectional samples** of solar cell structures were prepared using Ga ions in a FEI Helios Nanolab 400S focused ion beam (FIB) workstation. Focused high energy gallium ions were accelerated at voltages between 30 kV and 5 kV to sputter the sample at specific positions.

Figure 2.4 shows different intermediate steps in cross sectional FIB preparation of a TEM lamella, acquired using secondary electrons. First (see fig. 2.4 a)) a protective layer is deposited by injection of a Pt precursor gas close to the area of interest. Where the electron or gallium beam hits the sample, secondary electrons are emitted and decompose the precursors, which leads to local growth of a Pt/Ga/C mixture. In a second step (see fig. 2.4 b)) 30 kV Ga ions are used to cut a \( \approx 3 \mu m \) thick TEM lamella, which is only attached to the sample at the upper right part. Then the FIB manipulator needle is soldered to the lamella using Pt/Ga/C. Cutting the last connection with the sample allows a "lift out" of the lamella, which is then soldered to the TEM grid as shown in figure 2.4 c). Finally, the manipulator needle is cut off the lamella, which is then thinned down further using reduced Ga ion voltages and currents (see fig. 2.4 d)). The last thinning step with gallium ions was performed at 5 kV at 5° angle to the lamella surface to reduce the thickness of the amorphous surface layer forming during thinning.

Subsequent thinning with 500 V accelerated Ar ions at 10° incidence angle using the
Figure 2.4: Steps of TEM lamella preparation using FIB a) Protective layer deposition containing Pt, C and Ga, b) Cut TEM lamella still attached to the sample, c) Lamella transported to the TEM grid with the manipulator needle, and d) Top view of TEM lamella after thinning.

Fischione Nanomill was applied to reduce the thickness of the damaged layer on the surfaces of the FIB lamella.
2.3 TEM-based investigation methods

2.3.3. Electron diffraction techniques

Diffraction is a physical process defined as the interaction between a wave of any kind and an object of any kind [149], whereas scattering refers to the interaction of particles with objects.

Diffractions electrons can be investigated in the far-field of the object, in which the diffracted electrons can be regarded as plane waves. This far-field can be observed in the diffraction plane of a lens and corresponds to the Fourier transform of the object function [30]. The group of electron microscopic techniques in which the far-field in the diffraction plane of the objective lens is imaged and analyzed directly are referred to as electron diffraction techniques.

In this thesis, electron diffraction techniques such as selected area electron diffraction (SAED), nanobeam electron diffraction (NBED) and automated diffraction tomography (ADT) were applied to investigate the phase and crystallographic defects of hundreds of crystalline NPs and of single nanocrystals.

The kinematic scattering theory describes the diffraction of an electron wave \( \vec{k}_0 \) by a crystalline sample, which can be described by its reciprocal lattice vectors \( \vec{g} \), in a specific direction \( \vec{k}_g \) according the Laue equation:

\[
\vec{k}_g - \vec{k}_0 = \vec{g} + \vec{s}.
\]  

(2)

If the small excitation error \( \vec{s} \) is neglected, the Laue equation and the Bragg equation are equivalent. Therefore, \( \vec{s} \) describes the deviation from the exact Bragg orientation. Diffraction is possible for \( \vec{s} \neq 0 \) as the investigated crystalline specimen is very thin in electron beam direction. Therefore, \( \vec{s} \) points are usually aligned in the direction perpendicular to the lamella surface. In the case of nanostructured samples such as NPs, other directions are possible.

In the scattering process, the kinetic energy of the electrons does not change, which leads to an additional requirement: \( |\vec{k}_g| = |\vec{k}_0| \). Only the direction of the beam changes upon scattering. All diffracted beams lie on a sphere, the "Ewald sphere". If excitation errors are neglected, lattice planes for which \( \vec{g} \) does not lie on the Ewald sphere do not contribute to electron diffraction. If the sample is rotated, different reciprocal planes can be observed with a different set of \( \vec{g} \).

The intensity of the diffracted beam is influenced by several effects. Because of its strong interaction, the electron wave can be diffracted multiple times within the sample, which is referred to as dynamic scattering. Furthermore, inelastic and thermal diffuse scattering do play a role. Dynamic scattering can be calculated using the Bloch wave approach, in
which the electron wave inside the sample is represented by Bloch waves, which interfere at the sample exit surface. Using the Schrödinger equation for relativistic energies, the intensities of the diffracted beams can be calculated [30, 132].

The intensities of the diffracted beams and the undiffracted beam $I_0$ depend strongly on the sample thickness $t$. When absorption and thermal diffuse scattering are neglected and a two beam diffraction condition is chosen (where the crystalline sample is oriented so that only one set of lattice planes described by $\vec{g}$ contributes to the diffraction pattern), the intensity of the excited beam $I_g$ is given by [132]:

$$I_g = 1 - I_0 = \frac{1}{1 + s_s \xi_g} \sin^2(\pi \sqrt{1 + s_s^2 \xi_g^2} \frac{t}{\xi_g}).$$  \hfill (3)

Here, $s$ is approximated as the norm of $\vec{g}$, orientated in direction $\vec{k}_0$. $\xi_g$ is the extinction length, which depends on the lattice parameters and beams involved, the atomic numbers and the acceleration voltage used, and is in the order of several 10 nm [162].

The dependence of $I_g$ and $I_0$ on the sample thickness is plotted in figure 2.5 a) for $s = 0$. Both intensities are modulated by the extinction length $\xi_g$. This behavior is also referred to as the Pendellösung effect.

![Figure 2.5: Dynamically diffracted beam intensities as a function of sample thickness, according to equation 3. In case a) the sample is orientated exactly in the 2-beam conditions ($s = 0$) and for b) the sample tilt introduces an excitation error of $s = 0.35 \frac{1}{nm}$](image)

If it is assumed that $\vec{s} \perp \vec{g}$, the corresponding sample tilt from the ideal 2-beam condition can be estimated with $|\vec{s}| = \tan(\beta) \cdot |\vec{g}|$ from the Ewald sphere construction. An excitation error of $s = 0.35 \frac{1}{nm}$ of an $|\vec{g}| = 4 \frac{1}{nm}$ diffracted beam (e.g. $[110]$-beam of $\alpha$-Fe$_2$O$_3$) corresponds to a sample tilt of $\beta = 5^\circ$ (for $\vec{s} \perp \vec{g}$). The resulting intensities of the central
and the diffracted beams are presented in figure 2.5 as a function of the sample thickness. Such excitation errors cause a slight change of the modulation period and the intensities of both beams.

**Selected area electron diffraction (SAED)** was used to determine the phase of randomly orientated NPs. The SAED patterns were obtained using the selected area aperture (see chap. 2.3.1) from mostly sample areas with a diameter of 4000 nm. In the case of inhomogeneous samples, the selected area was reduced to a diameter of 100 nm. For a large number of randomly orientated NPs in the selected area, it can be assumed that all \( \vec{g} \) contribute to the resulting "powder diffraction pattern". This consists of rings of diffraction spots and gives the modulus of all reciprocal lattice \( |\vec{g}| \) distances present.

Figure 2.6 a) shows a typical SAED pattern of \( \beta\text{-FeSi}_2 \) NPs. Beside the sharp diffraction rings of the NPs, a background introduced by the supporting carbon grid on which the NPs were prepared. Spatial frequencies below \( 2 \frac{1}{\text{nm}} \) are blocked by the beam blanker used to protect the CCD camera from the high intensity central beam.

![SAED pattern](image)

Figure 2.6: Example electron diffraction pattern of \( \beta\text{-FeSi}_2 \) NPs. a) as acquired, b) rotationally averaged before and after background subtraction.

The diffraction pattern was rotationally averaged as shown in figure 2.6 b). To fit the background, spline functions were fitted between 8 points and subtracted. For spatial frequencies higher than \( 2 \frac{1}{\text{nm}} \) the fitted background is considered to match the actual background of the SAED pattern.

The measured reciprocal lattice distances \( \frac{1}{d_{\text{ref}}} \) allow the phase of the investigated NPs to be determined by comparing with reference reciprocal lattice distances. Reference reciprocal lattice distances obtained by XRD can also be used for the comparison, as
shown in chapter 3.4.2. Deviations between the electron diffraction pattern and the reference XRD pattern of the (221) and (312) reciprocal lattice planes will be discussed in chapter 3.4.2.

In this thesis, all reciprocal lattice distances measured with SAED are compared to reference reciprocal lattice distances found by XRD to determine the phase of the NPs by comparison. The advantage of SAED over XRD is that the patterns can be recorded from selected areas using apertures.

For rotational summation of the SAED patterns, the digital micrograph plugin DiffTools was used [103].

**Nanobeam electron diffraction** (NBED) was used to record patterns from areas in the order of 4 nm² e.g. from a single nanoparticle. Therefore, a convergent electron beam illuminates a specific area $A_{\text{ill}}$ of the sample. As the electron beam is convergent, the diffraction spots become diffraction disks (see figure 3.12 b) in chap. 3.4.2).

To identify the single NP phase and present crystallographic defects, the experimentally obtained NBED patterns were compared to simulated patterns using the JEMS program [142]. All NBED patterns were acquired using a 50 μm C2 aperture and a spot size of 8, which allowed a convergence angle of $1.6 \pm 0.1$ mrad and an area of illumination as small as 4 nm².

The SAED and NBED patterns presented were recorded in an FEI Tecnai F20 microscope at 200 kV in diffraction mode with a 2000 x 2000 pixel CCD camera. The patterns were calibrated using Au NPs sputtered onto parts of the TEM grid using a Cressington 108 auto sputter coater.

NBED can be combined with tilt series recording and reconstruction of 3-dimensional diffraction patterns by the automated electron diffraction tomography (ADT) technique (see review article [78]). ADT was used to detect planar defects within single NPs. Crystallographic defects such as twinning or other planar defects can be observed directly by specific features of the 3-dimensional reciprocal lattice e.g. streaking of specific diffraction spots [30].

ADT is similar to the acquisition of the NBED tilt series, which is then reconstructed.

For ADT, an automated script is used to rotate the NP of interest in the range of ±60° in 1° steps. Rotating the microscope stage induces shifts in the x- and y- directions in the order of 100 nm [78]. After each rotation step, the electron beam is shifted back towards to position of the NP of interest. Therefore, annular dark field microprobe STEM images were acquired between every rotational step. The NBEDs themselves were acquired in the microprobe STEM mode. To reduce the convergence angle and the resulting diameter of the NBED disks, a 10 μm C2 aperture was used. The incidence beam was defocused
2.3 TEM-based investigation methods

to further reduce the convergence angle. The diffraction lens was aligned accordingly to obtain sharp diffraction patterns for every tilt step of the series. The ADT was performed in an FEI Tecnai F30 microscope operated at 300 kV. The electron diffraction tomography datasets were processed using ADT3D software package from Nanomegas and Matlab scripts [78]. The reconstructed 3-dimensional diffraction patterns were investigated using the UCSF Chimera program [123]. The 3-dimensional diffraction patterns are visualized in this thesis by 2-dimensional projection (see fig. 3.13).
2.3.4. Transmission electron microscopy imaging

Transmission electron microscopy (TEM) offers a remarkable number of imaging techniques, which allow NP properties to be studied from the $\mu$ scale, where agglomeration can be observed, down to the 50 pm scale where atomic arrangements at interfaces and NP surfaces can be studied. Here, the bright field, dark field and high resolution TEM techniques will be introduced. For these techniques, diffraction contrast and phase contrast play a major role.

Diffraction contrast is dominant in the bright field (BF) and dark field (DF) TEM imaging modes. In both cases, the electron wave transmitted through the sample is filtered by the objective aperture in the back focal plane of the objective lens (see chap. 2.3.1). In BF TEM, only the central beam $\vec{k}_0$ contributes to the image, diffracted beams do not contribute.

In the case of a crystalline NP, the proportion of diffracted electrons depends to a large degree on the orientation and thickness (see chap. 2.3.3). When the nanocrystal orientation and thickness leads to strong electron diffraction, the central beam intensity is reduced and the crystalline NPs appear dark in the BF image. Weakly diffracting NPs appear in brighter contrast in the BF image (see fig. 4.4 a)). Amorphous material does not show strong diffraction contrast.

BF TEM images were used to investigate the size and shape of the NPs. The size distribution of separated NPs were evaluated using the CSD program [51]. To detect the NP size, the semi-automatic algorithm distinguishes NPs from the background by applying a threshold level. For every manually chosen window, the threshold is calculated to minimize the intensity variance of the pixels assigned to the background and the NP [116].

In DF TEM, the objective aperture position is chosen to exclude the central beam. Only those beams that have been diffracted in a particular set of solid angles selected by the objective aperture contribute to the image. Crystalline NPs orientated accordingly contribute strongly to the DF-TEM image (see figure. 4.4 b)). Due to dynamical scattering thickness, fringes can be observed (see chap. 2.3.3 or figure. 4.4 d)). Scattering in amorphous material also contributes weakly to DF TEM images.

In this thesis, DF imaging was used to identify single or polycrystalline NPs.

The BF TEM and DF TEM images presented in this thesis were acquired using an FEI Tecnai F20 microscope at 200 kV acceleration voltage equipped with a field emission gun and a $2k \times 2k$ CCD camera.

In high-resolution TEM (HR TEM), phase contrast plays an important role. To
introduce phase contrast, the interaction of the sample with the electron wave and the
imaging of the resulting object exit wave function (OEWF) will be given in summary.
These aspects are presented in more detail in appendix A.

Within the sample, the electron wave is altered by the electrostatic potentials of the sample
and changes by propagation. In the multi-slice approach, the two processes are treated
separately. Therefore the sample is separated into thin slices. The projected potentials
\( V_p(x, y) \) of each slice of the thickness \( t \) lead to a phase shift \( \phi \) of the electron wave function
according to \( \phi(x, y) = \sigma V_p(x, y)t \) with the interaction constant \( \sigma \). The propagation
between the planes of projected potentials is described by the Fresnel propagator (see
appendix A).

With sufficiently thin slices, the resulting OEWF agrees with the analytical solution of
the relativistically corrected Schrödinger equation, which can be solved by the Bloch wave
ansatz for periodic crystal potentials [30].

In the following, the simple exit wave function of a one atom thick sample will be given to
highlight the formation of phase contrast. In weak phase object approximation (WPOA,
see appendix A for details) the exit wave function \( \psi_e(\vec{r}) \) of a one atom thick sample is
given by:

\[
\psi_e(\vec{r}) \approx \psi_0(1 + i\phi(x, y)) = \psi_0(1 + i\sigma V_p t).
\]

\( \psi_0 \) describes the plan incidence electron wave with an amplitude of 1, terms quadratic in
\( \phi(x, y) \) have been neglected.

The exit wave function just below the sample is projected onto the CCD camera, which
can only detect differences in intensity. During projection, the aberrations of the objective
lens alter the electron exit wave function, which can be described by a convolution with
the complex microscope point spread function \( P(x, y) \).

For the example of the one atom thick sample in WPOA, the detected image intensity \( I \)
is given by:

\[
I(\vec{r}) = |\psi_e(\vec{r}) \otimes P(x, y)|^2 \approx 1 - 2\phi(x, y) \otimes \Im\{P(x, y)\}.
\]

Again terms quadratic in \( \phi(x, y) \) have been neglected.

This example shows that the imaginary part of the point spread function \( \Im\{PSF(x, y)\} \)
gives contrast to the phase of the OEWF. More details on the microscope aberrations are
presented in appendix A.

To interpret the contrast, the HR TEM images have to be compared with simulations. In
this thesis HR TEM image simulations were calculated using the multi-slice algorithm incorporated in the JEMS software package [142]. Unless stated otherwise, HR TEM studies were performed, an image corrected FEI Titan 80-300 TEM was used at 300 kV. The aberrations of the objective lenses were corrected up to the fourth order.

### 2.3.5. Scanning TEM imaging

For this thesis, scanning TEM (STEM) was used in combination with EELS (see chap. 2.3.6) to study local chemical compositions of NPs.

Electrons are scattered on the atomic nuclei at angles that depend on the atomic number $Z$. The interaction with the nucleus can be described by Rutherford scattering, which is proportional to $Z^2$. The sample electrons present lead to a slightly reduced exponent [121]. In STEM imaging, a high angle annular dark field (HAADF) detector with a minimum detection angle greater than 50 mrad is used to record this chemically sensitive signal. For such high detection angles scattering with the atomic core becomes dominant, which can be approximated by Rutherford scattering with an intensity dependence of approximately $Z^2$ [121]. Also, other effects such as screening of the surrounding electrons or the displacement of atoms due to strain do have an impact on the image intensity [53]. In comparison with simulations, quantitative information on sample thickness and composition can be obtained [135, 94].

For spatially resolved HAADF, the electron beam is focused to a point and scanned over the sample. The resolution of the image intensity $I_{\text{image}}(\vec{r})$ is limited by the probe size of the incidence electron beam given by the point spread function (see chap. 2.3.4) of the condenser system according to:

$$I_{\text{image}}(\vec{r}) = I_O(\vec{r}) \otimes P(x, y)^2,$$

where $I_O(\vec{r})$ is the object intensity (see e.g. review of [122]).

HAADF imaging was performed using a probe aberration corrected FEI Titan 80-300 (S)TEM at 300 kV and an FEI Titan $^3$ 60-300 at 200 kV. Camera lengths between 48 mm and 77 mm were used corresponding to minimum detection angles of 50 mrad and 80 mrad respectively.
2.3.6. Electron energy-loss spectroscopy and energy filtered TEM

Electron energy-loss spectroscopy (EELS) and energy filtered TEM (EFTEM) was used to investigate the local composition and bonding states of the pristine and embedded NPs.

Both techniques are based on the inelastic scattering of the TEM electrons by the sample. By Coulomb interaction, the inelastically scattered TEM electrons excite the sample and release a defined amount of energy depending on the original and final sample energy state.

In the case of EELS, the dispersed electron beam is recorded directly on a CCD camera in an energy dispersive plane (see chap. 2.3.1). A series of EELS spectra, each from different sample position, can be acquired in combination with STEM to obtain STEM/EELS linescans or STEM/EELS maps (often referred to as EELS spectrum images).

Figure 2.7 shows a typical electron energy loss (EEL) spectrum of an $\alpha$-Fe$_2$O$_3$ NP. It contains the zero loss peak (ZLP) of elastically scattered electrons. The FWHM of the ZLP reveals the energy resolution of the microscope (0.8 eV if a field emission gun is used).

On the energy loss scale, the ZLP is followed by the plasmon peaks formed by mobile collectively oscillating charge carriers.

![Figure 2.7: EEL spectra of an $\alpha$-Fe$_2$O$_3$ NP showing the characteristic regions of the ZLP, plasmons and core loss peaks](image-url)
The energy loss region above 50 eV reveals information about the composition and bonding state of the sample. Here, strongly bonded inner shell sample electrons are excited to higher energy states (see Fe M, O K or Fe L edge in figure 2.7). The inelastic scattering probability for high energy transitions like O K or Fe L excitations is rather low. Additionally, the EEL spectra contain a strong background (BG) signal, which originates from plural-scattering events and from tails of the preceding ionization edge.

Figure 2.8: EEL spectra of an \(\alpha\text{-Fe}_2\text{O}_3\) NP together with a background fit and the absolute difference between spectrum and fit.

In order to analyze a specific EELS edge, the background \((I_{BG})\) has to be removed. Figure 2.8 shows a typical EEL spectrum of an O K edge. The background was fitted in an energy window of \(E_{BG} = 80\) eV by a power law function in the form of \(I_{BG} = A \cdot E^r\) wherein A and r are the fitting parameters. Additionally, the absolute difference between the original spectrum and the fitted background is plotted. Even 100 eV prior to the background energy window, the deviation between the background and the original spectrum shows the same number of counts as the background subtracted O K signal. The deviation of the background from simple power law behavior is known in the literature as the parameter r itself depends on the energy, still it is commonly used for EELS quantification [162, 36]. This deviation limits the energy window, which can be used to analyze the edge \(E_{edge}\) of interest (O K in this case).

All EELS edges analyzed in this thesis were background subtracted using a power law
2.3 TEM-based investigation methods

function. The background energy window widths $E_{BG}$ were chosen to be: a) small enough to avoid contribution of preceding edges, b) small enough to reduce the deviation of the original spectrum, and c) large enough to reduce the impact of the spectrum noise on the background fit. The background energy window position was chosen to end 5 eV before the EELS edge onset of interest to avoid overlap with the EELS edge signal.

The energy windows used to evaluate the edge signal $E_{edge}$ were chosen to be of the same width as their background energy windows and to start at the EELS edge onset.

The accuracy of the relative composition profile obtained by integrating the $E_{edge}$ energy window was estimated for each edge by the noise of the profile in areas where no compositional changes are expected.

The bonding state influences the energy of the edge onset or the edge signature. In the case of electron loss near edge spectroscopy (ELNES), the edge onset and signature are recorded and analyzed. Relative peak highs of the edge fine structure or the distance between peaks in the edge fine structure can be compared to the literature to determine the bonding state [25, 50].

For STEM/EELS an STEM HAADF image is recorded. For every pixel of beam position, an EEL spectrum is acquired in parallel. From this set of EELS spectra a two dimensional composition map or a bonding state map can be obtained.

Due to white noise and readout noise of the CCD camera there is a specific minimum number of electrons needed per spectrum to evaluate the specific elemental signal. In the case of electron beam sensitive samples, the maximum number of electrons available for the measurement is limited before the sample degenerates. Therefore, the low dose StripeSTEM technique was used [56]. With StripeSTEM, one EEL spectrum is recorded per row of pixels or beam positions in the STEM HAADF image. High spatial resolution perpendicular to the direction of the pixel rows can be achieved, whereas the necessary dose per spectrum is spread parallel to the direction of the pixel rows. From this data, a one-dimensional composition of bonding state "line scan" can be evaluated.

Also, in case of conventionally recorded STEM/EELS maps containing $n^2$ pixels, the signal to readout noise ratio can be increased by $n^{0.5}$ by summing up all n pixels in one row. StripeSTEM shows a signal to readout noise ratio increased by n in comparison to the conventional STEM/EELS map, due to the significantly reduced number of CCD camera readouts.

The spatial resolution of the StripeSTEM linescan depends on the specimen drift and acquisition times. Atomic resolution can be achieved [56].

StripeSTEM experiments were performed using a probe aberration corrected FEI Titan 80-300 (S)TEM at 300 kV equipped with a Gatan Imaging Filter (GIF) Tridem and a
field emission gun. Typically, spot size 6, a camera length of 77 mm and a 2.5 mm GIF entrance aperture were used during the STEM/EELS experiments. STEM/EELS maps were acquired in a probe corrected FEI Titan 60-300 TEM at 300 kV using a GIF quantum. Background subtraction was performed using the CSI program [27].

For **energy filtered TEM** (EFTEM) the electron spectrometer and the microscope is operated as depicted in figure 2.3 a). A TEM image of the sample is dispersed by a magnetic field. A slit is introduced in the energy dispersive plane to obtain only electrons in a certain energy window. Subsequent electron optics allows acquisition of an EFTEM image. Series of EFTEM images were recorded with different energy windows to obtain compositional information.

Figure 2.9 shows a $\beta$-FeSi$_2$ example, in which a series of 16 EFTEM images was recorded with an energy window of 20 eV, each shifted by 20 eV. Integrating the intensity in a specific area of every image gives the displayed energy loss spectrum for this area. Similar to EELS spectra, a power law background subtraction was performed using the EFTEM images marked in green (see fig. 2.9). The DigitalMicrograph software was used to determine the relative O K and Fe L edge intensity. Performing this evaluation for every pixel of the EFTEM spectrum image gives the O K and Fe L edge maps as depicted in chapter 3.4.3, figure 3.14.

![Energy loss spectrum obtained from EFTEM spectrum image of $\beta$-FeSi$_2$ from 16 EFTEM images between 450 eV and 770 eV, window and step size of 20 eV. The intensity of every EFTEM image was spatially integrated. EFTEM images used for background subtraction are colored green, EFTEM images used to evaluate the O K and Fe L intensity after background subtraction are colored yellow and blue respectively.](image)
The high tension of the microscope was shifted between each of the 16 acquired 20 eV energy windows. The CCOR corrector of the PICO microscope allowed the chromatic aberration of $C_c$ to be reduced to a value in the order of $C_c = 5 \mu m$ [46, 65]. Disregarding all other aberrations and microscope instabilities, the resolution $d_{Cc}$ can be approximated by $d_{Cc} = (\frac{2\Delta E}{\Delta E} \alpha C_c)$ [155, 162]. A semi-collection angle of $\alpha = 35$ mrad was assumed [46] and a primary energy in the order of $E_0 = 80$ keV was used. The resulting $d_{Cc} = 30$ pm are below the instrument information limit of 80 pm. Therefore, the impact of the chromatic resolution on the EFTEM spectrum image can be disregarded.

EF-TEM maps recorded in a microscope that is not Cc corrected and having a $C_c$ of 2 mm, $\alpha = 4$ mrad, $\Delta E = 20$ eV and $E_0 = 80$ keV would allow an EFTEM spectrum image resolution of approximately 1.5 nm.

The spatial drift of the different EFTEM images was statistically determined using the SDSD correction program [136].

EFTEM studies were performed in the spherical and chromatic aberration-corrected FEI Titan PICO microscope equipped with a Gatan Imaging Filter quantum. Voltages of 80 kV were used to minimize beam damage. DigitalMicrograph software (Gatan) was employed for image processing.

### 2.3.7. Energy-dispersive X-ray spectroscopy

Energy-dispersive X-ray spectroscopy (EDX) was used for compositional analysis of the sample. After the TEM electrons scatter inelastically and excite the sample, the nuclei relax upon emission of an X-ray photon characteristic in energy (see book of [162]).

The energy resolution of EDX ($\approx 140$ eV) is limited by the photon detector, as the semiconductor detectors are optimized to reach the highest possible sensitivities. EDX linescans were recorded in combination with STEM to obtain qualitative compositional profiles. The background of the EDX spectra obtained was subtracted using a linear background fit. The intensities of the characteristic elemental K lines were integrated in 300 eV energy windows, not containing signal of other elements.

The TIA (TEM imaging and analysis) software from FEI was used to record and evaluate the STEM/EDX linescans. The STEM/EDX experiments presented here were acquired in a FEI Tecnai TEM operated at 200 kV in STEM mode. The EDX were acquired using a 30 mm$^2$ SiLi detector (Model: PV97-61700-ME) from the company EDAX. C2 apertures of 50 µm, spot sizes between 4 and 6, and a sampling of 1 spectrum per nm were used.
2.3.8. Sample degeneration and measuring the electron dose

During the TEM investigation the sample may suffer from beam damage. Three types of damage mechanisms are known: radiolysis, specimen heating and knock-on damage. In the case of radiolysis, chemical bonds break, possibly leading to a change in the chemistry and structure of the specimen. The effect of radiolysis can be reduced by increasing the acceleration voltage of the TEM electrons as the cross section for electron interaction becomes smaller.

Specimen heating by the electron beam may lead to sample degeneration or phase transformation. The final temperature depends on the sample geometry, electron beam current and thermal conductivity. Usually, specimen heating plays a minor role in the case of metals or semiconductors, as the heat conductivity is sufficiently high [162]. In the case of NPs where heat dissipation is reduced, specimen heating may become relevant. Increasing TEM voltages and reducing currents lead to a reduction of specimen heating. The most prominent damage mechanism for metals and semiconductors is knock-on damage. Here, sample atoms are displaced or scattered out of the sample. Knock-on damage can be reduced by decreasing TEM voltages and is proportional to the electron dose.

If the sample of interest is sensitive to the electron beam, it is recommended to determine the critical electron dose or electron dose current.

The electron dose was determined using the current on the fluorescent screen and the counts of the CCD camera, which give the dose current characterized by the microscope manufacturer.

The dose current measured using the CCD camera and the fluorescent screen is linear over 4 orders of magnitudes. The dose current fluctuation over the fluorescent screen is ±5%. The fluorescent screen and the CCD camera give the same dose currents within ±5% of accuracy. The measured dose currents are regarded as indicators for the actual dose currents, which gives at least the correct order of magnitude. The electron doses presented in this thesis were determined from the measured dose currents and the irradiation time. Electron beam damage experiments were performed in an FEI Tecnai microscope at 200 kV.
3. $\beta$-FeSi$_2$ NPs as potential absorbers for a-Si:H solar cells

3.1. Introduction

$\beta$-FeSi$_2$ is a semiconductor suitable for thermoelectric, light-emitting and light-sensitive applications. It is also non-toxic, abundant in nature and compatible with existing silicon-based technology [84].

The $\beta$-phase of FeSi$_2$ forms in a narrow compositional range below 982 °C [96]. The complex unit cell of FeSi$_2$ is shown in figure 3.1. The unit cell with 48 atoms is orthorhombic with the space group $Cmca$ and lattice parameters of $a=0.986$ nm, $b=0.779$ nm and $c=0.783$ nm [35].

![Figure 3.1: Crystal structure of $\beta$-FeSi$_2$ viewed along different crystallographic orientations [35]. Red: Fe atoms; Blue: Si atoms.](image)

$\beta$-FeSi$_2$ can be synthesized by solid-state reaction of Si and Fe at elevated temperature from bulk material [167], thin films [87] on Si substrates or nanocrystals embedded in crystalline Si [163].

Optical investigations using photoluminescence or absorption revealed both a direct band gap of 0.83 eV – 0.85 eV [17, 127, 41] and an indirect band gap of 0.73 eV - 0.78 eV [127, 41]. A high absorption coefficient of $10^5 \frac{1}{\text{cm}}$ was reported [17], which makes it a promising material for optical absorbers.

Undoped $\beta$-FeSi$_2$ may show n-type or p-type conduction depending on the exact growth parameters. The conduction type of undoped $\beta$-FeSi$_2$ can be changed when it is grown in Fe- or Si-rich conditions [100, 147]. EPR measurements revealed the presence of Fe and Si vacancies in $\beta$-FeSi$_2$, which serve as donors or acceptors respectively [147, 89].

$\beta$-FeSi$_2$ was investigated as a material system for thermoelectric applications as it has a high Seebeck coefficient $S$ of $\approx 200 \frac{\mu V}{\text{K}}$ [61]. The performance of a thermoelectric material does not only depend of the Seebeck coefficient $S$ but also on its electrical resistivity $\rho$ and thermal conductivity $\kappa$ giving the figure of merit $Z = \frac{S^2}{\rho \kappa}$. In the case of bulk
β-FeSi₂, Z higher than $5 \cdot 10^{-5} \frac{1}{K}$ [61, 110, 119]. Z can be further increased by geometric modification or embedding of minority phases, which decreases the thermal conductivity [61].

β-FeSi₂ is also interesting as a material for light emitting diodes and solar cells as it is compatible with existing silicon-based technology [127, 84, 150, 166].

Layers of β-FeSi₂ grown on Si substrates have been studied for more than 20 years as potential photon emitters or absorber layers in solar cells. It was found that device performance can be impaired by vacancies, planar defects and strain, which will be discussed in the following.

- Silicon or iron vacancies lead to mid band gap energy states [148]. Investigations on β-FeSi₂ layers suggest that Si vacancies are formed during MOVPE growth or ion-beam synthesis [150, 151, 3, 148]. Annealing at temperatures around 800°C leads to a reduction of the Si vacancies in the β-FeSi₂ by diffusion of Si from the substrate [150, 151, 3]. Another possible way to reduce the number of Si vacancies in β-FeSi₂ layers is by Al doping, which enhances the PL signal and solar cell performance [15, 151, 166]. Liu et al. [89] revealed that in the case of Fe vacant β-FeSi₂ layers on an Si substrate, Si interdiffusion yields stoichiometric β-FeSi₂. Although Si interdiffusion partly compensates for Fe and Si vacancies, they could still be found after 2 h of treatment at 800°C [89].

- Domain boundaries or crystallographic defects such as intrinsic planar defects described as (100)[011]/2 reduce the crystal quality of β-FeSi₂. (100)[011]/2 planar defects were found in bulk and in 150 nm thick layers of β-FeSi₂ prepared on Si substrates using solid-phase epitaxy [171]. They may be present in NPs of β-FeSi₂ and may introduce additional states within the band gap.

- Strain is introduced by the lattice mismatch at epitaxial β-FeSi₂/Si interfaces. Residual strain from the lattice mismatch modifies the band gaps [152]. In addition, dislocations within the Si [145, 146] were observed, which act as recombination centers, reducing the device performance [144]. Lattice deformation at β-FeSi₂/Si interfaces and the number of dislocations do increase during annealing [146, 152].

Despite these issues, layer based β-FeSi₂ solar cells reach conversion efficiencies of up to 3.7% [90]. However the growth process involves annealing at 880°C for several hours, which is needed to improve the high crystal quality of β-FeSi₂ layers on Si substrates. Therefore, high production costs are expected.
The issues found for $\beta$-FeSi$_2$ thin films are not expected to be present in the case of $\beta$-FeSi$_2$ NPs embedded in a-Si, because:

1. The number of vacancies may be reduced due to alternative growth processes. Remaining vacancies may relax easily to the NP surface where they may be passivated by the a-Si:H.

2. Domain boundaries or planar defects may not occur depending on the defect density and the NP size.

3. Strain effects may play a minor role as the a-Si:H adjusts bonding angles during deposition to a certain extent.

Another advantage of $\beta$-FeSi$_2$ NP absorbers in a cell of a-Si:H are lower production costs as embedding temperatures below 200°C are possible. The NPs themselves can be optimized by annealing without a significant increase in the solar cell costs as their fraction is low.

The fabrication of the necessary free-standing, phase pure $\beta$-FeSi$_2$ NPs has been a major issue using any physical or chemical deposition process. Recently, Bywalez et al. [22] succeeded in preparing free-standing $\beta$-FeSi$_2$ nanocrystals using chemical vapour synthesis in a hot wall reactor.

To find out whether these $\beta$-FeSi$_2$ NPs fulfill the criteria to serve as absorbers for solar cell applications (see chap. 1) the $\beta$-FeSi$_2$ NPs will be analyzed and discussed with respect to their structural and chemical properties.

The chapter 3.2 will begin with a short introduction to the gas phase synthesis used to grow the NPs investigated here. Chapter 3.3 will provide an overview of the average NP phase, mean composition and absorption measured by non-local methods such as XRD, XPS, ERDA and PDS. TEM experiments were performed, revealing the shape, degree of aggregation, faceting, local composition and local bonding states using high resolution TEM, energy filtered TEM and electron energy loss spectroscopy as presented in Chapter 3.4. In Chapter 3.5, the growth conditions of the NPs were altered and post-treatment steps were applied in order to improve the NPs. Chapter 3.4.2 will present a detailed analysis of stacking fault domains found inside the NPs by high resolution TEM, nanobeam electron diffraction as well as 3-dimensional diffraction tomography. These results will be discussed together with DFT calculations of the formation energy and the band structure of the stacking fault domains found.
3.2. Synthesis of $\beta$-FeSi$_2$ NPs

The NPs investigated here are the first phase pure $\beta$-FeSi$_2$ NPs reported in the literature. They are prepared using direct gas phase synthesis in a hot wall reactor [22] as shown in figure 3.2.

Silicon and iron were provided by the precursors monosilane (SiH$_4$) and iron pentacarbonyl (Fe(CO)$_5$) in gas phase. Therefore, the (Fe(CO)$_5$) was evaporated with a thermalized bubbler and carried into the hot wall reactor by nitrogen (N$_2$) gas flow. The iron and silicon precursor containing gases were completely mixed with an additional flow of N$_2$ before entering the hot wall reactor, where they decomposed to form $\beta$-FeSi$_2$ NPs. At the end of the silica tube, the NPs were collected with a filter and bottled. To avoid formation of the high temperature $\alpha$-phase, a reaction temperature of 900 $^\circ$C was chosen.

The overall decomposition energy of Fe(CO)$_5$ (72 kJ mole$^{-1}$) is significantly lower than the decomposition rate of SiH$_4$ (179.2 kJ mole$^{-1}$). Simulations of this NP growth process show that Fe(CO)$_5$ decomposes more than 1000 times faster than SiH$_4$ [22]. These decomposition dynamics suggest that iron particles form, which are later transformed into $\beta$-FeSi$_2$ when a sufficient amount of Si is supplied by the decomposition of SiH$_4$. It should be noted that precursors also contain the elements carbon, hydrogen and oxygen, which are present during the growth process.

After a successful recipe was found for producing phase pure $\beta$-FeSi$_2$ NPs, the growth was optimized, e.g. to avoid exposing the NPs to air, and post treatment annealing was performed to improve the NP properties. Table 3.1 gives an overview of the changed growth parameters and post-treatments.

In the following, sample $\beta$-FeSi$_2$ will be discussed in full detail. The properties of the further improved NPs will be discussed in a later step.
3.2 Synthesis of $\beta$-FeSi$_2$ NPs

Table 3.1: List of the studied $\beta$-FeSi$_2$ samples.

<table>
<thead>
<tr>
<th>Sample name</th>
<th>Post-treatment</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\beta$-FeSi$_2$</td>
<td>long-term exposure to air</td>
</tr>
<tr>
<td>500 $^\circ$C $\beta$-FeSi$_2$</td>
<td>exposure to air, 500 $^\circ$C annealing (1h, O part. pr. $10^{-4}$ mbar)</td>
</tr>
<tr>
<td>inert-$\beta$-FeSi$_2$</td>
<td>handled in inert atmosphere</td>
</tr>
<tr>
<td>inert-horizontal $\beta$-FeSi$_2$</td>
<td>handled in inert atmosphere</td>
</tr>
</tbody>
</table>
3.3. Macroscopic properties of $\beta$-FeSi$_2$ NPs

The $\beta$-phase of the crystalline NPs was confirmed using X-ray diffraction (XRD) [22] (see chap. 2.2.1).

The XRD pattern of figure 3.3 matches the reference data of $\beta$-FeSi$_2$ [167] nicely. Both were plotted in units of reciprocal lattice distances 1/d. The peak intensities and further diffraction data will be discussed in more detail in chapter 3.4.2.

Absorption of the $\beta$-FeSi$_2$ NPs was investigated using PDS (see chap. 2.2.2). Therefore, the NPs were drop-coated on a quartz glass substrate. The thickness of the NP layer on the substrate is unknown, so that only relative changes in the absorption can be measured. Figure 3.4 shows the PDS absorbance of the $\beta$-FeSi$_2$ NPs plotted against the incident photon energy. The band gap of $\approx 0.8$ eV is marked with a dotted line. Below the band gap, absorption is approximately one order of magnitude lower than the absorption above the band gap.

To learn more about the possible reason for this high sub-band gap absorption, further non-local methods such as XPS or ERDA were performed. For the ERDA measurements (see chap. chapter 2.2.6), the $\beta$-FeSi$_2$ NPs were prepared on a Ge substrate from ethanol suspension.
3.3 Macroscopic properties of $\beta$-FeSi$_2$ NPs

![Normalized Absorbance vs Energy](image)

Figure 3.4: PDS absorbance spectrum of $\beta$-FeSi$_2$ NPs. The dotted line indicates the band gap position around 0.8 eV

The ERDA results in figure 3.5 show the energy loss in the first thin part of the detector and the remaining recoil energy of the atoms measured in the second part of the detector. The measured $\Delta E/E$ ratio depends on the recoiled element and on the energy loss it suffered within the sample. The pronounced germanium tail originates from Ge atoms recoiled from different depths of the Ge substrate. Minor H, C and Na signals may originate from contamination of the wafer or of the ethanol NPs suspension used to prepare the sample. The Si and Fe signal allows determination of the Si/Fe ratio as $2.25 \pm 0.15$.

Figure 3.6 (a) and (b) from [2] depicts the binding energy of the electrons determined via XPS (see chap. 2.2.5) in the energy regions of the Si$\ell$ and Fe$\ell$ edge of the average NPs. The spectrum of the photon-generated electrons shows the Si$\ell$ edge with pronounced binding energies of 100 eV and 104 eV are characteristic for covalent bonded Si and SiO$_2$, respectively. The photon spectrum of the Fe$\ell$ edge with pronounced peaks at 708 eV and 721 eV is characteristic for covalently bonded iron. Binding energies between 709 eV and 711 eV are not present, indicating the absence of FeO, Fe$_2$O$_3$ or Fe$_3$O$_4$.

In conclusion, the macroscopic investigations of the $\beta$-FeSi$_2$ sample show that the $\beta$-phase is the only crystalline phase found. The Si/Fe ratio of $2.25 \pm 0.15$ does not match the equilibrium phase diagram, suggesting the presence of additional amorphous material containing Si. XPS indicates the presence of SiO$_2$.

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$^2$S. Niesar, WSI of the TU München, private communication 2012
Figure 3.5: Elastic recoil detection analysis of $\beta$-FeSi$_2$ NPs

Figure 3.6: XPS spectra of $\beta$-FeSi$_2$ NPs showing the electron binding energy distribution in the region of the (a) silicon L edge and the (b) iron L edge.
3.4. Structural properties and local chemical composition of $\beta$-FeSi$_2$ NPs

The results of various (S)TEM methods on the $\beta$-FeSi$_2$ NPs will be discussed in this chapter. Crucial NP properties (see chap. 1) including agglomeration, size and shape, faceting, local composition and bonding as well as crystallographic defects will be investigated.

3.4.1. Size and Shape of $\beta$-FeSi$_2$ NPs

Figures 3.7 shows $\beta$-FeSi$_2$ NPs at low magnification after dispersing them using acetone, ethanol, isopropanol, distilled water, toluene, or no solvent. No additional ultrasonic treatment was performed. In all cases the NPs, which show dark contrast, are deposited onto a lacey carbon layer. Agglomerates larger than 200 nm can be observed regardless of the solvent used. A comparison of the various solvents shows that preparation in toluene results in the smallest size of agglomerate like structures. Here, clusters with diameters between 100 nm and 1 $\mu$m remain (see fig. 3.7 f)). Additional sonification using an ultrasonic finger (Brandson sonifier, see chap. 2.3.2) does not allow the size of the clusters to be reduced further. This suggests that the NPs are sintered together.

Figure 3.8 (a) shows a BF TEM image of $\beta$-FeSi$_2$ NPs deposited on a lacey carbon grid. The nanocrystals form a chain-like structure consisting of 20 nm crystals. The average size of the aggregated crystals was estimated by fitting irregular round shapes to the particle complex. A high resolution image of a $\beta$-FeSi$_2$ nanocrystal viewed along the [111] zone axis direction is shown in figure 3.8 (b). The crystalline core is surrounded by a 1.7 $\pm$ 0.4 nm thick amorphous shell, which will be further investigated in chapter 3.4.3. The crystallographic orientation of the NP core is preserved through the sintering bond to the next NP. Also, DF TEM images (not shown here) reveal that adjacent particles are often orientated in similar crystallographic directions. Hence, the NPs are sintered together and from aggregates containing more than 10 NPs. Aggregates larger than 200 nm in diameter are common, and these are too big considering the requirements for NP based solar cells (see chap. 1). In chapter 3.5, mechanical milling is discussed as one possibility for breaking the sintered nanocrystals and reducing the cluster size further.

The crystalline edge of the $\beta$-FeSi$_2$ core, right at the interface to the amorphous shell, was investigated in more detail using high resolution imaging. Electronic properties of the NPs could change significantly if the last atomic layer of the $\beta$-FeSi$_2$ core is determined by iron or silicon respectively. For example, DFT calculations of the most stable (001)
Figure 3.7: TEM images of $\beta$-FeSi$_2$ NPs prepared using various solvents for dispersion, no additional ultrasonic treatment steps were used. a) acetone, b) ethanol, c) isopropanol, d) no solvent, e) distilled water and f) toluene.
3.4 Structural properties and local chemical composition of $\beta$-FeSi$_2$ NPs

Figure 3.8: (a) BF TEM image shows the nanocrystalline aggregates revealing a core shell structure. The aggregates contain 20 nm NPs. (b) High resolution TEM image shows a crystalline $\beta$-FeSi$_2$ core orientated in the [111] zone axis sintered to another NP, both surrounded by a $\approx$2 nm amorphous shell.

surface predict a metallic behavior induced by dangling iron bonds\(^3\).

Figure 3.9 a) shows an aberration-corrected HR TEM image viewed along [011]. The image was recorded in a defocus series with an underfocus of approximately 10 nm. The corresponding multislice simulated HR TEM image is presented in figure 3.9 b). The HR TEM image of the $\beta$-FeSi$_2$ crystal structure was simulated with a sample thickness of 4.4 nm, spherical aberration of $-20 \mu$m and a defocus of -12 nm was used (see chap 2.3.4). The experimental and the simulated HR TEM images match well. Overlaying the simulated HR TEM image with the crystal structure used for the simulations (see fig. 3.9 b)) allows the Fe and Si atomic columns to be assigned to the flower-like spot pattern observed in the simulated and experimental images. Figure 3.9 c) shows the atomic Fe and Si columns assigned to the experimental HR TEM image in the marked area up to the edge of the nanocrystal core. No distinct faceting is found. The nanocrystal surface contains both Fe and Si atomic columns in stoichiometric composition.

\(^3\)T. Schena, PGI-1 of FZ Jülich, private communication

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β-FESI₂ NPS AS POTENTIAL ABSORBERS FOR A-Si:H SOLAR CELLS

3.4.2. Phase and defects of β-FeSi₂ NPs

ED, NBED and ADT (see chap. 2.3.3) are applied to study the phase and crystallographic defects of the β-FeSi₂ NPs in more detail.

The phase of the crystalline NP core was analyzed using XRD [22] as already discussed in chapter 3.3. Figure 3.10 compares the rotational averaged electron diffraction pattern from figure 3.7 and the XRD diffraction pattern with the reference literature XRD data of β-FeSi₂ [167]. The electron diffraction pattern of the β-FeSi₂ NPs was obtained from the selected area shown in figure 3.7 (d). Both ED and XRD patterns match each other and the XRD reference data of β-FeSi₂ nicely. This also shows that reciprocal lattice distances obtained by electron diffraction can be directly compared to the reciprocal lattice distances from reference XRD data.

The β phase of the nano crystals is confirmed. However, the intensities of the (221) and (312) reflections are strongly reduced compared to the β-FeSi₂ reference structure model. This reduction of XRD intensities with (hkl) reflections that fulfill h+l≠2n can be modeled by (100)[011]/2 planar defects [167].

In the following, the (100)[011]/2 planar defects will be further discussed. Figure 3.11 illustrates a) an ideal β-FeSi₂ crystal and b) the same domain containing one (100)[011]/2
3.4 Structural properties and local chemical composition of $\beta$-FeSi$_2$ NPs

Figure 3.10: Comparison between XRD, rotationally averaged background subtracted ED and literature XRD data of $\beta$-FeSi$_2$ (as already presented in chapter 2.3.3).

planar defect at a unit cell position of $a = \frac{3}{4}$. Si atoms are colored blue whereas the red indicates Fe atoms. As a guide to the eye, distinct groups of Fe atoms are connected by a red line. The stacking fault location is marked with a black line. A large density of these defects was already reported for bulk and thin film samples of $\beta$-FeSi$_2$ [171, 170]. These stacking faults form at unit cell positions of $a = \frac{1}{4}$ and $a = \frac{3}{4}$, where they introduce only minor changes in the atomic distances and bonding angles [171, 167].

Figure 3.11 c) illustrates a $\beta$-FeSi$_2$ crystal domain with (100)[011]/2 planar defects at every possible lattice plane. This stacking fault domain is similar to the ideal domain with exchanged b- and c-axis, as depicted in figure 3.11 d). The term similar is used as the lattice parameters b and c of the stacking fault domain and the domain of exchanged b- and c-axis differ by 0.5% [167].

The ideal domain a) and the domain d) of exchanged b- and c-axis can be imagined as the "left hand" and "right hand" of the very same unit cell, the transformation can be divided into a mirror operation with an additional rotation about the a axis. Figure 3.11 e) illustrates the ideal domain in [012] projection mirrored at a plane parallel to [100] and [012]. Neglecting the strain, only a rotation about the [100] axis by $\approx 37^\circ$ is needed to transform the mirrored domain e) into the ideal domain of exchanged b and c axis d).
Figure 3.11: Domains of $\beta$-FeSi$_2$ oriented in [012] zone axis direction a) without stacking faults, b) containing one stacking fault, and c) containing stacking faults at all $a = \frac{1+2n}{4}$ positions of the unit cell. d) shows a $\beta$-FeSi$_2$ domain constructed by exchanging the b and c axis in [021] zone axis direction, whereas e) is constructed by a mirror transformation of the ideal domain a) with a mirror plane parallel to [100] and [012]. Blue and red dots indicate the projected positions of the oxygen and iron atoms, the (100)[011]/2 planar defects are highlighted with black lines. Red lines and striped regions guide the eye towards the differences in the atomic arrangement.

The projection and diffraction pattern of the ideal and mirrored domains are invariant. Therefore, TEM images and diffraction patterns of stacking fault domains of $\beta$-FeSi$_2$ orientated in [012] zone axis direction can be approximated as $\beta$-FeSi$_2$ orientated in [021] zone axis direction.

Figure 3.12 (a) shows a high-resolution TEM image. From the region marked with a square the Fourier transformation was calculated, and is shown in the inset. The measured lattice distances of the HR TEM image and the spatial frequencies of its Fourier transform indicate a crystal oriented in the [012] or [021] zone axis direction. Spatial frequencies that would allow a distinction are streaked in the [100] direction and fulfill the condition $k + l \neq 2n$. The nanobeam electron diffraction pattern presented in figure 3.12 (b) was acquired from the same NP and reveals the same streaking as the Fourier transform. The [100] direction and the $k + l \neq 2n$ condition of the streaks allow these planar defects to be identified as (100)[011]/2 [171]. Figure 3.12 (c) shows an enlarged part of the HR TEM image in which two types of contrast patterns are visible, indicating two domains. The insets show multislice simulations performed using the JEMS program [142] of $\beta$-FeSi$_2$ crystals orientated along the [012] and [021] zone axis direction. Simulation parameters
Figure 3.12: (a) HR TEM image of planar defects in a $\beta$-FeSi$_2$ NP. The square indicates the area of the calculated Fourier transformation shown in the inset. (b) NBED pattern recorded from the NP shown in (a). The arrows indicate streaks which appear if the condition $k + l \neq 2n$ is fulfilled. (c) Enlarged HR TEM image of the area marked in (a) with insets of simulated images of $\beta$-FeSi$_2$ along (1) [021] and (2) [012] directions [60].
of 200 kV acceleration voltage, 3 nm thick $\beta$-FeSi$_2$, a spherical aberration of 1200 nm and 120 nm defocus were used (see chap. 2.3.4). The good qualitative match between the experimental and simulated images suggests that two domains are present which can be described by an exchange of the b- and c-axis. This observation complies with domains of subsequent (100)[011]/2 planar defects.

The (100)[011]/2 planar defects are only visible for certain orientations since HR TEM images are projections of three-dimensional (3D) structures, and conventional NBED only excites diffraction spots in one plane of the reciprocal space. To learn more about the 3D structure of the $\beta$-FeSi$_2$ nanoparticles, automated diffraction tomography (ADT) [77] was applied, in which a tilt series of NBED patterns was collected from which the three-dimensional diffraction pattern was reconstructed (see chap. 2.3.3).

Figure 3.13 (a) shows the projection of the 3D diffraction pattern along the [001] direction of a $\beta$-FeSi$_2$ NP. A 2D diffraction pattern along the [001] direction would only show $(hkl)$ diffraction spots that fulfill the excitation condition $l = 0$. The projection of the 3D diffraction pattern also contains spots with $l \neq 0$. Figure 3.13 (b) shows the same 3D diffraction pattern projected along the [011] direction. The arrows mark lines of reflections streaked along [100]. Only spots that fulfill the $k + l \neq 2n$ condition show streaking. Therefore, only (100)[011]/2 planar defects are present.

![Figure 3.13: Reconstructed 3-dimensional diffraction pattern of a single $\beta$-FeSi$_2$ nano crystal projected along (a) [100] and (b) [011]. In (b), the arrows mark lines of reflections streaked along [100]. [60]](image)

In summary, (100)[011]/2 planar defects were unambiguously identified by diffraction methods, i.e. XRD, ED and ADT as well as by HR TEM imaging.
3.4 Structural properties and local chemical composition of β-FeSi₂ NPs

3.4.3. Chemical composition of the core/shell structure

An amorphous shell was observed surrounding the β-FeSi₂ NP core (see chap. 3.3). In this chapter the chemical composition of the core/shell NPs will be investigated. As the shell was found to be sensitive to the electron beam (see chap. 3.5.4) EF TEM studies were performed at low acceleration voltage and low dose EELS techniques such as StripeSTEM were used (see chap. 2.3.6).

![Figure 3.14](image-url)

Figure 3.14: a) BF TEM image of a crystalline β-FeSi₂ NP b) Background subtracted maps of O K (red) and Fe L (green) obtained by a C₅ and C₇ corrected EFTEM at 80kV [60].

Figure 3.14 a) and b) show a BF TEM image and the complementary Fe and O EFTEM map of a β-FeSi₂ NP (see chap. 2.3.6). The TEM image resolves the lattice fringes of the crystalline core, which is surrounded by an amorphous shell. Despite the low acceleration voltage of 80kV a spatial resolution below 0.1 nm was achieved by correction of the chromatic aberration (see chap. 2.3.6). To map the O and Fe distribution (see fig. 3.14 b)) a series of EF TEM images between 440 eV and 780 eV were acquired in 20 eV steps with a window size of 20 eV, containing the O K-edge at 532 eV and the Fe L-edge at 709 eV. After background subtraction, the O K map and Fe L map were plotted on top of each other and color-coded in red and green as shown in figure 3.14 b). The spatial resolution of the Fe and O map is estimated to better than 0.1 nm (see chap. 2.3.6). The Fe signal from the NP core is clearly surrounded by an oxygen shell. Unfortunately, the 2 nm thick amorphous shell (see fig. 3.14) was reduced to 0.7 nm during acquisition of the EFTEM series. That is why a second acquisition of the Si edge could not be conducted.
Still, the elemental signal distributions obtained (see fig. 3.14 b)) indicate the presence of an oxygen shell containing no iron.

Figure 3.15: $\beta$-FeSi$_2$ a) and c) HAADF images with box and arrow indicating the area for StripeSTEM elemental analysis shown in b) and d), respectively. b) reveals Fe M and Si L profiles after background subtraction and integration from the area marked in a). Accordingly, d) presents the background subtracted and integrated Fe L and O K profiles from the area marked in c) [60].

Further elemental analysis of the nanocrystals was done using the low dose StripeSTEM EELS technique [56] (see chap. 2.3.6). Compared to conventional EEL spectrum imaging, lower doses are possible with StripeSTEM due to the spreading of the intensity in the fast scanning direction (see chapter 2.3.6). Despite the high acceleration voltage of 300 kV, no indication of beam damage was observed.

Figure 3.15 a) and c) display STEM HAADF images of the $\beta$-FeSi$_2$ NPs used for chemical investigation. The STEM HAADF contrast is reduced in a $\approx 2$ nm thick shell region, confirming the core/shell structure of the NPs. Both figures highlighted the areas where StripeSTEM experiments (see chap 2.3.6) were performed to determine compositional profiles in the direction indicated by an arrow. Figure 3.15 b) and d) show the corresponding background subtracted EELS signals of Si, Fe and O measured. The
Fe M-edge at 54eV and the Si L edge at 99eV (see fig. 3.15 b)) show a constant Fe/Si ratio inside the particle. Towards the edge of the particle, the Fe signal drops prior to the Si signal. A 2 nm thick shell region is observed where only Si but no Fe signal is detected. The error bars of ±5% and ±6% of the maximum Fe and Si signals were estimated from the noise levels. Figure 3.15 d) compares the signal of the O K edge with the signal of the Fe L edge. In the middle of the particle, the oxygen signal is constant. In the region of the NP shell, a strongly increased O signal is observed, indicating an O-rich shell. It is concluded that the amorphous shell at the surface of the β-FeSi$_2$ NPs is rich in Si and O. Within the margin of error, no Fe was detected within the shell, and the Fe/Si ratio stays constant across the NP core.

![Image](image.jpg)

**Figure 3.16:** (a) HAADF STEM image of a β-FeSi$_2$ NP (b) background subtracted EEL spectra of the O K edge onset from areas marked in (a), both acquired using the StripeSTEM technique with HAADF detector collection angles between 70 mrad and 200 mrad [60].

In order to study the atomic configuration in the shell region, ELNES of the Si L edge was studied. Figure 3.16 a) displays a HAADF STEM image recorded at the edge of a β-FeSi$_2$ NP together with b) background subtracted EELS spectra of the Si L edge recorded from different areas of image 3.16 a). The bright contrast in the upper part of the HAADF image originates from the thick, strongly scattering FeSi$_2$ core. In the region marked with the number 4, reduced contrast indicates the weaker scattering shell. The EELS spectra (see fig. 3.16 b) from NP core areas 1 and 2 show a Si L-edge onset at 99eV, which is characteristic of covalently bonded Si [97]. In areas (3, 4 & 5) of the NP shell, the Si L-edge onset of 104 eV is observed and is in good agreement with amorphous SiO$_2$ (104.8 eV) [50]. The shift of the Si L edge onset suggests that the amorphous shell
of the FeSi$_2$ contains SiO$_2$ bonds.

In summary, we observed aggregates of $\beta$-FeSi$_2$ NPs larger than 200 nm. The NPs are covered with an amorphous shell containing silicon and oxygen. The EELS and XPS fine structures analysis suggest that the amorphous shell contains SiO$_2$ like bonds, whereas no significant FeO$_x$ was observed.
3.5. Improving $\beta$-FeSi$_2$ NPs

The $\beta$-FeSi$_2$ NPs investigated in chapter 3.3 and 3.4 are not ideal with respect to the NP requirements for NP-based solar cells (see chap. 1):

- The size of the aggregates up to 1000 nm in size is unsuitable, as the charge carrier mobility in the surrounding a-Si:H restricts the thickness of the intrinsic layer.
- The 2 nm thick SiO$_2$ shell may hinder carrier extraction.
- High sub-band gap absorption indicates the presence of defects offering a route for carrier recombination. Crystallographic defects have been observed, which may introduce these sub band gap states.

In this chapter, post-treatments are applied to the existing NPs and the growth conditions of the new $\beta$-FeSi$_2$ NPs are altered in order to improve their properties with respect to the requirements.

3.5.1. Size reduction of $\beta$-FeSi$_2$ aggregates

The size of the aggregates can be reduced by mechanical milling. Figure 3.17 shows the nano crystals embedded in a-Si:H after milling with 650 μm ZrO$_2$ milling beads for 5 hours and subsequent removal of the ZrO$_2$ beads by decantation.

![Figure 3.17: Zero loss peak energy filtered TEM image shows individual $\beta$-FeSi$_2$ nanocrystals embedded in amorphous a-Si after ZrO$_2$ nanoparticle milling.](image)

Single nano crystals are present, proving that mechanical milling is capable of breaking down the aggregates.
3.5.2. Removing the SiO$_2$ shell around $\beta$-FeSi$_2$ NPs

To remove the NP shell, either its growth has to be suppressed or post- treatments have to be applied. Post-treatments using etching agents such as HF and NH$_4$F were tested to remove the native SiO$_2$ shell. Regardless of the etching agent concentration no treatment was found that reduces the shell without changing the NP core$^4$.

Hence, options for suppressing the growth of the SiO$_2$ shell were investigated. Therefore, the process of shell formation has to be understood in more detail.

Two formation processes of the SiO$_2$ shell are reasonable. First, the SiO$_2$ shell may form already during growth of the $\beta$-FeSi$_2$ NP in the hot wall reactor. (The oxygen needed could be supplied by the used Fe(CO)$_5$SiH$_4$ precursors.) Second the SiO$_2$ shell may form due to oxidation after the NP growth, as the NPs were stored in air.

In order to find out whether the amorphous shell formed during the growth of the $\beta$-FeSi$_2$ NPs or in a later oxidation step, the hot wall reactor was improved to prevent air exposure after the NP growth.

The inert-$\beta$-FeSi$_2$ sample was produced and handled in inert conditions (see chapter. 3.2), except for 2 min exposure to air for the TEM sample preparation. Figure 3.18 a) and b) show typical BF TEM and high resolution TEM images of the inert-$\beta$-FeSi$_2$ sample. NPs with a size around 20nm were found on the lacey carbon grid. The NPs are surrounded by an approximately 2nm thick shell which is sensitive to the electron beam.

Figure 3.18 c) compares the rotationally averaged ED patterns from the $\beta$-FeSi$_2$ sample and the inert-$\beta$-FeSi$_2$ sample. The small variations in the intensities may originate from the background removal (see chap. 2.3.3). It is concluded that the NPs of the inert-FeSi$_2$ sample are also $\beta$-phase.

To investigate the composition of the shell more closely, Fourier transform infrared (FTIR) spectroscopy (see chap. 2.2.3) has been performed. Figure 3.19 compares the spectral frequencies between 500 and 1600 cm$^{-1}$ of the inert-FeSi$_2$ NPs after different periods of exposure to air. The sample was prepared and investigated in inert gas conditions to exclude any post-growth oxidation at timestep 0 min. Additionally, the infra-red spectrum of the $\beta$-FeSi$_2$ sample, exposed to air for several weeks, is plotted.

The observed frequencies in the range between 1000 and 1265 cm$^{-1}$ can be attributed to different vibration states of Si-O-Si chains or Si-O bonds $^{[33, 92, 39]}$. At the timestep 0 min the sample was not exposed to air at all, Si-O vibrational states were present. After 15 min of exposure to air, no significant changes were observed. It can be concluded that

$^4$S. Niesar, WSI of the TU München, private communication
3.5 Improving $\beta$-FeSi$_2$ NPs

Figure 3.18: Inert prepared $\beta$-FeSi$_2$ NPs a) BF TEM b) high resolution TEM image c) rotationally averaged and background subtracted ED pattern
Figure 3.19: Fourier transform infrared spectroscopy showing the vibration states of Si-O-Si bonds depending on the time exposed to air. The spectrum marked with an arrow was acquired from the $\beta$-FeSi$_2$ sample exposed to air for several weeks, whereas the other spectra originate from the inert-vertical-sample.

2 min of air exposure during TEM sample preparation does not change the amorphous shell. With longer exposure times, absorption increased and shifted towards the signature of the $\beta$-FeSi$_2$ sample that had been exposed to air for several weeks. During TEM investigation of sample $\beta$-FeSi$_2$ and sample inert-$\beta$-FeSi$_2$, no indications of additional Si or SiO$_x$ nanoparticles were found. It is concluded that the observed infrared absorption takes place in the amorphous shell. It does contain silicon and oxygen even when fully prepared and investigated in inert gas conditions. Exposure to air leads to a slight additional oxidation.

From this result, it is concluded that an SiO$_x$ shell forms during growth in the hot wall reactor. Its growth cannot be suppressed simply by inert production.
3.5.3. Annealing of $\beta$-FeSi$_2$ NPs

Annealing of $\beta$-FeSi$_2$ NPs may allow impurities like Fe or Si vacancies to relax to the core shell interface or surface, which may reduce the sub-band gap absorption. On the other hand, the $\beta$-FeSi$_2$ NPs are only stable up to a certain, unknown temperature.

In this chapter, the thermal stability of the NPs and the influence of annealing on sub-band absorption will be investigated. All annealing treatments were carried out in a vacuum or inert atmosphere conditions in order to prevent additional oxidation.

Initially, the thermal stability of the $\beta$-FeSi$_2$ NPs was investigated in a TEM in situ heating experiment. The $\beta$-FeSi$_2$ NPs were prepared on a SiN chip containing a heating spiral. A dedicated heating holder from the Nanofactory company was used for in situ heating of the sample. The temperature of the heating spiral was determined by its resistivity. The temperature was increased in 100°C steps. After 10 minutes at each temperature step, TEM images and electron diffraction patterns were acquired.

![TEM images of $\beta$-FeSi$_2$ NPs during in situ heating experiment at 200°C, 500°C, 600°C, and 700°C.](image)

For each temperature, the phase and morphology of the NPs were investigated. Figure 3.20 shows BF images of the $\beta$-FeSi$_2$ samples at temperatures of 200°C, 500°C, 600°C, and 700°C at two different magnifications each. For temperatures up to 600°C no change in morphology is observed. Above 600°C, the morphology changes significantly. The NPs
merge, their diameters increase to 50 nm and facets can be observed. In parallel, electron diffraction patterns were acquired at every temperature step as shown in figure 3.21.

Figure 3.21: Rotationally averaged electron diffraction patterns of $\beta$-FeSi$_2$ NPs during in situ heating experiment at 200°C, 500°C, 600°C and 700°C.

Up to 600°C, no changes in the diffraction pattern can be observed (see fig. 3.21). It is concluded that the $\beta$-FeSi$_2$ are stable during annealing in microscope-like vacuum ($\approx 10^{-7}$ mbar) up to 600°C.

Further ex situ annealing experiments took place under vacuum conditions with an oxygen partial pressure in the order of $10^{-4}$ to $10^{-5}$ mbar at 500°C for one hour. NPs from the $\beta$-FeSi$_2$ sample were annealed in a Pt case in order to avoid sample modifications driven by chemical reactions with the surrounding material. The annealed NPs will be referred to as 500°C-$\beta$-FeSi$_2$.

Figure 3.22 shows BF TEM images of the NPs prepared from the 500°C-$\beta$-FeSi$_2$ sample. $\beta$-FeSi$_2$ NP agglomerates with diameters below 2 µm can be observed at low magnification. Apart from them a very small proportion ($\approx 1\%$) of agglomerates show BF contrast darker than the contrast of the typical $\beta$-FeSi$_2$ NP agglomerates (see marked regions in fig. 3.22 a)). Figure 3.22 b) shows one of the rare areas of the sample that contains both agglomerate types, those with brighter BF contrast marked with 1 and those with darker contrast marked with 2. Figure 3.22 c) shows an area containing NPs from both
Figure 3.22: TEM BF images of $\beta$-FeSi$_2$ NPs after ex situ annealing at 500°C. a) shows two NP agglomerates with darker BF contrast marked with a cross and a square. b) and c) show the square marked region at higher magnification.
agglomerate types marked with 1 and 2. The NPs from agglomerate type 1 exhibit the typical $\beta$-FeSi$_2$ core shell structure. The NPs from agglomerates of darker BF contrast (type 2) are partly faceted, closer packed, and have a broader size distribution.

The crystallographic phases of the two observed types of NPs were investigated using selected area electron diffraction as presented in figure 3.23. The agglomerates of type 1 (majority phase) show the same diffraction pattern as the $\beta$-FeSi$_2$ NPs before annealing. The rarely found agglomerates of type 2 show electron diffraction that is consistent with Fe$_3$O$_4$ (see fig. 3.23). Additional energy dispersive X-ray analysis (not shown here) supports these findings.

![Figure 3.23: Background subtracted electron diffraction patterns from selected areas of the 500°C-$\beta$-FeSi$_2$ sample containing the majority $\beta$-FeSi$_2$ phase and the minority Fe$_3$O$_4$ phase in comparison with the ED before annealing and the Fe$_3$O$_4$ reference diffraction data [42].](image)

The PDS absorbance before and after annealing is presented in figure 3.24. After annealing the sample at 500°C -FeSi$_2$ exhibits slightly reduced sub-band gap absorption for energies below 0.8 eV.

This result is surprising, because Fe$_3$O$_4$ is known to be a half-metal [158], having both metallic and semiconducting properties depending on the electron spin. Therefore, the Fe$_3$O$_4$ NP agglomerates formed should increase the sub-band gap absorption. Two competing effects, reduced sub-band gap absorption due to the annealing of defects and increased absorption due to the Fe$_3$O$_4$ NPs may play a role.
3.5 Improving $\beta$-FeSi$_2$ NPs

In summary, the $\beta$-FeSi$_2$ NPs are stable up to 600 $^\circ$C when annealed in an electron microscope vacuum of $\approx 10^{-7}$ mbar. Annealing with an O partial pressure in the range between $10^{-4}$ mbar and $10^{-5}$ mbar does result in partial phase transformation.

In order to judge whether heat treatment helps to reduce the sub-band gap absorption of the $\beta$-FeSi$_2$ NPs, annealing has to be improved to prevent the formation of Fe$_3$O$_4$.

3.5.4. Electron beam irradiation

Now, the amorphous shell surrounding the $\beta$-FeSi$_2$ nanoparticles (see fig. 3.8) will be investigated in more detail. The 1.7 $\pm$ 0.3 nm thick amorphous shell was found to be sensitive to electron irradiation.

Figure 3.25 shows the same NP after three steps (a) as prepared, (b) after irradiation with an electron dose of more than 2000 $\mu$C pm$^{-2}$ at 200 kV acceleration voltage and (c) after further exposure to air for 70 days. The electron dose was determined according to chapter 2.3.8. The initially 1.7 $\pm$ 0.4 nm thick amorphous shell is reduced to a thickness of 0.6 $\pm$ 0.2 nm and is not sensitive to electron beam irradiation anymore. After 70 days of exposure to air, a new shell formed with a thickness of 2.1 $\pm$ 0.2 nm, which is sensitive to the electron beam again. The shell thickness for each step is given by the average of 40 measurements at different positions around the particle. The given accuracy is the standard deviation.

![Figure 3.24: PDS absorbance spectra of $\beta$-FeSi$_2$ NPs before and after annealing at 500 $^\circ$C.](image-url)
Figure 3.25: BF TEM images show $\beta$-FeSi$_2$ nanocrystals and the surrounding shell (a) before, (b) after an electron dose above 2000 $e^{-}/\text{pm}^2$ and (c) after 70 days of exposure to air.

of all measurements, which is also a measure for the variance of the shell thickness.

Figure 3.26: Diameter of the amorphous shell depending on electron dose irradiation.

Figure 3.26 shows the plot of the thickness of the amorphous shell against the electron dose a NP was exposed to. For total electron doses less than 600 $e^{-}/\text{pm}^2$ no reduction of the shell thickness was observed. Above 600 $e^{-}/\text{pm}^2$ the thickness of the shell decreases to a minimum value. In comparison with the literature, we find that SiO$_2$ is known to transform into Si at electron doses in the magnitude of 600 $e^{-}/\text{pm}^2$ for 200kV electron in the reported ranges of beam current (4-100 $\text{A/cm}^2$)[34]. This agrees with the beam sensitivity of the amorphous shell and suggests that the remaining shell is rich in Si, which can reoxidise again.
Free-standing, phase pure $\beta$-FeSi$_2$ NPs have been prepared successfully using gas phase synthesis [22]. Before this result, only a few reports on the synthesis of particulate $\beta$-FeSi$_2$ can be found. Wan et al. [156] succeeded in producing $\beta$-FeSi$_2$ nanoclusters and islands inside crystalline Si using electron beam evaporation of iron and silicon with subsequent annealing at 850 °C for 5 h. This long annealing time at high temperatures of the nanoparticles inside the matrix is economically less feasible than the separate production of the NPs with a later embedding process at low temperatures. Dahal and Chaika reported on a solution-based method for producing $\beta$-FeSi$_2$ nanoparticles together with other unspecified side products [28]. Kameyama et al. [67] have already produced $\beta$-FeSi$_2$ nanoparticles in a gas phase process. However, various Fe$_x$Si$_y$ phases were produced at the same time. This comparison with the literature shows that the $\beta$-FeSi$_2$ investigated here are exceptional. They were the first and so far only free-standing phase pure $\beta$-FeSi$_2$ NPs reported. Moreover, their growth in a hot wall reactor allows large quantities to be produced; industrial fabrication for e.g. absorbers in solar cells becomes feasible.

The $\beta$-FeSi$_2$ NPs investigated here fulfill many of the requirements for NP based solar cells (see chap. 1) as they contain only material abundant in nature, show a suitable band gap and a high absorption coefficient exceeding $10^5$ for energies higher than the band gap. However, the results on these 20 nm big $\beta$-FeSi$_2$ NPs obtained in chapter 3.3 and 3.4 reveal aspects that may not satisfy the requirements:

- The NPs are sintered and form aggregates with diameters up to 1000 nm.
- (100)[011]/2 planar defects were observed.
- High sub-band gap absorption was observed.
- The $\beta$-FeSi$_2$ NPs are surrounded by an 2 nm thick amorphous shell.

To study the origin of these aspects, the growth conditions of the NP were changed and post-treatment steps were applied (see chapter 3.5).

In the following, the impact of these aspects on the NP based solar cell will be discussed together with possibilities for improving the NPs.
3.6.1. Sintering and aggregation of $\beta$-FeSi$_2$ NPs

In chapter 3.4.1, various solvents and sonification techniques were applied to disperse the agglomerated NPs. Even for the best dispersion obtained, using toluene and sonification, residual clusters of NPs with sizes between 100 nm and 1000 nm remain. Adjacent NPs show similar crystallographic orientation and no shell is observed between them. Therefore it is concluded that the residual clusters are aggregates of sintered NPs. These large aggregates have implications on the thickness of the intrinsic a-Si layer, which is used to embed the NPs. The i-Si:H layer thickness is limited by the charge carrier mobility, therefore typical thicknesses of the intrinsic layer in a-Si:H pin solar cells are below 200 nm (see chap. 1).

Chapter 3.5.1 shows that ZrO$_2$ particle milling can be used to break the sintered NPs apart. However, ZrO$_2$ particle milling is known to introduce strain [66]. Possible modifications of the $\beta$-FeSi$_2$ NPs due to a milling process has to be investigated further.

3.6.2. Influence of (100)[011]/2 planar defects

$\beta$-FeSi$_2$ NPs were found to contain planar (100)[011]/2 defects using ED, NBED and ADT (see chap. 3.4.2). Other crystallographic defects were not observed. (100)[011]/2 planar defects have already been observed in the case of bulk and thin film $\beta$-FeSi$_2$ [171, 170, 167]. To the knowledge of the author, their formation in nanoparticulate $\beta$-FeSi$_2$ has not been reported before.

HR TEM images (see fig. 3.12) reveal domains of subsequent planar (100)[011]/2 defects at every $a = \frac{1}{4}$ and $a = \frac{3}{4}$ plane of the unit cell. Different kinds of planar defect domains, e.g. with one planar (100)[011]/2 defect per unit cell, may also be formed. These domains of planar (100)[011]/2 defects may introduce energy states, may act as traps for charge carriers and may reduce the efficiency of the NP-based solar cells. To investigate their influence on the band-gap and band structure and to determine the formation energy of different (100)[011]/2 defect domains, ab initio calculations were performed [60].

Three different domain models were investigated, each containing domains of ideal $\beta$-FeSi$_2$ and domains of stacking faults. Figure 3.27 shows the super cells used to calculate formation energy and band structure according to Model I and Model III. Blue and red atoms represent O and Fe positions, and red lines highlight the structural differences. Additional black dotted lines indicate the position of the grain boundaries. See figure 3.12 a) and c) for a comparison with the ideal domain and the stacking fault.

Models I (see fig. 3.27) and II consist of two domains each, one ideal $\beta$-FeSi$_2$ and a second
3.6 Discussion

Figure 3.27: Illustration of c(2x2) super cells according to Models I and III. Model I contains the ideal domain (see fig. 3.11 a)) and the stacking fault domain (see fig. 3.11 c)) with domain boundaries at $a = \frac{3}{4}$ and $a = \frac{7}{4}$. Model III contains the ideal domain and a domain of lower density stacking faults with (100)[011]/2 shift vectors at every second possible position $a = \frac{3}{4}$ and $a = \frac{7}{4}$. Red lines connect the positions of certain red Fe atoms as guides to the eye. The dashed lines indicate the domain boundaries [60].

containing (100)[011]/2 planar shifts at every possible $a = \frac{1}{4}$ and $a = \frac{3}{4}$ unit cell position. In the case of Model I, the stacking fault domain starts at $a = \frac{3}{4}$ whereas in Model II the stacking fault domain starts at $a = \frac{1}{4}$. Model III (see fig. 3.27) is similar to Model I, the only difference being that the stacking fault domain contains only one (100)[011]/2 planar per unit cell at the position $a = \frac{3}{4}$.

All supercells used for the ab initio calculations are non-primitive unit cells containing 2 repeat units in b- and c- direction (c(2x2)). 1+1 supercells, as depicted in figure 3.27, consist of one ideal c(2x2) unit cell and one c(2x2) unit cell containing stacking faults stacked in [100]- direction. In the case of 2+2 super cells, the domains are bigger and contain 2 ideal and 2 stacking fault unit cells.

Table 3.2 shows the additional formation energy needed to change ideal $\beta$-FeSi$_2$ into domain structures according to Models I, II and III. Formation energies of the strain relaxed super cells are given per c(2x2) unit cell. Interestingly, the formation energies do not change significantly between domains having one unit cell (1+1) and domains having two unit cells (2+2), even though in the 1+1 case the number of domain boundaries per c(2x2) cell is larger by a factor of two. The domain structures of Model I and II
are energetically favorable, only 42 meV formation energy is needed per c(2x2) unit cell. Constrained bulk-calculations indicate that interchanging the b and c axis introduces a strain of 40 meV. Hence, the formation energy of domains containing two stacking faults per unit cell is governed by strain. The domain boundary is energetically inexpensive. The formation energy increases by more than a factor of 4 if the defect domain contains less than two (100)[011]/2 planar defects per unit cell, as shown by Model III. It is concluded that under equilibrium growth conditions single (100)[011]/2 planar defects will not form, since domains with two (100)[011]/2 planar defects per unit cell are far more energetically favorable. Therefore, the observed crystallographic defect should not be referred to as "(100)[011]/2 planar defect" but rather as "stacking fault domains" or "strained domains of exchanged b- and c- coordinates".

In the case of epitaxial β-FeSi₂/Si structures, it is reported that strain changes the direct transition energies [99, 79]. To the knowledge of the author, the strain effect of the stacking fault domains on the band structure has not been studied so far. To investigate this influence, the band structures of β-FeSi₂ with and without stacking fault domains were calculated. Figure 3.28 shows the band structure of ideal β-FeSi₂ and of β-FeSi₂ containing stacking fault domains according to Model I. The band structure shows only minor changes. The band gap of β-FeSi₂ containing stacking fault domains according to Model I is slightly increased. The band structure in the Γ-X direction gives an effective electron mass of $\mu_e = 2.28 \cdot 10^{-31} \text{kg}$ from which the de Broglie wavelength $\lambda$ can be calculated according to $\lambda = \frac{h}{\sqrt{2\mu_e kT}} = 15.6 \text{nm}$. As the 20 nm diameter of the NPs exceeds the de Broglie wavelength, bulk-like electronic properties are expected.

In summary the density functional theory calculations [60] show: (a) domains of (100)[011]/2 stacking fault at every $a=\frac{1}{4}$ and $a=\frac{3}{4}$ unit cell positions are energetically favorable over domains of lower stacking fault density, (b) the formation energy these stacking fault domains is governed by the strain induced by the exchange of the b- and c- axis, (c) boundaries with domains from ideal β-FeSi₂ (according to Model I) do not change the band gap and (d) bulk like properties can be expected for faulted NPs as the calculated de Broglie wavelength is 15.6 nm.
3.6 Discussion

Figure 3.28: Band structures of $\beta$-FeSi$_2$ containing (red) and not containing (black) domains of two (100)[011]/2 planar defects per unit cell according to Model I. As the unit cell was doubled in the [100] direction, the bands are folded back into the $\Gamma X$ direction [60].

Therefore, the observed domains of planar defects do not compromise the absorption characteristics of the $\beta$-FeSi$_2$ nanoparticles.
3.6.3. Sub-band gap absorption of $\beta$-FeSi$_2$ NPs

The $\beta$-FeSi$_2$ NPs investigated here do show high sub-band gap absorption (see chap. 3.3). In order to use the NP as absorbers for solar cells, the sub-band gap absorption must be reduced, as the associated energy states would offer a route for charge carrier recombination.

Unfortunately, the origin of this high sub-band gap absorption is unclear. So far, domains of (100)[011]/2 planar defects could be excluded (see chap. 3.6.2). The $\beta$-FeSi$_2$ NP core surface is not faceted and contains both Fe and Si atomic columns. A surface determined by only Fe or Si may also induce sub-band gap states$^5$ which was not observed.

In the case of bulk or thin film $\beta$-FeSi$_2$, Si or Fe vacancies were found to introduce mid-band gap states [150, 151, 3, 148], which could account for the sub-band gap absorption. It was reported that these vacancies can be reduced by annealing at temperatures around 800$^\circ$C, which allows interdiffusion of the silicon atoms [89, 3, 148]. In situ TEM annealing experiments at vacuum levels of $10^{-7}$ mbar proved the $\beta$-FeSi$_2$ NPs to be thermally stable up to 600$^\circ$C (see chap. 3.5.3).

To investigate whether annealing also leads to reduced sub-band gap absorption of the $\beta$-FeSi$_2$ NPs, they were annealed at 500$^\circ$C under inert atmosphere conditions with an O partial pressure in the region of $10^{-4}$ to $10^{-5}$ mbar. Upon annealing, a minority of the nanoparticle aggregates were transformed into Fe$_3$O$_4$ (see chap. 3.5.3), which is known to be a half-metal and should significantly contribute to the sub-band gap absorption. Surprisingly, reduced band-gap absorption was observed, which could be explained by a reduction of mid-band gap states in the $\beta$-FeSi$_2$ NPs during annealing. A further reduction in sub-band gap absorption is expected for annealing conditions with O partial pressures similar to the TEM annealing experiment, where no Fe$_3$O$_4$ was formed.

To study the influence on the sub-band gap absorption, the $\beta$-FeSi$_2$ have to be annealed in O partial pressures conditions similar to the TEM in situ annealing experiment.

3.6.4. SiO$_x$ shell surrounding the NPs

TEM imaging revealed that the 20 nm big $\beta$-FeSi$_2$ NPs are surrounded by a 2 nm thick amorphous shell. Non-local chemical analysis such as XPS as well as local composition and bonding state analysis using EFTEM and STEM/EELS prove that the shell consists of SiO$_x$ (see chap. 3.3 and 3.4.3).

The SiO$_x$ shell may contain defect states or introduce states at the interface with the $\beta$-FeSi$_2$ NP. Furthermore, the amorphous shell will change the band structure, which

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$^5$T. Schena, PGI-1 of Forschungszentrum Jülich, private communication, 2013
leads to barriers for the charge carriers.

Now, the impact of 2 nm thick charge barriers will be estimated. The charge carrier tunneling probability $T$ can be calculated using the time-independent Schrödinger equation. Reducing the problem to a one-dimensional potential wall leads to

$$T = \left(1 + \frac{V^2 \sinh(kd)^2}{4E(V-E)}\right)^{-1},$$

with $k = \sqrt{\frac{2m(V-E)}{\hbar}}$, Planck’s constant $\hbar = 2\pi\hbar$ [32]. Assuming a carrier mass of $m = m_e/2$ and a barrier width of $d = 2$ nm leads to tunneling probabilities dependent on the carrier energy $E$ and the barrier energy $V$ as depicted in figure 3.29.

![Tunneling Probability, Barrier Width = 2nm](image)

Figure 3.29: Tunneling probabilities for a 2 nm thick potential wall for charge carrier energies smaller than the potential wall calculated in 0.1 eV steps.

For the sake of clarity, only trapped states where the $E < V$ are shown. Due to the huge barrier width of 2 nm, tunneling probabilities $T$ are smaller 4%, for the calculated range of $E$ and $V$. This estimation suggests that in the case of the observed 2 nm thick amorphous shell tunneling can be neglected regardless of $E$ and $V$, only charge carriers with energies higher than the barrier have a reasonable chance of passing it.

If a SiO$_2$ shell (band gap of 9 eV, work function of 5 eV [48]) and a $\beta$-FeSi$_2$ NP (band gap of 0.8 eV, work function of 4.8 eV [153]) are considered, electron and hole barrier energies around 4.5 eV are expected. For comparison, the energy of the photons in the terrestrial solar spectrum is less than 4.1 eV (300 nm) with a maximum peaks around 2.75 eV (450 nm) [14]. Effectively, no charge carriers excited by the terrestrial solar spectrum will be able to pass a 2 nm thick SiO$_2$ barrier.

As the 2 nm thick shell could be a suboxide SiO$_x$, barriers of lower energy are possible. Also these barriers will reduce the solar cell efficiency as the energy needed to pass the
barrier is lost and fewer electrons (from the higher energy part of the solar spectrum) contribute.

Figure 3.30 shows the carrier tunneling probability for 0.7 nm thick potential walls, calculated similarly to figure 3.29. For barrier energies smaller than $V < 2 \text{ eV}$ and charge carriers with energies of $E > V - 0.5 \text{ eV}$, tunneling probabilities between 10% and 60% are estimated. It is concluded that a SiO$_x$ suboxide shell thinner than 0.7 nm may be tunneled by the charge carriers.

In order to use the $\beta$-FeSi$_2$ NPs as absorbers in solar cells, ways to remove the 2 nm thick shell or reduce its thickness have to be found.

As a first step, the formation process of this shell will be discussed.

The formation of the SiO$_x$ shell was investigated by specific exposure to oxygen after growth. Even when produced and handled in inert atmosphere, a SiO$_x$ shell is present, which was found to oxidize further in air on a 5 h timescale (see chap. 3.5.2).

Assuming no O leaks at the precursor feed in, the hot wall reactor and the filter collecting the NPs, it is concluded that the shell forms during growth in the hot wall reactor, where oxygen is provided by the Fe(CO)$_5$ precursor.

To speculate about the exact growth mechanism of the shell in the hot wall reactor it is considered that:

- Simulations showing that the Fe(CO)$_5$ decomposes more than 1000 times faster than the SiH$_4$ precursor [22].
The precursor ratio used to grow the $\beta$-FeSi$_2$ has to be Si-rich. A Si/Fe precursor ratio below 2.9:1 leads to the formation of unwanted FeSi phases [22].

The Si/Fe ratio of the core shell $\beta$-FeSi$_2$ NP was determined to be $2.25 \pm 0.15$ (see ERDA results in chap. 3.3).

Therefore, it is assumed that NP growth starts with the nucleation of the iron core growing and transforming into $\beta$-FeSi$_2$, as the Si precursor decomposes later. Due to the Si/Fe precursor ratio of 2.9:1, Si is still present after the Fe precursor has been consumed. Part of the Si nucleates around the $\beta$-FeSi$_2$ NPs. This NP shell oxidizes due to the presence of CO in the 900°C hot wall reactor. This assumption is reasonable, since the standard formation enthalpy $\Delta H_f^0$ of solid SiO$_2$ (-905 kJ/mol [85]) is significantly higher than $\Delta H_f^0$ of CO and CO$_2$ in gas form (-110 kJ/mol and -394 kJ/mol [85]). Depending on the exact intermediate reaction steps, the ambient temperature of 900°C may be high enough to allow the reaction. However, a detailed investigation of the chemical route is beyond the scope of this work.

After exposure to air, the 2nm thick SiO$_x$ shell oxidizes further (see chap 3.5.2). This post-treatment may lead to a stoichiometric SiO$_2$ shell that contains no sub-band gap states.

Now, different approaches to remove the SiO$_x$ shell will be discussed so that charge carriers can leave the NPs and contribute to the solar cell efficiency.

The first possible approach is to oxidize the shell toward SiO$_2$ and later break the sistering bonds by ZrO$_2$ milling. This route is seen as promising as there is no shell between the sintered NPs, and ZrO$_2$ milling allows the sintering bonds to be broken (see chap. 3.5.1). However, possible influences of the milling process on the $\beta$-FeSi$_2$ NPs have to be investigated.

Post-treatments applied using etching agents such as HF or NH$_4$F were not successful in removing the SiO$_2$ shell without destroying the entire NPs. The NP shell was found to be sensitive to the electron beam (see chapter 3.5.4). The reduction of the shell thickness down to a minimum diameter of 0.7nm as well as the doses required for it comply with a reduction of the shell towards Si. For such shell thicknesses, carrier extraction via tunneling may be possible (see 3.30). Post-treatment of the NPs using a plasma process, which could be high energy photon assisted, may lead to a reduction similar to the electron beam effect. Another approach in order to obtain $\beta$-FeSi$_2$ NP without a surrounding SiO$_x$ shell could be achieved by optimizing the growth. The author speculates that the Si/Fe precursor ratio may have to be reduced in order to reduce or avoid the growth of the shell. The
high Si/Fe precursor ratio is needed for the formation of pure $\beta$-FeSi$_2$ as the Si precursor decomposes slowly. Choosing a different set of precursors that do not contain any oxygen or even preheating the Si precursor may allow a stoichiometric Si/Fe precursor ratio of 2 and the growth of $\beta$-FeSi$_2$ NPs without a surrounding shell. In summary, the observed SiO$_x$ shell forming during NP growth has to be removed to allow $\beta$-FeSi$_2$ NP absorbers to contribute to the efficiency of a future $\beta$-FeSi$_2$ NP-based solar cell. The results from post-treatment steps and $\beta$-FeSi$_2$ NPs with altered growth conditions obtained so far suggest several approaches for removing or changing this shell: first, oxidation and ZrO$_2$ particle milling, second, post-treatment of the NP to reduce the SiO$_x$ layer similarly to the electron beam, and third, improvement of the growth process. All of these approaches require further investigations.

3.6.5. Summary

The $\beta$-FeSi$_2$ NPs investigated here are interesting as absorbers in a-Si based solar cells, as they are the first phase-pure $\beta$-FeSi$_2$ NPs reported in the literature. At the moment they do not fulfill all of the criteria for serving as NP absorbers in solar cells, in terms of: the aggregate size, the high sub-band gap absorption (see chap. 1). Furthermore, the 2 nm thick SiO$_x$ shell surrounding the NPs must be removed as it prevents charge carrier extraction. Results on modified $\beta$-FeSi$_2$ NPs suggest promising approaches of improving the NPs in order to meet the criteria.

NP aggregates larger than 200 nm can be reduced in size by ZrO$_2$ ball milling. The high sub band gap absorption does not originate from the observed domains of (100)[011]/2 planar defects. A comparison with the literature suggests that the high sub-band gap absorption may originate from Fe or Si vacancies. Within the observed thermal stability of the NPs (up to 600 °C ) annealing at vacuum conditions better than $10^{-7}$ mbar may lead to a reduction in the number of defects and the sub-band gap absorption. Other results suggest approaches for removing the SiO$_2$ shell, which forms during growth. ZrO$_2$ particle milling before embedding will lead to NPs only partly surrounded by the amorphous shell. Other approaches, like optimizing the growth conditions or a reductive post-treatment similar to the electron beam damage observed in the TEM, seem promising too.

Embedding the optimized $\beta$-FeSi$_2$ NP seems to have high prospects for creating a NP-based solar cell, superior to the a-Si:H reference cell.
4. α-Fe₂O₃ NPs as absorbers for a-Si:H solar cells

4.1. Introduction

Hematite (α-Fe₂O₃) is a semiconductor material suitable for solar cells and photon-assisted water splitting [69]. Its components are non-toxic and abundant in nature. The unit cell, which is displayed in three viewing directions in figure 4.1 is R̅3c space group, contains 46 atoms with lattice parameters of a = b = 0.504 nm, c = 1.374 nm and α = β = 90° and γ = 120°.

![Figure 4.1: Crystal structure of α-Fe₂O₃ according to [16]. Red: Fe atoms, green: O atoms.](image)

The α-phase of Fe₂O₃ is thermodynamically stable up to temperatures of 1457°C [16]. Despite its stability it transforms into Fe₃O₄ in reducing atmospheres. 1 bar H₂ atmosphere reduces α-Fe₂O₃ to Fe₃O₄ after 30 min at 360°C [6]. For atmospheres of H₂ (5%) + Ar (95%) and pressures reduced to 5 mbar the transformation was observed at 450°C and 500°C, respectively [24, 6]. CO atmospheres reduce bulk α-Fe₂O₃ at 500°C [55] and even under vacuum conditions α-Fe₂O₃ transforms to Fe₃O₄ at 900°C [24]. The reduction from α-Fe₂O₃ to Fe₃O₄ takes place without formation of intermediate phases. Annealing Fe₃O₄ in air leads to a transformation into the thermally less stable γ-Fe₂O₃ phase at 300°C and finally to α-Fe₂O₃ above 475°C [165, 168].

Early studies report a direct band gap between 1.9 eV and 2.2 eV [105, 68] and a high absorption coefficient of 10⁵ cm⁻¹ above 2.2 eV [68] suitable for absorbers in solar cells. In the spectral region between 1.3 eV and 2.0 eV an absorption coefficient around 10³ cm⁻¹ with a peak at 1.4 eV is observed [95]. This absorption can be explained by transitions between the Fe 3d states in the context of ligand field theory [95, 139, 114]. These states introduce recombination effects, which lead to the low minority-carrier diffusion length below 5 nm [68, 10]. The comparison with the absorption coefficient in the order of 10⁵ cm⁻¹ shows that nanostructuring is necessary to use it for photon-assisted water splitting [10, 19, 23, 140, 81, 69].

α-Fe₂O₃ has been intensely studied as a photo-anode for water splitting in a photo-
electrochemical cell, as it is stable in aqueous solutions with pH values above 4 [68]. Disadvantages of α-Fe₂O₃ for solar water splitting are the low carrier diffusion length and the energetic position of the flat band potentials, which are too low in energy for direct water reduction [29, 140]. An additional voltage has to be applied to realize photon-assisted water splitting or tandem solar cells have to be realized reaching a solar-to-hydrogen efficiency in the order of 1% [19]. The conductivity of α-Fe₂O₃ depends strongly on its crystallographic orientation [112, 11] and can be further enhanced by doping, e.g., using Pt [59]. Kim et al. [69] achieved solar-to-hydrogen efficiency of about 5% with oriented single crystalline Pt doped hematite nanowires. One advantage of the material system is that α-Fe₂O₃ is easy to produce in NP form in an aqueous solution and that its dispersion in water is stable without surface ligand molecules [118]. Therefore, α-Fe₂O₃ NPs are interesting objects for studying the embedding of NPs in an a-Si based solar cell.

4.2. Growth of α-Fe₂O₃ NPs and PECVD embedding

α-Fe₂O₃ NPs were synthesized from FeCl₃ in aqueous solution in accordance with Ozaki et al. [118] and were subsequently resuspended in ultraclean H₂O with a resulting NP concentration of about 2% by weight. This growth process attracted a lot of attention as additional small amounts of NaH₂PO₄ lead to spindle-type α-Fe₂O₃ [118, 115, 5]. Almeida at al. studied the different reaction steps by quenching the suspensions using liquid nitrogen [5]. They observed that the chemical reaction between FeCl₃ and H₂O leads primarily to the precipitation of β-FeOOH NPs. In a second step, further nucleation of α-Fe₂O₃ NPs is observed. At a later stage the β-FeOOH NPs start dissolving in favor of further nucleation of the thermodynamically more stable α-Fe₂O₃ NPs. The size distribution of the α-Fe₂O₃ NPs is sharp below 10 nm. Sharp NP size distributions are expected in the case of diffusion limited growth processes [120]. Along with the dissolution of the β-FeOOH NPs, the suspended α-Fe₂O₃ NPs sinter together. The NPs may rotate, which allows the energetically favorable sintering of NPs in the same crystallographic direction. After the β-FeOOH NPs are consumed the bigger sintered α-Fe₂O₃ NPs will grow in favor of small ones due to Oswald ripening. The NPs were embedded in a-Si:H using PECVD as described in chapter 2.1. Table 4.1 gives an overview on the PECVD grown samples investigated in chapter 4. The a-Si:H p-i-n solar cell (see tab. 4.1) will be used as a reference here, it was produced with the same PECVD growth parameters used for all solar cells presented in this thesis (see chap. 2.1 and [108]).
4.2 Growth of $\alpha$-Fe$_2$O$_3$ NPs and PECVD embedding

<table>
<thead>
<tr>
<th>Sample name</th>
<th>Substrate</th>
<th>Layers</th>
<th>Transfer</th>
</tr>
</thead>
<tbody>
<tr>
<td>a-Si:H p-i-n solar cell</td>
<td>ZnO:Al</td>
<td>p-Si:H, i-Si:H, n-Si:H</td>
<td>None</td>
</tr>
<tr>
<td>$\alpha$-Fe$_2$O$_3$ solar cell 1</td>
<td>ZnO:Al</td>
<td>p-Si:H, $\alpha$-Fe$_2$O$_3$ NPs, i-Si:H, n-Si:H</td>
<td>Air</td>
</tr>
<tr>
<td>$\alpha$-Fe$_2$O$_3$ solar cell 2</td>
<td>ZnO:Al</td>
<td>p-Si:H, $\alpha$-Fe$_2$O$_3$ NPs, i-Si:H, n-Si:H</td>
<td>Vacuum box</td>
</tr>
<tr>
<td>Triple layer $\alpha$-Fe$_2$O$_3$ NPs</td>
<td>c-Si</td>
<td>i-Si:H, ($\alpha$-Fe$_2$O$_3$ NPs, i-Si:H) $\times$ 4</td>
<td>Vacuum box</td>
</tr>
<tr>
<td>Test structure</td>
<td>c-Si</td>
<td>(i-Si:H) $\times$ 7</td>
<td>Multiple</td>
</tr>
</tbody>
</table>

Table 4.1: List of samples. ZnO:Al covered corning class is abbreviated as ZnO:Al.

The $\alpha$-Fe$_2$O$_3$ solar cell 1 (see tab. 4.1) contains an additional layer of $\alpha$-Fe$_2$O$_3$ NPs. The NPs were embedded after PECVD growth of the p-Si:H layer by spincoating and subsequent PECVD growth of the i-Si:H and n-Si:H layers. To spincoat the NPs the sample was transferred to the spincoating system and back. During the transfer the sample was exposed to air. Back in the PECVD chamber the sample was heated for 1 h to temperatures up to 150$^\circ$C in order to remove residual water before the subsequent PECVD process was performed.

$\alpha$-Fe$_2$O$_3$ solar cell 2 was transferred between the PECVD system and the spincoater in a vacuum box to avoid exposure to air.

The triple layer $\alpha$-Fe$_2$O$_3$ NP sample contains a c-Si substrate and a stack of four a-Si:H layers. PECVD growth was interrupted to spin coat $\alpha$-FeSi$_2$ NPs at each interface between the layers. The sample was transferred between the PECVD system and the spincoater in an vacuum box.

To study possible sources of contamination during NP embedding, a test structure sample was prepared. A sequence of first exposing the surface to specific surface treatments (e.g. exposure to air) and then embedding this surface with a-Si:H via PECVD was repeated 6 times. The various surface treatments are listed in chapter 4.5.2
4.3. Properties of pristine $\alpha$-Fe$_2$O$_3$ NPs

After the good crystalline quality of the pristine $\alpha$-Fe$_2$O$_3$ NPs is confirmed, this chapter will present the structure and composition of the NPs investigated by TEM methods.

4.3.1. Absorptance characteristics of the pristine $\alpha$-Fe$_2$O$_3$ NPs

The crystalline quality of $\alpha$-Fe$_2$O$_3$ NPs was investigated by measuring their absorptance using PDS. The PDS spectrum [83] in figure 4.2 shows the band gap of 2.1 eV, just below saturation level starting at 2.2 eV. At energies around 1.4 eV and 1.9 eV pronounced absorptance is observed, which agrees with the transitions of the Fe 3d states [95, 139, 114].

![Figure 4.2: PDS absorptance measurement of $\alpha$-Fe$_2$O$_3$ [83]](image)

Below 1.4 eV, a significant decrease in the PDS signal is observed, indicating good crystalline quality.

In the case of bulk Fe$_2$O$_3$, the states around 1.4 eV and 1.9 eV lead to low carrier diffusion length, around 5 nm [10]. Annealing experiments using similar $\alpha$-Fe$_2$O$_3$ NPs suggest that the crystalline quality can be further optimized by annealing [114].
4.3 Properties of pristine $\alpha$-Fe$_2$O$_3$ NPs

4.3.2. Structure and composition of pristine $\alpha$-Fe$_2$O$_3$ NPs

In this chapter, the phase, shape, size distribution and local composition of the pristine NPs will be analyzed using ED, BF and DF TEM imaging, as well as STEM/EELS analysis. The NPs were prepared from a stable aqueous dispersion as described in chapter 2.3.2.

Figure 4.3: a) BF TEM overview image of $\alpha$-Fe$_2$O$_3$ NPs. b) Particle size distribution evaluated from a). c) SAED pattern of the $\alpha$-Fe$_2$O$_3$ NPs and d) rotationally averaged and background subtracted DP of c) in comparison with $\alpha$-Fe$_2$O$_3$ reference data [16].

The BF TEM image 4.3 a) shows separated $\alpha$-Fe$_2$O$_3$ NPs on a lacey carbon grid. The NPs are not sintered. The size distribution of the NPs as determined using the CSD program (see chap. 2.3.4) is presented in figure 4.3 b). Average NP diameter and standard deviation are 54 nm and 10 nm respectively.
Figure 4.3 c) displays an electron diffraction pattern taken from the area shown in figure 4.3 a). The ring-like distribution of diffraction spots indicates randomly orientated crystals. The ED pattern was rotationally averaged and background subtracted as plotted in figure 4.3 c) together with reference XRD data of $\alpha$-Fe$_2$O$_3$ from [16] (see chap 2.3.3). All measured reciprocal lattice distances match the reference data, confirming the $\alpha$-phase of the Fe$_2$O$_3$ NPs. Other Fe$_y$O$_x$ phases such as magnetite and maghemite do not match the experimental data.

The BF TEM image 4.3 a) reveals that the $\alpha$-Fe$_2$O$_3$ NPs are partly faceted. Figures 4.3 b), c) and d) show DF TEM images of the same area. The DF images show NPs that appear uniformly bright (see NP 1 in fig. 4.3 b)). Others show a bright rim (see NPs 2 in fig. 4.3 b)) as the intensity of the diffracted beam is dependent on the thickness, known as thickness fringes (see chap 2.3.3). The BF and DF TEM images suggest the presence of grain boundaries or planar defects in $\alpha$-Fe$_2$O$_3$ NPs (see e.g. NP 3 in fig. 4.3 c) and NP 4 in fig. 4.3 d)).

Figure 4.4: Images of $\alpha$-Fe$_2$O$_3$ NPs a) BF TEM b), c) and d) DF TEM images with different objective aperture positions.

The contrast of NP 5 in 4.4 d) shows a bright rim at the NP edge attributed to the
thickness effect. Additional bright lines towards the center of the NP can be observed, suggesting steep thickness variations inside the NP.

Figure 4.5 a) shows a STEM HAADF image of a representative $\alpha$-Fe$_2$O$_3$ NP at higher magnification. The rim of the NP is rough at the top and the bottom part of the depicted NP, similar to a cauliflower structure. Lines of reduced HAADF intensity are detected towards the center of the $\alpha$-Fe$_2$O$_3$ NP. The contrast changes in figure 4.5 a) may be due to compositional or thickness variations; therefore EELS compositional studies were performed.

An EELS spectrum image was acquired for every square of 4 by 4 pixels of the HAADF image simultaneously using sub pixel scanning (see chap. 2.3.6). No changes in STEM HAADF contrast were observed after acquisition of the EELS spectrum image. From the EELS spectra the O and Fe maps shown in figure 4.5 c) and d) where determined by background subtraction and integration over the first 20 eV of the O K and Fe L edge.
respectively. Figure 4.5 b) shows linescans of integrated O and Fe signals across the NP from the area indicated by boxes in fig. 4.5 c) and d). The oxygen and iron concentration show the same ratio across the NP, including the line of reduced HAADF intensity, which is marked with an arrow in every image of fig. 4.5 and across the NP rim. As no chemical variations were observed within measurement accuracy the fluctuations in HAADF contrast are attributed to local thickness variations.
4.4. Embedding $\alpha$-Fe$_2$O$_3$ NPs

The pristine $\alpha$-Fe$_2$O$_3$ NPs were embedded in a solar cell structure of a-Si:H to serve as absorbers. First the efficiency of the resulting NP-based solar cell is given and the phase of the NPs after embedding is confirmed using Raman spectroscopy. Afterwards, this chapter investigates the $\alpha$-Fe$_2$O$_3$ NP solar cell using BF TEM, STEM and EELS to find structural and compositional aspects influencing the solar cell performance.

4.4.1. Performance of solar cells with $\alpha$-Fe$_2$O$_3$ absorber layers

The performance of the solar cell 2 containing an $\alpha$-Fe$_2$O$_3$ NP absorber layer was investigated by IV-characterization under AM 1.5 illumination [83]. Figure 4.6 shows the resulting IV curve in comparison to the reference a-Si:H p-i-n solar cell, in which no NPs were embedded.

![Figure 4.6: IV characteristic of p-i-n solar cells from a-Si:H with and without addition of a layer of $\alpha$-Fe$_2$O$_3$ NP during the growth process [83].](image)

The NP solar cell generates an open circuit voltage $V_{OC}$ of 738 mV, a short circuit current density $J_{SC}$ of $5.9 \text{ mA/cm}^2$ and a total efficiency $\eta$ of 1.3%. The characteristics of the reference solar cell are better, total efficiency reaches $\eta$ of 4.5%.

Reasons why the $\alpha$-Fe$_2$O$_3$ NP layer does not improve the properties of the solar cell will be investigated in the following TEM studies.
4.4.2. Crystallographic phase of the $\alpha$-Fe$_2$O$_3$ embedded NPs

Raman investigations were performed to confirm the phase of the NPs after embedding [83]. The embedding was performed as described for the $\alpha$-Fe$_2$O$_3$ solar cell 2 sample (see chapter 4.2), in which the growth was stopped after the first $\approx 20$ nm thin a-Si:H layer formed on top of the NPs. This sample geometry was chosen to improve the ratio between the NP and the a-Si:H Raman signal. Figure 4.7 shows the Raman spectra of the $\alpha$-Fe$_2$O$_3$ NPs before and after embedding. The characteristic modes of hematite and a-Si:H are highlighted with arrows. The hematite modes are still present after embedding. Raman

![Raman spectra comparison](image)

Figure 4.7: Comparison of the Raman spectra, before (blue) and after embedding (red) of the $\alpha$-Fe$_2$O$_3$ NPs [83]

signal from magnetite was not observed. However, the strongest magnetite mode around 672 cm$^{-1}$ is close to the 660 cm$^{-1}$ mode for hematite [64], so a partial transformation of a small volume fraction into Fe$_3$O$_4$ cannot be excluded.
4.4.3. Structure and composition of the $\alpha$-Fe$_2$O$_3$ NPs solar cell

The BF TEM image of figure 4.8 shows the $\alpha$-Fe$_2$O$_3$ solar cell 1 sample in cross section.

![BF TEM image of the cross section of the $\alpha$-Fe$_2$O$_3$ NP solar cell structure acquired at 200 kV.](image)

The $\alpha$-Fe$_2$O$_3$ NPs are of dark contrast inside the bright a-Si layers surrounded by the dark ZnO:Al bottom and the dark Al top contact. The NPs form a single layer. No large agglomerates were observed, proving the spin-coating step to be successful and controllable.

The layers of different contrast can be assigned to the p-, i- and n-Si layers. The thickness of the p-, i- and n-Si:H layers is constant in growth direction, as they follow the surface topography of the ZnO:Al layer. Underneath and next to the NPs, additional bright contrast is observed, which can be explained by a reduced thickness of the a-Si:H due to holes and voids. These features will be investigated more closely by HAADF STEM (see fig. 4.10).

To study the phase of the embedded NP using ED, a plan view TEM specimen was prepared from the triple layer $\alpha$-Fe$_2$O$_3$ NP sample (see chap. 4.2) using the MultiPrep Polishing System. A BF TEM image 4.9 a) of the specimen shows a high NP density. From this area the electron diffraction pattern presented in figure 4.9 b) was acquired. It contains sharp rings of reflections from the NPs. The broad, diffuse rings originated from the a-Si:H surrounding the NPs.

The comparison of the rotationally averaged and background subtracted SAED pattern with the XRD reference of $\alpha$-Fe$_2$O$_3$ [16, 42] reveals a good match. Other reference phases such as Fe$_3$O$_4$, $\gamma$-Fe$_2$O$_3$ or FeO do not match.
As no phase transformation was observed after embedding of the NPs, it is concluded that the α-phase is still dominant after the embedding process, which agrees with the Raman results (see chap. 4.4.2).

The α-Fe₂O₃ solar cell 1 sample was investigated more closely by STEM HAADF imaging and STEM/EELS as presented in figure 4.10. The STEM HAADF image 4.10 a) shows the α-Fe₂O₃ NPs and the surrounding a-Si in cross section. The dark contrast close to the NPs marked with 1 and 2 suggest the presence of holes and voids at the bottom of figure 4.10 a). This result is confirmed by the bright contrast in the BF TEM image 4.8 b) and by complementary TEM images at different foci. Hence, the NPs are not completely connected to the surrounding a-Si:H.

Above the NPs, e.g., in the area marked with a square (see fig. 4.10 a)) no voids were observed. In this area STEM/EELS linescans were acquired in order to investigate chemical changes near the interface. The StripeSTEM method was used to obtain one dimensional compositional information using a low electron dose (for details see chap. 2.3.6). Figure 4.10 displays the integrated and background subtracted O K and Fe L signal as a linescan integrated over the first 40 eV of the edges. The linescan clearly shows the O K signal rising 1 ± 0.3 nm before the Fe signal indicating an O shell around the Fe₂O₃ NPs. To learn more about the O shell, the fine structure of the O K edge onset was investigated in the region of the shell and inside the NPs. Both spectra are compared in figure 4.10 after background subtraction. The O K signal from the NP center shows a pre-peak at 532 eV characteristic for α-Fe₂O₃ [25]. In the region of the NP/a-Si:H interface, this pre-peak is not observed, which complies with O bonded to Si [21]. In Figure 4.10 d) the integrated intensity of the characteristic pre-peak at 532 eV is plotted.
4.4 Embedding $\alpha$-Fe$_2$O$_3$ NPs

Figure 4.10: a) STEM HAADF image of the embedded NPs of sample $\alpha$-Fe$_2$O$_3$ solar cell 1. b) Integrated intensities of background subtracted EELS signals of the O K and the Fe L edges plotted as a linescan. The chemical information originates from the area marked indicated in a) with a square and an arrow. c) Background subtracted O K edge onset in the NP center (red) and at the NP/a-Si interface (blue), both regions are indicated in c). d) Linescans as in b) together with the integrated background subtracted O K peak around 532 eV, marked with an arrow in c). The EELS data shown here are extracted from the same StripeSTEM experiment [83].
together with the OK main signal and the FeL signal. The energy windows used to integrate the OK pre-peak intensity and the OK main peak intensity are indicated in figure 4.10 c). The intensity of the pre-peak clearly follows the Fe signal, indicating a constant composition within the NP. The O main signal rises prior to the O pre-peak and Fe signal outside of the NP.

Further compositional analysis of the Si K edge was not able to distinguish the expected SiO$_x$ shell from the surrounding a-Si:H shell (not shown here). As no indications for other materials in the shell region were found and the OK edge onset complies with O bonded to Si, it is concluded that the shell is SiO$_x$.

The pristine NPs do not show any kind of shell. Therefore it is concluded that the 1 ± 0.3 nm thick SiO$_x$ shell is formed during the embedding process.
4.5 Sources of contamination during NP embedding

The previous chapter 4.4 revealed a shell SiO$_x$, which forms at the interface between the NPs and the a-Si:H during the embedding process. This shell is unwanted as it may hamper the charge carrier extraction and reduce the efficiency.

To investigate the possibility of O contamination, two test samples were prepared (see chap. 4.2) and are discussed in this chapter:

a) The $\alpha$-Fe$_2$O$_3$ solar cell 2 sample with no vacuum break during transfer of the sample between the spin coater and the PECVD chamber, and

b) The test structure sample containing a stack of a-Si:H layers, each exposed to different atmospheres and treatments and embedded with a subsequent a-Si:H layer.

4.5.1. Composition of the $\alpha$-Fe$_2$O$_3$ solar cell 2 sample

The transportation between the PECVD chamber and the spin-coating system was improved with a homemade vacuum transportation box, which allows embedding the NPs in inert conditions.

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Figure 4.11: a) STEM HAADF image of the inertly embedded $\alpha$-Fe$_2$O$_3$ NPs of the $\alpha$-Fe$_2$O$_3$ solar cell 2 (see chap. 4.2). b) Linescan of integrated intensities of background subtracted EELS signals of the O K and the Fe L edge. The chemical information originates from the area marked in a) with a square and an arrow. c) background subtracted O K edge onset in the NP (red) and at the NP/a-Si interface (black). The EELS data shown here are extracted from the same StripeSTEM experiment.

Figure 4.11 a) shows a STEM HAADF image of the inertly embedded $\alpha$-Fe$_2$O$_3$ NPs. The TEM lamella was prepared using FIB has a thickness in the order of 100 nm and was investigated 3 days after preparation. The bright NPs in the middle overlap in the projection of the TEM lamella. The bright ZnO:Al substrate in the lower part of image 4.11 a) is rough, therefore the interface between ZnO:Al substrate and p-Si:H layer appears blurred in the STEM image.
Half NPs at the lamella surface, which were partly removed during the lamella thinning process, are expected to show a lower STEM HAADF signal. This thickness dependency is assumed to be dominant as a high minimum detection angle above 80 mrad was chosen and no indication for compositional variations were found.

The box and arrow in image 4.11 a) highlights the area and direction of the STEM/EELS linescan presented in figure 4.11 b) and c). The StripeSTEM method was used and the experimental parameters were optimized in order not to damage the NP during investigation. The integrated background subtracted Fe L and O K signal indicates significant amounts of O outside of the Fe rich NP. Figure 4.11 c) shows the O K edge onset in the NP center (blue). It shows the pre-peak at 532 eV which complies with \( \alpha\text{-Fe}_2\text{O}_3 \). At the interface between the NP and the surrounding a-Si:H the O K edge onset complies SiO\(_2\) (see black spectrum in fig. 4.11 c)).

To investigate whether the shell surrounds the NPs completely STEM/EELS maps were acquired. Figure 4.12 a) shows a STEM HAADF image of a 35 nm big NP acquired after the STEM/EELS maps were recorded in the area marked with a box. No signs of beam damage were observed by a comparison of the STEM images acquired before and after the experiment (not shown here).

![Figure 4.12](image)

**Figure 4.12:** a) STEM HAADF image of the inertly embedded NPs the \( \alpha\text{-Fe}_2\text{O}_3 \) solar cell 2. b) Fe map from background subtracted EELS spectra of the Fe L edge integrated between 705 and 775 eV. c) O map from background subtracted EELS spectra of the O K edge integrated between 530 and 600 eV. d) O – Fe difference map calculated by subtracting the normalized Fe map from the normalized O map. Bright contrast indicates high amounts of O and low amounts of Fe.

Figure 4.12 b) shows the Fe L map determined from the background subtracted EEL spectra integrated over energies between 705 and 775 eV. In order to reach appropriate signal-to-noise ratios for sufficiently low electron doses, a spatial resolution of \( 1.2 \times 1.2 \text{ nm} \) was chosen. Assuming the NP to be homogeneous, the intensity of the Fe L signal is proportional to the thickness of the NP along e-beam direction. In the case of a sharply decreasing Fe L signal a sharp/edge on interface between the NP and the a-Si:H can be
observed, as in the top and bottom parts of the NP. Here, the O-shell can be detected. Figure 4.12 c) shows the O K map of the NP after background subtraction and integration between 530 and 600 eV. The O K signal of the α-Fe₂O₃ core and the surrounding SiOₓ shell both contribute to the O map.

In order to image the shell where O is present and Fe not, the normalized Fe L map was subtracted from the normalized O K map in figure 4.12 d). This difference map gives a bright contrast in regions of high O signal and low Fe signal as is the case in the shell. The bright shell can be observed all around the NP. Only in regions where the interface between NP and a-Si:H is not sufficiently edge on, the signal to noise ratio is not large enough to image the shell (e.g. in the upper right part of the NP).

In summary, the NPs are surrounded by a SiOₓ layer even though air exposure during embedding was avoided.

4.5.2. Influence of surface treatments on O incorporation

To further study different possible sources of O contamination during embedding, the test structure sample was grown and investigated. The sample contains a stack of a-Si layers, subsequently grown, exposed to surface treatments and embedded by the next a-Si layer. This test sample allows compositional analysis of different surface treatments in one microscope session under the very same experimental conditions, which allows a direct comparison.

The different surface treatment steps are listed in figure 4.13 a). The embedding of the differently treated surfaces was performed with exactly the same process as the embedding of the NPs (see chap. 2.1) including heating the sample in the PECVD chamber for 1 h at temperatures up to ≈150 °C before PECVD growth. Figure 4.13 b) shows a STEM HAADF image of the test sample. The c-Si substrate at the bottom and the different a-Si:H layers show the same contrast. The bright contrast on the top of the structure is a mixture of Pt, Ga and C deposited during FIB sample preparation. In between some of the equally ≈70 nm thick a-Si:H layers a reduced contrast can be observed. These contrast changes are induced due to the different surface treatment steps, which change the composition and density at the interface. In the region of the c-Si layer, spots of increased brightness can be observed, marked with a white arrow. They formed during the adjustment of the microscope and the electron energy filter due to carbon contamination induced by the electron beam.

During the acquisition of the STEM HAADF image, EELS spectra were recorded using the StripeSTEM technique. The resulting linescans of background subtracted and intensity
Figure 4.13: Surface contamination experiment using STEM HAADF and EELS of iteratively surface treated and embedded a-Si:H layers. a) List of surface treatment steps, b) STEM HAADF of the differently treated and embedded a-Si:H surfaces. c) STEM/EELS linescan across b) of background subtracted and integrated CK, OK and SiL edges. SiL edge intensity was subtracted by 1 for better visibility. Image, linescan and treatment step list were aligned to describe the same surface at a given height.

integrated CK, OK and SiL edges are plotted in figure 4.13 c). For better visibility, the maximum SiL intensity was normalized between -1 in the region of the native SiO$_2$ surface and 0 in the c-Si substrate region. Note that a SiL signal of less than 0 indicates a reduced Si density. The CK signal was normalized to the Pt-Ga-C layer deposited in the FIB, whereas OK intensities were normalized to the native SiO$_2$ surface.

In the region of the c-Si substrate a broad C signal can be observed, attenuating slowly in the growth direction. This signal is consistent with the C contamination found by HAADF. The bottom surface no. 1 is the native SiO$_2$ layer on c-Si which serves as a reference. The STEM image 4.13 b) shows a marked change in HAADF contrast, whereas the EEL spectra of fig. 4.13 c) show a high OK signal and a drastic reduction in SiL intensity. Interestingly, a weak C signal also peaks at the first surface, which can be explained by a thin layer of hydrocarbons present on top of the SiO$_2$ layer before embedding.

The subsequent surface no. 2 was treated by spin coating of a volume mixture of 75% ethanol and 25% H$_2$O as if NP would be suspended in it. Then, the surface was annealed at 400 °C for 30 min in a dedicated vacuum heating system. The sample was transferred from the PECVD chamber to the spin coating system using the vacuum transportation box. On this surface, the HAADF and the EELS signal of the CK, OK and SiK show pronounced peaks. Severe C and O surface contamination took place. The reason for
4.5 Sources of contamination during NP embedding

this contamination could be a chemical reaction between the ethanol and water with the a-Si:H surface during annealing at 400 °C.

The surface no. 3 was treated by transferring the sample from the PECVD system (via the loading chamber) to the spin-coating system and back using the transportation box on a timescale of 1h. Neither the HAADF intensity nor the EEL spectra of this third interface give any indication of a C or O contamination. Also, the Si density here is equal to the a-Si:H layers. On the 1h timescale needed for preparation, the vacuum transportation box and the atmosphere of the spin coating system and PECVD loading chamber are sufficient to avoid contamination.

Surface no. 4 was exposed for two days in the loading chamber vacuum of the PECVD system. The STEM image 4.13 b) shows a change in HAADF contrast. The EELS intensities of surface 3 show a pronounced C peak together with a Si signal reduction (see 4.13 b)). A weak O peak is observed with a signal to noise ratio of 2 just above detection limits. The dominant C contamination is assumed to originate from hydrocarbons on the surfaces inside the loading chamber, which are sufficiently mobile to reach the sample surface on a 2-day timescale. The oxidation is assumed to originate from the residual low O partial pressure, which plays a minor role.

In the case of surface treatment no. 5, a volume mixture of 75% ethanol and 25% H2O was spin coated on the surface as if NPs would be suspended in it. The vacuum transportation box was used. HAADF contrast as well as the O and C EEL signal do not show a change in composition within measurement accuracy. In case of the less noisy Si signal however, a reduction could be observed with a signal to noise ratio of 2. This observed change in composition indicates the presence of C and/or O after exposing the surface to ethanol and H2O. This small change in composition could originate from the last atomic layer of H2O or ethanol not removed by the annealing step performed.

The last surface treatment no. 6 was spin coating of toluene, a quickly evaporating organic solvent, using the vacuum transportation box for transferring the sample. HAADF intensity and EEL spectra of surface no. 6 do not show O or C contamination directly or indirectly.

In summary, these results allow to judge which steps are critical for embedding any kind of NPs in solar cell structures using PECVD. The transfer between the spin coater and the PEVCD chamber on typical timescales of 1 h does not introduce O contamination, as surface no. 4 reveals. The solvent used for the NP suspension does have a strong influence, as the fast evaporating toluene leaves no contamination, whereas the ethanol water mixture induces contamination. Vacuum heating at temperatures far above the usual 150 °C does not decrease surface contamination.
4.6. Discussion

The pristine $\alpha$-Fe$_2$O$_3$ are on average 54 nm in diameter, their size distribution is sharp with a standard deviation of 10 nm. The $\alpha$-phase of the NPs was confirmed using electron diffraction. PDS spectra indicate good absorption characteristics (see chap. 4.3.1). A minority carrier diffusion length in the order of $\approx 5$ nm is expected from a comparison with bulk $\alpha$-Fe$_2$O$_3$ (see chap. 4.3.1).

BF, DF and (S)TEM studies revealed that the NPs are partly faceted and irregularly shaped, resembling a cauliflower structure (see chap. 4.3). Single crystalline as well as polycrystalline NPs are present. HAADF and BF TEM images indicate lines of reduced thickness towards the NP center. No indication of compositional inhomogeneities of the NPs could be observed using EELS (see chap. 4.3).

The cauliflower NP morphology is not surprising considering the growth process of the NPs, as reported in the literature (see chapter 4.2). Basically, the FeCl$_3$ precursor decomposes in aqueous solution and forms primarily $\beta$-FeOOH NPs as well as $\alpha$-Fe$_2$O$_3$ NPs with a diameter of 10 nm. After the precursor is consumed additional 10 nm $\alpha$-Fe$_2$O$_3$ NPs form upon decomposition of the $\beta$-FeOOH NPs. The $\approx 10$ nm NPs sinter together, preferably in the same crystallographic direction [5].

The lines of reduced thickness agree with the projection of the rough cauliflower-like NP structure.

Pristine $\alpha$-Fe$_2$O$_3$ NPs were embedded in a solar cell structure by spincoating the NP suspension on an a-Si:H surface and further PECVD growth. The resulting $\alpha$-Fe$_2$O$_3$ NP solar cells reaching efficiencies of 1.3% are not superior to the reference a-Si:H solar cell not containing NPs. Two aspects were found which may reduce the efficiency.

First, the presence of the NPs influenced PECVD growth. Underneath the NPs, holes in the subsequently grown a-Si:H layer were observed using TEM and STEM HAADF imaging. Additionally, void-like structures begin underneath the NPs and extend into the a-Si in growth direction. It is concluded that the diffusion perpendicular to the growth direction is minor, as such a process would lead to a filling of the holes and voids. During the a-Si:H growth, H$_2$ is provided in order to passivate energy states inside the a-Si. It is expected that the hydrogen provided also passivates interface states between the holes and the a-Si:H matrix to some extent$^6$. Further experiments are needed to judge the influence of the voids on the solar cell efficiency.

Second, a $1 \pm 0.3$ nm thick SiO$_x$ shell was found at the interfaces between the NPs and the surrounding a-Si:H layer, having formed during the embedding process. This SiO$_x$shell

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$^6$R. Carius, IEK-5 of Forschungszentrum Jülich, private communication, 2013
shell around the NPs may reduce carrier extraction (see discussion of the $\beta$-FeSi$_2$ NP shell in chap. 3.6.4). Unfortunately, the exact stoichiometry of the shell cannot be determined by EELS linescans as the NP shape at the interface is unknown. Still, the EELS line scans do show a pronounced O signal in the region of the shell compared to the O signal in the NP core region (see fig. 4.10 in chapter 4.4). Therefore the SiO$_x$ shell composition is estimated to be at least $x = 1$ or higher.

Now, possible O sources that allow the formation of a $1 \pm 0.3$ nm thick SiO$_1$ shell will be discussed:

1. A possible source of O for the formation of the SiO$_x$ shell is contamination. PECVD growth was interrupted at the p-Si:H layer in order to embed the NPs. A test sample of multiple a-Si:H layers was grown in order to study the contamination introduced by NP embedding. STEM/EELS analysis showed that the transfer between the spin-coater and the PECVD chamber does not introduce contamination or oxidation. Additional exposure to a mixture of ethanol and water leads to contamination just above detection limits, indicated by a reduced Si signal. The Si reduction observed at a 2 nm thick native SiO$_2$ layer is stronger by a factor of $\approx 20$. If the exposure to ethanol and water leads to a SiO$_2$ interface, its thickness would be in a range of 0.1 nm, the same order of magnitude as the distances between Si and O atoms in SiO$_2$. If the ethanol/water exposure also leads to C contamination, the expected SiO$_2$ layer thickness would be even less. The formation of an oxide monolayer after exposing the a-Si:H to an aqueous solution is reasonable as the applied heat treatment at 150 $^\circ$C in vacuum is expected to remove all water from the surface apart from the last chemisorbed water monolayer [172]. As SiO$_2$ and $\alpha$-Fe$_2$O$_3$ are both hydrophilic [161, 118], the NPs are also expected to be covered with a monolayer of water before the a-Si:H PECVD growth starts. This leads to the conclusion that at most the first monolayer ($\approx 0.1$ nm) of a SiO$_2$ shell (or a $\approx 0.2$ nm thick SiO$_1$ shell) surrounding the NPs can be explained by contamination. Assuming a NP with a diameter of 60 nm surrounded by a $1 \pm 0.3$ nm thick SiO$_1$ shell, the shell growth would consume $(3 \pm 1) \cdot 10^5$ O atoms, whereas contamination supplies at most $6 \cdot 10^4$ O atoms. Therefore, other sources must supply at least $\approx 2.4 \cdot 10^5$ O atoms.

2. The missing O atoms may originate from transformation of the $\alpha$-Fe$_2$O$_3$ NP. The resulting NP after embedding could be non stoichiometric $\alpha$-Fe$_x$O$_1$ NP, where $x = 0.7 \pm 0.01$. 
3. Furthermore, a partial phase transformation towards stoichiometric phases of (70 \pm 10)\% \alpha-Fe_2O_3 and (30 \pm 10)\% Fe_3O_4 could explain the missing O atoms. This transformation could be driven by the H plasma present during the embedding of the NPs. Even annealing of \alpha-Fe_2O_3 in H_2 atmosphere at 360^\circ C leads to a phase transformation into Fe_3O_4 [5]. However, transformation of 30 \% of each NP towards Fe_3O_4 was excluded by the electron diffraction and the Raman results. The detection limit of these methods is estimated to be 15 \% of Fe_3O_4 volume fraction.

4. The missing O for the formation of the SiO_x shell could be provided by partial transformation of the \alpha-Fe_2O_3 towards FeO in a fast non-equilibrium process. 11\% of the NP volume would have to transform to provide the missing O atoms, which would agree with a \approx 1.1 \text{nm} thick FeO shell surrounding the \alpha-Fe_2O_3 NP core. Transformations towards FeO was not observed by EELS from the O K edge fine structure as plotted in figure 4.10 d). The detection limit would allow observation of a FeO shell thicker than 0.3 \text{nm} (see fig. 4.10 d)).

5. Another possible origin of the missing O atoms needed for the SiO_x shell formation is a transformation of \alpha-Fe_2O_3 towards Fe. This transformation would consume \approx 4\% of the NP volume corresponding to an Fe shell thinner than 0.2 \text{nm}. In this case, a sharp, bright rim in the HAADF signal would be expected as the Z number density of Fe (2607 nm^3) is significantly higher than the Z number density of \alpha-Fe_2O_3 (1380 nm^3). An Fe shell surrounding the \alpha-Fe_2O_3 was not observed. The detection limit is estimated to be a shell thickness of 0.1 \text{nm}

6. Also, multiple reduction processes, e.g., the formation of a sub-stoichiometric \alpha-Fe_2O_3 core surrounded by a low amount of other phase (below detection limit) are possible.

7. Another possibility is that the SiO_x shell formed at the interface between the \alpha-Fe_2O_3 NP and the a-Si:H after the specimen was prepared for TEM investigation. When the NPs are not completely embedded in the TEM lamella, oxygen diffusion at the interface could take place leading to the observed shell. In the case of columnar grown Si, preferred oxidation at the interfaces of the Si columns is observed after an oxidation period of two months [76].

Mutoh et al. [109] investigated the oxidation of the surface of CVD grown hydrogenated amorphous Si using AES. Figure 4.14 shows the measured oxygen signal as a function of air exposure time. The intensity is normalized to the intensities
obtained after 2 and 4.5 months of air exposure, which are comparable to the oxygen signal of native SiO₂ on crystalline Si. Due to the mean free path of the oxygen Auger electrons of 1 nm 80-90% of the oxygen signal originates from the first 0-2 nm [109]. After 20 h an O signal of only 10% compared to the completely oxidized shell was observed. It is concluded that the oxidation speed of a-Si:H layers is generally low.

A further TEM lamella of a-Si:H embedded α-Fe₂O₃ NPs was prepared in which the time of air exposure between FIB preparation and STEM investigation was in the order of 2 min. This air exposure time is 5 orders of magnitude lower than the time needed for complete surface oxidation and 3 orders of magnitude lower than the time needed to reach 10% of complete surface oxidation [109]. Therefore, it is concluded that oxidation after TEM lamella preparation does not play a role. Still, the SiOₓ shell at the NP and a-Si:H interface could be observed. It is concluded that the SiOₓ shell forms during sample growth.

Assuming the shell composition to be SiO₁, then the amounts of O introduced by interrupting the PECVD growth and using water to disperse the α-Fe₂O₃ NPs does not explain the observed shell. Other sources of O contamination can be excluded (see aspect 1 in the discussion above). The missing O atoms for the formation of the shell could be provided by a transformation of the NP into sub-stoichiometric α-Fe₀.₇O₁ (see aspect 2). Multiple transformations (see aspect 6) are also possible. Although the transformation process of the NP could not be identified, it is concluded that the α-Fe₂O₃ NP provided the additional O for the SiOₓ shell formation.
In conclusion, it was observed, that the presence of the NPs influence PECVD growth. The voids observed in the vicinity of the NPs may introduce additional energy states, which may not passivated by the hydrogen provided during growth. Further experiments are needed to evaluate their impact on solar cell performance. Furthermore, a $1 \pm 0.3\text{nm}$ thick SiO$_x$ shell formed which is attributed to the decomposition of the $\alpha$-Fe$_2$O$_3$ NPs. This shell may reduce carrier extraction. Carrier extraction would be possible if the NPs were chemically stable and were not transformed during embedding. Ideal NPs for NP-based solar cells have to fulfill the additional criterion of being chemically stable. Despite the observed SiO$_x$ shell and the voids, a working solar cell was demonstrate (see fig. 4.6). Therefore, chemically stable NP absorbers and improved growth conditions are expected to lead to superior $\alpha$-Fe$_2$O$_3$ NP solar cells.
5. Cu-oxides and sulphide as absorbers for a-Si:H solar cells

The chemical stability of the NPs during the embedding process is a crucial requirement for the NP-based solar cells. When NPs decompose during the embedding process, they alter their properties and those of the surrounding i-Si:H, as observed in the case of the α-Fe$_2$O$_3$ NPs studied in chapter 4.

NPs from CuO, Cu$_2$O and Cu$_2$S were investigated, none of them are stable upon embedding. In this chapter, results of embedding CuO, Cu$_2$O and Cu$_2$S NPs will be presented in a condensed way for the sake of completeness.

5.1. Chemical stability of Cu$_2$O NPs

5.1.1. Short introduction on Cu$_2$O NPs.

Cu$_2$O, also known as cuprite, is a semiconductor with a band gap of 2.1 eV, its absorption coefficient exceeds $10^5 \text{cm}^{-1}$ for energies above 2.7 eV [134, 98]. The review articles of Rai [129] and Meyer et al. [98] summarize the challenges and developments of Cu$_2$O based thin film solar cells which did not exceed 3% efficiency before 2012. The main challenge is the chemical reaction at the interfaces of the Cu$_2$O layers towards CuO or Cu depending on the exact growth conditions. In 2013, Minami et al. [102, 101] reported on ZnO:Al/n-Ga$_2$O$_3$/p-Cu$_2$O solar cells with efficiencies of about 5.4%. The authors annealed sheets of Cu to 1000°C at different atmospheres for several hours to convert them into Cu$_2$O with the highest possible crystalline quality. Additionally, wet chemical etching (HCl) was applied to remove the CuO surface layer before the subsequent Ga$_2$O$_3$ and ZnO:Al layers were grown using pulsed laser deposition at room temperature [102]. These solar cells are expensive due to the high energy consumption involved in their production. Cu$_2$O NP based solar cells are expected to be less expensive to produce. Recently, Nishimura et al. found a wet chemical process to synthesize phase-pure Cu$_2$O NPs [113], which will be investigated in this chapter.

The chemical route employs copper (II) acetate monohydrate (H$_3$COOCu · H$_2$O) and oleylamine (C$_{18}$H$_{37}$N), acting as a surface stabilizing surfactant, 1-Heptanol (C$_7$H$_{16}$O) acts as a soft reducing agent, and tetramethyl ammonium hydroxide pentahydrate (N(CH$_3$)$_4^+$ OH$^-$ · 5H$_2$O) as a source of hydroxyl ions (OH$^-$) [113]. Depending on the reaction times and temperatures, the average NP size can be tuned between 10 nm and 140 nm and the phases CuO and Cu can be obtained alternatively [113].

The absorbance spectra of these Cu$_2$O NPs show band gaps depending on the NP diameter. A band gap of 2.5 eV was observed for NPs with an average diameter of 30 nm, which is
higher than the bulk band gap due to confinement effects [113].
Nishimura et al. also reported on annealed NPs in N\textsubscript{2} atmosphere in order to remove
the surface oleylamine ligands. At temperatures above 200°C FT-IR vibrational modes
of CH\textsubscript{3}, C=C bonds or the alkyl chain were significantly reduced. Above 300°C these
FT-IR modes could not be observed at all, indicating the removal of the surface ligands
[113].
These Cu\textsubscript{2}O NPs will be investigated with respect to their chemical stability upon
embedding as they are promising absorbers for solar cell application.

5.1.2. Pristine Cu\textsubscript{2}O NPs

Before the embedded NPs are discussed, a short overview on the size, morphology and
phase of the pristine NPs Cu\textsubscript{2}O NPs is given.
The NPs were provided by Nishimura according to [113] in toluene dispersion and prepared
for TEM investigations as described in chapter 2.3.2.
Figures 5.1 a), b) and c) show TEM images of the NPs at different magnifications. The
NPs are cubic in shape, have diameters between 25 nm and 85 nm and are neither sintered
nor agglomerated.

![Figure 5.1: Cu\textsubscript{2}O NPs at different magnifications. a) low magnification TEM image with SAD
aperture of the NPs contributing to the diffraction pattern of the image 5.2 b) and c) medium resolution BF TEM and TEM images showing the size and shape of the Cu\textsubscript{2}O NPs.](image)

Furthermore, patches of dark contrast larger than 200 nm in diameter can be observed
(see fig. 5.1 a) and b). Their contrast variation in the BF TEM image 5.1 b) is typical for
amorphous material, which may originate from organic molecules used during NP growth.
The phase of the Cu\textsubscript{2}O NP was confirmed via electron diffraction. The pattern shown in
5.1 Chemical stability of Cu$_2$O NPs

Figure 5.2: Electron diffraction pattern of the Cu$_2$O NPs depicted in figure 5.1 a). a) as recorded, arrows indicate the (111) and (220) lattice plane distances in crystalline Cu$_2$O. b) rotationally averaged and compared with XRD reference data from [117, 49, 45].

Figure 5.2 a). Figure 5.2 b) displays the data after rotationally averaging in comparison with different XRD reference diffraction data [117, 49, 45] (see chap. 2.3.3). No indications of other crystalline phases than Cu$_2$O are found.

In summary, the toluene dispersed Cu$_2$O NP sample contains impurities probably originating from residual organic molecules as well as cubic NP in Cu$_2$O phase with sizes between 25 nm and 85 nm.

5.1.3. Embedded Cu$_2$O NPs

The pristine NPs (as described in chapter 5.1.2) were embedded in an a-Si:H solar cell structure in order to investigate their chemical stability (see chap. 2.1).

Figure 5.3 shows a TEM image of the embedded NPs in cross section. A thick layer of roundish NPs labeled with "I" can be observed at the interface between the p-doped and i-doped a-Si:H layers (see I in fig. 5.3), the diameter of these NPs is below 10 nm. Structures labeled with "II" of similar contrast which are several 100 nm long range into the i-Si:H layer (see II in fig. 5.3). Moreover, contrast variations with a diameter of 1-2 nm are observed all over the i-Si:H layer (see NPs labeled with "III" in fig. 5.3). They could not be removed by further thinning of the TEM lamella using 1 kV Ar ions and are therefore regarded as NPs III.

To study the influence of the embedding process on the NPs more closely, the chemical composition and phase of these three features were investigated in more detail.
Figure 5.3: TEM image of the embedded Cu$_2$O NPs. The arrows highlight: I structures ranging into the i-Si:H layer, II NPs between the p-Si:H and i-Si:H layer, and III, small NPs found all over the i-Si:H layer.

Figure 5.4 a) shows an area containing the NPs I, structures II and small NPs III selected for the electron diffraction pattern 1 (DP1) depicted in figure 5.4 b). Due to the cross section geometry of the TEM lamella, only a small number of distinct diffraction spots contribute to the pattern 5.4 b). Additionally, broad closed rings indicate the presence of a huge number of very small Cu nanocrystals.

Figure 5.4 c) shows the rotational averaging DP1 together with a second electron diffraction pattern (DP2) was acquired from a similar area containing NPs I, structures II and small NPs II. Two electron diffraction patterns from different regions are plotted as the number of NPs contributing to a diffraction pattern is rather small (see fig. 5.4 a)). The comparison with reference XRD data of Cu, Cu$_2$O and ZnO [117, 45, 1] shows a good match of DP1 and DP2 with the Cu phase and the ZnO phase of the substrate. Spatial frequencies expected from the Cu$_2$O phase or the CuO phase were not observed, indicating a phase transformation.

The chemical composition of structure II was investigated using StripeSTEM (see chap. 2.3.6). The STEM HAADF image 5.5 shows structure II alongside the NPs III already observed in 5.3 a).

The corresponding EELS data is plotted in figure 5.5 b) as a linescan of the integrated and background subtracted O and Cu across structure II of fig. 5.5 a). It contains Cu, but no rise of the O signal is observed compared to the surrounding i-Si:H layer. Therefore, the long range structure is considered to be rich in copper and poor in oxygen.
5.1 Chemical stability of Cu$_2$O NPs

Figure 5.4: a) TEM image of the area diffraction pattern 1 (DP1) was acquired from. b) electron diffraction pattern 1. c) comparison of DP1 and DP2 acquired from a similar position with reference XRD diffraction data [117, 45, 1] and diffraction pattern embedded Cu$_2$O NPs.

Figure 5.5: StripeSTEM measurement across the long structure in the i-Si:H layer a) STEM HAADF image, arrow indicates the linescan direction (growth direction from left to right). b) Linescan of background subtracted and integrated EELS signal of O K and Cu L edge along the scan direction of the STEM image a).
The composition of the NPs I and the small NPs III was studied by StripeSTEM. The area of investigation is marked in the overview STEM HAADF image 5.6 a) and enlarged in figure 5.6 b). It contains, in area (1) the edge of a crystalline NP I, in area (2) a small NP III, and in area (3) a part of the i-Si:H layer not containing any NPs. The average lattice distance of the crystalline NPs from area (1) is 0.207 ± 0.002 nm. The estimated accuracy is higher than the pixel size of 6 pm as the distance across 20 lattice fringes was averaged. The influence of drift is neglected as the measured distance is almost parallel to the fast scanning direction of the STEM image. The measured lattice plane distance agrees nicely with the (111) lattice distance of the Cu phase (0.208 nm).

In the parallel recorded EELS spectra across the regions (1), (2) and (3) are plotted as linescans of the O K and Cu L edge in figure 5.7 a), both after background subtraction and integration over 50 eV energy windows according to chapter 2.3.6. In area (1) of the crystalline NP I a pronounced Cu L signal and a weak O K signal are observed. In area (2) containing the small NP III, small amounts of Cu are detected, not observed in area (3) where no NPs are present. A significant O K signal is observed outside of the crystalline NPs, indicating O rich i-Si:H. The rise of the O K signal in area (3) suggests an inhomogeneous O distribution in the i-Si:H layer.
5.1 Chemical stability of Cu\(_2\)O NPs

To prove that small amounts of O are present in the region (1) of the NP and small amounts of Cu are present in region (2), the EELS spectra integrated across all three regions are displayed in figure 5.7 b) Here, just one background subtraction in front of the O K edge was performed. The spectra are shifted in intensity for better visibility and scaled to the maximum of the O K edge. The intensity of spectrum (1) is divided by 2. Clearly, small amounts of O K signal were observed in region (1) and small amounts of Cu are present in the region of the small NP III.

In summary, no evidence was found for the presence of Cu\(_2\)O NPs. Electron diffraction, HR TEM and EELS results suggest the presence of pure crystalline Cu in the case of the 10nm NPs and Cu rich phases in the case of the 1-2nm NPs and the long range structures.

5.1.4. Summary on embedding Cu\(_2\)O NPs

The pristine cubic, 25nm and 85nm Cu\(_2\)O phase NPs are not chemically stable upon embedding via PECVD in a-Si:H. The embedding process leads to a change in morphology and phase towards crystalline, roundish Cu NPs smaller than 10nm. Additionally Cu, was found across the i-Si:H layer in the form of long structures NPs smaller than 2nm.

The investigated Cu\(_2\)O NPs are not chemically stable during the PECVD embedding process.
5.2. Chemical stability of CuO NPs

5.2.1. Short introduction on CuO NPs.

CuO, also referred to as tenorite, is a semiconductor with a band gap of 1.35 eV to 1.5 eV [72, 134, 93], with an absorption coefficient exceeding $10^5 \frac{1}{\text{cm}}$ above 2.1 eV [98]. A detailed review article on CuO, CuO nanostructures and their applications is given in [169]. Literature on CuO-based solar cells is very rare. Until now, CuO nanorods and nanoneedles were employed as cathodes in dye-synthesized solar cells reaching efficiencies of 1% [7, 88].

CuO NPs can be produced by the same route as the Cu$_2$O NPs investigated previously (see chap. 5.1.1) as they are formed in an intermediate step [113]. The chemical stability of these NPs upon PECVD embedding will be investigated in this chapter.

5.2.2. Pristine CuO NPs

To study the CuO NP size and shape before embedding, the pristine NPs were prepared on a holey carbon TEM grid using sonification (see chap. 2.3.2).

Figure 5.8: Pristine CuO NPs a) and b) BF TEM images at low magnification and medium magnification on a carbon support. c) HR TEM image at the edge of a carbon film.

TEM BF and HR images of figure 5.8 show the pristine CuO NPs at different magnifications. Their size varies between 5 nm and 30 nm, they are not faceted and crystalline (see fig. 5.8 b) and c)).

The phase of the CuO NPs was confirmed by electron diffraction. Figure 5.9 a) shows an electron diffraction pattern recorded from the area indicated in figure 5.8 a), containing a rather large number of nanocrystals. Figure 5.9 b) compares the rotational integration of the ED with XRD reference data [8], confirming the CuO phase. There is no indication
5.2 Chemical stability of CuO NPs

of the presence of a different phase.

![Electron diffraction pattern of pristine CuO NPs](image)

Figure 5.9: Electron diffraction pattern of pristine CuO NPs from the area indicated in figure 5.8 a) as detected b) after rotational integration in comparison with reference XRD data of [8]

5.2.3. Embedded CuO NPs

The pristine CuO NPs (see chap. 5.2.2) were embedded in an a-Si:H structure as described in chapter 2.1 in order to investigate their chemical stability.

Figure 5.10 a) shows a STEM HAADF image of the solar cell structure, containing the bright ZnO:Al TCO at the bottom, the p-Si:H dark layer, two layers of bright contrast NPs, another dark contrast layer labeled with SiO$_x$ as the EDX analysis of figure 5.11 suggests this composition. The contrast of the i-Si:H layer is slightly brighter. Flake-like NPs of bright contrast are present between the SiO$_x$ and the i-Si:H layer.

All these features could be observed using secondary electrons, BF or DF imaging in the FIB directly after finishing the TEM lamella. TEM investigations performed 2 weeks later showed additional features in some parts of the TEM lamella, which are sensitive to the plasma cleaning. These features are attributed to a decomposition of NPs at the surface of the TEM lamella. Areas of the lamella, where the additional features do not appear, are assumed to contain only NPs inside the TEM lamella not in contact with the lamella surface. These areas are regarded as representative of CuO NPs embedded in solar cell structure, they are studied and depicted in figure 5.10.

The formation of the SiO$_x$ layer was not intended. Still the difference in HAADF contrast indicates a difference in composition, density or both. NPs forming the double layer show diameters between 7 nm and 25 nm.
Figure 5.10: CuO NPs after PECVD embedding in an a-Si:H solar cell structure. a) STEM HAADF image, the black arrow indicates the direction of the EDX linescan of the figure. b) HR TEM image, arrows indicate the lattice plane distances.

Figure 5.10 b) shows one of these NPs at high resolution. The marked lattice plane distances of 0.21 nm ± 0.01 nm and 0.185 nm ± 0.01 nm were determined by averaging the distances of 30 lattice plane distances each. The relative angle between the lattice planes is 54 ± 1°. These numbers are consistent with (111) and (020) lattice planes of Cu oriented in [101] zone axis direction. (According to [117] expected distances and angles for Cu in [101] zone axis direction are 0.2087 nm, 0.1808 nm and 54.7°, respectively.) No NP with lattice plane distances characteristic for CuO was found. It is concluded that the embedded NPs are Cu phase.

To learn more about the composition of the SiO\textsubscript{x} layer, an EDX linescan was performed along the black arrow in figure 5.10 a). Figure 5.11 shows the integrated EDX intensities of the Cu K, O K, and Si K edges.

The linescan starts in the region of the ZnO:Al TCO up to distances of 40 nm, accordingly a strong O signal is observed. In the region of the p-Si:H layer (between 40 nm and 80 nm) a strong Si and a weak O signal are observed. The region containing the Cu NPs (80 nm to 120 nm) shows two pronounced and separate Cu peaks. The O signal rises before the Cu signal, does not change within this layer and can be detected in the subsequent 30 nm, described as SiO\textsubscript{x} layer in figure 5.10. In the SiO\textsubscript{x} layer, rather low levels of Si are detected in comparison with the i-Si:H layer starting at 145 nm. It is concluded that the SiO\textsubscript{x} labeled layer is rich in O and Si.
5.2 Chemical stability of CuO NPs

5.2.4. Summary on embedding CuO NPs

Pristine, phase pure CuO NPs with diameters between 5 nm and 30 nm were embedded in an a-Si:H based solar cell structure using PECVD. During the embedding process, the NPs were transformed into Cu phase. The released O incorporated into a 30 nm thick SiO$_x$ shell. The composition of the NPs between the SiO$_x$ and the i-Si:H layer was not further studied. However, the high HAADF intensity suggests a high density of heavy atoms such as Cu. One possible explanation is Cu diffusion, as already observed during the embedding of the Cu$_2$O NPs (see chap. 5.1.3).

In summary, the investigated CuO NPs are not chemically stable during the PECVD embedding process.

![Figure 5.11: Linescan of integrated and normalized EDX intensities of the CuK, O K, and SiK edge across the NP solar cell structure depicted in figure 5.10 a) at the position of the white dotted arrow.](image)
5.3. Chemical stability of Cu₃₁S₁₆ NPs

5.3.1. Short introduction to Cu₃₁S₁₆ NPs

The CuₓS material system contains several phases with a Cu/S ratio x close to 2, including low-chalcocite (Cu₂S), high-chalcocite (Cu₂S), djurleite (Cu₃₁S₁₆) and dignetite (Cu₉S₅) [166]. The formation energies of all the mentioned CuₓS phases are very close to each other [166]. The monoclinic low-chalcocite phase is stable up to 104°C and transforms reversibly into the hexagonal high-chalcocite phase [164]. Djurleite is stable up to 93°C [126]. NPs of the low-chalcocite phase transform into the djurleite phase on a timescale of 2 weeks at room temperature in N₂ atmosphere [91].

As all the mentioned phases show absorption coefficients in the region of 10⁵ cm⁻¹ [107] and band gaps of 1.2 eV (low chalcocite, [86]), 1.3 eV-2 eV (djurleite [107, 26, 111]) and 1.4 eV-1.6 eV (dignetite [111, 107]), the CuₓS material system is a promising candidate for absorbers in solar cells.

Cu₂S solar cells reach efficiencies exceeding 10% [54], but lack long term stability due to Cu interdiffusion [4].

The Cu₃₁S₁₆ NPs investigated here were produced in a wet chemical process involving stabilizing ligands according to [159]. The djurleite phase of the NPs was confirmed using XRD (see chap. 2.2.1). Figure 5.12 shows the comparison of the XRD results and the djurleite reference phase [37].

![Graph showing XRD results and XRD djurleite](image)

Figure 5.12: XRD of the pristine NPs [74] in comparison with the Cu₃₁S₁₆ phase [37].
As the djurleite unit cell contains 376 atoms [37] it is not enough to determine the NP phase from the XRD peak positions. Therefore, XRD data of different phases were simulated and compared with the experimental data, showing the best match with the djurleite phase [73].

5.3.2. Results on pristine Cu$_{31}$S$_{16}$ NPs

Figure 5.13 shows the pristine Cu$_{31}$S$_{16}$ NPs on a C-grid before embedding at different magnifications. The average NP size is 9 nm with a size standard deviation of 2 nm (evaluated from 200 NPs using [51]). Individual NPs and NP agglomerates are present. The agglomerates are one NP layer thick and they are separated by at least 1 nm indicating the presence of surface ligands. The HR TEM image of figure 5.13 c) shows that the crystalline NPs are faceted.

Figure 5.13: Cu$_{31}$S$_{16}$ NP at different magnifications. a) and b) TEM BF images c) HR TEM image
5.3.3. Embedded Cu$_{31}$S$_{16}$ NPs

The pristine Cu$_{31}$S$_{16}$ NPs were embedded using PECVD (see chap. 2.1) to investigate their chemical stability. Figure 5.14 a) shows a BF TEM image of the embedded NP in cross-section. The NP appear with darker contrast on the bright contrast of the a-Si:H pin junction, some of the NPs are roundish while others show banana-like morphologies. NPs are present at the p-Si:H and i-Si:H interface as well as inside the i-Si:H layer. The contrast of the p-Si:H layer underneath the NP is a little brighter than the contrast of the i-Si:H layer on top of it. Inside the p-Si:H layers, even brighter, roundish, NP-like structures can be observed. Their bright contrast and additional TEM images at high over- and underfocus suggest holes or low density material.

Figure 5.14: TEM images of embedded Cu$_{31}$S$_{16}$ NPs, acquired using an FEI Tecnai microscope at 200 kV.

Figure 5.14 b) shows a HR TEM of a NP inside the i-Si:H layer, far from the p-i interface. The orientation of the crystalline NP only allows one lattice plane distance to be determined. Measuring over 20 lattice planes gives an average lattice distance of 0.21±0.01 nm, which is consistent with the (111) lattice plane distance of crystalline Cu (0.209 nm [117]). The djurleite phase cannot be excluded as it contains a very high number of different lattice plane distances, and some of them agree with the experimental result.

Further investigations on the chemical composition of the embedded NPs were performed STEM HAADF and EDX. Figure 5.15 a) shows a STEM HAADF image of the embedded NPs. The contrast is strongly Z-dependent. For the chosen imaging conditions the STEM HAADF signal saturates in the ZnO:Al substrate and the Pt top layer deposited during the FIB sample preparation. The HAADF contrast of the NP varies significantly from...
NP to NP and inside the NPs. A homogeneous NP would show the highest HAADF signal at its center where the thickness is greatest. Often NPs are observed which appear partly brighter at their rim, as it is the case for the NP crossed by the arrow in figure 5.15 a). This indicates chemically inhomogeneous NPs.

Along the arrow of figure 5.15 a), the chemical composition was studied using EDX (see chap. 2.3.7).

The SiK signal allows to estimate the relative thickness of the NP surrounded by a-Si:H. In region 1 of the rim up to a distance of 20 nm a still large SiK signal was detected. The NP is thin in the rim region. Here, a strong HAADF signal and a strong CuK signal were observed, whereas only traces of S were detected. In region 2, the SiK signal indicates the thick NP core. Here a very pronounced SK signal was detected together with a reduced amount of Cu. At the lower rim of the NP orientated towards the p-Si:H layer both SK and CuK signals drop. EDX investigations at different positions (not presented here) also show separate NPs, one Cu and S rich at the p-Si:H and i-Si:H interface, and one Cu rich inside the i-Si:H layer.

The EDX results prove that the formerly djurleite NP degenerated during the embedding process.
5.3.4. Summary on embedding Cu$_{31}$S$_{16}$ NPs

The pristine Cu$_{31}$S$_{16}$ NPs with average size of 9 nm are faceted and separated from each other by their surface ligands. After embedding, different kind of NPs are observed. Their morphology as well as their composition varies. TEM BF images indicate the presence of Cu NPs, STEM HAADF images indicate and EDX investigations prove compositional differences. Close to the interface of the p-Si:H and i-Si:H layer the NPs are rich in Cu and S, whereas inside the i-Si:H layer the Cu NPs are S poor.

It is concluded that the Cu$_{31}$S$_{16}$ NPs degenerated and Cu diffused into the i-Si:H layer during PECVD embedding.
5.4. Discussion

In this chapter, NPs of different Cu-containing material systems were investigated with respect to their chemical stability during PECVD embedding in a-Si:H. Cu₂O and CuO NPs transformed into Cu NPs during PECVD embedding. In the case of the embedded CuO NPs, a defined 30 nm thick SiOₓ layer formed during the embedding process. Its growth is attributed to the reduction of the CuO NPs. Also in the case of the Cu₂O NPs, indications of O-rich a-Si:H were found.

Before the PECVD embedding started, the sample was annealed in the PECVD chamber at temperatures below 150 °C for 1 h and pressures below 10⁻⁴ mbar to remove residual water. At such low O₂ partial pressures and temperatures below 350 °C the pressure-temperature stability (PTS) phase diagram of the Cu-Cu₂O-CuO system (see [130]) suggests the transformation towards CuO. However, the PTS phase diagram describes the bulk behavior of the Cu-Cu₂O-CuO system. In the case of nanoparticulate material, transformation temperatures may be different. Still it shows that the system tends to oxidize even at such low O partial pressures. A transformation of the CuO and Cu₂O NPs during the annealing step is not expected. Therefore, the observed phase towards Cu is attributed to the subsequent PECVD growth. This reduction of the copper oxide NPs is expected to happen in favor of the observed SiO₂ formation, which is plausible as the standard formation enthalpy of SiO₂ is very high (-905 kJ/mol [85]) compared to the standard formation enthalpy of CuO (-156 kJ/mol [85]) or Cu₂O (-170 kJ/mol [85]).

Apart from the reduction of the NPs, a pronounced Cu diffusion could be observed in the case of the embedded Cu₂O and Cu₃₁S₁₆ NPs. Cu diffusion could also explain the observed NP outside of the NP layer in the case of the embedded CuO NPs. These observations are consistent with the literature as Cu is known to be a fast diffuser in Si, SiO₂ and a-Si:H [160, 143, 125].

In conclusion, CuO, Cu₂O and Cu₃₁S₁₆ were found to be incompatible with the PECVD embedding process. In the case of CuO and Cu₂O a complete phase transformation took place. These NPs are regarded as chemically very unstable. NPs from other material systems have to be used as absorbers in a NP-based solar cell.
6. Conclusion

This thesis is dedicated to an innovative and promising approach to enhancing the efficiency of low-cost a-Si:H solar cells. The idea is to incorporate semiconducting NPs as absorbers in a-Si:H solar cells. This approach makes use of the high absorption coefficients of the nanoparticles and the low production costs of a a-Si:H solar cell grown at low temperature. Producing NPs in a first step, and then embedding them in the solar cell in a second step offers new degrees of freedom for optimizing the nanoparticle absorbers.

The optimization options offered by this approach make NP material systems such as $\beta$-FeSi$_2$, $\alpha$-Fe$_2$O$_3$, Cu$_x$O or Cu$_2$S promising absorber materials, although high quality thin film solar cells from these material systems have not yet been grown successfully.

A range of promising candidate NPs was investigated using (S)TEM based methods with the aim of finding and optimizing suitable NP absorbers.

It was found that the FeSi$_2$ NPs studied are the first pure $\beta$-phase FeSi$_2$ NPs reported in the literature. As grown, they are surrounded by a 2 nm thick SiO$_x$ shell and they form aggregates. Furthermore, a large sub-band gap absorption was observed, which does not originate from the observed domains of (100)[011]/2 planar defects as DFT calculations show.

The $\beta$-FeSi$_2$ NPs were successfully optimized using several of the methods investigated. The NPs are thermally stable up to 600 °C at pressures of $10^{-7}$ mbar. Under these conditions, annealing is expected to reduce the sub-band gap absorption, as suggested by preliminary ex situ annealing experiments. It was found that the size of the NP aggregates could be reduced by ZnO$_2$ ball milling. The observed 2 nm thick SiO$_x$ shell surrounding the pristine NPs was found to form during NP growth in the hot wall reactor, supplied with O from the Fe(CO)$_5$ precursor. Electron beam irradiation allows to reduce the shell thickness. Similar surface treatments or optimized growth conditions may also serve to reduce shell thicknesses, allowing carrier extraction. It is expected that embedding of optimized $\beta$-FeSi$_2$ NPs will yield a NP-based solar cell superior to the a-Si:H reference cell. The case of $\beta$-FeSi$_2$ highlights the rich post-treatment possibilities, allowing the NPs to be optimized before they are embedded in the solar cell structure.

The as-grown $\alpha$-Fe$_2$O$_3$ NPs were found to be suitable for embedding. Amorphous Si:H solar cells based on $\alpha$-Fe$_2$O$_3$ NPs were produced, reaching an efficiency of 1.3%. This shows that it is possible to embed NPs in a working a-Si:H solar cell using PECVD. However, the $\alpha$-Fe$_2$O$_3$ NP-based solar cell was not superior to a a-Si:H reference solar cell. A $1 \pm 0.3$ nm thick SiO$_x$ shell was observed at the interface between the NPs and the a-Si:H layer, which can reduce the contribution of the Fe$_2$O$_3$ NPs to the solar cell.
efficiency. Various sources of O were investigated as possible origins of the SiO$_x$ shell formation. It is concluded that the PECVD embedding process chemically reduces the α-Fe$_2$O$_3$ NPs.

Embedding of the CuO NPs yields Cu NPs that are surrounded by a defined layer of oxidized a-Si:H. It is concluded that the main NP decomposition mechanism is chemical reduction.

The CuO NPs were completely reduced, as they show a standard formation enthalpy of CuO (-156 kJ/mol), which is fairly low compared to the standard formation enthalpy of SiO$_2$ (-905 kJ/mol). For comparison, a stepwise reduction of α-Fe$_2$O$_3$ requires 484 kJ, 604 kJ and 544 kJ per mol O$_2$, respectively. It is concluded that oxide NPs with higher standard formation enthalpies than SiO$_2$ are stable against reduction during the PECVD embedding process.

The Cu$_{31}$S$_{16}$ and Cu$_2$O NPs showed signs of Cu diffusion, which is attributed to the high mobility of Cu in a-Si:H at temperatures above 150°C.

In conclusion, chemical stability during embedding is a crucial property for the NPs. Two different mechanisms where found to cause the degeneration of the NPs, firstly chemical reduction of the NPs and secondly the diffusion of the NP elements.

Having identified these two decomposition mechanisms, it now becomes possible to select NPs that are stable during PECVD embedding. Such NP material systems are both oxygen-free and composed of materials with low mobilities in a-Si:H. Semiconductor materials such as FeS$_2$ and ZrS$_2$ are expected to fulfill these requirements [58, 82, 133]. Optimized β-FeSi$_2$ NPs are also still promising.

Another approach for manufacturing NP based solar cells is to change the embedding process and the material of the surrounding solar cell structure in order to be less demanding on the stability of the NPs. Organic solar cells, which can be produced by spin coating and baking at temperatures below 150°C [157] may be suitable.

Both approaches, either using chemically stable NP absorbers or using less disruptive embedding processes and materials, hold promise for the successful production of superior NP-based solar cells.
A. Phase contrast, aberrations and image simulation

To introduce the phase contrast observed in HR TEM images, two aspects have to be considered: firstly, the interaction of the electron wave with the sample leading to the exit plane wave function \( \psi_e \), and secondly the impact of the lens aberrations on \( \psi_e \).

These steps will initially be discussed with regard to the highly simplified case of a one atomic layer thick sample using the weak phase object approximation. Then, the multislice algorithm will be introduced, which allows HR TEM images of real world samples to be simulated.

A one atomic layer thick sample can be approximated as a phase object. In the phase object approximation, the incidence electron wave \( \psi_0 \) is changed in phase according to \([30]\):

\[
\psi_e(\vec{r}) = \psi_0 \cdot \exp[i\phi(x,y,t)] = \psi_0 \cdot \exp[i\sigma V_p t] \tag{6}
\]

\[
\psi_0(\vec{r}) = \exp[2\pi i (k_0 \vec{r})]. \tag{7}
\]

Here, \( t \) describes the thickness of the phase object and \( k_0 \) the direction of the incidence electron wave \( \psi_0(\vec{r}) \), which is perpendicular to the sample plane (x- & y-direction). The phase shift \( \phi(x,y,t) \) introduced by the phase object is given by the projected sample potential \( V_p \), the thickness \( t \) and the interaction constant \( \sigma \).

In the weak phase object approximation (WPOA), it is further assumed that the phase change is very small, \( \phi(x,y,t) \ll 1 \). Hence, \( \psi_e \) can be approximated by a Taylor series as:

\[
\psi_e(\vec{r}) = \psi_0(1 + i\phi(x,y,t) - \frac{\phi(\vec{r})^2}{2} + \ldots) \approx \psi_0(1 + i\phi(x,y,t)) \tag{8}
\]

Now, an ideal electron microscope (all aberrations are neglected) is assumed. \( \psi_e(\vec{r}) \) is projected onto the image plane, where only intensities can be recorded. The measured intensity \( I(\vec{r}) \) is given by:

\[
I(\vec{r}) = |\psi_0(\vec{r})(1 + i\phi(x,y,t))|^2 \approx 1. \tag{9}
\]

Terms quadratic in \( \phi(x,y,t) \) are neglected as \( \phi(x,y,t) \ll 1 \). All information of the sample encrypted in the phase change of \( \phi(x,y,t) \) is lost.

In real microscopes, the phase change \( \phi(x,y,t) \) introduced by the sample does contribute to the recorded intensity due to aberrations of the objective lens. In real space, the aberrations are described by the complex point spread function \( P(x,y) \), which alters the object exit wave function \( \psi_e(\vec{r}) \) by a convolution. The electron wave arriving at the image
plane \( \psi_1(\vec{r}) \) is given by:

\[
\psi_1(\vec{r}) = [\psi_0(\vec{r}_z^e)(1+i\phi(x,y,t)) ] \otimes P(x,y).
\tag{10}
\]

The complex point spread function \( P(x,y) \) can be represented by its real part \( \Re[P(x,y)] \) and its imaginary part \( \Im[P(x,y)] \) which gives:

\[
\psi_1(\vec{r}) = \psi_0(\vec{r}_z^e)(1+i\phi(x,y,t) \otimes \Re[P(x,y)] - \phi(x,y,t) \otimes \Im[P(x,y)]).
\tag{11}
\]

After neglecting terms quadratic in \( \phi(x,y,t) \), the intensity becomes

\[
I_1(\vec{r}) = |\psi_1(\vec{r})|^2 \approx 1 - 2\phi(x,y,t) \otimes \Im[P(x,y)].
\tag{12}
\]

The phase difference introduced by the weak phase object contributes to the image contrast due to the imaginary part of the \( P(x,y) \).

All of the samples investigated in this thesis where thicker than one atomic layer. Therefore, the simple POA and the WPOA cannot be used to determine the electron exit wave function. In the case of a crystalline sample, the exit plane wave function \( \psi_e \) can be found analytically using the relativistically corrected Schrödinger equation and the Bloch wave approach. Alternatively, \( \psi_e \) can be determined numerical using the multislice algorithm, in which the electron wave propagation and the interaction with the sample are treated separately from each other. For this purpose, the sample is divided into atomic layer thin slices with the thickness of \( t_s \). The potential distribution of each slice is projected into its center plane, called the phase grating. Free space is assumed between the planes of projected potentials.

The propagation of the wave between two phase gratings can be described by a convolution with the Fresnel propagator \( \mathcal{P}(x,y,t_s) = \exp[i\pi k_0 \frac{x^2+y^2}{t_s}] \) \cite{30}.

The \( j \) projected potentials \( V_j^p(x,y) \) can be assumed as phase objects in the POA, as slice thicknesses in the order of one atomic layer are used. The interaction of the electron wave and the projected potentials can be described by a phase function \( \mathcal{G}(x,y) = \exp[i\sigma V_j^p(x,y)] \). The electron wave function \( \psi_n(x,y,z) \) after interaction with the potential plain \( n \) can be calculated by:

\[
\psi_n(\vec{r}) = [\psi_{n-1}(\vec{r}) \otimes \mathcal{P}(x,y,t_s)] \cdot \mathcal{G}(x,y),
\tag{13}
\]

which leads to object exit wave function \( \psi(\vec{r}) \). The convolution with \( P(x,y) \) is performed in reciprocal space, where it becomes a multiplication with the contrast transfer function.
T in reciprocal space.

$$T(\vec{k}) = H(\vec{k}) \exp[2\pi i \chi(\vec{k})] = H(\vec{k}) \exp[2\pi i (\frac{1}{2} \Delta f \lambda k^2 + \frac{1}{4} C_s \lambda^3 k^4 + ...)].$$ \hspace{1cm} (14)

$\text{H}(\vec{k})$ indicates an aperture limiting the spatial frequencies projected, $\Delta f$ denotes the defocus and $C_s$ the spherical aberration. Higher order aberrations are not listed here. The reciprocal wave function at the image plane $\psi_I(\vec{k})$ is given by:

$$\psi_I(\vec{k}) = \mathcal{F} (\psi(\vec{r}) \otimes P) = \psi(\vec{k}) T(\vec{k}).$$ \hspace{1cm} (15)

$\mathcal{F}$ denotes the Fourier transformation.

The reciprocal image intensity $I(\vec{k})$ is given by

$$I(\vec{k}) = \int \psi_I(\vec{k}) \psi_I^*(k + k') d\vec{k},$$ \hspace{1cm} (16)

whereas $^*$ indicates the complex conjugated.

To simulate HR TEM images, the JEMS software package was used [142]. This performs the described steps of calculating the object exit wave function using the multislice approach and accounting for the microscope aberrations in Fourier space by multiplication with the contrast transfer function.
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