Quantitative Thickness Mapping In High-angle Annular Dark-field (haadf) Scanning Transmission Electron Microscopy (stem)

2008

Haritha Nukala

University of Central Florida

Find similar works at: http://stars.library.ucf.edu/etd

University of Central Florida Libraries http://library.ucf.edu

Part of the Materials Science and Engineering Commons

STARS Citation

http://stars.library.ucf.edu/etd/3670

This Masters Thesis (Open Access) is brought to you for free and open access by STARS. It has been accepted for inclusion in Electronic Theses and Dissertations by an authorized administrator of STARS. For more information, please contact lee.dotson@ucf.edu.
QUANTITATIVE THICKNESS MAPPING IN HIGH-ANGLE ANNULAR DARK-FIELD (HAADF) SCANNING TRANSMISSION ELECTRON MICROSCOPY (STEM)

by

HARITHA NUKALA
B.E, Andhra University, Visakhapatnam, 2004

A thesis submitted in partial fulfillment of the requirements for the degree of Master of Science in the Department of Mechanical, Materials and Aerospace Engineering in the College of Engineering and Computer Science at the University of Central Florida Orlando, Florida

Summer Term 2008
ABSTRACT

Only a few methods are currently available for the measurement of sample thicknesses in Transmission Electron Microscopy (TEM). These methods, Convergent-Beam Electron Diffraction (CBED) and thickness mapping in Energy-Filtered TEM (EFTEM), are either elaborate or complex. In this present work, I have investigated and come up with a simple straight-forward method to measure the local thickness of a TEM sample with the atomic number (Z-contrast) imaging using High-Angle Annular Dark Field (HAADF) Scanning Transmission Electron Microscopy (STEM).

HAADF STEM shows atomic number contrast for high scattering angles of the electrons, owing to predominant electron scattering at the potential of the nucleus similar to Rutherford scattering. The characterization of materials by STEM helps to identify microstructures and nanostructures within a sample and to analyze defects in samples. HAADF STEM imaging is capable of resolving atomic structures with better than 2 Å lateral resolution. However, HAADF STEM has so far not been systematically used to measure sample thicknesses.
In Z-contrast imaging, it was known that the intensity of the electrons scattered to high angles increases with increase in the atomic number (Z) of the element/compound with increasing thickness of the sample based on the equation,

\[ I \sim t \cdot Z^\alpha \]

Where \( t \), is the thickness and \( \alpha \), is a parameter between 1 and 2. This project was started with this simple approach, but the experimental results within the thesis show that the relation between the intensity and the atomic number is not well described by this equation. A more reliable parameter, \( \sigma_Z \), the interaction coefficient of the material was calculated.

Samples containing Ag₂Al platelets in Al matrix were used for calibration purposes. Additional samples containing layers of known elements/compounds were obtained from TriQuint Semiconductors and from the Physics department of UCF to calculate \( \sigma \) for various elements/compounds. These experimental values were used to measure the local thicknesses in nanoparticles and also the total volume of the nanoparticles.

This quantitative HAADF STEM analysis represents a new method, which can be added to the list of methods used for the purpose of measurement of the local thickness of a sample in the TEM.
This method is especially useful for the thickness measurement of nanoparticles. The other two methods, CBED and thickness maps in EFTEM are strongly affected by the sample orientation and therefore not appropriate for the study of nanoparticle thicknesses, whereas orientation effects are negligible for the conditions used in this HAADF STEM analysis.
Dedicated
to
My Bhagavan Mavayya (Uncle)
for the gift of Life that he has given me.
ACKNOWLEDGMENTS

I would like to take this opportunity to express gratitude to my advisor Dr. Helge Heinrich, who is one of the best teachers I have met, for introducing me to the field of Transmission Electron Microscopy. I am grateful to him for spending so much of his valuable time guiding me through every step of the way. I will always remember him for his friendly nature. I have learned a lot from you, and hope that you will pass your knowledge and experience on to many new student generations to come.

I am happy to acknowledge Dr. Raj Vaidyanathan and Dr. Neelkanth Dhere for serving on my thesis committee and for their valuable suggestions. They are one of the nicest Professors that I have met and interacted with during my studies at UCF, extremely knowledgeable and helpful. I would like to extend my appreciation to NREL and the Thin-Film PV Partnership who supported this research under contract no: XXL-5-44205-08 during the initial stages. I would like to thank TriQuint Semiconductors for extending the financial support to continue this project. I am also thankful to Dr. Aigner, Dr. Fattinger, and Dr. Kook from TriQuint Semiconductors and Dr. Roldan from Physics Department, UCF for providing me the samples for the project.
I would like to acknowledge AMPAC’s Materials Characterization Facility (MCF) for providing me the chance to learn different material characterization techniques. Special thanks to Zia and Kirk from MCF for their help with FIB and TEM. I will always cherish the lighter moments I shared with Zia, Kirk, Mikhail, Dr. Heinrich and Karen during my stay at MCF. I really appreciate the help extended by my friends and colleagues, Baio Yuan and Hilary Palmer, in sample preparation and data analysis during my stay in UCF.

My sincere gratitude is expressed towards Ms. Cynthia Harle, Ms. Kari Stiles and Ms. Judith Ramos for taking care of all the paperwork during the process of completion of my Master’s degree.

I would like to acknowledge all my wonderful friends, Maithiri, Abu, Vani Akka and Venkatesh Uncle in particular, whose support and encouragement helped me in moving towards my goal. Last but not the least, I would like to extend my thanks to my fiancé, Diwakar for helping, supporting and encouraging me at every step along the way.

Above all, I am eternally in debt to my uncle, Bhagavan Mavayya, my parents and sister for always believing in me and for all their plans to send me abroad for higher education. If it wasn’t for their unfailing love and support I wouldn’t have seen the light of this day!
TABLE OF CONTENTS

LIST OF FIGURES ........................................................................................................................................... xii

LIST OF TABLES ............................................................................................................................................... xvii

LIST OF ACRONYMS AND ABBREVIATIONS ............................................................................................... xviii

CHAPTER 1: MOTIVATION AND INTRODUCTION ......................................................................................... 1

1.1 Motivation .................................................................................................................................................. 1

1.2 Introduction ............................................................................................................................................... 3

1.2.1 The imaging process .......................................................................................................................... 4

1.2.2 Atomic number imaging (Z-Contrast imaging) .................................................................................. 7

CHAPTER 2: SAMPLE PREPARATION ............................................................................................................. 9

2.1 Focused Ion Beam (FIB) technique .......................................................................................................... 9

2.1.1 Ex-situ lift out of TEM samples ........................................................................................................ 11

CHAPTER 3: CHARACTERIZATION TOOLS ................................................................................................. 15

3.1 An Introduction to Transmission Electron Microscopy ........................................................................... 15

3.1.1 Components of a Transmission Electron Microscope ...................................................................... 17

3.1.2 Conventional Transmission Electron Microscopy ............................................................................. 20

3.1.2.1 Bright-field and dark-field TEM .............................................................................................. 20
3.1.2.2 Selected-area electron diffraction ................................................................. 22

3.1.3 High-resolution transmission electron microscopy (HRTEM) ......................... 22

3.1.4 Analytical TEM using Scanning transmission electron microscopy (STEM) .... 23

3.1.4.1 High-angle annular dark field (HAADF) scanning transmission electron microscopy ........................................................................................................ 23

3.1.4.2 Energy Dispersive X-ray spectroscopy (EDS) .............................................. 30

3.1.5 Electron energy loss spectroscopy (EELS) ....................................................... 32

CHAPTER 4: EXPERIMENTAL FACTS ............................................................................. 35

4.1 FIB milling with ex-situ lift-out ............................................................................ 35

4.2 Atomic number contrast imaging ......................................................................... 36

4.2.1 Quantitative HAADF STEM for materials science ......................................... 37

4.2.2 Calibration Methods in Z-Contrast Imaging to calculate the local sample thickness 42

4.2.2.1 Wedge method using Ag$_2$Al platelets ......................................................... 42

4.2.2.2 Thickness method using Ag$_2$Al platelets .................................................... 45

4.2.2.3 Wedge method using Pure Silicon wafer ..................................................... 47

4.3 Energy-filtered transmission electron microscopy ............................................... 48

4.3.1 Thickness Maps ............................................................................................... 51
CHAPTER 5: RESULTS AND DISCUSSION................................................................. 52

5.1 Results.............................................................................................................. 52

5.2 Towards Quantitative HAADF STEM ............................................................. 66

5.3 Limitations of this method............................................................................... 70

APPENDIX Calculation of the thickness of the sample from the projected thickness measured. 72

REFERENCES .......................................................................................................... 78
LIST OF FIGURES

Figure 1: Au-Fe nanoparticles with unknown thickness. Samples provided by Dr.Roldan, Physics department................................................................. 2

Figure 2: Schematic diagram of (a) a basic FIB system and (b) liquid metal ion source (reproduced from [Gian05])................................................................. 9

Figure 3: The FIB instrument FEI 200 TEM in use at Materials Characterization Facility (MCF) of UCF. ................................................................. 10

Figure 4: The steps of the ex-situ lift-out process. (a) Pt deposition to protect the sample surface, (b) a thin section is formed by cutting of the sides, (c) side view at 45° tilt of the thin section with the bottom cut visible, (d) low-magnification TEM image of sample sections deposited on a carbon film supported by a Cu grid. [Halb06]........................................... 13

Figure 5: The optical microscope used for the Ex-situ lift out of the TEM samples............ 14

Figure 6: The Quartz needle attached to the micro-manipulator. ........................................ 14

Figure 7: The 300 kV TEM (Tecnai F30), housed in MCF of UCF................................. 16

Figure 8: (a) Imaging and (b) diffraction mode of the transmission electron microscope (reproduced from [Seal08]) [Heim80]............................................ 19

Figure 9: Ray diagrams for (a) Bright-field imaging using direct beam and (b) dark-field imaging using a specific off-axis scattered beam.(reproduced from [Petr06])................................. 21
Figure 10: Arrangement for imaging in HAADF-STEM mode (reproduced from [Sena05]) .... 25

Figure 11: A Ronchigram which is used to center the condenser aperture and to stigmatize the incident electron beam. ........................................... .................................................. 27

Figure 12: Calculated electron probe intensity profiles. Microscope parameters suitable for Tecnai F30 (300kV, Cs = 1.2 mm). a: Δf = 0.0 nm, αconv = 9.0 mrad; b: Δf = -48.0 nm, αconv = 3.0 mrad; c: Δf = -48 nm, αconv = 9.0 mrad; d: Δf = -70.0 nm, αconv = 9.0 mrad. ................. 28

Figure 13: Schematic illustration of the Z-contrast imaging geometry-- a focused electron probe channels along the projected atomic column and undergoes a large-angle scattering event to the high-angle detector. Images and formed by scanning the electron probe across the surface and can be interpreted in terms of the projected specimen scattering power. (reproduced from [Petr06]) ........................................................................................................................................ 29

Figure 14: Sample geometry for analysis with an EDX detector (reproduced from [Halb06]) ... 32

Figure 15: Principle of a post-column electron energy loss spectrometer with the option of energy-filtered imaging. (reproduced from [Fult01]) ................................................................. 32

Figure 16: (a) an example of an EELS spectrum, (b) Schematic of the interaction of electrons with inner shell electrons (reproduced from [Halb06]) [Abou05]......................................................... 34

Figure 17: STEM BF, ADF and HAADF detectors and their annular ranges. The conventional ADF and BF detectors are shown as well as the HAADF detector set-up for Z-contrast imaging,
together with the range of electron scattering angles for each detector (reproduced from [Petr06])

Figure 18: The micrograph of the Ag₂Al platelets at an angle. The angle between the two red lines is measured as the angle made by the wedge. ................................................................. 38

Figure 19: The micrograph of the Ag₂Al platelets edge-on. The dashed red-line gives the measurement of the change in intensity. ................................................................. 44

Figure 20: The micrograph of tilted Ag₂Al platelets in [001] beam orientation used to measure the projected thickness of the platelets, as shown by the red lines. ........................................ 45

Figure 21: The micrograph of edge-on Ag₂Al platelets in the [112] beam orientation used for measuring the intensities of Ag₂Al and Al using the profile given beside the micrograph. The profile is the profile of intensities across the dashed red-line in the micrograph. ......................... 46

Figure 22: Geometry of the wedge shaped Silicon Wafer. ................................................................. 47

Figure 23: Simplified setup of the electron-optical path for energy-filtered imaging using a post-column energy filter (GIF) (reproduced from [Erni03])................................................................. 50

Figure 24: The micrograph of the Ag₂Al platelets in the edge-on position in the [101] beam orientation. .......................................................................................................................... 52

Figure 25: A calibrated HAADF STEM image in the left and its corresponding CTEM image in the right for the [101] orientation................................................................. 53
Figure 26: A tilted micrograph of the Ag$_2$Al platelets imaged in the [001] beam orientation where the projected thicknesses are measured

Figure 27: A micrograph in the [101] edge-on position where the red dashed-line represents the profile that is shown beside the micrograph from which the intensity of the platelets and the matrix surrounding it is measured

Figure 28: The micrograph representing a multilayer system supplied by TriQuint Semiconductors, and the profiles give a measure of the intensities of the various elements

Figure 29: A sample of a multilayer system supplied by TriQuint Semiconductors, that was used for determination of the interaction coefficient values for the elements, Au and Ti

Figure 30: Alternate Layers of Si$_{0.81}$Ge$_{0.19}$ and pure Si

Figure 31: The CTEM and STEM micrographs of Au$_{0.8}$Fe$_{0.2}$ nanoparticles, sample supplied by Dr.Roldan of UCF’s Physics Department

Figure 32: The constructed RGB image from STEM micrograph in Fig. 31 of the Au$_{0.8}$Fe$_{0.2}$ nanoparticles and the scale bar to represent the thickness (white particles are more than 10 nm thick)

Figure 33: The HAADF STEM micrograph that was used to determine the composition of Cu in the Al-Cu alloy, present in the finger. The measurement of the intensity of the Al-Cu alloy was taken from the profile

Figure 34: The phase diagram of Al-Cu
Figure 35: The micrograph of the HAADF detector to determine the overall intensity of the incident beam of electrons. ................................................................. 66

Figure 36: The plot of the interaction coefficient, $\sigma$ Vs the atomic number, $Z$ ....................... 69

Figure 37: Probable shapes of nanoparticles on the surface of the carbon film; (a) completely spherical, (b) elliptical and (c) lying flat on the surface. ................................................................. 71

Figure 38: Diffracction pattern of Ag2Al at zero station......................................................... 73

Figure 39: Cross-section of the sample in the edge-on position................................. 74

Figure 40: The cross-section of the sample is the tilted position................................. 75

Figure 41: The projection of the vectors on (001) plane and their geometry. ....................... 76
LIST OF TABLES

Table 1: List of parameters that were kept constant in the STEM mode of imaging. ................. 41

Table 2: Values of the intensity/thickness ratios for various elements/compounds. ................. 60

Table 3: The ratio of the intensity/nm for each element/compound Vs the intensity of the incident beam on the detector. .......................................................... 67

Table 4: The calculated values of σ, the interaction coefficient for the elements/compounds. .... 68
**LIST OF ACRONYMS AND ABBREVIATIONS**

<table>
<thead>
<tr>
<th>ACRONYM</th>
<th>DEFINITION</th>
</tr>
</thead>
<tbody>
<tr>
<td>ADF</td>
<td>Annular Dark Field</td>
</tr>
<tr>
<td>AFM</td>
<td>Atomic Force Microscopy</td>
</tr>
<tr>
<td>BF</td>
<td>Bright Field</td>
</tr>
<tr>
<td>CBED</td>
<td>Convergent-Beam Electron Diffraction</td>
</tr>
<tr>
<td>CCD</td>
<td>Charge-Coupled Device</td>
</tr>
<tr>
<td>CTEM</td>
<td>Conventional Transmission Electron Microscopy</td>
</tr>
<tr>
<td>Cu</td>
<td>Copper</td>
</tr>
<tr>
<td>DF</td>
<td>Dark Field</td>
</tr>
<tr>
<td>Eb</td>
<td>Binding Energy</td>
</tr>
<tr>
<td>E_{kin}</td>
<td>Kinetic Energy</td>
</tr>
<tr>
<td>E_0</td>
<td>Energy of Incident Electron Beam</td>
</tr>
<tr>
<td>EDS</td>
<td>Energy Dispersive Spectroscopy</td>
</tr>
<tr>
<td>EDX</td>
<td>Energy Dispersive X-Ray Spectroscopy</td>
</tr>
<tr>
<td>EELS</td>
<td>Electron Energy-Loss Spectroscopy</td>
</tr>
<tr>
<td>FEG</td>
<td>Field-Emission Gun</td>
</tr>
<tr>
<td>Abbreviation</td>
<td>Description</td>
</tr>
<tr>
<td>--------------</td>
<td>-------------</td>
</tr>
<tr>
<td>FIB</td>
<td>Focused Ion Beam</td>
</tr>
<tr>
<td>Ga</td>
<td>Gallium</td>
</tr>
<tr>
<td>HAADF</td>
<td>High-Angle Annular Dark Field</td>
</tr>
<tr>
<td>HRTEM</td>
<td>High-Resolution Transmission Electron Microscopy</td>
</tr>
<tr>
<td>LAADF</td>
<td>Low-Angle Annular Dark Field</td>
</tr>
<tr>
<td>nA</td>
<td>nanoAmpere</td>
</tr>
<tr>
<td>Ni</td>
<td>Nickel</td>
</tr>
<tr>
<td>nm</td>
<td>nanometer</td>
</tr>
<tr>
<td>pA</td>
<td>picoAmpere</td>
</tr>
<tr>
<td>Pt</td>
<td>Platinum</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>TDS</td>
<td>Thermal Diffuse Scattering</td>
</tr>
<tr>
<td>Z</td>
<td>Atomic Number</td>
</tr>
<tr>
<td>ZnS</td>
<td>Zinc Sulphide</td>
</tr>
</tbody>
</table>
CHAPTER 1:
MOTIVATION AND INTRODUCTION

1.1 Motivation

Characterization of materials has occupied a very important place from the very start of science era, as it is the only means to understand the material and its properties completely. There have been and are many different types of characterization techniques, measurement of properties like density, color, electrical conductivity, heat conductivity, and also destructive and non-destructive characterization techniques. To understand a material completely, it is very important to understand its microstructure, properties and behavior. One such characterization technique is the Transmission Electron Microscopy (TEM). The transmission electron microscope is a very powerful system which has a high lateral resolution of about 2 Å, which allows us to view the individual atomic columns and gives us an insight to the atomic structure of materials.

To get a comprehensive picture of a material it is really important to know all the three dimensions of the sample used to characterize the material. For the determination of the exact shape of a nanoparticle, the measurement of the sample thickness is very important. And the determination of the shape is of utmost importance in the characterization of nanoparticles. Though TEM has a high lateral resolution (as can be seen in Fig.1 in case of nanoparticles), it is extremely difficult to know the third dimension (sample thickness) in it.
The Atomic Force Microscope (AFM) provides a true three-dimensional surface profile; it mainly uses the height of its probe tip to measure the surface topography. The image is usually distorted at high edges on the surface as the tip is not sharp [Wiki08]. So in different ways, TEM and AFM are complementary to each other.

Figure 1: Au-Fe nanoparticles with unknown thickness. Samples provided by Dr.Roldan, Physics department

The objective of my thesis is to develop a new quantitative method in TEM, to determine the sample thickness locally. The intensity of the electrons scattered to high angles, affected by the thickness and atomic number are studied for different materials.
1.2 Introduction

In Scanning Transmission Electron Microscopy (STEM), an electron probe is used to create an image. The probe is scanned across the sample using deflection coils and a detector is used to capture the signal for each position. There are three different detectors used to collect specific parts of the diffraction pattern. These detectors are Bright-field (BF), dark-field (DF) and the high-angle annular dark-field (HAADF) detectors. Conventional TEM (CTEM) usually consists of bright-field, dark-field and high-resolution transmission electron microscopy (HRTEM).

Multiple scattering and dynamical scattering usually affects the CTEM methods. These effects are minimized by utilizing the electrons scattered to high angles. Two such methods which exploit these high scattered electrons for quantitative study are: conical dark-field transmission electron microscopy and HAADF STEM. Kirkland (1998) and Erni et al (2003) have developed methods for HAADF STEM contrast simulations [Seal08].

The measurement of sample thickness can be done in various ways. The thickness can be determined based on the geometry when all the required parameters are known. But the knowledge of all the required parameters is difficult. The sample thickness can also be measured using the Convergent Beam Electron Diffraction (CBED) method. This method is an age-old method and is quite complicated. Another alternative method is the Thickness Maps employed in the Electron Energy-Loss Spectroscopy (EELS). This is an easy method, but requires the knowledge of the value of the mean free path of the particular material being analyzed.
These values are specific to the materials and determination of these values is difficult.

In my thesis, I have described a method that can be added to the above methods in the determination of the sample thickness, which is simpler and easy to use than the above methods.

1.2.1 The imaging process
HAADF STEM is a valuable tool for the study of chemical homogeneities in materials containing elements of sufficiently different atomic numbers. Unlike the BF and DF detectors, the HAADF detector captures electrons scattered at higher angles. The HAADF STEM image formation process clarifies the origin of incoherence. Incoherent imaging is fundamental for a direct interpretation of the micrographs. In contrast to the partially coherent imaging process known for HRTEM, a lower number of ambiguities have to be considered. STEM imaging is essentially diffraction imaging. Precise relationship between the phases of the incident and scattered beams is characteristic of “coherent scattering” of electron which produces diffraction. The scattered wave is made up of component waves, called “wavelets”, which are produced by the different atoms in the sample. Constructive or destructive interferences occur at different angles around the sample in diffraction due to the phase differences in the wavelets. The total scattered wave has maxima and minima due to the interferences, which depends on the distances between the atoms and angles made by the atoms in the material [Fult01] [Cowl81].
At any given point in time, the structure of a wave along the position \( x \), can be described by the wave amplitude \( \psi(x) \). The mathematical form \( \psi(kx-\omega m) \) accounts for how the wave amplitude shifts in position with increasing time, \( m \). The phase of the wave is given by the argument, \( kx-\omega m \), which includes two constants for the wave: \( k \) (the wave vector), and \( \omega \) (the angular frequency).

In the scattering from different locations \( (r_j) \) in a material, the relative phases of the wavelets are preserved in coherent scattering. On the other hand, “incoherent scattering” does not preserve a phase relationship between the incident wave and the scattered wavelets. The total scattered wave, \( \psi_{coh} \), in coherent scattering is produced by adding the amplitudes of the scattered wavelets.

\[
\psi_{coh} = \sum r_j \psi r_j
\]  

Hence the constructive and destructive interferences of the wavelet amplitudes define the total coherent wave. The total coherent intensity is given by,

\[
I_{coh} = \left| \sum r_j \psi r_j \right|^2
\]  

But for incoherent scattering, the total intensity of the scattered wave is the sum of individual scattered intensities, as it does not preserve a phase relationship between the incident and the scattered wavelets.
The intensity of the coherent scattering involves addition of the wave amplitudes, and it depends on the relative phases of the scattered wavelets. Hence it depends on the relative positions of the N atoms in the group. Thus diffraction experiments use coherent scattering and incoherent scattering is not useful in those experiments.

Scattering processes are also defined as “elastic” or “inelastic” based on the change or no change in the energy of the wave after scattering. Thus four types of scattering can be constructed based on the permutations and combinations of elastic, inelastic, coherent and incoherent. Coherent elastic scattering is useful for diffraction hence important for electron and x-ray scattering. Incoherent inelastic scattering is useful in spectroscopy. Coherent inelastic scattering is useful in neutron scattering studies of elementary excitations in materials. And finally incoherent elastic scattering occurs when phase relationships between scattered wavelets are disrupted by the disorder in the material. The incoherent elastic intensity does not show sharp diffractions associated with crystalline periodicities, but has a broad angular dependence, which is the main aspect used in HAADF STEM imaging.

\[ I_{inc} = \sum_{rj} I r_j = \sum_{rj} |\psi_{rj}|^2 \]  

(1.3)
1.2.2 Atomic number imaging (Z-Contrast imaging)

Atomic number imaging or Z-Contrast imaging is one of the well-established high-resolution imaging techniques in STEM. They are formed from incoherent elastically scattered electrons. The incoherent images of the Z-contrast method are interpreted directly in terms of atom types and positions because as discussed in section 1.2.1(Eq 1.3) the scattered intensity in incoherent scattering is the sum of independent scatterings from individual atoms.

High-angle (75-150 mrad) elastically scattered electrons are collected with an annular dark-field detector, which form the Z-contrast images. An efficient dark-field imaging mode is provided by this type of annular detector which captures a large fraction of the high-angle electrons. The angle of scattering is larger than that required for a typical Bragg diffraction by an order of magnitude, so the relevant part of the scattering potential is smaller than typical atomic dimensions by an order of magnitude. The effective size of the atomic scattering potential which typically is 0.01 – 0.003 nm, is also smaller that the size of the electron beam probe of modern medium-voltage field-emission STEMs by an order of magnitude [Fult01]. Thus, a vertical column of atoms can be understood as a very sharp object in the plane of the sample. The obtained image resolution is a convolution of a “δ-function”. This “δ-function” has the spatial profile of the probe current (see Fig.1), along with any beam broadening that might occur. It is possible to use thin specimens so that beam broadening is minimized, because of the large cross-section for elastic scattering.
The incoherence of the HAADF images is a result of their large $\Delta k$ (change in the wave vectors of the incident and the scattered wave). At large $\Delta k$, coherent scattering is suppressed, but the thermal diffuse scattering is large and this dominates the signal. This makes quantitative image interpretation relatively straightforward, as there are no contrast oscillations with thickness and no contrast reversals with focus.

The scattered intensity is proportional to the atomic number of the scattering element, raised to some power between 1.5 and 2, depending on the detector angles. Many researchers have used this relationship for the quantitative differentiation between atoms of different elements for analysis of Z-contrast images of individual atoms, interfacial structures and chemical inhomogeneities.

But, for quantitative interpretation of high-angle scattering, many factors must be considered, most important being: specimen thickness, composition, orientation, structural defects, and thermal vibrations.
CHAPTER 2:
SAMPLE PREPARATION

2.1 Focused Ion Beam (FIB) technique

The Focused Ion Beam (FIB) technique is one of the methods of TEM sample preparation. A basic FIB instrument consists of a vacuum system and chamber, detectors, gas delivery system, a liquid metal ion source, ion column, stage, gas inlets and a computer to run the complete instrument as shown in Fig 2. It operates by focusing Gallium (Ga) ions on the sample in FIB, quite similar to a scanning electron microscope. The FIB instrument used in this work for sample preparation is shown in Fig.3.

![Figure 2: Schematic diagram of (a) a basic FIB system and (b) liquid metal ion source (reproduced from [Gian05])](image-url)
A sharp tungsten needle is in contact with a reservoir containing Ga ions, which wets the tip of the tungsten needle as shown in Fig 2(b). A high electric field of more than $10^{10}$ V/m at the tip is induced by a high extractor voltage of around 10 kV. A drop of Ga atoms ionized and ready to be emitted is formed at the tip of the needle. The Ga beam is deflected across the sample with the help of beam deflectors. As the beam scans the sample, a highly magnified image is created, which makes it possible to view the micro-structural features. An image is formed by using a secondary electron detector. The probe current can be varied from 10 pA to 20,000 nA. Smaller probe currents are used to remove material at specific locations, to make a thin sample, by using small beam diameters in the final preparation steps.

Figure 3: The FIB instrument FEI 200 TEM in use at Materials Characterization Facility (MCF) of UCF.
Large quantities of material are removed and trenches of several µm in depth are dug into the sample using high probe currents.

A layer of Platinum (Pt) is deposited to protect the sample area of interest, by a gas injection needle which can be positioned close to the sample area. This needle contains an organo-metallic material which decomposes to deposit Pt in the Ga ion beam. After the deposition of the Pt layer, the cutting of the TEM sample starts. The FIB sample stage has typically the ability to provide 5 axis motions- X, Y, Z, tilt and rotation. All these five motions are motorized which allows rapid processing at various angles to the specimen. The sample is cut, a few µm deep, around the strip of protective Pt layer.

2.1.1 Ex-situ lift out of TEM samples
There are two different types of lift-out techniques in FIB. In this section the ex-situ lift out technique is described as this was the method we used for preparing the TEM samples.

In this method, the Ga beam size is started off with a high current and then it is successively reduced till the sample is as thin as 1000 nm (shown in Fig 4(b)). The sample is tilted to 45°, and the bottom of the section is cut as shown in Fig 3(c).
The sample is thinned further on both sides of the section with ion currents below 100 pA [Gian05]. When the sample is around 50 to 100 nm thick, the sides of the section are cut off. The sample is then placed under an optical microscope (shown in Fig 5). A micromanipulator is attached to a thin quartz needle (shown in Fig 6). The tip of the needle is usually so thin that it cannot be seen with the naked eye.

The sample sticks to the tip of the quartz needle due to electrostatic forces when the needle is brought near the sample. The sample is removed from the specimen and placed on a Cu or Ni grid with an amorphous carbon film. The thin sample usually sticks easily to the carbon film when the quartz needle approaches the carbon film. This whole operation is done by looking at the magnified images being transmitted to a monitor from a camera attached to the microscope. The thin sample on the Cu grid is now ready for TEM analysis as shown Fig 4(d).
Figure 4: The steps of the ex-situ lift-out process. (a) Pt deposition to protect the sample surface, (b) a thin section is formed by cutting of the sides, (c) side view at 45° tilt of the thin section with the bottom cut visible, (d) low-magnification TEM image of sample sections deposited on a carbon film supported by a Cu grid. [Halb06]
Figure 5: The optical microscope used for the Ex-situ lift out of the TEM samples.

Figure 6: The Quartz needle attached to the micro-manipulator.
CHAPTER 3: CHARACTERIZATION TOOLS

3.1 An Introduction to Transmission Electron Microscopy

Transmission electron microscopy (TEM) is a premier tool for the micro-structural characterization of materials using a beam of high-energy electrons to examine objects [Gian05]. A TEM study can yield the following information about the material [Cmra95]---Topography, morphology, crystallographic and compositional information. The surface features and texture of a cross-sectional specimen form the topography. The morphology is made up by the size, shape, arrangement of particles and their inter-relations on the atomic scale. The crystallographic information is obtained by the arrangement of atoms, their degree of order and defect detection at atomic scale. The elements and compounds and their ratios give us the compositional information.

TEM is a two-dimensional imaging technique applied to three-dimensional systems. Thus, the interpretation of TEM micrographs and the chemical studies is not straightforward. The higher the resolution, the more complicated the interpretation becomes. A picture of a typical TEM is shown in Fig.7.
Figure 7: The 300 kV TEM (Tecnai F30), housed in MCF of UCF.
3.1.1 Components of a Transmission Electron Microscope

The components of a transmission electron microscope (as shown in Fig 8(a) and 8(b)) are an electron source (electron gun), condenser lenses, an objective lens, imaging system (consisting of the diffraction lens, intermediate lenses, and projector lenses depending on the type of microscope), and a viewing screen. The condenser lens system with at least two lenses essentially demagnifies the electron probe thus reducing the area illuminated by the electron beam. Electrons near the optical axis for illumination of the sample are selected by a condenser aperture.

The sample is centered within the upper and lower pole pieces of the objective lens (Fig 7). A parallel beam, generated by the upper part of the objective lens, enters the sample. A magnified image is created by the lower part of the objective lens. In the back focal plane of the lens, a diffraction pattern is formed, in addition to the magnified image. One or more Bragg reflections can be selected in the back focal plane (it’s also called the diffraction plane as a diffraction pattern is formed there) with an objective aperture to form magnified images of the sample with contributions transmitted through this aperture.

Additional magnification of the sample image or the diffraction pattern can be obtained by various lenses available in the imaging system. A selected area aperture can be inserted in the plane of the first image formed by the objective lens, which allows only electrons from a limited area of the sample to go through.
A fluorescent material like Zinc Sulphide (ZnS) is used on a viewing screen, in the camera system. The fluorescent screen can be tilted up to acquire micrographs on a CCD camera.

There are different kinds of detectors, like the bright-field (BF) or dark-field (DF) detectors or the high-angle annular dark-field (HAADF) detector in the scanning transmission mode (STEM). Electrons can be impinged on either one of them or the electrons can be captured by an electron energy loss spectrometer. The probe can be moved across the sample by the use of deflection coils.

The sample is mounted on a sample holder. A goniometer holds the sample holder in the gap between the upper and the lower pole piece of the objective lens. The sample can be tilted in different directions by means of double tilt holders.
Figure 8: (a) Imaging and (b) diffraction mode of the transmission electron microscope (reproduced from [Seal08]) [Heim80].
3.1.2 Conventional Transmission Electron Microscopy

The conventional TEM mode uses a broad, nearly parallel electron beam with a diameter of several micrometers. Apertures in the back focal plane and in the image plane may be applied to increase the contrast or to select an area of interest.

3.1.2.1 Bright-field and dark-field TEM

These techniques essentially give a crystallographic contrast for polycrystalline samples. The contrast is obtained by the insertion of an objective aperture in the back focal plane of the objective lens.

A single Bragg reflection is selected to contribute to the image. An aperture in the diaphragm is centered about this Bragg reflection in the diffraction pattern. All other beams other than the selected Bragg reflection are blocked, and hence do not contribute to the image. If the undiffracted beam (000) is centered by the objective aperture, it’s called bright-field condition (Fig 8(a)). Only the undiffracted beam and, for a larger aperture, a few of the low-indexed Bragg reflections also contribute to the image. The contrast in such a bright-field micrograph is enhanced when compared to an image without an aperture.
This method is quite useful in detecting Crystal defects. The reason behind this is that the diffraction contrast is modified locally by the defects, i.e. the number of electrons scattered to other Bragg reflections and lost to the undiffracted beam.

**Figure 9: Ray diagrams for (a) Bright-field imaging using direct beam and (b) dark-field imaging using a specific off-axis scattered beam. (reproduced from [Petr06])**

In dark-field imaging (Fig 8(b)) the incident electron beam is tilted with respect to the optical axis of the objective lens before the sample. Therefore, the electron diffraction pattern in the back focal plane is shifted. The electron beam is tilted in such a way, that one Bragg reflection is on the optical axis of the objective lens. The objective aperture is then centered around this Bragg reflection. All other reflections are excluded by the diaphragm and do not contribute to the image. Bright areas in dark-field imaging are from regions, which contribute to the specific Bragg reflection in the objective aperture, while all other regions are dark.
3.1.2.2 Selected-area electron diffraction

As seen in Fig 7(b), the diffraction pattern contains electrons from the whole area of the specimen that is illuminated. Such a pattern is not very useful because the specimen will often be buckled. Furthermore, the direct beam is often so intense that it will damage the viewing screen. Insertion of an aperture in the image plane of the microscope results in the blocking of those electrons which fall outside the dimensions of the aperture. This is a useful tool to acquire electron diffraction patterns from a certain area of interest on the specimen.

3.1.3 High-resolution transmission electron microscopy (HRTEM)

The HRTEM technique uses phase contrast to image lattice fringes and atomic structure unlike the conventional TEM techniques which operate at low/medium magnification mode (up to 200,000 X) and employ mass-thickness or diffraction contrast. The imaging of the atomic lattice requires its orientation in such a way that the atomic columns of this lattice are oriented parallel to the incident electron beam. High-resolution micrographs of crystal lattices can be acquired in modern transmission electron microscopes with high lateral resolution of about 2 Å or better.
3.1.4 Analytical TEM using Scanning transmission electron microscopy (STEM)

The scanning TEM mode is different from the conventional TEM mode since it uses a convergent electron probe with a few angstroms or nanometer in diameter. The probe scans the sample using a set of deflection coils. Such highly convergent beam allows probing with a high degree of specificity.

Electrons impinging on a specimen induce emission of X-ray while they also lose their energy owing to the interaction with the electron shells of the atoms. These processes can be used to chemically analyze areas of interest. Additionally, electron beams diffracted by atomic planes of specimen maybe detected by an annular detector in order to image the specimen.

3.1.4.1 High-angle annular dark field (HAADF) scanning transmission electron microscopy

High-angle annular dark field (HAADF) scanning transmission electron microscopy (STEM) is employed here using the FEI Tecnai F30 microscope, which is equipped with a scanning unit and a HAADF detector from Fischione (model 3000). The HAADF detector is an annular detector consisting of a scintillator-photomultiplier. This retractable detector is placed in a housing above the projection chamber of the Tecnai F30 microscope.
The spatial resolution is determined by the size of the focused incident probe. With electron beam sizes of less than 3 Å, imaging at atomic resolution is possible. The signal is collected, amplified and converted to gray levels for display.

The electron-optical path and the HAADF detector are schematically shown in Fig. 9. The electrons emitted by the Schottky field-emission electron gun are focused by the gun lens to a cross-over. The diameter of this cross-over can be reduced, which then acts as a virtual electron source. Choosing a suitable gun lens setting and demagnifying the electron probe in the condenser lens system, forms an electron probe, whose diameter, at the height of the specimen, is in the range of 0.2 nm. The incident electron probe is formed and affected by both, the aberrations of the objective lens and the condenser aperture C2. The condenser lens stigmator is used to stigmatize the electron probe.
Figure 10: Arrangement for imaging in HAADF-STEM mode (reproduced from [Sena05])

As indicated by the double colored lines in Fig 9, the electron probe is scanned across the thin foil by the deflection coils. Transmitted electrons can be detected as a function of scattering angle, for each scan position, either by a bright-field (BF), an annular dark-field (ADF) or a HAADF detector. The BF and the ADF detector are off-axis and not shown in the figure.
The HAADF detector below the specimen can be inserted optionally. The detector plane, between the specimen and viewing screen, corresponds to the diffraction plane. For each scan position, the high-angle scattering intensity of the corresponding diffraction pattern, integrated over a certain range of scattering angles which is determined by both, the camera length and the detector area, is measured by the HAADF detector. According to the scan position, these intensities are finally arranged to form a real space image.

Due to the convergence of the electron probe, at each scan position, a convergent electron microdiffraction pattern, called electron Ronchigram, is formed on the viewing screen and on the detector plane which is similar to the one shown in Fig.10. When positioning the electron probe on an amorphous part of the thin foil, the electron Ronchigram can be used to align and stigmate the electron probe [Jame99] [Brow01] [Rode02]. The spatial resolution achievable by HAADF STEM depends on the instrumental factors affecting the stability of the imaging process and the shape of the electron probe incident on the specimen. Thus a proper alignment of the electron probe is a necessity for high-resolution HAADF STEM.

The semi-angle of beam convergence $\alpha_{\text{conv}}$ of the incident electron probe is determined by the condenser aperture C2 with an aperture semi-angle $\alpha_{C2}$, i.e., $\alpha_{C2} = \alpha_{\text{conv}}$. 
Figure 11: A Ronchigram which is used to center the condenser aperture and to stigmatize the incident electron beam.

The aberration function of the objective lens, which depends on the constant of spherical aberration $C_s$ and on the defocus $\Delta f$, additionally affects the shape of the electron probe. In Fig.12, intensity profiles of the electron probe, calculated for different imaging parameters are shown.

For the Tecnai F30 microscope, the optimum semi-angle of the condenser aperture $\alpha_{C2}$ is 9.0 mrad and the optimum defocus $\Delta f_{\text{Scherzer,}i}$ is -48 nm. There is a set of condenser apertures which defines discrete settings for the condenser aperture semi-angle.
Figure 12: Calculated electron probe intensity profiles. Microscope parameters suitable for Tecnai F30 (300kV, Cs = 1.2 mm). a: Δf = 0.0 nm, αconv = 9.0 mrad; b: Δf = -48.0 nm, αconv = 3.0 mrad; c: Δf = -48 nm, αconv = 9.0 mrad; d: Δf = -70.0 nm, αconv = 9.0 mrad.

The Rutherford scattering, i.e., the predominant scattering at the electronic potential of the nucleus, becomes dominant at high scattering angles. Due to this the HAADF signal is strongly sensitive to the atomic number (Z) of the elements in the sample. Therefore, HAADF STEM is also known as Z-contrast STEM or Z-contrast imaging. A schematic of the formation of Z-contrast imaging geometry is shown in Fig 13.

In a HAADF micrograph, brighter spots typically represent the heavier atomic columns, and the darker ones, the lighter element atomic columns. HAADF is also strongly dependent on specimen thickness, so specimens with significant variation in thickness may show high intensity in thicker areas. In this case, the HAADF signal does not necessarily indicate a high atomic number.
De-channeling of the electron beam can also produce contrast variations from local strain fields, vacancies, dislocations and crystal tilt changes. Sample information can even be extracted (with loss of resolution) from much thicker regions. In these thick regions contrast reversals are seen depending upon composition and thickness.

![Figure 13: Schematic illustration of the Z-contrast imaging geometry](image)

Figure 13: Schematic illustration of the Z-contrast imaging geometry-- a focused electron probe channels along the projected atomic column and undergoes a large-angle scattering event to the high-angle detector. Images are formed by scanning the electron probe across the surface and can be interpreted in terms of the projected specimen scattering power. (reproduced from [Petr06])

The signals generated when the focused beam is moved across a specimen are generated due to the interaction between the electron beam and the specimen. These signals are characteristic to the specimen and vary with its characteristics, such as composition, structure, orientation and topography.
These changes in signals when the beam is scanned over the specimen in a rectangular raster can be detected by one of the STEM detectors. These detected signals can be used to build up the image of the specimen. [Tcmf02]

HAADF STEM imaging is now competitive with conventional BF TEM phase contrast for atomic resolution imaging of materials. It has been applied to a wide range of problems in which the local atomic structure at boundaries is significant, and is particularly useful when combined with EELS for studies of local elemental composition and bonding.

3.1.4.2 Energy Dispersive X-ray spectroscopy (EDS)

Secondary electrons are inner-shell electrons ejected by the electrons passing through the specimen. These empty inner-shell states are subsequently occupied by other inner-shell electrons from higher energy levels, which results in an X-ray spectrum characteristic to the specific element. These X-rays emitted from the specimen are detected by the X-ray detector.

A typical X-ray detector consists of Silicon (Lithium) or Germanium single crystal with a Beryllium window. When the X-rays hit the detector area, electron-hole pairs are generated. The energy of the incoming X-ray determines the number of charges produced. The number of X-rays with certain energy is plotted as a function of their X-ray energies, in an X-ray spectrum.
The position of the EDS detector is always above the specimen to minimize the background signal (e.g. from Bremsstrahlung X-rays generated in the forward direction) in the spectrum. The sample is typically tilted to an angle between 15° and 30° towards the detector to minimize absorption of low-energy X-rays within the sample (Fig 14). Therefore, even sample regions not hit by the electron beam or parts from the pole pieces near the sample can contribute to EDX spectra due to the generation of additional X-rays, which may be due to the excitation of atoms by the X-rays and secondary electrons generated in the illuminated volume.

Thus, particular care has to be taken to account for a possible excitation of X-rays in neighboring areas in quantitative EDX analysis.

EDS is well suited for the detection of heavy elements. The EDX spectra can be obtained in the following formats—

1. Point measurement – This is the spectra obtained by measuring the X-rays in a very small area (down to 1 nm diameter with reasonable count rate is possible) of the sample.

2. Line scan – This is the spectra obtained by positioning the small electron probe sequentially on points along a line. For each point position an EDX spectrum is obtained.

3. Area scan/ map – This is a spectra obtained by positioning the small electron probe sequentially on points on a two-dimensional grid to form a map of the area.
Figure 14: Sample geometry for analysis with an EDX detector (reproduced from [Halb06])

3.1.5 Electron energy loss spectroscopy (EELS)

Figure 15: Principle of a post-column electron energy loss spectrometer with the option of energy-filtered imaging. (reproduced from [Fult01])
Electron energy-loss spectroscopy (EELS) analyzes the energy lost by electrons after the electrons pass through the sample. The energy loss of the incident electron, $\Delta E$, is given by the equation (3.1), where $E_0$ is the energy of the incident electron, $E_b$ is the binding energy of the inner-shell electron and $E_{\text{kin}}$ is the kinetic energy of the ejected inner-shell electron.

$$\Delta E = E_0 - (E_b + E_{\text{kin}}) \quad (3.1)$$

Different electron energies can be separated by their location after passing through the homogeneous magnetic field, wherein the electrons are forced on a circular trajectory with a radius based on their velocity.

A zero-loss peak, a large peak of all electrons that have not interacted with the sample at all, a low energy loss Plasmon peak, Plasmons are collective oscillations of the free electrons in the material, and a signal background from multiple excitations and Bremsstrahlung, exponentially decreasing with increasing energy loss, make up the electron energy-loss spectrum, as shown in Fig 15a. Light elements and elements of medium atomic weight result in small energy losses, and hence this method is well suited for them, except H and He.

EELS can be used for compositional analysis, local thickness analysis and analysis of chemical bonds in a material.
Figure 16: (a) an example of an EELS spectrum, (b) Schematic of the interaction of electrons with inner shell electrons (reproduced from [Halb06]) [Abou05]
CHAPTER 4: EXPERTIMENTAL FACTS

4.1 FIB milling with ex-situ lift-out

A FEI 200 TEM Focused Ion Beam system operating at 30 KV was used to prepare cross-sectional TEM samples. Milling was initiated with a current of 3000 pA to cut trenches on either side of the Pt layer. As the milling progressed, the current was successively reduced with the thinning of the sample. Currents as low as 30 pA were used for the final thinning of the sample. The approximate dimensions of the final sample were 17 µm (length) x 5 µm (height) x 50 nm (thickness). The sample was lifted out using the ex-situ method. A Mitutoyo VM Zoom 40 optical microscope equipped with hydraulic micromanipulators was used to lift out the sample from the bulk and place it on Cu grid in a manner described in section 2.1.1.
4.2 Atomic number contrast imaging

High-angle annular dark field (HAADF) scanning transmission electron microscopy (STEM) has proved to be a valuable tool for the study of chemical inhomogeneities in materials containing elements of sufficiently different atomic numbers. HAADF STEM employed with a field-emission electron source benefits from three major features:

1. The point resolution determined by the electron probe is better than 0.2 nm for the Tecnai F30 with a field emission source and a spherical aberration of the objective lens of 1.2 mm. For an electron-probe diameter smaller than the inter-column distance of a zone-axis oriented crystal, the atomic columns are illuminated consecutively. Atomic-column resolved micrographs are thus possible.

2. HAADF STEM is to a good approximation an incoherent imaging technique. Incoherent imaging makes image interpretation straightforward. Generally, an intuitive interpretation of HAADF STEM micrographs is correct. There are no delocalization effects, no contrast oscillations with increasing foil thickness and no contrast reversals caused by focus changes. A simple transfer function describes the imaging process.

3. HAADF STEM micrographs show atomic-number (Z) contrast, owing to the dominant contribution of Rutherford scattering to the total elastic electron scattering at high scattering angles.
4.2.1 Quantitative HAADF STEM for materials science

Knoll and Ruska invented the Conventional Transmission Electron Microscope (CTEM), in the early 1930’s which was an extension of an earlier work, the oscilloscope. The invention of STEM followed shortly after that and its utility was greatly improved by Crewe et al with the addition of the cold field emission gun (FEG) source with a small source size and high brightness, in the late 1960’s.[Petr06]

In STEM mode the focused probe is scanned across the specimen in a raster and the image is built up one image point or pixel at a time as opposed to the whole image formed parallel at one time in CTEM.

The STEM has three types of detectors: the bright field (BF) detector and two different annular dark-field (ADF) detectors. The BF detector is positioned on the optic axis, and it detects the electrons that have passed through the specimen without significant deviation. The ADF detector collects the electrons that have been scattered to high angles.
Imaging of individual heavy atoms on an amorphous carbon substrate was made possible by high resolution STEM, which used low-angle (LA) ADF detector to collect scattered electrons from heavy atoms, in the 1970’s. [Crew70] But LAADF imaging mode has a disadvantage. The intensity in the LAADF imaging does not always depend on the atomic number as it is mainly due to dynamical diffraction.

Figure 17: STEM BF, ADF and HAADF detectors and their annular ranges. The conventional ADF and BF detectors are shown as well as the HAADF detector set-up for Z-contrast imaging, together with the range of electron scattering angles for each detector (reproduced from [Petr06])
Howie proposed the use of a high-angle (HA) ADF detector, which reduces the detection of coherent Bragg reflection and increases that of the incoherent thermal diffuse scattering (TDS). Thermal vibrations act to reduce the coherency of these events [Howi79]. A strong dependence on atomic number is seen in the resultant incoherent images.

It is shown that the atomic number of the scattering element, raised to some power between 1 and 2 [Lang73] is proportional to the scattered intensity. The proportionality depends on the detector angles and this could be used for the quantitative differentiation between atoms of different elements. The equation is written as

\[ I \sim t Z^\alpha \]

where \( I \), is the intensity, \( t \), the thickness of the sample, \( Z \), the atomic number and \( \alpha \), the parameter \( Z \) is raised to, where \( 1 < \alpha < 2 \).

HAADF STEM imaging is characterized by transversal incoherence between scattering contributions of different atomic columns, so that each column can be treated individually. Longitudinal incoherence allows the intensity of one atomic column to be expressed as a sum of the scattering intensities of the atoms, comprising the column. Thus the image intensity of a HAADF STEM micrograph can be analyzed directly, if the high-angle scattering intensities of the atoms in the crystalline specimen are known [Erni03].

The annular detection area of the HAADF detector is fixed, the inner and outer diameters were measured as 53 mrad and 322 mrad, respectively, for the setup used here, with the camera length of nominally 80 mm.
The angular working range for the electron detection can be adjusted by changing the camera length of the microscope. Choosing a small camera length means that electrons are detected, which are scattered to high angles. To extract quantitative information from the HAADF STEM image certain parameters have to be kept constant for calibration purposes. These parameters are listed in the table below.

The equation used to calculate the ratio of the intensities of the elements or compounds is

\[ I = I_{bg} + B \times \frac{\rho}{(A \times n)} \times t \times Z^\alpha \] ..............................(4.1)

where

- \( I_{bg} \) – Intensity of the background
- \( B, \alpha \) – parameters
- \( \rho \) – density of the material
- \( A \) – atomic weight
- \( n \) – neutron mass
- \( t \) – thickness of the sample
- \( Z \) – atomic number

The contrast and brightness settings used for the calibration were 46.875% and 12.500%. Similar settings were used for acquiring the quantitatively analyzed HAADF STEM micrographs.
Table 1: List of parameters that were kept constant in the STEM mode of imaging.

<table>
<thead>
<tr>
<th>Parameters</th>
<th>Values</th>
</tr>
</thead>
<tbody>
<tr>
<td>Camera Length</td>
<td>80 mm</td>
</tr>
<tr>
<td>Spot Size</td>
<td>7</td>
</tr>
<tr>
<td>Extractor Voltage</td>
<td>4400 V</td>
</tr>
<tr>
<td>Gun Lens</td>
<td>6</td>
</tr>
<tr>
<td>C2 Aperture</td>
<td>3</td>
</tr>
<tr>
<td>Contrast Setting</td>
<td>12.500%</td>
</tr>
<tr>
<td>Brightness Setting</td>
<td>46.875</td>
</tr>
<tr>
<td>Semi-convergence angle</td>
<td>7.17 mrad</td>
</tr>
</tbody>
</table>
4.2.2 Calibration Methods in Z-Contrast Imaging to calculate the local sample thickness

The calibration for the quantification of the Z-contrast method for the determination of the sample thickness can be done using one of several methods available. In this thesis I explain three different methods of calibration. They are:

1. Wedge method using \( \text{Ag}_2\text{Al} \) platelets,
2. Thickness method using \( \text{Ag}_2\text{Al} \) platelets, and
3. Wedge method using a pure Silicon wafer.

4.2.2.1 Wedge method using \( \text{Ag}_2\text{Al} \) platelets

In this method, micrographs of the \( \text{Ag}_2\text{Al} \) are imaged at different tilt angles. First the edge-on orientation of the \( \text{Ag}_2\text{Al} \) platelets in the sample is achieved by following the Kikuchi lines in the diffraction pattern. The beam orientation for this particular diffraction pattern can be found by indexing it. Several \( \text{Ag}_2\text{Al} \) platelets are in the edge-on position in this orientation.
The sample is imaged in the CTEM as well as the HAADF STEM mode, at different magnifications and also maintaining the several constant parameters. The sample is then tilted using the Kikuchi lines to an orientation which is determined from the diffraction pattern.

The sample being tilted now, some of the Ag$_2$Al platelets are at angles and thus seem much thicker than their original thickness. The sample is imaged in this orientation in CTEM and HAADF STEM mode, at different magnifications. Several such micrographs of the platelets are taken, both in the tilted and the edge-on conditions at different places of the sample. The angle made by the platelet wedge in the tilted micrographs is measured (as shown in Fig.18) in digital micrograph software. The apparent thickness of the sample is also measured in the tilted micrographs. Based on the geometry of the platelets when tilted with respect to (wrt) the platelets when they were edge on, the increase in thickness from the tilted micrographs can be correlated to the change in intensity in the edge-on micrographs, measured as shown in Fig.19, for both Al and Ag$_2$Al, thus giving us the values for counts/nm.
Figure 18: The micrograph of the Ag₂Al platelets at an angle. The angle between the two red lines is measured as the angle made by the wedge.

Figure 19: The micrograph of the Ag₂Al platelets edge-on. The dashed red-line gives the measurement of the change in intensity.
4.2.2.2 *Thickness method using Ag$_2$Al platelets*

In this method too the micrographs are imaged in the edge-on and tilted positions as mentioned in 4.2.2.1. In the tilted micrographs, the projected thickness of the Ag$_2$Al platelets is measured using the digital micrograph software (as shown in Fig.20) and the corresponding thickness is calculated using the equation that has been arrived at in the appendix using the geometry of the sample. In the edge-on micrographs the intensity for Al and Ag$_2$Al is measured.

![Figure 20](image)

**Figure 20:** The micrograph of tilted Ag$_2$Al platelets in [001] beam orientation used to measure the projected thickness of the platelets, as shown by the red lines.
Figure 21: The micrograph of edge-on Ag$_2$Al platelets in the [112] beam orientation used for measuring the intensities of Ag$_2$Al and Al using the profile given beside the micrograph. The profile is the profile of intensities across the dashed red-line in the micrograph.

Using the measured intensities and the calculated thickness, the counts/nm values can be determined for both Al and Ag$_2$Al, thus giving us the calibration values. The geometry of the thickness method is described in detail in Appendix 1.

The advantage of the wedge method is that it eliminates possible errors in the data evaluation due to surface contamination, which yields a more or less constant background. However, in the wedge method, the wedge angle is typically not very well defined with a high relative error in the range of 10%. This error can be avoided for the thickness method described above. The thickness method however yields reliable results only if the surface contamination is negligible.
4.2.2.3 Wedge method using Pure Silicon wafer

In this method a thin wafer of Si is polished on both sides completely. The wafer breaks off at precisely 90° angle to the surface if the wafer normal is [100]. This piece is placed in the sample holder of the TEM and this is tilted in the instrument in such a way that we can view the wedge made at the 90°. According to the geometry shown in Fig 22., the thickness of the sample can be determined directly.

Figure 22: Geometry of the wedge shaped Silicon Wafer.
4.3 *Energy-filtered transmission electron microscopy*

Some of the incident electrons lose part of their initial energy due to inelastic interactions. Information about the chemical composition of the sample (EEL spectrum), thickness of the sample (Thickness Maps) and also about the chemical bonds of the materials can be obtained from an EELS spectrum measured from a sample.

The background in the low-loss region, usually at energy losses below 100 eV, is mostly due to plural valence-electron or plural plasmon scattering. The background in higher-energy loss regions, usually greater than 100 eV, is caused by plural scattering of dissimilar scattering events with different electron energy losses, in particular by convolutions of plasmon losses. Zero-loss peaks are caused by elastically scattered electrons and quasi-elastically scattered electrons with energy losses below 1 eV caused by inelastic electron-phonon interactions. Plasmon-loss peaks, contributed by energy losses caused by excitations of collective oscillations of electrons in the conduction band, can be found at electron energy losses between 10 to 50 eV.

Inner-shell electrons of a selected element excited by a transmitted electron cause a rise in the intensity of the spectrum, which is called the ionization threshold. The ionization threshold sets in at an energy loss approximately corresponding to the binding energy of the ionized atomic shell. A sharp rise in intensity at the ionization threshold usually is a tell-tale sign of an inner-shell absorption edge.
This sharp rise in intensity is specific for an element, which is followed by an extended decay towards higher energy losses. Characteristic edges observable in the EEL spectrum are tabulated and can be used directly for a chemical analysis of the sample. The Tecnai F30 microscope with a post-column energy filter from Gatan, called Gatan imaging filter (GIF) is used for the purposes of this experiment. The main advantage with this type of spectrometer is that it is an independent add-on attachment to the microscope. A schematic of the imaging path within the microscope and the GIF mounted below the microscope column are shown in Fig.23. It is a simplified scheme with the electron-optical path suitable to perform the energy-filtered imaging and omitting the influence of the various correcting units.
Figure 23: Simplified setup of the electron-optical path for energy-filtered imaging using a post-column energy filter (GIF) (reproduced from [Erni03])
The acquisition of a thickness map is one of the several alternative techniques available for \textit{in situ} thickness measurement. Analysis of a convergent-beam diffraction pattern sometimes achieves 5\% accuracy, but the technique is time consuming with its need of dynamical contrast simulations and works only for crystalline specimens. Methods based on tilting the specimen and observing the lateral shift of surface features are less accurate and may interfere with subsequent microscopy of the same area. The easiest procedure for measuring specimen thickness within a region defined by the incident beam is to record an energy-loss spectrum and use simple integration to compare the area $I_0$ under the zero-loss peak with the total area $I_t$ under the whole spectrum. The thickness $t$ is given by,

$$
\frac{t}{\lambda} = \ln\left(\frac{I_t}{I_0}\right)
$$

where $\lambda$ is a total mean free path for all inelastic scattering in a material. Before applying the above equation, instrumental background should be subtracted from the spectrum. [Fult01]
CHAPTER 5: RESULTS AND DISCUSSION

5.1 Results

In section 4.2.2, I describe three different methods for thickness calibration purposes, but in this thesis I use the thickness method using Ag$_2$Al platelets to calibrate and obtain the results that I am about to present. For the calibration purposes, the sample containing Ag$_2$Al platelets was first tilted to get to an edge-on position, in this case being the [101] beam orientation.

Figure 24: The micrograph of the Ag$_2$Al platelets in the edge-on position in the [101] beam orientation.
The beam orientation was determined from the diffraction pattern. The micrograph of the Ag$_2$Al platelets is shown in Fig.24. The sample was then tilted to a beam orientation of [001] and also [101]. Micrographs were taken at both the beam orientations. Individual platelets were identified in the different micrographs with different beam orientations. The HAADF STEM images were calibrated using the corresponding CTEM bright field micrographs. Corresponding micrographs in HAADF STEM and CTEM are shown in Fig.25.

![Figure 25: A calibrated HAADF STEM image in the left and its corresponding CTEM image in the right for the [101] orientation.](image)

Now in the tilted micrograph, say the micrograph obtained in the [001] beam orientation, the projected thickness is measured (as shown in Fig.26) which is 304 nm.
Figure 26: A tilted micrograph of the Ag₂Al platelets imaged in the [001] beam orientation where the projected thicknesses are measured.
From this projected thickness, the thickness of the sample is calculated using the derived equation (6.1) (since the projections of the vectors on [101] plane are parallel to each other) from appendix A, which gives us the thickness to be 288 nm.

Now the intensity is measured from the micrograph in the edge-on position as shown in Fig.27, and the background intensity is subtracted from them.

Figure 27: A micrograph in the [101] edge-on position where the red dashed-line represents the profile that is shown beside the micrograph from which the intensity of the platelets and the matrix surrounding it is measured.
The ratio of intensity and the calculated thickness gives the counts/nm values for both Ag₂Al as well as Al, which are 39.2 counts/nm and 8 counts/nm respectively. This gives us the calibration required to calculate the intensity/thickness ratios for other elements from the various multilayer systems.

Based on the calibrated values for Al, the intensity/thickness ratios for various elements in the multilayer system (shown in Fig.28) are calculated assuming the thickness over the interfaces to be uniform. Let us take an example. From the multilayer system micrograph, it can be measured that the intensity in the Al region is 1450 counts. We know that the ratio for Al is 8 counts/nm, which gives us the thickness of the sample to be 181 nm (± 10 nm).

Now assuming that the thickness is uniform over the Al/W interface, we can calculate the intensity/thickness ratio for W to be 70.2 counts/nm. In a similar way the intensity/thickness ratio is calculated for AlN, SiO₂, Si.
Figure 28: The micrograph representing a multilayer system supplied by TriQuint Semiconductors, and the profiles give a measure of the intensities of the various elements.
Figure 29: A sample of a multilayer system supplied by TriQuint Semiconductors, that was used for determination of the interaction coefficient values for the elements, Au and Ti.

Figure 30: Alternate Layers of Si0.81Ge0.19 and pure Si.
The intensity/thickness ratio for Ag, is calculated using the composition law and the above relation.

The ratio was calculated for Au and Fe based on the relation between the atomic number and the intensities. The values calculated are presented in Table 2.

Using the above relations and methods the local thickness of nanoparticles can be measured which in principle gives us the volume of the nanoparticles (as shown in Fig.31).

The intensity/thickness ratio for the nanoparticles was calculated based on the composition law and the relation discussed above which gave the value to be 65.6 counts/nm. The intensity across the nanoparticles across which there is a red dashed-line (in the CTEM image of Fig.31) is measured. This gives a calculated value of 7 nm for the thickness of the nanoparticles. A calibrated RGB micrograph of the Au$_{0.8}$Fe$_{0.2}$ nanoparticles is shown in Fig.32.
Table 2: Values of the intensity/thickness ratios for various elements/compounds.

<table>
<thead>
<tr>
<th>Elements/Compounds</th>
<th>Intensity/Thickness ratio (Counts/nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ag$_2$Al</td>
<td>39.2 (≈ 3% error)</td>
</tr>
<tr>
<td>Al</td>
<td>8 (≈ 3.5% error)</td>
</tr>
<tr>
<td>W</td>
<td>70.2</td>
</tr>
<tr>
<td>Si</td>
<td>9.1</td>
</tr>
<tr>
<td>SiO$_2$</td>
<td>6.4</td>
</tr>
<tr>
<td>AlN</td>
<td>7.8</td>
</tr>
<tr>
<td>Ag</td>
<td>54.8 (derived from Ag$_2$Al)</td>
</tr>
<tr>
<td>Au</td>
<td>76.3</td>
</tr>
<tr>
<td>Fe</td>
<td>22.6</td>
</tr>
<tr>
<td>Ti</td>
<td>18.1</td>
</tr>
<tr>
<td>Cu</td>
<td>24.7</td>
</tr>
<tr>
<td>Ge</td>
<td>27</td>
</tr>
</tbody>
</table>
Figure 31: The CTEM and STEM micrographs of Au0.8Fe0.2 nanoparticles, sample supplied by Dr. Roldan of UCF’s Physics Department.
Figure 32: The constructed RGB image from STEM micrograph in Fig. 31 of the Au$_{0.8}$Fe$_{0.2}$ nanoparticles and the scale bar. to represent the thickness (white particles are more than 10 nm thick).

The RGB micrograph gives us a measurement of thickness of the nanoparticles directly, like a thickness map. The calibration to the color in terms of the thickness is given below the micrograph.
The total intensity of that particular nanoparticle is measured and then the area of the nanoparticle is calculated by multiplying it with 0.0625 nm (since 1 pixel has a lateral dimension of 0.25 nm). This gives us the volume of this specific nanoparticle, which was calculated to be 121 nm$^3$. Similarly, volumes of other nanoparticles are determined.

The measurement of the thickness of the nanoparticles is pretty important as the change in the thickness as well as the overall size of the nanoparticles may bring about a change in the catalysis and in luminescence-center-mediated excitation where they have very important functions [Savy07] [Croy07].

Thicknesses can only be determined if the composition is well known. However, this method can be used to determine compositions when the thickness is known. One example is the composition of a decomposed Al-Cu alloy in one of the multilayer systems provided by TriQuint. The sample reveals decomposed Al-Cu grains in a matrix of Al-Cu alloy. The thickness of the sample is directly determined from the HAADF intensity for the Al-Cu alloy phase, which was measured to be 89 nm.
Figure 33: The HAADF STEM micrograph that was used to determine the composition of Cu in the Al-Cu alloy, present in the finger. The measurement of the intensity of the Al-Cu alloy was taken from the profile.
The Al-Cu grains show higher intensity, and assuming no changes in thickness for this FIB sample, we get a composition of Cu to be 49% by weight from the measurement of the intensity from the profile (as shown in Fig 33). This value is pretty close to the composition of the $\theta$ phase in the phase diagram of Al-Cu, which is shown in Fig.34.

Figure 34: The phase diagram of Al-Cu.
5.2 Towards Quantitative HAADF STEM

The thesis shows that the HAADF STEM method can be made quantitative to allow for the measurement of the sample thicknesses or compositions. The results shown in table 2 depend on the amplifier characteristics of the HAADF detector and on the intensity of the incident beam. Therefore, they should be made independent of the incident electron probe current.

To perform this task, the normal diffraction mode for STEM was switched off and the electron beam was scanned across the HAADF detector through a hole in the carbon film, of the TEM sample (as shown in Fig 35). This yields a measure of the local and overall intensity of the incident beam, measured with the HAADF detector when the undisturbed electron beam impinges directly on the detector. This was measured to be 37200 counts. When we divide the intensity/nm value for any of the elements and compounds in the table 2 by the intensity of the incident beam on the detector, we get a measure of the fraction of electrons scattered onto the detector per 1 nm of the respective material. This is given in Table 3.

Figure 35: The micrograph of the HAADF detector to determine the overall intensity of the incident beam of electrons.
Table 3: The ratio of the intensity/nm for each element/compound Vs the intensity of the incident beam on the detector.

<table>
<thead>
<tr>
<th>Element/Compound</th>
<th>Fraction of electrons scattered onto detector (/nm) x 10^{-4}</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ag₂Al</td>
<td>11</td>
</tr>
<tr>
<td>Al</td>
<td>2.2</td>
</tr>
<tr>
<td>W</td>
<td>19</td>
</tr>
<tr>
<td>Si</td>
<td>2.4</td>
</tr>
<tr>
<td>SiO₂</td>
<td>1.7</td>
</tr>
<tr>
<td>AlN</td>
<td>2.1</td>
</tr>
<tr>
<td>Ag</td>
<td>15</td>
</tr>
<tr>
<td>Au</td>
<td>21</td>
</tr>
<tr>
<td>Fe</td>
<td>6.1</td>
</tr>
<tr>
<td>Ti</td>
<td>4.9</td>
</tr>
<tr>
<td>Cu</td>
<td>6.6</td>
</tr>
<tr>
<td>Ge</td>
<td>7.3</td>
</tr>
</tbody>
</table>
Table 4: The calculated values of $\sigma$, the interaction coefficient for the elements/compounds.

<table>
<thead>
<tr>
<th>Element/Compound</th>
<th>$\sigma$, Interaction Coefficient ( nm$^2$/atom) x 10$^{-6}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ag$_2$Al</td>
<td>18</td>
</tr>
<tr>
<td>Al</td>
<td>3.5</td>
</tr>
<tr>
<td>W</td>
<td>29</td>
</tr>
<tr>
<td>Si</td>
<td>4.7</td>
</tr>
<tr>
<td>SiO$_2$</td>
<td>2.5</td>
</tr>
<tr>
<td>AlN</td>
<td>1.1</td>
</tr>
<tr>
<td>Ag</td>
<td>24</td>
</tr>
<tr>
<td>Au</td>
<td>35</td>
</tr>
<tr>
<td>Fe</td>
<td>6.9</td>
</tr>
<tr>
<td>Ti</td>
<td>8.3</td>
</tr>
<tr>
<td>Cu</td>
<td>7.5</td>
</tr>
<tr>
<td>Ge</td>
<td>16</td>
</tr>
</tbody>
</table>
Furthermore, by dividing the data from Table 3 by the atomic density of a material, we get the value for $\sigma$, the interaction coefficient of the scattering cross-section for the electrons scattered to the corresponding scattering angles of the HAADF detector. These values are shown in Table 4. A plot was drawn between the interaction coefficient values and the atomic number, which gives an increasing curve as shown in Fig.36. This plot is in sync with the theory stating that, the intensity increases with the increase in the atomic number.

![Graph showing the relationship between $\sigma$, the interaction coefficient, and the atomic number, Z.](image)

**Figure 36: The plot of the interaction coefficient, $\sigma$ Vs the atomic number, Z**
During the first part of the project, the calibration was done and $\alpha$, the atomic number parameter was determined. But the values obtained for some of the elements were either too small ($< 1$) or too big ($> 2$) which is against the theory stating that the value of the parameter is to lie between 1 and 2. Hence it was concluded during this thesis work that, the relation of intensity with atomic number is not clearly described.

5.3 Limitations of this method

This thesis addresses several difficulties faced during the Z-contrast imaging using the HAADF STEM mode, and there are some limitations of this method. The thickness of the sample can be calculated only locally. The identification of particular nanoparticles in the STEM mode and in CTEM bright field mode was quite a challenge as all of them look alike.

Care should be taken while imaging nanoparticles as radiation damage can be significant and might sometimes cause structural changes [Seal08].
The local thickness measurement in nanoparticles does not give us any information about its overall shape relative to the surface, as to whether it is lying flat on the surface or if it completely spherical (as shown in Fig.37), which is quite important.

![Diagram of particle shapes](image)

**Figure 37: Probable shapes of nanoparticles on the surface of the carbon film; (a) completely spherical, (b) elliptical and (c) lying flat on the surface.**

It is also quite difficult to measure the thickness of layers which are quite porous and not homogeneous, as in the case of CIGS Solar Cells.
APPENDIX
Calculation of the thickness of the sample from the projected thickness measured.
The mathematics used in the calculation of the thickness depends strongly on the geometry of the TEM sample and its crystallographic orientation. It requires the knowledge of the surface normals, the normals to the platelets, the angles between the beam direction and the surface normal and the angles of tilt employed to tilt the sample. Let us consider a diagram of the cross-section of the sample when the sample is in the edge-on position (as shown in Fig. 39).

![Diffraction pattern of Ag2Al at zero station.](image)

**Figure 38:** Diffraction pattern of Ag2Al at zero station.
The normal of the sample surface was determined by indexing the diffraction pattern (shown in Fig. 38) when the sample was not tilted in the transmission electron microscope (i.e., not tilted, and not in edge-on position). Let us name the platelet that we are using for the purpose of this calculation, Platelet A. The normal of the Platelet A is determined, when the platelet is viewed in the edge-on position. In this case let us assume the beam orientation in the edge-on position to be [101], which gives the normal of Platelet A to be [11-1]. The intersection of the Platelet A ([11-1]) with the surface of the sample ([213]) gives the vector [-451]. The vector parallel to the surface normal and parallel to Platelet A passing through the bottom intersection point of the Platelet A and the sample is [213]t/(14)^0.5.

Figure 39: Cross-section of the sample in the edge-on position.

Now, the sample is tilted through an angle following the Kikuchi lines and the micrographs are obtained in the [001] beam direction.
We consider a diagram that displays the cross-section of the sample in this tilted position (shown in Fig 40). As seen in this diagram, the projected thickness measured in the tilted micrograph is in fact the distance \( d_p \) measured between the projection of the vector representing Platelet A on the (001) plane, since the beam orientation in the tilted position is assumed to be [001]. Hence \( d_p \) is given by measuring the distances between the projections of vectors [-451] and [213]t/(14)^{0.5} on the (001) plane. These projections are respectively [-450] and [210]t/(14)^{0.5}.

![Diagram](image)

**Figure 40:** The cross-section of the sample is the tilted position.
From Fig.40, based on the geometry,

\[
\cos \theta = \frac{t}{tp} \quad (6.1)
\]

Now looking at the projection part of the diagram on (001) shown in Fig.40, as seen in Fig 41,

\[
\cos \alpha = \frac{[210], [-450]}{\sqrt{5}, \sqrt{14}} = -\frac{3}{\sqrt{210}}
\]

\[
\sin \alpha = \frac{67}{\sqrt{70}} = \cos \beta
\]

Figure 41: The projection of the vectors on (001) plane and their geometry.
But from the geometry of the diagram as seen in Fig.41,

\[ \cos \beta = \frac{dp}{di} \]

Where \( d_i \) is the length of the vector \([210]t/(14)^{0.5}\),

i.e.

\[ d_i = \frac{\|[210]t\|}{\sqrt{14}} = \frac{\sqrt{5}}{\sqrt{14}} \cdot t \]

Now,

\[ dp = d_i \cdot \cos \beta = \frac{\sqrt{5}}{\sqrt{14}} t \cdot \frac{\sqrt{67}}{\sqrt{70}} = \frac{\sqrt{67}}{14} t \]

Thus,

\[ t = \frac{14}{\sqrt{67}} dp \] \hspace{1cm} (6.2)

Hence, in calibrations, when the projected thickness is measured, using equation (6.2), we can calculate the thickness of the sample.
REFERENCES


