Quantitative analysis of lattice strains and crystal polarity in semiconductor nanomaterials using Convergent Beam Electron Diffraction

by

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Abstract

In this thesis, different Convergent Beam Electron Diffraction (CBED) methods were developed and verified for the investigation of local lattice strains between ≈ 10nm wide Si$_{1-x}$Ge$_x$-Si Strained Layer Superlattice (SLS) layers and crystal polarity of novel CdS nanostructures. As part of strain calculations, the shifts & splitting of Higher Order Laue Zone (HOLZ) lines were quantified for the deformation along the electron beam direction and the asymmetric crystal growth of CdS structures was studied based on the analytical intensity calculations performed using double diffraction phenomenon and many-beam intensity profiles plotted using JEMS® software.

The lattice strain evaluation methodology involves extraction of HOLZ lines using Hough transformation and quantifying the shifts in HOLZ line positions for a unique set of lattice parameters/strain variations. Due to the appearance of split HOLZ lines at the outer interfaces of the SLS structures, the quantification method adopted for HOLZ lines shifts cannot be applied for this particular case. It is shown that the splitting of HOLZ lines are related to the surface relaxation occurred during the Transmission Electron Microscope (TEM) specimen preparation and using the kinematical simulation, the experimental magnitude of the split HOLZ lines is well reproduced and subsequently, the specimen deformation is determined.

The quantification methodologies of shift and split HOLZ lines are validated by comparing the determined profiles to Finite Element simulations that were modelled by considering the surface relaxations in TEM thin foils. Based on the appearance of the experimental CBED patterns, it is shown that even at relatively thicker regions of TEM specimen, there exists a impact of surface relaxation on the SLS structure and is demonstrated that the best achievable accuracy of the evaluated lattice parameters are in the range of $2 \rightarrow 4 \times 10^{-4}$ nm.

Based on a simple method that requires no specimen tilt from its exact zone axis orientation, the crystal polarity of CdS nanostructures is experimentally determined. The characterization technique is mainly dependent upon the multiple scattering among the zone axis reflections which has caused the asymmetric intensity distribution in \{0002\} beams. It is shown that the considered method is viable for a crystal thickness of 16nm which is less than one extinction distance of $\pm0002$ reflections.
Declaration

I hereby declare that this thesis is entirely my own work, with due acknowledgement being made in the text where work has been conducted in collaboration with another. This thesis has not been submitted for the award of a Degree at any other University.

Naga Vishnu Vardhan Mogili
To my late grandpa
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Concerning the software’s used in the current research; initially I would like to thank Prof. Pierre Stadelmann (EPFL, Switzerland) for provided JEMS software and several valuable clarifications regarding the HOLZ lines simulations. I further thank, Dr. David Holec (University of Leoben, Austria) for giving HANSIS software code and useful tips for enhancing the contrast of HOLZ lines appearances.

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<th>Description</th>
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<tr>
<td>ADF</td>
<td>Annular Dark Field</td>
</tr>
<tr>
<td>BF</td>
<td>Bright Field</td>
</tr>
<tr>
<td>CBED</td>
<td>Convergent Beam Electron Diffraction</td>
</tr>
<tr>
<td>CBIM</td>
<td>Convergent Beam Imaging</td>
</tr>
<tr>
<td>CCD</td>
<td>Charge Coupled Device</td>
</tr>
<tr>
<td>CDF</td>
<td>Centred Dark Field</td>
</tr>
<tr>
<td>CLC</td>
<td>Centre of Laue Circle</td>
</tr>
<tr>
<td>CM</td>
<td>Condenser Mini-lens</td>
</tr>
<tr>
<td>CMOS</td>
<td>Complementary Metal Oxide Semiconductor</td>
</tr>
<tr>
<td>DF</td>
<td>Dark Field</td>
</tr>
<tr>
<td>FCC</td>
<td>Face Centred Cubic</td>
</tr>
<tr>
<td>FEG</td>
<td>Field Emission Gun</td>
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<tr>
<td>FEM</td>
<td>Finite Element Modelling</td>
</tr>
<tr>
<td>FOLZ</td>
<td>First Order Laue Zone</td>
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<tr>
<td>FWHM</td>
<td>Full Width Half Maximum</td>
</tr>
<tr>
<td>HAADF</td>
<td>High Angle Annular Dark Field</td>
</tr>
<tr>
<td>HOLZ</td>
<td>Higher Order Laue Zone</td>
</tr>
<tr>
<td>HRTEM</td>
<td>High Resolution Transmission Electron Microscopy</td>
</tr>
<tr>
<td>JEMS</td>
<td>Java Electron Microscopy Software</td>
</tr>
<tr>
<td>Acronym</td>
<td>Description</td>
</tr>
<tr>
<td>-----------</td>
<td>--------------------------------------------------</td>
</tr>
<tr>
<td>KM Fringes</td>
<td>Kossel – Möllenstedt Fringes</td>
</tr>
<tr>
<td>LAADF</td>
<td>Low Angle Annular Dark Field</td>
</tr>
<tr>
<td>LACBED</td>
<td>Large Angle Convergent Beam Electron Diffraction</td>
</tr>
<tr>
<td>LCD</td>
<td>Liquid Crystal Display</td>
</tr>
<tr>
<td>LPE</td>
<td>Liquid Phase Epitaxy</td>
</tr>
<tr>
<td>MBE</td>
<td>Molecular Beam Epitaxy</td>
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<tr>
<td>MOSFET</td>
<td>Metal Oxide Semiconductor Field Effect Transistor</td>
</tr>
<tr>
<td>OM</td>
<td>Objective Mini-lens</td>
</tr>
<tr>
<td>PIPS</td>
<td>Precision Ion Polishing System</td>
</tr>
<tr>
<td>ROI</td>
<td>Region Of Interest</td>
</tr>
<tr>
<td>SAED</td>
<td>Selected Area Electron Diffraction</td>
</tr>
<tr>
<td>SE</td>
<td>Secondary Electrons</td>
</tr>
<tr>
<td>SEI</td>
<td>Secondary Electron Imaging</td>
</tr>
<tr>
<td>SEM</td>
<td>Scanning Electron Microscope</td>
</tr>
<tr>
<td>SLS</td>
<td>Strained Layer Superlattice</td>
</tr>
<tr>
<td>SOLZ</td>
<td>Second Order Laue Zone</td>
</tr>
<tr>
<td>STEM</td>
<td>Scanning Transmission Electron Microscope</td>
</tr>
<tr>
<td>TDS</td>
<td>Thermal Diffuse Scattering</td>
</tr>
<tr>
<td>TEM</td>
<td>Transmission Electron Microscope</td>
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<tr>
<td>ZOLZ</td>
<td>Zero Order Laue Zone</td>
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## List of Symbols

<table>
<thead>
<tr>
<th>Symbol</th>
<th>Definition</th>
</tr>
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<tbody>
<tr>
<td>$a, b, c$</td>
<td>translation vectors in real space</td>
</tr>
<tr>
<td>$a^<em>, b^</em>, c^*$</td>
<td>translation vectors in reciprocal space</td>
</tr>
<tr>
<td>$c$</td>
<td>velocity of light</td>
</tr>
<tr>
<td>$d_{hkl}$</td>
<td>interplanar distance</td>
</tr>
<tr>
<td>$e$</td>
<td>electron charge</td>
</tr>
<tr>
<td>$E$</td>
<td>accelerating voltage</td>
</tr>
<tr>
<td>$\xi_g$</td>
<td>extinction distance</td>
</tr>
<tr>
<td>$f$</td>
<td>lattice misfit</td>
</tr>
<tr>
<td>$F(\theta)$</td>
<td>structure factor</td>
</tr>
<tr>
<td>$f_\theta$</td>
<td>atomic scattering factor</td>
</tr>
<tr>
<td>$f_x$</td>
<td>atomic scattering factor of x-rays</td>
</tr>
<tr>
<td>$g$</td>
<td>diffraction vector</td>
</tr>
<tr>
<td>$G$</td>
<td>reciprocal lattice point</td>
</tr>
<tr>
<td>$\gamma$</td>
<td>relativistic factor</td>
</tr>
<tr>
<td>$h$</td>
<td>Plank’s constant</td>
</tr>
<tr>
<td>$hkl$</td>
<td>Miller indices</td>
</tr>
<tr>
<td>$I_g$</td>
<td>diffracted beam intensity</td>
</tr>
<tr>
<td>$\vec{k}$</td>
<td>diffracted beam wave vector</td>
</tr>
<tr>
<td>$\vec{k}_0$</td>
<td>incident beam wave vector</td>
</tr>
</tbody>
</table>
List of Symbols

\( K \)  
incident wave vector including crystal potential

\( \lambda \)  
electron wave length

\( \Lambda \)  
width of strained layers in an SLS

\( m \)  
relativistic electron mass

\( m_e \)  
electron Mass

\( n \)  
integer number

\( \phi_g \)  
diffracted wave amplitude

\( s \)  
deviation parameter

\( s' \)  
effective deviation parameter

\( t \)  
specimen thickness

\( \theta \)  
scattering angle

\( \theta_B \)  
Bragg angle

\( U_0 \)  
crystal potential

\( v \)  
electron velocity

\( V_0 \)  
unit cell volume

\( Z \)  
atomic number
1.1 Convergent Beam Electron Diffraction technique

With the advancement and improvements of Transmission Electron Microscope components such as stable double-tilt specimen stages, Field Emission guns and enhanced vacuum systems, the Convergent Beam Electron Diffraction (CBED) technique is regularly adopted for the quantitative analysis of crystal structures in material science analysis [1-3]. The main fundamental challenge in materials science is to establish a relationship between the crystalline structure of the material and its properties. Due to the sub-nanometre sized electron probes of CBED technique, it is possible to generate information from a localised region, which is beyond the reach by any other diffraction method. By correlating CBED with High Angle Annular Dark Field (HAADF) imaging, both structural and compositional details of the analysed local region can be interpreted [4]. With the increase in the complexity of the materials design and the use of new and advanced materials, the need for the information at nanoscale is very important for explaining material properties. In multilayer and quantum well structures, the knowledge of the local lattice parameters helps to infer the interfacial strain variations. Moreover, the crystal structural information of newly synthesised nanomaterials assists in understanding different macroscopic phenomena.
1. Introduction

With the availability of Field Emission guns, CBED analysis can be performed at an area of diameter from 1 to 10nm with a strain sensitivity of $2 \times 10^{-4}$ [5-6]. More details regarding the CBED technique and its implementation in an electron microscope are discussed in chapters 2 and 3.

In brief, the aims of this thesis are to implement a new methodology for quantifying the CBED patterns obtained from the interfaces of multilayer superlattice structures for studying strain variations across the layers and validate the quantified methods by comparing to finite element simulations. Furthermore, investigate novel non-centrosymmetric nanostructures using high spatial resolution CBED technique and determine the surface polarity that is resulting in asymmetric crystal growth.

1.2 Overall motivation and objectives

1.2.1 Lattice strain evaluation

In a zone axis orientation, the central disc of a CBED pattern generally consists of dark fine lines called Higher Order Laue Zone (HOLZ) lines. Apart from their application for symmetry analysis, these lines are very sensitive to any lattice deformation. Based on this observation, for the first time Jones et al. [7] reported that lattice parameters can be determined from the HOLZ line intersections and indicated that dynamical effects should be considered for more accurate measurements. Later on, due to the development of TEM and the essential spatial resolution offered by CBED, the interest in the technique was significantly increased and many groups have applied for different materials. Some of the important demonstrations of lattice parameters/strain evaluation are as follows: Zuo et al. [8] worked on single crystal YBa$_2$Cu$_3$O$_{7-\delta}$ and determined a, b lattice parameters by adopting kinematical theory simulations with a dynamical correction. Weber et al. [9] investigated lattice distortions in GaAs layers and Kaiser et
al. [10] determined lattice parameters in 3C-SiC films grown on 6H-SiC substrate. Furthermore Kramer et al. [11] measured the axial strains in Al interconnects by introducing Hough transformation for HOLZ line positions. In relation to the strained-layer heteroepitaxy, Chems et al. [12] analysed elastic strains using the CBED rocking curves obtained from Low Order and HOLZ reflections in Si-Ge SLS structures of plan view samples. Moreover, assuming no surface relaxation due to the specimen thinning, Pike et al. [13] carried out strain analysis on cross-sectional Si-Ge SLS from HOLZ line intersections.

In the studies performed on cross-sectional TEM samples, the strain or deformation with respect to the reference lattice is calculated by matching strain dependant simulated patterns to experimental patterns. Moreover, these matching strategies are broadly classified under area [14] or distance methods [8]. In case of the area method, the area delimited by HOLZ lines is measured and compared to corresponding theoretical HOLZ lines whereas in distance method, a set of distances between HOLZ lines crossing is measured and compared to the simulated HOLZ lines. Basically both the methods are similar because the areas are directly linked to the distances between the HOLZ lines intersection points by Heron’s formula [15].

By adopting HOLZ lines distance method, Armigliato et al. [16] applied CBED technique for $\text{Si}_{1-x}\text{Ge}_x$/Si heterostructures and determined the lattice parameters from the acquired CBED patterns. They have considered the lattice relaxation due to the thinning of the specimen but the analysis methodology was not illustrated. Latter Akaogi et al. [17] considered a method and determined all the six lattice parameter from one CBED pattern without adopting any assumptions regarding the crystal lattice symmetry and applied it to $\text{Si}_{1-x}\text{Ge}_x$/Si heterostructure. However, authors did not consider the ambiguity issues related to the non-uniqueness in the determined lattice parameters. In
early work by Humphreys et al. [18], it was pointed out the categorical statements regarding lattice parameters or strain that were determined using the CBED technique. From Maier et al. [19] work, it was made clear that the solution obtained from a CBED pattern cannot be unique because most of CBED patterns can be simulated by a number of different lattice parameters. The authors concluded by noting that a general recipe to the use of CBED patterns for the evaluation of lattice parameters does not exist, since there are many parameters involved in the process. They propose by making an intelligent choice of Zone axis orientation for the analysis and making an educated assumption regarding the specimen, the problem can be approached. Hence, the main objective of the current study of lattice strain evaluation is to develop a new methodology by addressing the ambiguity problem that is resulting in unique CBED patterns and quantify the HOLZ lines obtained from Si and Si$_{1-x}$Ge$_x$ regions.

1.2.2 Crystal polarity determination

The absence of a symmetry centre in crystal structures like wurtzite has a direct impact on its macroscopic properties such as, chemical reactivity of crystal surfaces, growth characteristics and asymmetry in mechanical hardness [20-22]. By determining the absolute polarity of the studied crystals, it is possible to interpret the corresponding structural models and to understand the particular crystal formation mechanism. Among various techniques including selective etching [23], x-ray diffraction [24] and ion channelling [25] that may be used to determine crystal polarity, the CBED technique performed in TEM is of special interest due to its ability to be performed on nanostructures.

Based on the structure-factor phase relationship in an off axis CBED pattern, for the first time Tafto and Spence et al. [26] demonstrated the GaAs crystal polarity. This method includes tilting the [011] specimen about 10° along the (200) plane and from the
intensity difference observed in diffraction discs due to dynamical three beam interactions, the crystal polarity was determined. Performing polarity analysis without any computer simulation and possessing independence to the specimen thickness are the primary advantages of this method.

However, in the case of nanomaterials, tilting a particular structure for the required four-beam condition and implementing the Tafto & Spence method may be highly challenging. In addition to this, Lu and Cockayne et al. [27] have determined the polarity of Cadmium Telluride (CdTe) samples using Tafto & Spence method but reported its failure for the materials with large degree of non-centrosymmetry such as Cadmium Sulfide (CdS) and Zinc Telluride (ZnTe). Hence in the currently undertaken CdS nanostructures, the main objective is to use a focused electron probe of CBED technique and determine the crystal polarity of the nanostructure based on the asymmetric intensity difference among $g_{0002}$ and $g_{0005}$ discs of zone axis CBED pattern.

1.3 Organisation of thesis

With the knowledge of the current research work motivations that were discussed in the present chapter, the synopsis of the remaining thesis is as follows:

Chapter two illustrates the background theoretical aspects of electron-specimen interaction and diffraction concepts related to parallel & convergent incident beams. All the major concepts that are important in understanding the CBED technique and origin of HOLZ lines in the CBED patterns are briefly described. Further in chapter two a brief outline of kinematic and dynamical theories of electron diffraction is discussed.

Chapter three presents the overview of JEOL 2100F Transmission Electron Microscope (TEM) that was used for obtaining all the different experimental micrographs. CBED
patterns are acquired in both TEM and Scanning TEM (STEM) modes of operations with different spots sizes and convergence angles at various camera lengths. For lattice strain analysis, CBED patterns are recorded along the line scans performed across the SLS structures whereas for polarity evaluation, CBED patterns obtained in TEM-CBED mode are preferred. In order to understand how CBED patterns are acquired in various modes, the different components of TEM are briefly discussed. Furthermore, a short description of the major steps involved in TEM sample preparation is presented.

Chapter four details the investigated lattice strain results obtained from the bands of individual Si$_{1-x}$Ge$_x$-Si Strained Layer Superlattice (SLS) structure. The surface relaxations which are always present in the thinned cross-sectional TEM foils does create a problem in the interpretation of CBED patterns. As an addition to this, the dynamical effects that exist in low index zone axis enhance the problem. So before lattice parameter/strain evaluation, a suitable zone axis is determined using the computer simulations performed in JEMS® software written by Stadelmann et al. [28]. Then by means of spectrum imaging in STEM mode, CBED patterns are acquired along the line scans performed over the bands of SLS and quantified for the strain variations.

Chapter five describes the crystal polarity analysis results of Cadmium Sulfide (CdS) nanostructures. The asymmetric intensity distribution among the zone axis CBED discs that has resulted from the violation of Friedel’s law in non centrosymmetric crystal is theoretically demonstrated for a crystal thickness less than the extinction distance of \{0002\} beams. The considered method of experimental analysis is shown to be viable for a CdS nanostructure with 16nm thickness along the electron beam direction.

Chapter six outlines the summary of the main conclusions derived from Chapters four and five.
In appendix A and B, the steps involved in structure factor calculation and the derivation of final exit wave function that was used for calculating the CdS intensity are shown respectively.
1.4 References


Chapter 2

Theory of Convergent Beam Electron Diffraction (CBED) technique

The main aim of this chapter is to discuss the theoretical aspects that are crucial for understanding the results shown in Chapters 4 & 5. In regard of that, the concepts are presented starting with electron scattering and diffraction illuminated by parallel and convergent beams. Then, the electron scattering phenomenon is discussed, based on the interaction of electrons with an individual atom & the atoms inside a crystal lattice. The diffraction concepts are introduced by discussing the differences between Bragg’s law and Laue conditions. To have a better understanding of the HOLZ and Kikuchi lines formation which are the part of Convergent Beam Electron Diffraction (CBED) patterns, Bragg’s law is extended to the third dimension and discussed. With knowledge of important concepts related to CBED patterns such as the deviation parameter, extinction distance and Centre of Laue Circle (CLC), kinematic theory and its assumptions are discussed. Finally, with a brief overview of dynamical theory, the concept of dispersion surface is discussed and its effect on the HOLZ line positions is illustrated.
2. Theory of Convergent Beam Electron Diffraction (CBED) technique

2.1 Electron Properties

Based on De Broglie hypothesis, electrons possess a dual nature where they can be described as having wave and particles properties [1]. Due to this, it is possible to explain the interaction between an electron and specimen. Initially, if the electron is considered as a particle, it carries a single negative fundamental unit of charge \( e \) of \( 1.6 \times 10^{-19} \) C and has a mass, \( m_e \) of \( 0.9 \times 10^{-30} \) kg. If a single electron is accelerated by a large voltage \( V \), then its velocity, \( v \) can approach the velocity of light, \( c \), of \( 2.998 \times 10^8 \) ms\(^{-1}\) and based on relativistic effects, mass increases as [2]:

\[
m = \frac{m_e}{\sqrt{1 - \left(\frac{v}{c}\right)^2}} = \gamma m_e
\]  

(2.1)

Where \( \gamma \) is relativistic factor equal to \( \left(1 - \left(\frac{v}{c}\right)^2\right)^{-1/2} \). Considering the electron as a wave, its wavelength (\( \lambda \)) is given by \( h/(mv) \), where \( h \) is Planck’s constant \( (6.636 \times 10^{-34} \) J.Sec)\). The energy given to the electron during acceleration \( eE \) is related to the energy represented by the relativistic change in mass:

\[
eE = (m - m_e)c^2
\]  

(2.2)

Thus the wavelength of the electron may be related to the potential difference or accelerating voltage \( E \) [2] as

\[
\lambda \ (\text{in nm}) = \frac{h}{2eEm_e + e^2E^2/c^2} = \left[\frac{1.5}{(E + 10^{-6}E^2)}\right]^{1/2}
\]  

(2.3)

If relativistic effects are ignored, then equation(2.3) reduces to \( \lambda = \sqrt{1.5/E} \) nm.

However, at the accelerating voltages that are most commonly used in electron microscopy (20 kV and above), the electrons are accelerated to a velocity which is a
significant fraction of the velocity of light [1]. Table 2.1 shows the effect of relativity of some common accelerating voltages that are employed in TEM. It can be observed that at an accelerating voltage of 100kv, there exists a difference of about 4.4% in the calculated wavelength values based on with and without considering relativistic effects. Moreover, the effect of relativistic effect becomes more significant for the electrons with energies greater than 100kv.

<table>
<thead>
<tr>
<th>Accelerating voltage / kv</th>
<th>$\lambda$ (non-relativistic) / nm</th>
<th>$\lambda$ (relativistic) / nm</th>
</tr>
</thead>
<tbody>
<tr>
<td>100</td>
<td>0.00387</td>
<td>0.00370</td>
</tr>
<tr>
<td>120</td>
<td>0.00354</td>
<td>0.00335</td>
</tr>
<tr>
<td>200</td>
<td>0.00274</td>
<td>0.00251</td>
</tr>
</tbody>
</table>

### 2.2 Electron scattering

When high energy electrons are incident on the specimen, either the same electrons, or electrons produced via a variety of secondary effects (such as Auger electrons) exit the surface to form an image or a measured signal [1]. Hence, by understanding this interaction, it is possible to interpret the chemistry and structure such as arrangement of atoms inside the unit cell of the specimen. During a scattering process both the amplitude and phase of the electron wave may be altered, leading to energy loss during the process. Based on this mechanism the scattering process is described as elastic scattering (no energy loss) or inelastic scattering (with energy loss).
2. Theory of Convergent Beam Electron Diffraction (CBED) technique

2.2.1 Elastic scattering by an individual atom

Elastic scattering is generally coherent (i.e. the phase relationship between scattered waves from different atoms is preserved) and involves no change in energy of the primary electron, although there may be large changes in direction. The communication between an electron and an isolated atom is either electron–nucleus or electron–electron interaction caused by Columbic force present between two charged bodies. When there is a direct collision between a primary electron (electron with an energy > 50ev) and the nucleus of an atom, it results in large angle elastic scattering also known as Rutherford scattering [2] where the scattering angle is greater than 5°. When there is an interaction between an incident electron and the electrons present in the electron cloud of an atom, it leads to small angle scattering which is typically in a range of 10 – 100 milliradians. The efficiency of an atom in scattering waves is described in terms of the atomic scattering factor \( f_\theta \) which depends on both the scattering angle \( \theta \) and the incident electron wavelength \( \lambda \) and is given by [3-4]

\[
f_\theta = \left( \frac{me^2}{2h^2} \right) \left( \frac{\lambda}{\sin \theta} \right)^2 \left( Z - f_x \right)
\]  

(2.4)

where \( Z \) is the atomic number and \( f_x \) is the atomic scattering factor of x-rays.

In equation(2.4), the parameter \( m \) needs to be replaced with equation(2.1) to include the relativistic effects of high accelerating voltage electrons. Based on the atomic scattering amplitudes [5] of Silicon, Sulphur, Germanium and Cadmium elements, a graph of \( f_\theta \) as a function of \( \sin \theta/\lambda \) at 200kv accelerating voltage is plotted in Figure 2-1.
2.2 Electron scattering

Figure 2-1 Atomic scattering factors of Si, S, Ge, Cd as a function of $\sin \theta / \lambda$ at 200kv

With the increase in the atomic number $Z$, the $f_\theta$ value is increased but its amplitude falls off rapidly at larger angles. From the plotted $f_\theta$ values of Cd and S, the structure factor of CdS crystal is calculated and the discussed more in appendix A.

2.2.2 Elastic scattering by crystal atoms

As crystalline solids are made of many atoms, the electron beam cannot be scattered just by one isolated atom. Hence, to understand the scattering process from the entire crystal lattice, the structure factor $F(\theta)$ needs to be introduced. It describes the amplitude of electron scattering from a particular $(hkl)$ set of crystallographic planes. It is defined as[1],

$$F(\theta) = \sum_i f_i e^{i\varphi} = \sum_i f_i e^{2\pi i(hx + ky + lz)}$$  \hspace{1cm} (2.5)
2. Theory of Convergent Beam Electron Diffraction (CBED) technique

Where $f_i$ represents the atomic scattering factor from $i$ atoms with coordinates $x_i, y_i, z_i$
and $e^{2\pi i (kx_i + ly_i + mz_i)}$, $(h, k, l)$ represents the phase of the electron wave and Miller indices respectively.

2.2.2.1 Bragg’s law and Laue conditions

Initially the diffraction of electrons by a single crystal in the current section is discussed
by means of kinematical theory. As the theory is mainly based on the geometry of the
interaction, the terms “scattering” and “diffraction” are used interchangeably. However
the term scattering specifically refers to the case of a beam of incident radiation striking
a small particle (say atom) and giving rise to an angular distribution of emergent
radiation which depends on the nature of the individual particle and not on their relative
positions. Whereas diffraction is used when interference effects between waves
scattered by many atoms give rise to modulations of the intensity distribution which
may be measured to give information on the relative positions of atoms [6]. The theory
of kinematical diffraction relies on the following assumptions but they cannot always be
ture as follows:

1. There is no attenuation of the incident wave in the crystal so that the incident
   wave has the same amplitude at each scattering point.
2. Each scattered wave travels through the crystal without being re-scattered by
   other scattering points.
3. There is no absorption of either the incident or the scattered waves in the crystal.

More details on kinematic theory are discussed in section-2.4. Nevertheless, the
kinematical approach is still satisfactory for a general description of diffraction
patterns.
2.2 Electron scattering

Figure 2-2 Reflection of plane wave at Bragg angle $\theta$ from one set of crystal lattice plane

Figure 2-2 depicts the situation describing the diffraction phenomenon in terms of Bragg’s law for a particular set of crystal lattice planes. Strong diffracted beams (constructive interference) occur if the path difference ABC is an integral number of wavelengths $n\lambda$. This gives:

$$n\lambda = 2d_{(hkl)} \sin \theta$$  \hspace{1cm} (2.6)

Figure 2-3 Scattering of plane wave by two atoms separated by a distance ‘a’

As an alternative approach to Bragg’s law, based on Laue conditions, diffraction may be considered in terms of scattering by individual atoms. This approach is more
quantitatively related to the reciprocal lattice of the crystal. Figure 2-3 illustrates this case for a one dimensional crystal lattice having 2 atoms separated by distance ‘\(a\)’. In the case of a three dimensional crystal with \(a, b, c\) as cell parameters, constructive interference occurs when [1]:

\[
a \left( \sin \gamma_1 - \sin \delta_1 \right) = h \lambda
\]

\[
b \left( \sin \gamma_2 - \sin \delta_2 \right) = k \lambda
\]

\[
c \left( \sin \gamma_3 - \sin \delta_3 \right) = l \lambda
\]

Equations (2.7) are known as Laue conditions and they need to be satisfied by the incident wave to get diffracted by the three dimensional crystal lattice. As these equations can be reduced to Bragg’s condition, they are also referred to as 3-dimensional representation of Bragg’s law and its visualisation is discussed in the next section.

### 2.2.2.2 Three-dimensional description of Bragg’s law

Figure 2-2 illustrates the formation of electron diffraction pattern obtained with an incident parallel beam because all the incident electrons have the same orientation. Nevertheless, they are not well adapted for the description of electron diffraction patterns obtained with a convergent incident beam. In this case, electrons having different orientations can satisfy Bragg’s law simultaneously to produce diffracted beams. Thus, for each set of \((hkl)\) lattice planes, it is useful to consider the geometrical locus where the incident rays satisfy Bragg’s law [7]. As shown in Figure 2-4, this is a cone (often called Kossel cone) located around the lattice plane normal, and with vertex semi-angle \(\pi/2 - \theta_h\).
2.2 Electron scattering

Figure 2-4 Kossel cones (geometrical loci of incident rays satisfying Bragg’s law) location for a set of lattice planes. In (a, b) the Kossel cones for incident and diffracted beams having vertex semi-angle $\pi/2 - \theta_B$ and oriented to the $(hkl)$ lattice planes is shown & in (c, d) similar process is shown for $(\overline{h} \overline{k} \overline{l})$ lattice planes (redrawn from [7])

As the Bragg angle $\theta_B$ is identical with the incidence angle $\theta$ for a particular $(hkl)$ lattice plane, the incident and diffracted cones are also identical. The diffraction phenomenon can also occur on the other side of the $(hkl)$ planes, i.e. for the set of $(\overline{h} \overline{k} \overline{l})$ lattice planes corresponding to the $\overline{h} \overline{k} \overline{l}$ incidence and diffracted Kossel cones
as illustrated in Figure 2-4 (c), (d). This phenomenon is crucial in understanding the formation of Kikuchi and HOLZ lines in Convergent Electron Diffraction Patterns. Hence, it is further discussed in the following sections.

### 2.2.3 Reciprocal lattice

The reciprocal lattice is a geometrical construction which may be used as a tool in conjunction with the Ewald sphere construction to simplify considerably the interpretation of electron diffraction patterns. If $a$, $b$, $c$ are unit cell translation vectors (i.e. the vector that connects two lattice points) in real space and $a^*, b^*, c^*$ are unit cell translation vectors in reciprocal space, then their directions are related as [1]

$$a^* \cdot b = a^* \cdot c = b^* \cdot a = b^* \cdot c = c^* \cdot a = c^* \cdot b = 0$$  \hspace{1cm} (2.8)

which can be understood as $a^*$ is normal to $b$ and $c$, and so on. Moreover their lengths are related as:

$$a^* \cdot a = b^* \cdot b = c^* \cdot c = 1$$ \hspace{1cm} (2.9)

Hence, the two important properties of reciprocal lattice vector $g_{(hkl)}$ are,

1. The vector $g_{(hkl)}$ to the point $(hkl)$ of the reciprocal lattice is normal to the plane $(hkl)$ of the crystal lattice.
2. The magnitude of $g_{(hkl)}$ is $1/d_{(hkl)}$ where $d_{(hkl)}$ is the interplanar spacing of the family of $(hkl)$ planes.

Generally the reciprocal lattice is defined as an array of points which corresponds to a particular $(hkl)$ lattice planes and each point is referred to as “nodes”.

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2.3 Specimen illumination (Parallel & Convergent beams)

Figure 2-5 Formation of electron diffraction pattern with (a) incident parallel beam (b) incident convergent beam with beam convergence angle ‘α’

Figure 2-5 shows a simplified ray diagram of electron diffraction pattern formation with incident parallel and convergent beams. As the crystal is oriented in such a way that the electron beam illuminates a single set of parallel crystal planes, the diffraction patterns consist of a row of spots/discs. In this three beam condition (one transmitted & two diffracted beams), when the specimen is illuminated with parallel incident beams then a spot diffraction pattern is obtained in which the diffraction spots are separated by Bragg angle \( \theta_B \) and if the illumination is done with a converged probe, it results in a diffraction pattern with discs instead of spots. The convergent beam disc can be regarded as the collection of spot patterns because each point in the central disc is a
2. Theory of Convergent Beam Electron Diffraction (CBED) technique

resultant of parallel incident beams having all possible orientations within the convergent incident beam. Hence Convergent Beam Diffraction patterns are the intensity map of transmitted and diffracted intensities as a function of the orientation of the incident beam with respect to the set of \((hkl)\) lattice planes.

2.3.1 Ewald sphere

![Ewald sphere construction in reciprocal space](image)

The Ewald sphere construction as shown in Figure 2-6 is an elegant method for determining the diffraction wave-vectors from a crystal. It is drawn in reciprocal space with the end point of incident beam vector \(\vec{k}_0\) as the origin. A \(hkl\) diffracted beam is produced when a \(hkl\) node of the reciprocal lattice is exactly located on the Ewald sphere. In Figure 2-6, this situation occurs for the \(hkl\) node located at point ‘G’. If \(\vec{k}_0\) and \(\vec{k}\) are the wave vectors used to describe both the direction and the wavelength of
the incident and diffracted beams, then the Ewald sphere construction shows that Bragg’s law can also be written as [8]:

\[ k - k_0 = g_{hkI} \]  \hspace{1cm} (2.10)

2.3.2 Deviation parameter

Figure 2-7 Schematic illustration of excitation error (or) deviation parameter in-case of parallel (a), converged (b) incident beams and their respective diffraction patterns are shown in (c, d). The contrast of the diffraction patterns is reversed to give an improved appearance and the Convergent incident beam case is exactly in the two-beam (i.e. one transmitted and one diffracted beam) condition
2. Theory of Convergent Beam Electron Diffraction (CBED) technique

In the case of X-ray and neutron diffraction, to obtain a diffracted beam, the crystal must be tilted in such a way that a \( hkl \) node should lie exactly on the Ewald sphere. However, for electron diffraction, it is more flexible because from Equation(2.3), it is evident that the wavelength of an electron is very small, which makes the radius of the Ewald sphere \( R = 1/\lambda \) very large. As the specimens investigated under electron microscopy are thin foils having very small thickness, the nodes of the reciprocal lattice are no longer spots but are extended along the direction of least specimen thickness as shown in Figure 2-7. These transformed short rods are known as “relrods”\[7\]. The length of these relrods depends upon on the equation \( 2/t \) or \( 2/\xi_g \) where \( \xi_g \) is the extinction distance of \( hkl \) reflection.

The deviation parameter \( s \) is an expression which represents the misorientation of the set of \( hkl \) lattice planes with respect to the exact Bragg orientation. In the case of a parallel incidence beam, by convention, ‘s’ is positive if the node of the reciprocal lattice is lying inside the Ewald sphere \[7\].

In Figure 2-7(a) as the node of reciprocal lattice is outside the Ewald sphere, its sign is negative. However, for a converged beam of incidence, it is more complicated. Due to the fact that the different oriented beams satisfy Bragg’s law simultaneously, the convergent-beam diffraction pattern as shown in Figure 2-7 (d) is regarded as a map of transmitted and diffracted intensities versus the deviation parameter \( s \). The maximum of diffracted intensity and the minimum of transmitted intensity are observed for the value of \( s = 0 \). Moreover \( s > 0 \) and \( s < 0 \) are symmetrically disposed with respect to the \( s = 0 \) line. Based on the deviation parameter, it is possible to tilt the specimen for the required diffraction contrast imaging and the significance of the parameter is further
2.3. Specimen illumination (Parallel & Convergent beams)

illustrated in the brief overview of kinematic and dynamical theories discussed in sections – 2.4, 2.5.

2.3.3 Extinction distance

As discussed in earlier sections, when the specimen is illuminated by an electron beam, it scatters in different directions as it propagates from top to bottom surface of the crystal thickness. Assuming the incident beam is in two-beam condition (i.e. only one diffracted beam is strongly excited) the transmitted and diffracted beams each are split up into two branches at the top surface of the crystal. The difference between each of the branches consists of a difference in wavelength depending upon the considered specimen and chosen beam conditions (i.e. <220> or <400> beams). Due to this wavelength difference, interference occurs between the branches and the electron beam will become extinct and re-emerges as it progresses through the crystal. This phenomenon illustrates the extinction distance as, the characteristic distance between two minima or maxima of the transmitted or diffracted electron beams. In other words, the intensity of the electron beam at the exit surface of the specimen depends upon on the path length of the electrons inside the specimen equal to the local thickness of the specimen. In the case of wedge shape samples as used in the present work, this leads to the phenomenon of thickness fringes [1]. At exact Bragg orientation, based on the distance between these fringes, local thickness of the specimen has been determined as discussed in section 4.5.

2.3.4 Zone axis Ewald sphere or Higher Order Laue Zone (HOLZ)

In Figure 2-6, it was shown that when the Ewald sphere intersects with a reciprocal lattice point, a diffracted beam is produced. Generally, the reciprocal lattice is a three-

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1 Extinction distance is a characteristic distance which shows up in both Kinematic and Dynamical treatment of electron diffraction. Its mathematical expression is shown in Dynamical Theory of Electron Diffraction part as discussed in section 2.5.
dimensional lattice and in any given zone axis pattern, a nearly planar section is observed through its lattice. Moreover, the radius of the Ewald sphere is large enough compared to the spacing between reciprocal lattice points. Hence, the Ewald sphere intersects the reciprocal lattice planes that are present parallel in a zone axis orientation as shown in Figure 2-8, and the intersection is at rather large distance from the origin of reciprocal space.

Figure 2-8 (a) Schematic illustration of High Order Laue Zone (HOLZ) (b) Schematic diagram of its corresponding diffraction pattern (adapted from [8])
The set of reciprocal lattice points belonging to a zone axis pattern can be described by means of Zone equation or condition [1]:

\[ hu + kv + lw = n \]  

(2.11)

Where \((hkl)\) represents lattice planes, \([uvw]\) is the beam direction and \(n\) is an integer.

In Figure 2-8(a), it is observed that when the Ewald sphere intercepts the reciprocal lattice points present in layer \(n = 0\) and nearby to the origin ‘o’, a set of reflections are seen in the central area of the diffraction pattern of Figure 2-8(b). This set of reciprocal lattice points are referred to as Zero Order Laue Zone (ZOLZ). In the same way if some of the reciprocal lattice points present in layer \(n = 1\) intercept with Ewald sphere, then a concentric pattern of spots are formed around ZOLZ, and they are referred to as First Order Laue Zone (FOLZ). Based on the value of \(n\), the reciprocal lattice points are referred to as FOLZ or Second Order Laue Zone (SOLZ) and so on. Generally apart from ZOLZ, all the other orders are referred as High Order Laue Zone (HOLZ).

2.3.5 Centre of Laue Circle (CLC)

In sections 2.3 to 2.3.4, the formation of a diffraction pattern or its conceptual illustrations are based on the incident electron beam that was directed along the optic axis of the microscope. In practice, this ideal configuration may not always be found. The incident beam may be tilted, due to misalignment in a microscope or when the electron beam samples several differently oriented crystal lattice volumes. Moreover, it could also occur on purpose, by modifying the orientation of the incident beam with respect to the \((hkl)\) lattice planes.
Figure 2-9 (a) Schematic diagram illustrating Centre of Laue Circle (CLC) phenomenon (b, c) Effect of CLC or beam misorientation ‘ρ’ on the CBED patterns (modified from [7, 9])
When the electron beam is tilted by an angle ‘$\rho$’ as shown in Figure 2-9(a), the crystal reciprocal lattice is also tilted in such a way that the Ewald sphere intersects the ZOLZ plane and forms a circle corresponding to the position (0KL) and this position is referred as Centre of Laue Circle (CLC). In the case where there is no tilt in the electron beam direction then all the circular ZOLZ, FOLZ, SOLZ planes will have CLC at (000) as shown in Figure 2-8(a). As CBED discs consist of a lot of information compared to spot diffraction patterns, the beam tilt has more impact on CBED patterns. With a small tilt angle ‘$\rho$’ in the incident beam direction with respect to optic axis (Figure 2-9(c), it results in a shift of both transmitted and diffracted discs by a distance $t = f \rho$. However, it is important to note that the HOLZ lines present inside the CBED discs remain motionless because their position depends only on the orientation of the lattice planes with respect to the optic axis [7].

2.3.6 Kikuchi lines and Higher Order Laue Zone (HOLZ) lines

In many respects, crystallographic formation of Kikuchi lines is similar to the HOLZ lines. So in this section initially, formation of Kikuchi lines is discussed and further details regarding HOLZ lines are illustrated.

2.3.6.1 Kikuchi lines

Kikuchi lines are observed when a thick specimen is illuminated by means of parallel or convergent incident beams. (Here the thick specimen can be understood as the one which can incorporate multiple scattering along the electron beam direction.) In both the cases (parallel or convergent incident beams), it is possible to view Kikuchi lines but their appearance is much sharper when they are formed in CBED patterns.

Figure 2-10 illustrates the mechanism involved in the formation of Kikuchi lines due to parallel and convergent incident beams. As shown in Figure 2-10(a), due to the parallel
incident beam, the mechanism consists of an inelastic scattering followed by a second diffraction which is elastic in nature. It is possible if after initial inelastic scattering process, two beams of different intensities are focussed at Bragg angles (positions A, B in the Figure 2-10(a)) to a set of \( hkl \) lattice planes. Here if the intensities of both the beams are identical then it is not possible to see any observable effect [7]. However, based on the scattering angles of these beams, the final intensity at positions C and D are obtained. In the present considered case (Figure 2-10(a)), the beams combined at position C have a smaller scattering angle, hence possess greater intensity compared to position D and appear darker (deficient Kikuchi line).

Figure 2-10(b) illustrates the Kikuchi lines formation when the incident beam is a convergent beam. On comparison of Figure 2-10(a, b), it can be observed that illuminated area is much smaller in convergent beam case for the formation of Kikuchi lines. Moreover, as long as the beam convergence angle is greater than the Bragg angle i.e. \( 2\alpha > 2\theta_B \), there will always be some electrons in the probe at the Bragg angle to the planes to fulfil the elastic scattering phenomenon. Due to this, Kikuchi lines formed under convergent incident beam are much sharper than parallel incident beams [7]. Apart from these differences, the Kikuchi line formation is similar to parallel incident beam.

In section 2.2.2.2, it was shown that for a given set of planes, the Bragg condition is satisfied for all the electrons travelling along a conical surface with an opening angle \( \pi/2 - \theta_B \). Extending the analysis of darker and brighter spots at positions C and D in Figure 2-10(a, b) to the three-dimensional case, the incident, diffracted and transmitted rays lies on Kossel cones.
2.3. Specimen illumination (Parallel & Convergent beams)

Figure 2-10 Schematic diagram (a, b) illustrating origin of Kikuchi lines due to parallel and convergent incident beams (c) Intersection of Kossel cones with the Back Focal Plane or viewing screen of TEM (redrawn from [7])
Due to the small Bragg angle, the hyperbolae that were obtained from the intersection of Kossel cones with TEM Back Focal plane tend to appear as straight lines on the viewing screen as shown in Figure 2-10(c). The line near the optic axis of Figure 2-10c appears darker than the background due to the involvement of low scattering beams and it is referred to as deficient Kikuchi line while the one that appears brighter is called an excess Kikuchi line.

Kikuchi lines may be used to determine the exact specimen orientation with respect to the incident beam. Due to the large divergence associated with the Kikuchi patterns (about 10° in semi-angle) the zone axis orientations are easily identifiable. Moreover they are also used to determine the deviation parameter for a particular reflection ‘g’.

2.3.6.2 HOLZ lines

Kikuchi lines discussed so far are basically evolved from ZOLZ planes. When the Ewald sphere intercepts with the HOLZ plane (Figure 2-11), Bragg’s law is satisfied and HOLZ lines are formed. Hence, a HOLZ line is the locus of the Bragg condition for a HOLZ reflection (G). Like Kikuchi lines, HOLZ lines also appear in pairs and the schematic diagram shown for Kikuchi lines formation (Figure 2-10(c)) is applicable for the formation of HOLZ lines. Both Kikuchi lines and HOLZ lines arise from the same elastic Bragg-scattering mechanism but the difference between them lies in the source of electrons in each case. In-elastically scattered wide cones of electrons inside the crystal contribute to the formation of Kikuchi lines whereas smaller cones generated by the HOLZ region leads to the formation of HOLZ lines.

Due to the large angular separation between the HOLZ lines pair, darker lines (deficient HOLZ lines) appear in the central disc of CBED patterns and its brighter counterparts (excess HOLZ lines) appear as HOLZ ring around the central disc. In the schematic
kinematical model shown in Figure 2-11, the deficient and excess HOLZ lines are indicated as small curves. At realistic accelerating voltages, the curvature between Ewald sphere and HOLZ reflection disc is very small and the line segments appear nearly straight. As the HOLZ lines correspond to the HOLZ reflections with large ‘g’ vectors, their positions are very sensitive to any change in the lattice parameters [10].

The location of HOLZ lines that can be observed in the central disc of a CBED pattern and Kikuchi lines seen in electron diffraction patterns can be computed in a similar way. For the former HOLZ lines case, a single line needs to be mathematically formulated whereas for latter Kikuchi lines case, two lines needs to be simulated. The code for the HOLZ lines simulation can be found in [11] and all the required HOLZ lines simulation used in this thesis are performed using JEMS® software [12].

Figure 2-11 Schematic diagram showing the formation of HOLZ lines based on kinematic approximation (redrawn from [13])
In case of small angle approximation, the Bragg’s law stated in equation (2.6) can be rewritten as:

\[ 2d_{hkl} \theta_B \approx \lambda \] (2.12)

Where \( d_{hkl} \) is the interplanar spacing of \((hkl)\) lattice planes and in case of cubic crystal,

\[ d_{hkl} = \frac{a}{\sqrt{h^2 + k^2 + l^2}} \] (here ‘a’ is crystal lattice parameter) and wavelength \((\lambda \propto E^{-1/2})\)

Differentiating \((\theta_B, \lambda)\) and \((\theta_B, (d_{hkl} \text{ or } a))\) separately,

\[ \frac{\Delta \theta_B}{\theta_B} = -\frac{\Delta E}{2E} \quad ; \quad \frac{\Delta \theta_B}{\theta_B} = -\frac{\Delta d_{hkl}}{d_{hkl}} = -\frac{\Delta a}{a} \] (2.13)

This indicates that the change in accelerating voltage and lattice parameter modifies the Bragg angle plane that give rise to HOLZ line. In other words, for a given voltage variation, shifts in the HOLZ line position can be misinterpreted as lattice parameter change. To solve this ambiguity, initially from a strain-free region, the accelerating voltage is calibrated and then the shifts in the HOLZ lines are analysed for the change in the lattice parameters.

### 2.3.7 Inelastic scattering

Generally inelastic scattering is incoherent in nature in which the phase relationship between scattered waves is lost and involves a loss in the energy of the incident electrons. The energy analysis of the in-elastically scattered electron beam forms the basis for Electron Energy Loss Spectroscopy (EELS) [14]. The in-elastically scattered beam is generally concentrated about the incident beam directions compared to the more widely spread elastic scattering. There are mainly four types of inelastic scattering.
mechanisms such as Phonon, Plasmon, single electron excitations and direct radiation losses. All the inelastic electrons appear as diffuse background in the CBED patterns and strongly affect the analysis of HOLZ line positions. By means of zero loss energy filtering, it is possible to eliminate the inelastic electrons and improve the appearance of HOLZ lines in CBED patterns. However, by employing some evaluation algorithms such as Radon or Hough transformation, the detection of HOLZ lines in unfiltered CBED patterns can be improved [15].

2.4 Kinematical theory of electron diffraction

To analyse the diffraction patterns (either discs in CBED or spots in selected area diffraction) completely, examination of transmitted and diffracted intensities is required. Mainly the intensity of a \((hkl)\) reflection depends upon the nature of the set of \((hkl)\) diffracting planes, value of deviation parameter \(s\) and the specimen thickness \(t\). Moreover the intensity depends upon the interactions between diffracted beams with the transmitted beam and also interactions between various diffracted beams. There are two theories available to calculate the diffracted intensities; the kinematical theory and the dynamical theory. Both the theories can be applied in two-beam or many beams conditions. In the current section Kinematical theory of electron diffraction and its assumptions are briefly illustrated.

The kinematical theory is the simplest approach for describing mathematically the process of electron diffraction. It is based on the following assumptions:

1. The incident beam intensity is equal to the transmitted beam intensity in other words, there is no absorption as the beam passes through the crystal.
2. The diffracted beam is not re-scattered such that there is no multiple scattering permitted.
2. Theory of Convergent Beam Electron Diffraction (CBED) technique

Obviously, these assumptions can only be fulfilled when the scattering of the electrons is through very thin crystals which are oriented far from exact Bragg condition, in other words, when deviation parameter ‘s’ is large. Moreover, it is applicable for the crystals whose thickness is less than about half the extinction distance [16-17] and no absorption is taken into account.

2.5 Dynamical theory of electron diffraction

To overcome the problems indicated in kinematic theory of electron diffraction, dynamical theory was developed. This assumes that the diffracted beam can be strong and therefore can undergo multiple diffractions. Thus there may be significant interaction between the straight through beam and the diffracted beams. Furthermore, the effect of absorption may also be incorporated into the theory. To understand the behaviour of an electron inside the crystal, the time-independent Schrödinger equation needs to be solved as it describes the wave function of an electron. In this section only important solution of dynamical equations such as the Howie-Whelan equations [18] derived from the Schrödinger equation are presented and very brief insight into the theory is discussed further. For detailed descriptions and derivations, it is recommended to refer to the literature [1, 10, 19-20].

In the case of two-beam kinematic theory, the intensity $I_g$ of a diffracted beam produced by an incident beam with an intensity $I_o = 1$ is given by:

$$I_g = \left| \phi_g \right|^2 = \left( \frac{\pi}{\xi_g} \right)^2 \frac{\sin^2(\pi ts)}{(\pi s)^2}$$  \hspace{1cm} (2.14)
Where $\phi_g$, $\xi_g$, $t$, $s$ represent diffracted wave amplitude, extinction distance, specimen thickness and deviation parameter respectively. Here the extinction distance $\xi_g$ is based on the particular value of $g_{hkl}$ of a material and is given by:

$$\xi_g = \frac{\pi V_0 \cos \theta}{\lambda F_g}$$

(2.15)

Where $V_0$ being the volume of the unit cell.

However, as equation(2.14) does not consider multiple diffractions, based on Howie and Whelan’s mathematical formulation it is possible to understand the variation of amplitudes $\phi$ of incident and diffracted waves as a function of $z$ which is the distance through the crystal. In the two-beam condition the pair of Howie-Whelan differential equation are given as:

$$\frac{d\phi_u}{dz} = \left(\frac{i\pi}{\xi_u}\right)\phi_u + \left(\frac{i\pi}{\xi_s}\right)\phi_s \exp(2\pi isz)$$

$$\frac{d\phi_s}{dz} = \left(\frac{i\pi}{\xi_u}\right)\phi_u + \left(\frac{i\pi}{\xi_s}\right)\phi_s \exp(-2\pi isz)$$

(2.16)

By solving equations(2.16), the diffracted beam intensity can be written as

$$I_s = |\phi_s|^2 = \left(\frac{\pi}{\xi_s}\right)^2 \frac{\sin^2 (\pi ts')}{(\pi s')^2}$$

(2.17)

Equation (2.17) is similar to the solution from kinematical theory except that the deviation parameter $s$ is replaced with effective deviation parameter $s'$ which is given by
$s' = \left( s^2 + \frac{1}{s_g^2} \right)^{1/2}$ \hspace{1cm} (2.18)

From the Howie Whelan equation (2.16), it can be understood that diffraction phenomenon is not a unidirectional issue along the crystal thickness. As the electrons propagate along the crystal, the intensity from the incident beam transmits to the diffracted beam and in the forward scattering event, the intensity from the diffracted beam transmits again back into the incident beam. However the solutions are derived considering electron scattering will travel only in directions $K_0$ and $k_0 + g$ which may not be necessarily valid inside the crystal.

The Bloch waves which are the Eigen functions obtained by solving the Schrödinger equation illustrates the wave propagation through the crystal. However, the Bloch waves are rather mathematical and pure theoretical physics. Hence the pictorial representation of Bloch waves is referred to as dispersion surface. Therefore, the modified Schrödinger equation in terms of Bloch wave coefficients $C_g$ is given as \[10, 20\]:

$$\left[ K^2 - (k + g)^2 \right] C_g + \sum_{b \neq g} U_{g-b} C_b = 0 \hspace{1cm} (2.19)$$

Where $K$ in terms of magnitude of wave vector in vacuum $\chi$ and crystal potential $U_b$ is given by,

$$K^2 = \chi^2 + U_b \hspace{1cm} (2.20)$$

In the case of two beam approximation only the Bloch wave amplitudes $C_0$ and $C_g$ are need to be considered and the equation (2.19) can be written as
2.5 Dynamical theory of electron diffraction

\[
\begin{vmatrix}
K^2 - k^2 & U_{eg} \\
U_g & K^2 - (k + g)^2
\end{vmatrix} = 0
\]  

(2.21)

As equation (2.19) is referred to as the standard dispersion equation of high energy electron diffraction, the two-beam version of it (equation(2.21)) is represented by dispersion surfaces as shown in Figure 2-12.

Figure 2-12 Illustration of dispersion surfaces in two-beam approximation (modified from [1])

As the Ewald sphere shown in Figure 2-6 is drawn without considering the crystal inner potential, the centre of the sphere is determined based on the magnitude of the wave vectors \( k_0 = k = 1/\lambda \). However if the construction is performed by considering the mean inner potential of the crystal, the centre of the sphere is determined based on equation (2.20) and as \( K > (k_0 \text{ or } k) \), the centres are shifted as shown in Figure 2-12. As a
result both incident and diffracted beams split up into two branches and the loci of the starting point of these branches lie on the dispersion surface.

![Diagram](image)

**Figure 2-13 Schematic diagram illustrating HOLZ lines formation based on dispersion surfaces (redrawn from [13])**

Due to the multiple scattering in the dynamical theory, the HOLZ line positions often deviate from the kinematic positions. Based on the dispersion surfaces, it is possible to interpret the dynamical effects such as shift, curvature and multiplicity of HOLZ lines. Figure 2-13 shows the dispersion surface construction for the formation of HOLZ lines in which the HOLZ lines are described as the intersection of two dispersion surfaces centred at ‘O’ and ‘G’. Dynamical effects among the HOLZ lines in a particular zone axis occur due to two different types of interactions among the Laue zones [21]. The first kind i.e. when the interactions between the zero order reflections with HOLZ lines
creates thickness induced HOLZ lines shift and the second kind i.e. the interaction among the HOLZ lines introduces bending of lines near the point of intersection. In the considered zone axis for the strain evaluation, by simulating various dynamical patterns at different thicknesses and discarding the HOLZ line intersections indicating bending of lines, both the dynamical effects are investigated further and discussed in chapter-4.

In brief conclusion, all the major theoretical aspects that are related to electron diffraction are discussed in this chapter. The primary focus was given to Convergent Beam Electron Diffraction concepts as it was used for both lattice strains and polarity analysis there are presented in chapter 4 & 5.
2.6 References


Chapter 3

Instrumentation and Experimental details

The main aim of this chapter is to present the principal functions of various components in the Transmission Electron Microscope (TEM) that were used for acquiring different experimental images for the analysis presented in chapters 4 & 5. In order to achieve the quantitative evaluation successfully, complete knowledge of the complex electron microscope setup and its various operating modes is crucial. Hence in section 3.1, the TEM column is divided into 5 subdivisions including the Illumination system, Specimen stage, Imaging system, Deflection coils & Stigmators and Lens aberrations with each subdivision discussed separately. Then different operating modes of the microscope are presented briefly in section 3.2. Finally various types of samples such as powder and cross-sectional TEM samples that are used for the analysis with their preparation methodology and their respective TEM sample coordinate axes are discussed.
3. Instrumentation and Experimental details

3.1 The Transmission Electron Microscope

When an object is placed between a light source and screen, the magnified image of the object is placed upon the screen but it is out of focus. The only way to obtain acceptable magnification and an in-focus image is to place a lens between object and the screen. Then the image is in the form of shadow graph with contrast variations. The optically dense material prevents the illumination getting through to the screen and less optically dense material allows less or more illumination through, creating the image termed a shadow graph. This is the basic principle of a transmitted image formation in a light or electron microscope. An ideal microscope should provide three features namely Resolution, Contrast and Magnification. According to Sir George Airy’s theory [1], it was illustrated that when using a lens, the image points are made up of central core accommodating 84% of the intensity with diffuse discs around the central core which are referred as Airy discs. This phenomenon was further investigated by Abbé who wrote an equation that describes the resolution of a microscope. It was based on least possible distance between the overlap of two Airy discs. The resolution of a microscope is limited to a great extent by illuminating media and this is the main reason for using electron as source of illumination compared to light.

In the case of Transmission Electron Microscope or a Transmission Light Microscope, the main action of a lens is to magnify or de-magnify the object with relation to the image plane. If the object is further away from the lens than the image plane, then the action of the lens is to de-magnify. If the object is very close in relation to the first image plane then the action of the lens is to magnify. Both types of lens are used in the Transmission Electron Microscope (TEM). The schematic diagram of an electron lens is shown in Figure 3-1 and generally it is made up of coils of copper wire. By passing the current through these coils, a magnetic field is created at the centre. The upper and
lower faces of the gap would act as north or south poles of the magnet. In order to increase the field strength, a device known as pole piece is placed within the lens core to concentrate the magnetic field still further. The size of the gap between the two pole faces relates to the strength of the pole piece, the smaller the gap the higher the strength.

![Schematic diagram of magnetic lens](image)

**Figure 3-1** Schematic diagram of magnetic lens (a) Complete view and (b) Cross-sectional view (adapted from [2])

Figure 3-2 shows the cross-sectional view of the JEOL 2100F Transmission Electron Microscope (TEM) column. As can be observed, between electron gun and viewing window, it consists of various sets of lens systems such as two or three condenser / objective lenses instead of a single lenses. The functionality of each of the lens system is discussed by dividing the TEM column as illumination system, specimen stage, imaging system and described as follows.

### 3.1.1 Illumination system

The illumination system comprises of the electron gun together with the condenser lenses that focus the electrons on to the specimen. Its design and operation determine the diameter of the electron beam at the specimen and the intensity level in the final TEM image.
3. Instrumentation and Experimental details

Figure 3-2 Cross section of JEOL 2100F column used for the study (adapted from JEOL 2100F equipment documentation, JEOL™ company)
3.1.1.1 Electron gun

The electron gun produces a beam of electrons whose kinetic energy is high enough to enable them to pass through thin areas of TEM specimen. Figure 3-3 shows the basic configuration of gun assembly. It consists of three basic components. A cathode assembly which has a very fine aperture, sitting within the cathode assembly is the filament and then sitting opposite to the cathode assembly is the anode. The anode and cathode makes two electrodes of electron gun. The holes around the cathode allow the vacuum to get in so that the filament will last as long as possible. Once the electron source produces electrons, they are accelerated by high voltage towards the zero potential anode.

Figure 3-3 Electron gun assembly (a) Schematic diagram of illumination system (b) Electron gun units (adapted from [2])
3. Instrumentation and Experimental details

Figure 3-4 shows the simplified version of an electron gun circuit. The filament supply with around 3 volts of voltage heats the filament to 1700 K (for Schottky FEG) [3-4]. The accelerating voltage is applied to the Wehnelt or grid cap, which is placed over the filament in the cathode assembly. Due to the electrical relationship between the cap and the filament, there is a complete control over number of electrons that passes down to the column. In order to generate potential (voltage) difference between the cap and the filament either a variable resistance or a separate power supply is placed between the two components, known as bias system. As the potential between the two components is varied, the flow of electrons leaving the cathode also varies. When the filament is very near to the potential of the grid nearly all the electrons are funnelled down through the system, resulting in high beam current, high brightness and large source size. As the bias, or potential difference increases, the mouth of the grid cap acts as an electrostatic lens, funnelling the electrons even closer together and limiting the electron flow through the aperture; this results in lower beam current, less brightness, smaller source size, and with less heating being used, longer filament life is achieved. There is also a field between the Cathode and Anode which is also involved with bringing the emitter electrons to a focus known as the virtual source. The strength of this field also relates to the accelerating voltage, lowering the voltage decreases the field.

Generally there are two main mechanisms by which electron sources operate: Thermionic emission and Field emission. In thermionic sources, the electrons are given sufficient thermal energy to overcome the potential barrier (work function) and escape the source. The source material in thermionic sources either has a high melting temperature (tungsten, W) or a low work function (Lanthanum hexaboride, LaB$_6$). In Field emission sources a large electric field is applied on the source to allow the electrons to tunnel through the potential barrier and emit. The Field emission requires
3.1 The Transmission Electron Microscope

the surface of the emitter to be completely free from contamination and oxides. In cold field emission this is achieved by operating at room temperature but under Ultra High Vacuum conditions (< $10^{-11}$ Torr) [4].

![Figure 3-4 Schematic diagram of gun circuit assembly (adapted from [2])](image)

In thermal Field emission also called Schottky Field Emission Gun (FEG), the surface is kept free from contamination by heating the tip to $\sim 1800$ K and without the need to operate under such high vacuum conditions [5]. Moreover in Schottky FEGs the surface of the emitter is often covered with a thin layer of ZrO$_2$ in order to lower its work function. The JEOL 2100 microscope used in the present work is fitted with a Schottky FEG.

3.1.1.2 Condenser lens system

The lens system immediately below the gun is that of the condenser, its task is to collimate the beam and guide it onto the selected area of the specimen. Figure 3-5 shows the simplified condenser lens system arrangement and its ray diagram. The
3. Instrumentation and Experimental details

electron beam that leaves the gun always tends to be very high. The condenser lens reduces the beam energy and allows it to place the beam on the areas that are desirable to view on the sample. The first condenser lens (C1) takes the virtual source and reduces its size and projects it on to the second condenser lens (C2).

Figure 3-5 Schematic diagram of Condenser lens system (adapted from [2])

Generally, the C1 lens is a strong magnetic lens which is capable of performing large demagnification process. By strengthening the C1 lens, smaller probe sizes can be
achieved and the currents along the C1 lens determine the spot size of the analysis. The C2 lens is a weak magnetic lens which provides little or no magnification. The condenser mini-lens (CM) which is a part of Condenser-Objective system is used to illuminate the specimen with a divergent, parallel or convergent incident beam. It provides little or no magnification but allows the diameter of illumination at the specimen to be varied continuously over a wide range. The CM lens assembly also contains an aperture (called condenser aperture) whose diameter can be changed in order to control the convergence semi-angle (α) of the specimen illumination.

Below the gun unit, there are two sets of coils in groups of four. These are gun alignment coils which enable to tilt or shift the electron beam in order to align the electron gun. Above the specimen, another two sets of coils are present which when tilting and shifting the beam together allow to scan or raster along the surface of the sample. Moreover at the base, eight stigmator coils are available to correct the astigmatism that is present in the beam.

3.1.2 The specimen stage

The specimen stage is designed to hold the specimen as stationary as possible, as any drift or vibration would be magnified in the final image, impairing the spatial resolution of the analysis. There are two basic designs of the specimen stage: side-entry and top-entry. As the TEM that has been used in the present work is attached with side-entry specimen stage model, only its details are discussed. Figure 3-6 shows the schematic diagram of a side-entry specimen stage model. It provides much simpler specimen exchange compared to top-entry model. The most outstanding feature of this model is the ability to provide eucentric tilting stage which allows tilting without image movement. The contamination during the examination is reduced by means of a cold fingers equipped around specimen rod and stage.
Some of the disadvantages of this model such as mechanical vibrations or thermal expansion of specimen holder can be largely reduced by careful design of the specimen holders used [3].

### 3.1.3 Imaging system

The purpose of the imaging lens system in the TEM is to produce a magnified image or an electron diffraction pattern of the specimen on the viewing screen or camera system. The TEM used in the present work consists of set of 5 lenses: the objective, 1\textsuperscript{st} intermediate lens, 2\textsuperscript{nd} intermediate lens, 3\textsuperscript{rd} intermediate lens and projector lens. Apart
from this, it also consists of a twin lens called the Condenser-Objective mini-lens which is located in illumination and imaging system.

3.1.3.1 Objective lens

It is the most important lens in TEM since it is the strongest and due to its position in the TEM column, it accomplishes the major part of the magnification. It is characterized by two different planes: the back focal plane (focal plane lying behind the objective lens), in which the diffraction pattern is formed and the image or the selected area plane. As this is the first lens in the imaging system, any distortions in it are further magnified by other lenses that are present below. Hence, the aberrations (imperfections) in this lens need to be minimised as much as possible for any successful work.

3.1.3.2 Condenser-Objective mini-lens

In general there are two types of objective lens: the high contrast lens known as asymmetric lens and twin or symmetric lens. The TEM used in the present work consists of symmetric lens design which is based on Rieke-Ruska model [6]. As mentioned earlier in section 3.1.1.2, the Condenser Mini-lens (CM) which is located above the specimen provides very large convergence angles as well as very small probe sizes. The Objective Mini-lens (OM) positioned below the objective aperture is used for magnification purposes, specifically low magnification. When there is a flow of current through the CM lens, it generates a field that reinforces the field of the upper objective lens. Therefore the beam crossover of the condenser lenses is raised up at the front focal plane of the upper objective lens resulting in more parallel beam of illumination over the specimen. This is the case for normal TEM imaging mode of operation. If there is no current flow through the CM lens, then it generates a field that cancels out the field of the upper objective lens and the beam crossover of the condenser lenses then takes place at the eucentric height of the specimen. This result in very small illumination
spots that is primarily used are Convergent Beam Electron Diffraction and Scanning Transmission Electron Microscope modes of operation.

### 3.1.3.3 Intermediate lens

As the name suggest, the Intermediate lenses are situated between the Objective lenses and Projector lenses. The two main purposes of this lenses is to attain a wide range of image magnifications by changing its focal length in small steps and to produce a diffraction pattern at the projector object plane by reducing its excitation current.

### 3.1.3.4 Projector lens

It is the last lens in the imaging system which produces the image or the diffraction pattern of the specimen over the entire TEM screen. Generally the Projector lens is a strong lens with a small focal length which is capable of capturing the electrons that are scattered at a large angle with respect to the optic axis.

Figure 3-7 shows the ray diagram of electron beam as it passes through different lenses in JEOL 2100F TEM. Specifically Figure 3-7a – b illustrates the specimen illumination by parallel and converged beam of incidence, Figure 3-7c shows the image magnification once the image is formed by the Objective lens and Figure 3-7d represents diffraction pattern formation in back focal plane of the Objective lens. As the specimen is illuminated with a parallel beam in this ray diagram, diffraction spots are obtained and they are limited by introducing Selected Area aperture. With an addition to the condenser aperture, JEOL TEMs are equipped with an additional alpha selector\(^2\) for adjusting the probe convergence angle more precisely.

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\(^2\) Alpha selector is mainly used for changing the specimen illumination ranging from full convergent beam to parallel incident beam. Alpha selector value set to 9 on JEOL TEMs gives full convergent beam which is generally used in STEM mode. In TEM high resolution mode, Alpha value set to 1 is preferred as it gives narrow parallel beam.
Figure 3-7 Ray diagrams of parallel & Convergent beam illumination system (a–b) and imaging & diffraction modes (c–d) respectively [adapted from JEOL 2100F manual]
3. Instrumentation and Experimental details

3.1.4  Deflection coils & Stigmators

In sections 3.1.1 to 3.1.3, different types of TEM lenses and its main operations are discussed. Apart from these lenses, JEOL 2100 TEM has deflection coils for changing the angle of the electron beam. They are small coils of wires mounted around the electron beam at the top and the base of the condenser system.

The deflection coils which are also called as alignment coils are used for aligning the electron gun with the condenser system and the total illuminating system with the imaging system. When the electron beam is passing through the column and unable to find an earth when it strikes a surface, the electrons get stagnated causing build-up of electrical charge on the wall of the instrument. As a result, strength of the lens tends to be stronger in one direction than another which leads to the phenomenon referred as astigmatism in the recorded images.

The beam with astigmatism is in the form of an ellipse when a lens is out of focus and the beam spot is larger than it should be when the lens is in focus. To compensate this problem, two devices known as stigmators are fitted into the condenser and objective lens of the column. The stigmators are made up of 8 coils at the same level working with equal and opposite currents. Each pair of coils is balanced in such a way that by adjusting the stigmators it is possible to adjust the shape of the electron beam to be perfectly round.

3.1.5  Lens aberrations

Like the lenses made out of glass, magnetic lenses also possess physical (Chromatic) and geometrical (Spherical and Astigmatism) aberrations which distort the image and leads to the loss in the image resolution. In section 3.1.4, one of the geometrical types of
aberration known as astigmatism is discussed; in the current section other types of aberrations are very briefly described.

3.1.5.1 Chromatic aberration

Chromatic aberration relates to the stability of the high voltage source, the variation in heat energy applied to an electron and the stability of all the lenses, resulting in not one fixed focal point but a cycling through a range of focal points. Higher energy electrons are focused later than lower energy electrons or weaker lens strengths focus later than stronger lens strengths. This aberration may also be caused through the specimen being too thick for the accelerating potential in use and a high degree of electron energy is lost within the specimen.

3.1.5.2 Spherical aberration

Spherical aberration relates to the distance off axis that electrons travel when they spiral through an electron lens. The further off axis the electrons travel when passing through a lens the higher the effective lens strength due to the electron spending a longer time within the electron lens field, and the earlier they come into focus.

In the cases of Chromatic and Spherical aberration the result is a focal point which is the area of minimum beam spread, minimum aberration effect, known as the Disc of Minimum Confusion. Based on the degree of spherical aberration, the lens further can give raise to two different types of distortions such as Barrel or Pincushion type distortions. Due to the presence of these two distortions, the lens does not have identical properties (i.e. magnification, degree of rotation) over its area.
3.2 Transmission Electron Microscope operating modes

As discussed in section 3.1.3.1 the objective lens produces either first image pattern of the specimen or its diffraction pattern. Hence the microscope may be operated to produce either a diffraction pattern from a specific region of the specimen or one of the several imaging modes such as Bright Field, Dark Field and High resolution micrographs. For any quantitative analysis of a particular material, detailed correlation between the diffraction pattern and its image is required. In the current section, different imaging and diffraction modes that has used in the thesis has been illustrated briefly.

3.2.1 TEM imaging modes

3.2.1.1 Bright Field & Dark Field imaging

Bright Field (BF) and Dark Field specifically Centred Dark Field (CDF) are the most commonly used imaging modes for crystalline materials. If the objective aperture is placed in the back focal plane of the objective lens to intercept the diffracted beam and only allow the transmitted beam to form an image as shown in Figure 3-8 (a), then obtained image is referred to as a Bright Field image.

![Figure 3-8 Simplified ray diagram of (a) Bright Field (BF) and (b) Centred Dark Field (CDF) image formation](image)
Alternatively if the objective aperture is displaced from the optic axis to intercept the transmitted beam and allow the diffracted beam to contribute to the image formation, then it is referred as displaced aperture Dark Field image. However due to spherical aberration and astigmatism in electron beam, the image quality of displaced aperture Dark Field image is very low. In order to retain the resolution of the BF mode, the illumination incident on the specimen is tilted so that the diffracted electrons travel along the optic axis as shown in Figure 3-8(b). This technique is known as Centred Dark Field (CDF) imaging and is performed by using beam tilt device on JEOL 2100F TEM.

Under exact Bragg condition, the BF and DF images are nearly complementary to each other. The BF images are formed by excluding diffracted electrons and in contrast DF images are created mainly using diffracted electrons. Consequently they are simply high magnification maps of the intensity distribution across the transmitted or diffracted beams produced by the interaction of the specimen illuminated with the incident electron beam. Hence this mode of imaging is referred as diffraction contrast imaging.

3.2.1.2 Phase contrast imaging

Experimentally, the primary difference between diffraction contrast and phase contrast is that phase contrast requires more than one beam to form the image. The phase contrast mechanism is extremely sensitive to experimental conditions and is used primarily for atomic column imaging and biological TEM. Phase contrast is based on the difference in the diffracted and incident beams’ phases which produces variations in image intensity according to the local projected potential in the sample. This provides the ability for lattice resolution imaging. Interpretation of such lattice images requires detailed analysis of the instrumental conditions such as sample thickness, objective lens defocus and Contrast Transfer Function (CTF) of the microscope. In the present work as
3. Instrumentation and Experimental details

the quantification is limited to electron diffraction patterns (HOLZ lines), the details of instrumental conditions for phase contrast imaging are not discussed any further.

3.2.1.3 Absorption contrast imaging
Absorption or mass/thickness contrast is a high angle scattering phenomenon. The denser or more massive an atom is, the more likely it is to scatter an incoming electron to a high angle. Correspondingly, the thicker the sample is, the better the chances are for an incoming electron to scatter to high angles. Such electrons are scattered out of the image collection system (most typically by the objective aperture) and thus a region of low intensity would appear in the image.

3.2.2 TEM diffraction modes
In Transmission Electron Microscope, based on the way the specimen is illuminated, the diffraction modes are fundamentally classified as Selected Area Electron Diffraction (SAED) and Convergent Beam Electron Diffraction (CBED) modes. To project a diffraction pattern on the viewing screen the strength of the intermediate lenses is changed so that the plane of the screen is conjugate with the back focal plane of the objective lens. To produce a diffraction pattern using parallel illumination, a selected area (SA) aperture is inserted in the image plane of the objective lens. This plane is conjugate with the object plane of the objective lens and therefore the SA aperture selects the area of the specimen from which the diffraction pattern is taken. Its simplified ray diagram is shown in Figure 3-9(a) which is equivalent to Figure 3-7(d). If the beam is focused to a spot on the specimen, a CBED pattern is formed in the back focal plane of the objective lens as shown in Figure 3-9(b). As discussed in Chapter 2, the CBED diffraction pattern consists of discs with details about crystal lattice and its symmetry.
Figure 3-9 Ray diagrams illustrating different diffraction modes in TEM (a) Selected Area Electron Diffraction (SAED) (b) Convergent Beam Electron Diffraction (CBED) (c) Large Angle Convergent Beam Electron Diffraction (LACBED) (d) Convergent Beam Imaging (CBIM)
In the present work, apart from CBED mode of operation, its variant techniques such as Large Angle Convergent Beam Electron Diffraction (LACBED) [7] and Convergent Beam Imaging (CBIM) [8] techniques are performed based on the requirement of the experiment. The illumination conditions for both these techniques are almost similar to the CBED mode but in case of LACBED, the specimen is raised or lowered by a distance ‘h’ from its normal position in the object plane as shown in Figure 3-9 (c). As a result apart from reciprocal lattice information, LACBED pattern consists of shadow image of the illuminated area. In case of CBIM technique, the specimen is located at the eucentric height but the incident beam is focused above or below the specimen. Figure 3-9 (d) shows the simplified ray diagram of CBIM technique for which the illumination is focused below the specimen. Like LACBED patterns, the CBIM patterns provide information on both the direct space (the image of the illuminated area) and the reciprocal space. For LACBED patterns, the reciprocal information is in focus and the image is out of focus but for CBIM, the opposite is true i.e. only image is in focus.

3.2.3 Scanning Transmission Electron Microscopy

With the addition of scanning coils in TEM as shown in Figure 3-10(a), it is possible to scan the focused probe over the specimen in similar way as Scanning Electron Microscope (SEM). The main advantage of this mode of operation compared to TEM mode is imaging lenses are not used to form the images. Hence the defects in the imaging lenses do not affect the image resolution. The objective and projector lenses are just used to change the effective camera length between the specimen and detector plane. Moreover from Figure 3-10(a), it can also be seen that the specimen illumination in STEM mode is achieved by using a converged beam. Hence by stopping the scanning beam, it is possible to perform Convergent Beam Electron Diffraction (CBED) in STEM mode of operation. Because of this feature it is possible to acquire a CBED
3.2 Transmission Electron Microscope operating modes

pattern from a desired position in STEM image. Also, STEM mode gives smaller probes than TEM mode, because in STEM mode, the objective Pre-Field is being used to focus the beam whereas in TEM mode, only the condenser mini-lens is used.

Once after electrons leave the specimen in STEM, the scattered beams are selected either by Bright Field (BF) or Annular Dark Field (ADF) detectors. The electrons that have been scattered through very small angles (< 20 mrad) normally form STEM Bright Field images. These are identical to TEM Bright Field images. But in STEM mode due to the absence of chromatic aberration, it is possible to image a very thick sample which is not possible in TEM mode. When the electrons are scattered through at higher scattering angles, by means of an Annular Dark Field detector, the STEM dark field images are produced. Based on the degree of scattering angle as shown in Figure 3-10(b), the obtained images are divided into Low Angle Annular Dark Field (LAADF) or High Angle Annular Dark Field (HAADF) images. Figure 3-10(c) shows the range of different signals that are obtained when the STEM probe samples the specimen. At higher scattering angles, the coherent effects of elastic scattering are neglected and the scattering is entirely Thermal Diffuse Scattering (TDS) [9].

When the scattering angle is in the range of 20 to 60 milliradians (LAADF), the scattering process might consist of one or two Bragg diffracted beams and this operating range may be used for imaging strain contrast at the interfaces [9]. But at higher angles greater than 60 milliradians (HAADF), this Bragg scattering is completely attenuated by thermal vibrations and the collected signal is dominated by incoherent TDS approaching atomic number (Z) dependence [10]. Therefore the intensity of atom columns in HAADF-STEM imaging depends on the average atomic number Z of individual atom columns (approx. proportional to the square).
Figure 3-10 (a) Schematic representation of ray paths in CBED/STEM mode (adapted from [11]) (b) Simplified diagram of STEM Bright Field (BF), Annular Dark Field (ADF) and High Angle Annular Dark Field (HAADF) Detectors and their annular range with respect to the inner diameter of the detector (c) Schematic diagram showing signals that are produced in STEM image formation (adapted from [12])
3.3 Sample preparation

The qualitative interpretation of HAADF-STEM images is relatively straightforward (i.e. when a bright spot is appeared, it can be concluded that it is an atom column as its intensity is independent of microscope defocus). But for quantitative interpretation of HAADF-STEM images, i.e. determination of chemical composition of atom columns based on intensities requires extensive image calculations based on Multi-slice or Bloch wave approaches and image matching [13]. The quantitative interpretation details of HAADF imaging are not further discussed as they are not employed in the present study.

3.3 Sample preparation

In this thesis, the studies are performed on different Nanomaterials and epitaxial thin films grown over <001> and <111> substrates. Hence different techniques are applied for preparing the TEM samples accordingly.

3.3.1 Nanomaterials

To examine nanomaterials which are in the form of powder under TEM, they are initially dispersed in a suitable solution and the mixture is suspended over a holey carbon film supported by copper grids. The chosen solvent should be compatible with the nano-material and in the present study ethanol was used as a solvent as it was found to be chemically inert on evaporation over copper grids and moreover no agglomeration of nano-particles are obtained. Preparing the TEM samples in this way is relatively simple but however it is not suitable for epitaxially grown thin films.

3.3.2 Cross-sectional TEM sample of thin films

Figure 3-11 illustrates the basic steps involved in the preparation of cross-sectional TEM samples.
Figure 3-11 Schematic diagram illustrating cross-sectional TEM sample preparation
3.3 Sample preparation

Initially as shown in Figure 3-11(a, b) the wafer is cleaved perpendicular to its flat edge i.e. <110> direction with a diamond scriber into two pieces of dimensions ~ 2mm x 6mm. Then a sandwich structure is prepared by joining the upper faces i.e. area of interest of the pieces with a fast curing epoxy such as Gatan’s G-2 epoxy. By means of a tuned piezo cutting tool (such as Gatan 601 Ultrasonic cutter), at the middle of the stack as shown in Figure 3-11(c), the structure is sliced into a cylindrical form having diameter of 2.3mm. To avoid cross contamination that would have resulted from the cutting process, the cylindrical structure is cleaned thoroughly with isopropanol and glued into brass tube having a diameter of 3mm. When the epoxy inside the brass tube is completely annealed, using a thin blade diamond tipped saw, the assembly is sliced into a series of discs having a thickness of around 400μm. By mechanically grinding on either side of each disc against polishing pads sized 5 - 40μm, its thickness is reduced to 80μm and cleaned thoroughly with isopropanol to eliminate contamination. Before performing the ion milling process, the discs are dimpled i.e. spherical shaped deepening on either side using Gatan’s Dimple grinder (Model No. 656) as shown in Figure 3-11(f) to a thickness of around 30μm at the centre of the disc. Finally Ar-ion milling process was performed using the Gatan Precision Ion Polishing System (PIPS), for obtaining the electron transparency at the centre of the disc.

The parameters of the ion milling process needs to be chosen based on the material used. For a silicon based wafer as used in the present work, at the start of the milling process to have a high etching rate, the beam energy of 4 kv with ion guns focused at 5° (top) and 3° (bottom) are used. Once the perforation started to appear, to have a low etching rate and larger electron transparent region, the beam energy was reduced to 2.5kv and ion guns are focussed at 4° (top) and 2° (bottom). As the PIPS system used in the present work is equipped with a CCD attached to a LCD display, the entire process
can be monitored and based on the interference fringe colour pattern [14] near the edge of the perforation, the ion milling process was stopped when the desirable thickness level has been attained. Moreover, during the milling process, the ion beam modulation option from which the continuous exposure of the specimen to the incident beam is avoided and liquid nitrogen stage was employed to reduce the specimen heating during the preparation.

3.3.2.1 TEM sample crystal axes

![Diagram showing crystal axes orientation for (a) (001) and (111) silicon wafers and (b) Cross-sectional TEM sample crystal axes orientation for <001> and <111> silicon wafers]

<table>
<thead>
<tr>
<th>Direction</th>
<th>&lt;001&gt; Si wafer</th>
<th>&lt;111&gt; Si wafer</th>
</tr>
</thead>
<tbody>
<tr>
<td>Thinned direction or Zone axis</td>
<td>(110)</td>
<td>(112)</td>
</tr>
<tr>
<td>Parallel to interface</td>
<td>(110)</td>
<td>(110)</td>
</tr>
<tr>
<td>Perpendicular to interface</td>
<td>(001)</td>
<td>(111)</td>
</tr>
</tbody>
</table>

Figure 3-12 Cross-sectional TEM sample crystal axes orientation for <001>, <111> silicon wafers
In the present work, thin films grown over both $<001>$ and $<111>$ silicon substrates are analysed. As a result, the cross-sectional TEM samples that are prepared from these wafers possess different crystal axes due to the different crystal growth directions. In the current section, the crystal axes directions of both the systems are illustrated. Here the brackets $[...]$ and $<...>$ are used to indicate crystallographic direction and families of directions, whereas brackets $(...)$ and $\{...\}$ are used to represent crystallographic plane and families of planes respectively. Figure 3-12(b) shows a silicon wafer with major flat edge. The flat edge for both $<001>$ and $<111>$ wafers is identical i.e. $[110]$ direction.

The cross-sectional TEM samples are prepared from these wafers by cleaving the wafer perpendicular to its flat edge and as a result, the $<001>$ grown substrate consists of $[110]$ direction as zero-tilt zone axis whereas $<111>$ grown substrate has $[112]$ direction as its zero-tilt zone axis. Based on this, the TEM samples have crystal axes directions as indicated in Figure 3-12.

In a brief conclusion, an outline of main components of TEM is described. A particular emphasis was given to different operating modes of JEOL 2100 Field Emission TEM, as the majority of work presented in this thesis is carried out using it. Finally, sample preparation methods of different materials used in this work are discussed.
3.4 References


Chapter 4

Interfacial Strain analysis in Si$_{1-x}$Ge$_x$-Si Strained Layer Superlattice structure

In this chapter the Convergent Beam Electron Diffraction (CBED) technique is implemented over an individual Si$_{1-x}$Ge$_x$-Si Strained Layer Superlattice (SLS) structure for evaluating the lattice strains between the SLS bands which are in the size range of approximately 10nm wide. Before evaluating the HOLZ lines inside the CBED discs, the effect of surface relaxation occurred due to the thinning of cross-sectional TEM thin foils is discussed in section 4.3 and the geometry of the SLS bands is examined using high resolution HAADF imaging in section 4.4.

As the analysis presented in this chapter is mainly discussed with respect to the specimen thickness along the electron beam direction, the adopted method of thickness determination using CBED is illustrated in section 4.5. Furthermore, due to the large dynamical effects in zero-tilt zone axis of <001> cross-sectional TEM sample, strain analysis using CBED needs to be performed in different high index zone axis. Thus, to determine the appropriate orientation for the analysis, various zone axes along the <004> kikuchi line was investigated by means of JEMS® software and verified for any dynamical shifts among HOLZ line intersections in the considered zone axis due to thickness variations. In addition to this, calibration of TEM accelerating voltage which
is a prerequisite for the lattice parameter/strain analysis using HOLZ line positions is presented in section 4.6.

Using a focused electron probe in Scanning TEM mode, CBED patterns were acquired along the line scans performed outside and across the bands of the considered SLS nanostructure. As the behaviour of the HOLZ lines appearance acquired from outside & inside of the SLS tends to be different, similar quantification process is not applicable for both the cases. The split HOLZ lines which are composed of two strong outer lines with weak inner fringes are quantified for lattice plane bending angle as illustrated in section 4.7 and the shifts in the HOLZ line position are evaluated for a unique set of lattice parameters as discussed in section 4.8. Moreover, the lattice strain variation across the bands of the SLS structure is determined for different specimen thicknesses as shown in section 4.9 and in section 4.10, the analysed bending angles & strain variation plots were compared to finite element simulations to validate the results.
4.1 Introduction

Characterisation of elastic strains is a crucial process in the development of advanced devices in the semiconductor industry [1]. The quantitative knowledge of local lattice parameters/strains leads to a better understanding of the underlying physical mechanism related to the mobility of electrons and to achieve optimised strain engineering in the device performances [2]. Strains present in the semiconductor devices arise from various origins. In electronic components (MOS, CMOS), strains are non-intentionally produced during the growth process such as oxidation or deposition of materials with different mechanical properties from those of silicon. In the case of epitaxially grown thin films such as SiGe alloys epitaxially grown on Si substrates, the strains are directly induced due to the lattice mismatch between the two materials. To study these lattice strains, techniques such as Micro-Raman spectroscopy or X-Ray diffraction are quite easily accessible methods that gives analysis results with reasonable sensitivities [3]. However the spatial resolution offered by them is usually greater than 500nm which is insufficient for strain investigation in the modern devices [4]. In the present work by employing CBED technique in Transmission Electron Microscope (TEM) equipped with Field Emission Gun, the strain analysis in Si-SiGe epitaxial layers is performed in order to achieve high spatial resolution and greater sensitivity.

4.2 Material properties

Both Silicon (Si) and Germanium (Ge) are group IV semiconductors which are crystallised in a diamond lattice structure. They are regarded as two Face Centred Cubic (FCC) Bravais lattices that are displaced to each other one quarter of the space diagonal [5]. As shown in Figure 4-1, in a diamond lattice, each atom is bonded to four equivalent nearest-neighbour atoms located at the corners of a regular tetrahedron with
nearest distance of $\frac{\sqrt{3}}{4}a$ where ‘$a$’ is the lattice constant. One conventional cubic cell consists of four such tetrahedrons. These diamond structures are the resultant of directional covalent bonding through sharing the four valence electrons of one atom with its four nearest neighbours.

At 300K, the lattice constants of Si and Ge are 0.5431nm and 0.56575nm [6] respectively. Due to this there exists a lattice misfit ($f$) between these two materials which is given by:

$$f_{\text{Si-Ge}} = \frac{a_{\text{Ge}} - a_{\text{Si}}}{a_{\text{Si}}} = 4.18\%$$  \hspace{1cm} (4.1)

Due to the miscible nature of Si and Ge materials, they can form $\text{Si}_{1-x}\text{Ge}_x$ alloy of diamond lattice structure with $x$ ranging from 0 to 1. Based on the Vegard’s law, the
lattice constant of $\text{Si}_{1-x}\text{Ge}_x$ can be calculated as $[7]$, $a_{\text{SiGe}} = a_{\text{Si}} + (a_{\text{Ge}} - a_{\text{Si}})x$. However
from the experimental analysis of Dismukes et al. [6], it was shown that there exists a slight deviation (no more than $10^{-3}$ Å) from Vegard’s law. Hence the lattice constant of $\text{Si}_{1-x}\text{Ge}_x$ alloy at room temperature is given by the equation-(4.2) [8] and has been considered in this thesis wherever required.

$$a_{\text{SiGe}}(x) = 0.5431 + 0.0200326x + 0.0026274x^2$$ (4.2)

### 4.3 Strain description

#### 4.3.1 Bulk epitaxial layers

Due to the high quality growth of Si-SiGe heteroepitaxial layers over the single crystal silicon substrate, it was always considered as a particular interest in the device applications and fundamental research. Depending upon the alloy composition, it is possible to achieve alloy band gap wave length in the range of 1 to 1.5μm which is a very useful range in several bipolar and discrete opto-electronic devices [9]. As the band gaps, band offsets and band structures are strongly dependent upon the strain state within the individual epitaxial layers, experimental characterisation of layer strains does possess considerable significance. As the Ge lattice constant is around 4% greater than Si lattice constant, when a thin layer of SiGe is epitaxially grown on a Si substrate, the SiGe film is laterally compressed to match the in-plane substrate lattice. However, in the bulk epitaxial layers, when a thin film of Si is grown on SiGe layer, the thin Si film does not possess the tensile strain state. The mechanism illustrated in Figure 4-2(b) is valid for bulk epitaxial layers where only SiGe layers undergo compressive strains and Si layers maintain lattice matching with thick silicon substrate beneath.
Based on the deposition rate of the thin film on the substrate, it is possible to obtain mono-crystalline orientation between the individual thin films and the substrate. Once it is achieved, the film growth can be considered as pseudomorphic or coherent in nature and the layers share a common in-plane lattice constant. Due to this, a mismatch strain arises along the growth direction <001> and it is defined as

\[ m_{001} = \frac{a_{001} - a_s}{a_s}; \quad a_s = \text{Substrate lattice constant} \] (4.3)

![Figure 4-2 Schematic diagram (a) individual layers and substrate in strain-free state (b) Bulk Superlattice structure with compressed SiGe layers](image)

Generally when the magnitude of this lattice mismatch is < 1%, it is possible to achieve a coherent growth rate in thin films. As the width of the thin film is increased beyond the critical thickness, then the conditions are much favourable for the introduction of misfit dislocations at the interface. In case of thinned epitaxial layers, the superlattice can be considered as a stack of alternatively arranged strained thin films. Generally this
is only valid if the width of the silicon layers present between SiGe layers is less than
twice the width of SiGe layers. In other words, if the silicon layers inside a Si-SiGe SLS
are three to five times wider than the alloy layers, then the Silicon layers retain the
undeformed bulk structure [10].

4.3.2 TEM samples

In section 3.3.2, the various steps involved in TEM sample preparation were briefly
discussed. Generally transparency to electrons depends upon the electron wavelength
and on the extinction distance, specific to a material and its diffracting planes.
Conventional imaging techniques (dark and bright fields) and diffraction (SAED)
require specimens to be few hundreds of nanometres thick and for HRTEM imaging, it
requires even smaller thickness, below approximately 50nm depending on the material
analysed. Moreover in CBED patterns to view Higher Order Laue Zone (HOLZ) lines,
the specimen needs to be few hundreds of nanometre thick. Here the important point to
consider is, as the specimen is thinned down from its bulk state, the strain state is
altered at its free surfaces as illustrated in Figure 4-3. The schematic diagram shown in
Figure 4-3 was drawn by Prof. Shohei Nakahara [11].

Surface/strain relaxation in periodic superlattices is well established field and has been
the main objective of the theoretical work performed by Treacy and Gibson [12-13].
Their work was based on an <001> oriented strained superlattice cubic material and
using Fourier series, the authors analytically calculated the strain gradient generated by
the cross-sectional thinning along [100] direction of the interface plane. If ‘t’ is the
thickness in the thinning direction and ‘A’ being the total width of the strained layers in
an SLS, then from earlier study conducted by Gibson et al. [14], it was concluded that
the level of relaxation is fixed and is based on the ratio of ‘t’ and ‘A’.
4. Interfacial Strain analysis in $\text{Si}_{1-x}\text{Ge}_x$-$\text{Si}$ Strained Layer Superlattice structure

Figure 4-3 Schematic diagrams of (a) Bulk Si-SiGe Strained Layer Superlattice (SLS) structure (b) Slice of TEM specimen obtained from bulk SLS (c) An illustration of tetragonal distortion at the Si-SiGe interface [15]

In Figure 4-3(c), it is shown that at the interface of the Si and SiGe layers due to their lattice mismatch, the Si layer is in tension and SiGe layer is in compression resulting in tetragonal distortion. However, this is only true when relaxation effects are not taken into consideration [16]. Due to the thinning of the TEM specimens, the strained film can undergo completely or partially relaxed along the thinned direction. This leads to the change in distortion symmetry from tetragonal to orthorhombic symmetry [17-18].

4.4 Specimen geometry

The specimen used in the present study is a cross-sectional Si/SiGe calibration sample known as Mag-I-Cal™ [19]. As shown in Figure 4-4(b), it consists of few Strained Layer Superlattice (SLS) structures separated by depositing silicon layers of around 1200nm thick. As the width of this silicon layer is relatively large, it acts as a substrate for each individual SLS structure and the tensile force arising due to lattice mismatch
between individual SLS and substrate is limited to the very edges of the layer. This effect was schematically shown as strain contrast in Figure 4-4(a).

The individual SLS (Figure 4-4(c)) consists of a period of five SiGe layers (thickness of 9.6nm – 11.9nm) separated by Si spacer layers (thickness of 10.7nm – 14.2nm). As the thickness of these Si spacer layers is nearly similar to SiGe layers, the mismatch strains may be distributed in both the layers[10]. All the layers were grown using a Vacuum Generators (VG) V80 Molecular Beam Epitaxy (MBE) system operating at a base pressure of $5 \times 10^{-9}$ Pa on <100> oriented Czochralski Si substrate [19].

![Figure 4-4 (b), (c) [110] Bright Field STEM micrographs of cross-sectional Si/SiGe Strained Layer Superlattice (SLS) structure (a), (d) Schematic representation of interfacial strain contrast formed due to lattice mismatch](image)

Figure 4-5(a) shows the high resolution STEM – High Angle Annular Dark Field (HAADF) image of one particular SiGe band of an individual SLS structure recorded with 60 mrad – 159 mrad as inner and outer collection angles of ADF detector.
4. Interfacial Strain analysis in $\text{Si}_{1-x}\text{Ge}_x$-$\text{Si}$ Strained Layer Superlattice structure

Figure 4-5 (a) [110] STEM – HAADF image of a SiGe layer in an individual SLS structure (b) Corresponding intensity profile covering Si-SiGe interfaces on either sides of SiGe layer
Generally, the spatial resolution of the HAADF technique is based on the size of the scanning coherent electron probe and in the present case it was set to 0.2nm which is smaller than the size of the lattice parameter of the silicon unit cell. As a result, it is possible to image the atomic structure of the unit cell.

As the High Resolution TEM (HRTEM) images are formed due to the reconstruction of diffracted beams, they are sensitive for both objective lens defocus and specimen thickness [20]. However, as discussed in section 3.2.3, the HAADF images possess weak thickness dependence exhibiting no reversals as in HRTEM images and micrographs are simply blurred due to the changes in defocus. Hence, Figure 4-5(a) represents an intuitively interpretable atomic-scale map of the superlattice projection.

In Figure 4-5(a), it is clearly visible that there exists alternative darker and brighter bands inside SiGe layer and due to this, there is no uniformity in the intensity profile taken from SiGe band (Figure 4-5(b)). This may be due to the growth of Si, Ge monolayers obtained from Ge-atom pump mechanism of MBE technique that are exhibiting interfacial ordering phenomenon as explained by Jesson et al. [21]. As the HAADF image represents the direct image of ordering in Si-Ge system, Ge atomic columns are seen with brighter contrast and Si atomic columns appear darker. From low resolution Bright Field STEM images of SLS structure (Figure 4-4(b, c)) and the high resolution HAADF image (Figure 4-5(a)), it can be confirmed that the layers do not possess any noticeable planar or misfit dislocations at the interface and the growth is coherent in nature resulting in elastically strained layers.

**Background**

In this chapter, by evaluating the positions of strain induced deficient HOLZ lines that are present in the central disc of CBED pattern, the local lattice strain distribution across
the SLS layers is quantified. Due to large dynamical effects present in the zero tilt [1 -1 0] zone axis, a different high index zone axis is considered and the orientation is examined based on the HOLZ lines visibility and sensitivity with respect to the lattice distortions. To eliminate the ambiguity issues related to the evaluated lattice parameters using CBED technique, appropriate assumptions regarding the crystal lattice geometry are considered and the shifts in the HOLZ line positions are quantified for a unique set of lattice parameters. However, the illustrated method is applicable only for the sharp and unsplit HOLZ line patterns. In case of split HOLZ lines which occur mainly at the outer interface of the SLS structure, using kinematically simulated HOLZ line patterns, the bending or displacement field of crystal planes along the illuminated column is determined. As the accurate knowledge of the TEM accelerating voltage is a prerequisite for the strain evaluation, the voltage is calibrated frequently from the HOLZ line patterns obtained from the strain free silicon substrate.

4.5 **Specimen thickness measurement**

For any quantitative analysis in TEM, accurate knowledge regarding the foil thickness is crucial. Most of the work presented in this thesis is performed with respect to the specimen thickness (t). In all possible cases where the sample thickness is greater than one extinction distance ($\xi_g$), it is achieved by measuring the intensity oscillations inside the CBED discs that satisfy the (400) two beam condition. Moreover, the method that was adopted here is one of the most accurate methods available with quoted errors as low as 2% [22-23].

From Howie-Whelan equations for the dynamical two beam case, the intensity of the diffracted beam is given as [24-26]:

85
4.5 Specimen thickness measurement

\[ I_g = \frac{\pi^2 \sin^2 \left( \pi s' \right)}{\xi^2_g \left( \pi s' \right)^2} \]  

(4.4)

Where \( s' \) and \( \xi_g \) are the effective deviation parameter and extinction distance respectively. This indicates that the intensity \( I_g \) modulates for a fixed thickness as a function of deviation parameter \( s' \). As discussed in section 2.3.2, in case of CBED, the intensities of different deviation parameter \( s' \) can be simultaneously recorded. Due to this feature, the modulation is visible as Kossel-Möllenstedt fringes with decreasing intensity inside the CBED diffracted disc as shown in Figure 4-6(a).

The diffraction intensity shown in Equation (4.4) is similar to the solution derived from kinematical theory except the deviation parameter \( s \) is replaced with the effective deviation parameter \( s' \) and \( s \) & \( s' \) are related to each other as:

\[ s' = \sqrt{\frac{s^2 + \frac{1}{\xi^2_g}}{s}} \]  

(4.5)

Figure 4-6(b) represents the (400) CBED disc intensity variation and in it minimum intensity is obtained when \( s' \) * \( t = \) integer:

\[ \frac{1}{t^2} \left( s_i^2 + \frac{1}{\xi^2_g} \right) = n^2 \]  

(4.6)

Where \( s_i \) is the deviation of \( i^{th} \) minimum from exact Bragg condition and 'n' is a positive integer. Rearranging equation (4.6), the specimen thickness can be determined using:

\[ \left( \frac{s_i}{n} \right)^2 + \left( \frac{1}{n^2} \right) \left( \frac{1}{\xi^2_g} \right) = \frac{1}{t^2} \]  

(4.7)
4. Interfacial Strain analysis in $\text{Si}_{1-x}\text{Ge}_x\text{-Si}$ Strained Layer Superlattice structure

Figure 4-6 (a) Two beam CBED discs setup using (400) reflection showing Kossel-Möllenstedt or thickness fringes obtained from the Si substrate (b) Plot of (400) disc intensity distribution (c) Measurements of thickness fringe spacing $\Delta \theta_i$ for $i^\text{th}$ fringe with respect to the deviation parameter $s = 0$ position and Bragg angle $\theta_B$ between $s = 0$ positions in transmitted (000) and diffracted (400) discs
Figure 4-7 Plot of $\left( \frac{s_i}{n} \right)^2$ vs. $\left( \frac{1}{n} \right)^2$ for a systematic variation of integer $n = 1$ to 7. Legend on the right side of the plot indicates the linear fitting values and $n = 2$ appear to be the optimum fit.

In Figure 4-6(c), the bright fringe in (400) disc corresponds to the deviation parameter $s = 0$ indicating that it is oriented exactly to the Bragg condition and the values of $s_i$ are deduced based on the distances $\theta_i$ and using them in the following equation:
4. Interfacial Strain analysis in $\text{Si}_{1-x}\text{Ge}_x\text{-Si}$ Strained Layer Superlattice structure

\[ s_i = \frac{\lambda \theta_i}{2\theta_B d^2} \quad (4.8) \]

Here $\lambda$, $\theta_B$, $d$ are electron wavelength, Bragg angle and interplanar spacing of the reflecting planes respectively. In equation (4.7), if the extinction distance ($\xi_g$) of the considered set of conditions is known for sufficient accuracy then by substituting different $s_i$ values obtained from fringe spacing, the thickness can be calculated. However, the value of the extinction distance needs to corrected based on the n-beam condition and the Debye-Waller factor [23]. So as equation (4.7) represents a linear form, by plotting a graph of $(\frac{s_i}{n})^2$ versus $\left(\frac{1}{n^2}\right)$, from the slope and the y-intercept of the plot, it is possible to determine both thickness and extinction distance of the analysis simultaneously. Figure 4-7 illustrates the fitting procedure that was performed on the experimental two beam CBED pattern (Figure 4-6(a)). The measured values are represented by circular markers and corresponding fit as solid lines. The integer value $n$ is varied sequentially from $n = 1$ to 7 and checked for a correlation coefficient that is nearly unity. In the present case, $n = 2$ appears to be the optimum fit giving $1.5 \times 10^{-5}$ as the y-intercept value. This results in a specimen thickness of $259 \pm 5$ nm. By reducing the inelastic scattering in CBED patterns using energy filter, more accurate methods have been discussed in the literature [27]. But due to the unavailability of energy filter, the method that has been discussed was adopted in the entire work.
4.6 Lattice strain measurements

4.6.1 Zone axis orientation

Due to the excess number of HOLZ lines and dynamical nature possessed by them, the zero degree tilt axis which is [1 -1 0] zone axis cannot be used for analysing the lattice parameters using the CBED technique. So the specimen needs to be tilted parallel to Si$_{1-x}$Ge$_x$/Si interface which is perpendicular to the [001] growth direction for analysis. Figure 4-8 shows the Large Angle CBED (LACBED) pattern taken along the [340] zone axis orientation. Due to the defocused illumination in LACBED mode, it is possible to see the shadow image of the analysed region. The HOLZ lines that are nearly parallel and perpendicular to the SLS interface were indexed based on the cubic silicon lattice structure.

In Figure 4-8, it can be clearly seen that the behaviour of the HOLZ lines that are parallel to the SLS interface differ from the one which are oriented perpendicular. The HOLZ lines (-1 1 ±9) exhibit split nature as they approach the interface whereas the HOLZ lines (7 -5 ±1) remain sharp even though they pass over the SLS structure. The reasons for the split behaviour of (-1 1 ±9) HOLZ lines are discussed in section 4.7, but the important point for the present discussion is that the zone axis that is considered for the evaluation of lattice parameters needs to be composed of HOLZ Lines that are orientated parallel and perpendicular to the SLS interface. In the present work the arrangement of HOLZ lines in several zone axes that are oriented along <004> Kikuchi line were examined. Before considering [340] zone axis as the best option for the analysis, other zone axes were compared.
4. Interfacial Strain analysis in $\text{Si}_{1-x}\text{Ge}_x$-Si Strained Layer Superlattice structure

Figure 4-8 [340] LACBED pattern with shadow image of an individual $\text{Si}_{1-x}\text{Ge}_x$-Si SLS structure

In this research all the required HOLZ lines simulations were carried out using Java Electron Microscopy (JEMS®) software [28]. It is possible to perform the simulation of HOLZ lines either kinematically or dynamically. In the case of kinematic HOLZ line simulation, the HOLZ lines positions are given by Bragg’s law and by considering crystal lattice symmetry and TEM accelerating voltage, the patterns were generated. By using the ‘HOLZ shift’ feature, it is possible to implement first-order dynamical
4.6 Lattice strain measurements

diffraction corrections for kinematically simulated patterns. Moreover, generation of HOLZ lines using this type of simulation is very quick and the effect of simulation parameters such as convergence angle (α), lattice constants, camera length, zoom factor are instantly identifiable. On the other hand, dynamical simulations were performed based on Bloch wave approach. As this type of simulation considers the specimen thickness and the multiple scattering effects inside the specimen, the intensity variation in the generated HOLZ line patterns represent a typical experimental pattern. Depending upon the number of beams considered generally the dynamical simulation of one HOLZ line pattern takes about an hour or even more.

Figure 4-9(a – g) represents the HOLZ lines geometry in seven different zone axes that were examined as part of the present work. All the CBED patterns were recorded from strain free regions of the silicon substrate at room temperature and their corresponding dynamically simulated CBED patterns were shown on the right side of the experimental pattern.

Figure 4-9 (a) Experimental and dynamically simulated HOLZ lines in [670] zone axis at 200kv accelerating voltage and the significant HOLZ lines intersection points were marked over simulated pattern
Figure 4-9 (b – d) Experimental and dynamically simulated HOLZ lines at 200kv accelerating voltage in [560], [450], [340] zone axes respectively and the significant HOLZ lines intersection points were marked in each zone axis of simulated pattern.
Figure 4-9 (e – g) Experimental and dynamically simulated HOLZ lines at 200kv accelerating voltage in [230], [350], [120] zone axes respectively and the significant HOLZ lines intersection points were marked in each zone axis of simulated pattern.
4. Interfacial Strain analysis in Si$_{1-x}$Ge$_x$-Si Strained Layer Superlattice structure

<table>
<thead>
<tr>
<th>Zone axis</th>
<th>Tilt angle</th>
<th>Intersection points nearly parallel to [110] direction</th>
<th>Intersection points nearly parallel to [001] direction</th>
<th>Intersection points affected due to dynamical effect</th>
</tr>
</thead>
<tbody>
<tr>
<td>[6 5 0]</td>
<td>4.39°</td>
<td>–</td>
<td>4, 5</td>
<td>–</td>
</tr>
<tr>
<td>[5 6 0]</td>
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<td>2, 3</td>
<td>7, 8</td>
<td>1</td>
</tr>
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<td>[4 5 0]</td>
<td>6.34°</td>
<td>5</td>
<td>–</td>
<td>3</td>
</tr>
<tr>
<td>[3 4 0]</td>
<td>8.13°</td>
<td>2</td>
<td>6, 9</td>
<td>4</td>
</tr>
<tr>
<td>[2 3 0]</td>
<td>11.30°</td>
<td>7</td>
<td>3</td>
<td>–</td>
</tr>
<tr>
<td>[3 5 0]</td>
<td>14.03°</td>
<td>–</td>
<td>4, 6, 8, 9</td>
<td>–</td>
</tr>
<tr>
<td>[1 2 0]</td>
<td>18.43°</td>
<td>–</td>
<td>7, 9, 10</td>
<td>–</td>
</tr>
</tbody>
</table>

Table 4.1 – Analysis of different HOLZ lines geometries in several zone axes oriented horizontally to <110> projection in Silicon cubic crystal and the HOLZ lines intersection points with less than 15° are treated as parallel to the respective direction

Table 4.1 illustrates the HOLZ lines geometry in seven different zone axes that were oriented along the <0 0 4> Kikuchi band. From Figure 4-8, it was evident that the HOLZ lines that are nearly parallel to [-1 1 0] direction are most affected and split HOLZ lines were seen and the HOLZ lines that are nearly parallel to [0 0 1] direction remained unaffected. This indicates that an intelligent choice about a particular zone axis should possess a combination of HOLZ line pairs that are oriented parallel to both [-1 1 0] and [0 0 1] directions. Based on this observation, all the HOLZ lines intersection points in different zone axes CBED patterns were examined.

In all the dynamically simulated CBED patterns of a particular zone axis (right side images of Figure 4-9(a – g)), the HOLZ line intersection points which are clearly visible
in its corresponding experimental pattern were numbered sequentially starting from 1 to 10. The HOLZ line pairs which are inclined less than a $15^\circ$ of inclination angle with respect to [0 0 1] or [-1 1 0] directions are treated as parallel to the respective direction. Moreover, the HOLZ line intersection point which is affected due to dynamical effects cannot be used for the lattice parameter analysis. Some of zone axes which consist of dynamically affected HOLZ line intersection points are listed down in Table 4.1.

With a small tilt angle of about $4^\circ$ - $6^\circ$ from the [1 1 0] projection, the zone axes [6 5 0] and [4 5 0] are easily accessible. However, the former zone axis does not consist of any HOLZ line intersection points that are oriented parallel to the [1 1 0] direction and the latter one does not possess any intersection points oriented parallel to the [0 0 1] direction. Thus these two zone axes were therefore not very promising candidates for the lattice parameter analysis.

The HOLZ lines of the [5 6 0] zone axis appear to be a better option, as they consist of HOLZ lines that are oriented parallel to the [-1 1 0] and [0 0 1] directions. However from Figure 4-9(b), it can be seen that the intensity of HOLZ lines is very low. This is because the zone axis consists of only two First Order Laue Zone (FOLZ) lines and all other lines are evolved from higher Laue zones. The appearance of these higher Laue zone lines are much diminished once they are recorded from strained regions of SLS structure. Hence, this zone axis was not considered for the CBED analysis.

Due to the similar problem as indicated for the [6 5 0] zone axis, the [3 5 0] & [1 2 0] zone axes were not considered as they do not posses any HOLZ line pairs that are oriented parallel with respect to the (1 1 0) direction. Finally, this leaves a choice to be made between the [3 4 0] or [2 3 0] zone axes. Both the axes consists of HOLZ lines that are parallel to the [0 0 1] and [1 1 0] directions but the tilt angle with respect to the
4. Interfacial Strain analysis in Si$_{1-x}$Ge$_x$-Si Strained Layer Superlattice structure

[1 1 0] projection is different among them. When the CBED technique is implemented on MOSFET devices, the required tilt angle needs to be kept as low as possible in order to improve the lateral resolution of the analysed region in between source and drain of the semiconductor devices [29]. With smaller tilts from the [1 1 0] zone axis, the projection effect can be reduced and a large region of interest is available in the MOSFET channel for investigation. However, in the case of SLS structures, as the specimen is tilted parallel to the Si$_{1-x}$Ge$_x$/Si interface, the lateral resolution does not cause a significant problem. Either way to keep the tilt angle smaller, the [3 4 0] zone axis was chosen and all the required CBED patterns for lattice parameter evaluation were recorded from this particular zone axis.

4.6.2 Effect of specimen thickness on HOLZ line positions

Mansfield et al. [30] have shown that HOLZ line positions may be sensitive for the changes in the specimen thickness particularly for a zone axes where two or more strongly excited Zero Order Laue Zone (ZOLZ) dispersion surface branches interact with HOLZ layers. However, authors have commented that this effect is considerably reduced in a zone axis where dynamical effects are relatively weak. To confirm this, the [3 4 0] zone axis HOLZ lines positions were dynamically simulated for different thicknesses and further examined.

Figure 4-10 shows the dynamically simulated HOLZ lines patterns of the strain-free silicon lattice for different specimen thicknesses. When the thickness is about 50nm (Figure 4-10(a)), the visibility of HOLZ lines is very low and cannot be used for lattice parameter determination.
Figure 4-10 Effect of specimen thickness on HOLZ line positions that were dynamically simulated at thicknesses (a) 50nm (b) 150nm (c) 200nm (e) 300nm and the corresponding intensity profile obtained from the marked regions in (c), (e) are shown in (d), (f) respectively.
4. Interfacial Strain analysis in $Si_{1-x}Ge_x$-Si Strained Layer Superlattice structure

Figure 4-10 Effect of specimen thickness on HOLZ line positions that were dynamically simulated at thicknesses (g) 400nm (i) 500nm and the corresponding intensity profile obtained from the marked regions in the patterns are shown in (h), (j) respectively.

With the increase in thickness, the contrast of the HOLZ lines also improved but cannot find any shift in HOLZ line position due to the dynamical effects. This confirms that [3 4 0] zone axis possesses weak dynamical effects compared to any other high symmetry zone axis investigated in the present study. Figure 4-10(d, f, h, j) represents the intensity profile of (-1 1 9) HOLZ line for different specimen thicknesses. With the increase in the thickness levels, the width of HOLZ line is reduced and becomes sharper. As the dynamical simulation has taken the electron absorption into account, with the increase in specimen thickness, the background intensity of the CBED pattern is reduced.
4.6 Lattice strain measurements

4.6.3 TEM accelerating voltage calibration

Generally, the nominal voltage indicated by the microscope is not very accurate in nature. In order to evaluate the strain from the experimental patterns, the comparison of the simulated patterns should be performed at a precisely known accelerating voltage value of the TEM session. From section 2.3.6, it was evident that HOLZ lines are very sensitive for the changes in both lattice parameters and the TEM accelerating voltage. As the HOLZ line in [3 4 0] zone axis exhibit little or no dynamical effects, the distance between the HOLZ line intersection positions is used for the accurate accelerating voltage evaluation [31].

Figure 4-11(a) represents the deficit HOLZ lines present in the central disc of an experimental [3 4 0] zone axis pattern obtained from the strain-free silicon substrate. Based on careful tracing of the experimental pattern, an outline of the HOLZ line positions was drawn as shown in Figure 4-11(b) and the lines were indexed related to cubic silicon crystal symmetry. By changing the accelerating voltage from 201.4kv to 202.5kv with a step size of 0.1kv, a series of [3 4 0] CBED patterns were dynamically simulated and found that the HOLZ lines (7 -5 ±7), (-1 1 ±9), (7 -5 ±5), (7 -5 ±3) are very sensitive with respect to the considered voltage variation range. Hence the distances between these lines is indicated as L1 – L3 as shown in Figure 4-11(b) and used for voltage analysis. Figure 4-11(c) illustrates the linear variations of L1, L2, and L3 distances with respect to the change in the accelerating voltages and using the corresponding fitting equations, the accelerating voltage of the experimental setup was determined. All the required distances in the experimental pattern (Figure 4-11(a)) are measured by considering a reading error of one quarter of HOLZ line width which relates to the accelerating voltage of 201.86kv with an accuracy of ± 0.04kv.
Figure 4-11 (a) Strain-Free silicon [3 4 0] experimental CBED pattern with HOLZ lines at nominal voltage of 200kv (b) Skeletonised [3 4 0] CBED pattern with indexed HOLZ lines (c) Plot of L1, L2, L3 calibration curves relating to the TEM accelerating voltage

In the present method, the camera length was calibrated from the experimental pattern (Figure 4-11(a)) obtained from the strain-free Si region and it is kept constant for all the
simulated patterns. The CBED patterns that are analysed in sections 4.7 and 4.9 are recorded from several TEM sessions. From one TEM session to another, it was found that there was a small variation about 0.1 to 0.2kv in the calibrated accelerating voltage values. Hence, at the start of every analysis, the accelerating voltage was calibrated for the pattern obtained from a strain-free Si region and that particular value was used for the entire JEMS simulation to evaluate HOLZ lines obtained from strained regions.

4.7 Split HOLZ lines

In a LACBED pattern (Figure 4-8) obtained near an individual SLS structure, splitting behaviour was displayed by the HOLZ lines that were inclined parallel to the Si$_{1-x}$Ge$_x$-Si interface. In order to quantify the splitting nature more precisely with respect to the interface, by means of a focused electron probe, the [3 4 0] HOLZ lines were recorded in Scanning TEM (STEM) mode of operation. As a consequence, it is possible to measure the electron probe distance with respect to the interface more accurately.

Figure 4-12(a) illustrates the bright field STEM image of an individual SLS structure oriented along the [3 4 0] zone axis and each observatory electron beam position is represented with a dark solid circle (A, B, C). From the [3 4 0] HOLZ line patterns obtained from the corresponding probe position A – C as shown in Figure 4-12(b), it can be observed that the magnitude of the splitting is mainly dependent upon the distance from Si$_{1-x}$Ge$_x$-Si interface. Moreover it can be noted that all the HOLZ lines do not exhibit the same extent of splitting but they do split symmetrically with respect to the origin point of sharp HOLZ Lines (i.e. pattern obtained from position A).
4. Interfacial Strain analysis in \( \text{Si}_{1-x}\text{Ge}_x - \text{Si} \) Strained Layer Superlattice structure

Figure 4-12 (a) STEM Bright Field image of an individual SLS structure with electron beam positions (A, B, C) that are at distances 428.6nm, 230.6nm, 161.3nm respectively from \( \text{Si}_{1-x}\text{Ge}_x - \text{Si} \) interface (b) [3 4 0] experimental HOLZ lines illustrating HOLZ lines splitting evolution when they are obtained from probe positions A, B, C respectively (c) Corresponding kinematically simulated [3 4 0] HOLZ line patterns
Specifically, the (-1 1 ±9) HOLZ lines which are nearly parallel to the interface as highlighted in Figure 4-12(b) undergo maximum splitting compared to other HOLZ lines in the [3 4 0] zone axis.

Split HOLZ lines are assumed to arise due to inhomogeneous strain fields along the electron beam direction caused due to linear or planar defects at the interface [32], plane bending around precipitates that are not occupying the entire TEM lamella [33] or surface relaxation during the TEM sample preparation [34-35]. From atomic resolution HAADF image (Figure 4-5) and the low resolution bright field STEM image (Figure 4-4(b)), it can be confirmed that no defects exist at the interface and all the individual SLS structures have occupied entire TEM lamella uniformly. Hence with neither defects at the interface nor non-uniform thin film SLS structure, it is apparent that the cause for split HOLZ lines is due to the surface relaxation.

Based on this observation, the experimental widths of the HOLZ lines (Figure 4-12(b)) were quantified by overlapping the kinematically simulated HOLZ line patterns in such a way that they match experimental split HOLZ lines as shown in Figure 4-12(c). In the present case all the calculated patterns were generated using the parameters (i.e. accelerating voltage, convergence angle, crystal orientation) that were precisely calibrated over the strain-free region of the silicon substrate for each TEM analysis. Moreover the overlaid patterns possess a different Centre of Laue Circle (CLC) to represent the electron beam sampling different regions of the bent lattice plane at the interface.
4. Interfacial Strain analysis in Si$_{1-x}$Ge$_x$-Si Strained Layer Superlattice structure

Figure 4-13 (a) Illustration of symmetrical lattice plane bending with respect to split HOLZ lines (b) Kinematically simulated split HOLZ lines (c) Formation of a triplet split HOLZ lines after electron beam interacting three regions of a bent lattice plane. Schematics (a, c) are drawn by Prof. Shohei Nakahara [11, 15]
4.7 Split HOLZ lines

Lattice plane bending is a well-known phenomenon of surface relaxation that occurs in any multilayer epitaxially grown systems [35-38]. Figure 4-13 schematically illustrates the relationship between the lattice planes bending assumption with respect to the experimental split HOLZ lines shown in Figure 4-12(b).

In the experimental pattern (Figure 4-12) obtained from electron beam position ‘B’, there are no intermediate fringes whereas the pattern obtained from beam position ‘C’ does contain an intermediate fringe. Due to this, the patterns obtained from the beam positions A, B, C are referred to as Singlet, Doublet and Triplet respectively for the present discussion.

As shown in Figure 4-13(a, b) the split HOLZ line pattern can be understood as an overlap of two or more CBED patterns obtained from a rotated lattice. When the lattice plane rotation angle is zero then sharp HOLZ lines can be expected. However, due to the surface relaxation if there exists any rotation of lattice planes, the rotated lattice acts as different interacting volumes for the electron beam direction along the crystal thickness and produces HOLZ line patterns from each of the volumes. Based on the number of intermediate fringes observed in experimental split HOLZ lines, it is possible to estimate the number of interacting volumes of the bent lattice planes. In Figure 4-13(c), the formation of triplet split HOLZ line pattern is elucidated by showing three different HOLZ line patterns that were obtained from its corresponding interacting volumes of the bent crystal planes. Moreover, as these crystal volumes have small difference in their orientation with respect to electron beam direction, the evolved HOLZ line patterns possess slightly different Centre of Laue Circles (CLC). Hence, in JEMS software, the experimental width of the triplet patterns is able to be produced by overlapping three HOLZ lines that differ slightly in their CLC’s.
4. Interfacial Strain analysis in Si\textsubscript{1-x}Ge\textsubscript{x}-Si Strained Layer Superlattice structure

Figure 4-14 Schematic diagram illustrating the relationship between the lattice plane bending angle with respect to the width of the split HOLZ line [11, 15]

Figure 4-14 illustrates the quantification process of a bent lattice planes with respect to observed split HOLZ Line. As the separation of a split HOLZ line is directly proportional to the assumed bending angle, the parameter 2\(\Delta\) is directly measured from the width of an experimental split HOLZ line and converted it as angle of rotated lattice plane (2\(\beta\)). All the measured split HOLZ lines were calibrated with respect to the Bragg angle of <0 0 4> kikuchi line which is 1.0588° for a 200kv accelerating beam voltage. Figure 4-15 shows the plots of lattice plane bending angle calculated from the width of (-1 1 9) split HOLZ line for different specimen thicknesses on either side of an individual SLS structure. With increase in the distance from the interface, the magnitude of the bending angle was reduced. For a specimen thickness of 190nm, at a distance less than 50nm from the interface, the split HOLZ lines patterns were too distorted and didn’t reveal any information. This may be due to the effect of a large degree of strain and surface relaxations. At a distance \(\approx 250\)nm from the interface, the bending angle is effectively zero indicating that the misfit strains are no longer affecting the rotation of lattice planes.
Figure 4-15 Plot of lattice plane bending angle versus distance from the interface for different specimen thicknesses on either side of an individual SLS structure
With the increase in the level of specimen thickness, the distorted region near the interface and the distance at which the bending angle tends to become zero are also increased. As discussed in section 4.3.2, based on Gibson and Treacy’s analytical model [12-13], it was illustrated that the surface relaxation tends to be fixed with respect to the ratio of specimen thickness (t) to the superlattice wavelength (i.e. total width of Si$_{1-x}$Ge$_x$ & Si layer widths in an individual SLS) (Λ). In the present study, even for a thickness of ≈470nm and Λ of 24nm, which corresponds to t/Λ of about ≈19.58, there exists a considerable impact of surface relaxation on the specimen. In order to verify the quantification process of split HOLZ lines discussed so far, the plots shown in Figure 4-15 were further compared to Finite Element calculations in section 4.10.

**4.8 Shift of HOLZ lines**

To evaluate the strains inside an individual Si$_{1-x}$Ge$_x$-Si superlattice, CBED patterns were recorded with a step size of 1nm along the line scan performed normal to the edge of the SLS. Figure 4-16(a) depicts the low magnified STEM bright field image of the individual SLS structure showing Si$_{1-x}$Ge$_x$ layers with darker contrast. Figure 4-16(b, c) show the [3 4 0] HOLZ line patterns that were obtained from the electron beam positions labelled as D, E, F, G, H, I in Figure 4-16(a). The identifiable shift in the HOLZ lines intersections due to the mismatch strain between Si$_{1-x}$Ge$_x$ and Si layers are highlighted with black and white arrows on the micrographs. On comparing Figure 4-12 and Figure 4-16, it can be understood that as the degree of non-homogenous strain due to the surface relaxation is greater in the regions outside the SLS, bending of lattice planes and split HOLZ lines does occur. However, due to the decrease in non-homogenous strain levels along the electron beam direction, a shift in the HOLZ line positions was observed from the patterns taken inside the SLS structure.
4.8 Shift of HOLZ lines

Figure 4-16 CBED patterns obtained from Si$_{1-x}$Ge$_x$ & Si layers illustrating shift in HOLZ line intersections (a) STEM Bright Field image of an individual SLS structure with electron beam positions over the layers (b, c) [3 4 0] HOLZ lines obtained from Si$_{1-x}$Ge$_x$ and Si layers respectively
In general, two types of surface relaxations occur in superlattice structures: One between Si\(_{1-x}\)Ge\(_x\) and Si layers inside the SLS structure and a second one between entire individual Si\(_{1-x}\)Ge\(_x\)-Si SLS and Si substrate [39-40]. They can be termed as local and overall relaxations respectively. As the patterns shown in Figure 4-16(b, c) were recorded from a very thick region (470nm along beam direction), the impact of local surface relaxation was less and it was possible to see HOLZ lines with good contrast from first and second bands of Si\(_{1-x}\)Ge\(_x\) and Si layers respectively of an individual SLS. However, when the patterns were recorded from a thinner region (235nm along beam direction), the local surface relaxation effect was dominant and could not acquire HOLZ lines with good contrast from the bands that were located on either ends of an individual SLS structure.

**4.8.1 Data evaluation using Hough transformation**

To evaluate the lattice strains based on the shifts in the HOLZ line positions, it is very crucial to measure the distances between HOLZ lines intersections precisely. Due to the unavailability of energy filter for the present work, the HOLZ line patterns that were obtained from strained regions were prone to noise and high background intensities resulting from inelastic scattering. As Hough transformation is robust to noise, initially both experimental and simulated HOLZ line patterns were analysed using Hough transformation (HT). The HOLZ line detection using HT was employed by using the software code written by Holec *et al.* [41]. Figure 4-17 illustrates the transformation of a particular straight line in image space to a point in the so-called Hough space. If \(\theta'\) is the angle between the line ‘p’ and the abscissa, and \(\vec{R}'\) is the vector normal to line ‘p’ then the straight line in two-dimensional image space can be represented as:
4.8 Shift of HOLZ lines

Figure 4-17 Schematic diagram illustrating Hough transformation of line p in (a) image space and (b) Hough space (Redrawn from [42])

\[ R' = x \cos \theta' + y \sin \theta' \] \hspace{1cm} (4.9)

Where x and y are the Cartesian coordinates of the experimental image plane. The Hough transformation of line ‘p’ described by \( R' \) and \( \theta' \) is a point with coordinates \((R', \theta')\) in Hough space as shown in Figure 4-17(b). By extending this analogy to an experimental HOLZ line pattern shown in Figure 4-18(a), for a particular HOLZ line ‘p’, its corresponding intensity \( I(R', \theta') \) in Hough space (Figure 4-18(b)) is obtained by integrating along ‘p’ in experimental pattern (i.e. image space) and it is given by [41]:

\[ I(R', \theta') = \int I(R' \cos \theta' - t \sin \theta', R' \sin \theta' + t \cos \theta') dt \] \hspace{1cm} (4.10)
4. Interfacial Strain analysis in $\text{Si}_{1-x}\text{Ge}_x\text{-Si}$ Strained Layer Superlattice structure

Figure 4-18(a) Inverted contrast [3 4 0] CBED pattern with detected HOLZ lines (in red colour) for Hough transformation superimposed on experimental HOLZ lines (b) Corresponding Hough transformed map of the experimental pattern representing HOLZ lines with spots and the detected HOLZ lines were indicated with red-coloured circles
4.8 Shift of HOLZ lines

Hence, the resultant transformation in Hough space of all the HOLZ lines present in an experimental pattern gives raise to several spots of varying intensities as shown in Figure 4-18(b). Every spot in the Hough map indicates a particular HOLZ lines with its centre representing the parameters \((R', \theta')\) of the image space. The accuracy of the analysis depends upon the considered sampling parameters of the Hough space i.e. \(n(R)\) and \(n(\theta)\). In the present work, for a 512 x 512 pixel image, the Hough space parameters, \(n(R)\) and \(n(\theta)\) are chosen as 1000 and 1440. This corresponds to a resolution of 0.51 pixels and 0.35° along \(n(R)\) and \(n(\theta)\) respectively.

4.8.2 Non-uniqueness of the CBED lattice parameters

As HOLZ lines evolve from higher Laue zones with large extinction distance and exhibit no sensitivity to the thickness variations (4.6.2), from the geometry of the HOLZ line positions, it is possible to evaluate all the lattice parameters of the investigated material. However, the obtained set of independently determined lattice parameters cannot be unique [43-46]. Figure 4-19 shows three dynamically simulated [3 4 0] HOLZ line patterns that illustrates the same geometry of HOLZ line positions even though they were simulated with different set of lattice parameters.

To avoid this ambiguity of non-uniqueness of the obtained solution from CBED patterns, apart from making assumptions regarding the crystal lattice symmetry, Morawiec et al. [44] has indicated an alternative approach. It was proposed that by projecting the Region of Interest (ROI) in multiple zone axes and by analysing all the different HOLZ line patterns that represented the same ROI, the ambiguity problem can be eliminated.
4. Interfacial Strain analysis in $\text{Si}_{1-x}\text{Ge}_x\text{Si}$ Strained Layer Superlattice structure

Figure 4-19 Dynamically simulated $[3 4 0]$ HOLZ lines with lattice parameters (a) $a = 0.54089\text{nm}$, $b = 0.54309\text{nm}$, $c = 0.54199\text{nm}$, $\alpha$, $\beta$ = 90°, $\gamma$ = 90.2° (b) $a$, $b$, $c$ = 0.54309, $\alpha$, $\beta$, $\gamma$ = 90° (c) $a = 0.54529\text{nm}$, $b = 0.54309\text{nm}$, $c = 0.54419\text{nm}$, $\alpha$, $\beta$ = 90°, $\gamma$ = 89.80°

However, in the current SLS structure it was not possible because after obtaining a series of CBED patterns along a line scan from a ROI in one zone axis orientation, the nanometre sized STEM electron probe builds up contamination over the ROI due to prolonged exposure. The patterns that were subsequently obtained from a different zone axis from the same ROI were diminished due to this contamination. Hence in the present work the quantification of HOLZ line shift was performed by reducing the number of independent lattice parameters based on the following assumption regarding the distorted crystal.
4.8 Shift of HOLZ lines

(a) As no defects were seen at the Si$_{1-x}$Ge$_x$-Si interface (Figure 4-5(a)), the growth is treated as pseudomorphic in nature and the thin layers of the TEM sample undergo orthorhombic distortion [17-18].

(b) The simulations are performed on a transformed silicon cubic unit cell having the crystal axes coordinates of the in-plane parameter $a_{(1 \ 1 \ 0)}$, electron beam/thinning direction parameter $b_{(1 \ 1 \ 0)}$ and growth direction parameter $c_{(0 \ 0 \ 1)}$.

(c) To maintain the pseudomorphic relationship between the thin film and the substrate, the in-plane lattice parameter $a_{(1 \ -1 \ 0)}$ is kept as the bulk silicon value assuming that there exists no relaxation in that direction.

4.8.3 Silicon unit-cell coordinate transformation

For considering the crystal lattice symmetry assumptions and reducing the number of lattice parameters for simulating the HOLZ line patterns in JEMS® software, the reference frame of the cubic silicon crystal was changed to orthorhombic crystal symmetry. Assuming that $(a, b, c)$ & $(a', b', c')$ are the crystal coordinate axes of cubic and orthorhombic lattices respectively, then $a_{(1 \ -1 \ 0)}$, $b_{(1 \ 1 \ 0)}$ and $c_{(0 \ 0 \ 1)}$ are related to $a'$, $b'$, $c'$ as [47],

\[
\begin{align*}
 a' &= 1a - 1b + 0c \\
 b' &= 1a + 1b + 0c \\
 c' &= 0a + 0b + 1c
\end{align*}
\]

In matrix form it can be represented as
4. Interfacial Strain analysis in \( Si_{1-x}Ge_x-Si \) Strained Layer Superlattice structure

\[
(a', b', c') = (a, b, c) \times \begin{pmatrix} 1 & 1 & 0 \\ -1 & 1 & 0 \\ 0 & 0 & 1 \end{pmatrix} \tag{4.12}
\]

The transformation equation can be rearranged as

\[
(a, b, c) = (a', b', c') \times \begin{pmatrix} 0.5 & -0.5 & 0 \\ 0.5 & 0.5 & 0 \\ 0 & 0 & 1 \end{pmatrix} \tag{4.13}
\]

If \([u \ v \ w]\) and \([u' \ v' \ w']\) represent the electron beam directions in cubic and orthorhombic crystal lattices respectively then from equations (4.13) & (4.12), they can be written as:

\[
\begin{align*}
u & = 0.5(u' + v') \\
v & = 0.5(v' - u') \\
w & = w'
\end{align*} \quad \Rightarrow \quad \begin{align*}
u' & = u - v \\
v' & = u + v \\
w' & = w
\end{align*} \tag{4.14}
\]

Figure 4-20 represents the modified silicon lattice structure in orthorhombic form and consists of 4 atoms in its basis. Due to the reduction in the number of atoms in the orthorhombic unit cell compared to the cubic form, the required simulations can be performed much more quickly. Moreover, the lattice constants of the current transformed structure are:

\[
a_{(1 \ 1 \ 0)} = b_{(1 \ 1 \ 0)} = 0.38403 \text{nm} \quad \text{and} \quad c_{(0 \ 0 \ 1)} = 0.54309 \text{nm} \tag{4.15}
\]
4.8.4 Geometry of HOLZ line shifts in [3 4 0] zone axis

In section 4.6.1, it was found that the [3 4 0] zone axis orientation is favourable for lattice parameters evaluation and from LACBED pattern of an individual SLS structure (Figure 4-8), it was observed that there exists a clear impact on HOLZ line positions based on the subtended angle of a particular HOLZ line with respect to the Si$_{1-x}$Ge$_x$-Si interface. In the present section, before choosing the suitable HOLZ line intersections for lattice parameter evaluation, the subtended angles of different HOLZ line positions in the considered zone axis were carefully examined. Figure 4-21(a, b) shows the experimental and simulated HOLZ lines obtained from strain-free silicon in the [3 4 0] incident beam direction. The indexing of the HOLZ lines were performed based on cubic lattice symmetry of silicon crystal and moreover the HOLZ lines that were evolved from First Order Laue Zone (FOLZ) and Second Order Laue Zone (SOLZ) were indicated on experimental (Figure 4-21(a)) and simulated (Figure 4-21(b)) patterns respectively.
Figure 4-21 (a, b) Central discs of experimental and dynamically simulated [3 4 0] zone axis CBED patterns illustrating indexed First Order Laue Zone (FOLZ) and Second Order Laue Zone (SOLZ) HOLZ lines of strain-free cubic silicon crystal lattice respectively.
### Table 4.2 HOLZ lines subtended angles with respect to the Si$_{1-x}$Ge$_x$-Si interface

<table>
<thead>
<tr>
<th>Intersection point</th>
<th>HOLZ lines</th>
<th>Angle to the Si$_{1-x}$Ge$_x$-Si interface</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>($7 \bar{5} 7$), ($7 \bar{5} 7$)</td>
<td>≈ 51°</td>
</tr>
<tr>
<td>2</td>
<td>($\bar{1} 1 9$), ($\bar{1} 1 9$)</td>
<td>≈ 8.7°</td>
</tr>
<tr>
<td>3</td>
<td>($7 \bar{5} 5$), ($7 \bar{5} 5$)</td>
<td>≈ 60°</td>
</tr>
<tr>
<td>4</td>
<td>($7 \bar{5} 3$), ($7 \bar{5} 3$)</td>
<td>≈ 71°</td>
</tr>
<tr>
<td>5</td>
<td>($7 \bar{5} 1$), ($7 \bar{5} 1$)</td>
<td>≈ 83°</td>
</tr>
<tr>
<td>6</td>
<td>($10 \bar{8} 6$), ($10 \bar{8} 6$)</td>
<td>≈ 64.5°</td>
</tr>
<tr>
<td>7</td>
<td>($\bar{6} 4 \bar{1} 0$), ($\bar{6} 4 \bar{1} 0$)</td>
<td>≈ 35.5°</td>
</tr>
<tr>
<td>8</td>
<td>($\bar{9} 7 \bar{1}$), ($\bar{9} 7 \bar{1}$)</td>
<td>≈ 85°</td>
</tr>
</tbody>
</table>

Though dynamical simulations are rather time consuming, they exhibit the experimental patterns well in detail as shown in Figure 4-21. As the silicon crystal possess a Face Centred Cubic (FCC) lattice, the experimental HOLZ lines (Figure 4-21(a)) depict a mirror symmetry perpendicular to the [0 0 1] direction. All of the relevant HOLZ line intersections of the [3 4 0] zone axis were marked sequentially from 1 – 8 and their inclination angle with respect to [1 -1 0] direction is shown in Table 4.2. Moreover the measured angles were indicated from an undistorted silicon crystal. To understand the moving behaviour of the HOLZ line intersection points 1 – 8 in strained regions, different HOLZ line patterns were simulated by creating a distortion in $b_{(1 1 0)}$ and $c_{(0 0 1)}$ directions separately and examined further.
4. Interfacial Strain analysis in $Si_{1-x}Ge_x-Si$ Strained Layer Superlattice structure

Figure 4-22 Dynamically simulated CBED patterns illustrating shift in HOLZ line positions for the variations in $b_{(110)}$ lattice parameter (b), (c) and $c_{(001)}$ lattice parameter (d), (e)
Figure 4-22 illustrates the shift in the simulated HOLZ line positions due to the variations in both $b_{(1 \ 1 \ 0)}$ and $c_{(\theta \ 0 \ 1)}$ lattice parameters. Figure 4-22(a) shows the [1 7 0] zone axis HOLZ lines in other words the orthorhombic form of the [3 4 0] zone axis, in the strain-free condition. When a distortion of 0.0043nm is created in $b_{(1 \ 1 \ 0)}$ direction, then Figure 4-22(b, c) represents the shifts in HOLZ line positions due to the considered distorted lattice. Similarly when a distortion of 0.0043nm is introduced in $c_{(\theta \ 0 \ 1)}$ direction, then Figure 4-22(d, e) indicates the respective HOLZ line shifts in the strained lattice direction.

On comparing Figure 4-22(b, c) with Figure 4-22(d, e), it can be understood that the HOLZ line intersection points (1 – 8) which are inclined less than 70° with respect to Si$_{1-x}$Ge$_x$-Si interface (shown in Table 4.2) were affected due to the changes in both the $b_{(1 \ 1 \ 0)}$ and $c_{(\theta \ 0 \ 1)}$ directions and causes shift in the HOLZ lines positions. However, the intersection points that are oriented greater than 70° were affected only due to the distortion in the $b_{(1 \ 1 \ 0)}$ direction and result in the shifts in HOLZ line positions. To be precise, it can be confirmed that the HOLZ lines which are aligned nearly perpendicular to the Si$_{1-x}$Ge$_x$-Si interface were affected only due to the changes in $b_{(1 \ 1 \ 0)}$ lattice parameter. Therefore, based on the distance between the intersection points 5 and 8 which are the points that were inclined nearly perpendicular to the Si$_{1-x}$Ge$_x$-Si interface, the $b_{(1 \ 1 \ 0)}$ lattice parameter was determined. As an experimental HOLZ line pattern obtained from a strained region consists of distortion impact from both $b_{(1 \ 1 \ 0)}$ and $c_{(\theta \ 0 \ 1)}$ lattice parameters, initially after determining the $b_{(1 \ 1 \ 0)}$ parameter, the $c_{(\theta \ 0 \ 1)}$
lattice parameter was found subsequently by adopting a bilinear interpolation technique. The quantification process was elucidated by considering an experimental pattern that was obtained from electron beam position ‘D’ in Figure 4-16 and discussed further.

4.8.5 Determination of unique set of lattice parameters from shift of HOLZ lines

Figure 4-23(a, b) illustrates the [3 4 0] HOLZ lines obtained from strain-free silicon substrate and Si$_{1-x}$Ge$_x$ layer of an individual SLS structure. As indicated in Table 4.2, all of the experimental HOLZ line intersections were numbered sequentially from 1 – 8 and the clearly identifiable shifts in intersections points were highlighted with arrow marks in both the micrographs.

For quantifying the shift of HOLZ lines shown in Figure 4-23(b), multiple HOLZ line patterns were simulated using the orthorhombically transformed silicon unit cell
described in section 4.8.3. The entire set of required simulated HOLZ lines were performed by keeping the parameter $a_{(1 \ 1 \ 0)}$ to bulk silicon value assuming that no distortion occurs along the infinite long Si$_{1-x}$Ge$_x$-Si parallel interface (section 4.8.2). At the calibrated accelerating voltage and camera length, the parameters $b_{(1 \ 1 \ 0)}$, $c_{(0 \ 0 \ 1)}$ were varied in a range as indicated in Table 4.3 and an array of HOLZ lines patterns with a step size of 0.0015nm and 0.005nm respectively were simulated. As the number of simulated patterns is nearly 100, kinematical simulation with first order dynamical correction was adopted to reduce the required time for the simulation.

<table>
<thead>
<tr>
<th>Fitting linear equations</th>
<th>Variation range &amp; $R^2$ value</th>
</tr>
</thead>
<tbody>
<tr>
<td>(5 – 8) distance</td>
<td></td>
</tr>
<tr>
<td>$2020.92 \ b_{(1 \ 1 \ 0)} - 659.29 \ @ c_{(0 \ 0 \ 1)} = 0.54309 nm$</td>
<td></td>
</tr>
<tr>
<td>(5 – 7) distance</td>
<td></td>
</tr>
<tr>
<td>$-1632.9 \ b_{(1 \ 1 \ 0)} + 682.48 \ @ c_{(0 \ 0 \ 1)} = 0.5331 nm$</td>
<td>$0.38252 \ nm \leq b_{(1 \ 1 \ 0)} \leq 0.40052 \ nm$</td>
</tr>
<tr>
<td>$-1675.4 \ b_{(1 \ 1 \ 0)} + 711.49 \ @ c_{(0 \ 0 \ 1)} = 0.5381 nm$</td>
<td>$0.53310 \ nm \leq c_{(0 \ 0 \ 1)} \leq 0.56810 \ nm$</td>
</tr>
<tr>
<td>$-1578.3 \ b_{(1 \ 1 \ 0)} + 685.88 \ @ c_{(0 \ 0 \ 1)} = 0.5431 nm$</td>
<td>$R^2 (0.995 – 0.998)$</td>
</tr>
<tr>
<td>$-1705.5 \ b_{(1 \ 1 \ 0)} + 747.98 \ @ c_{(0 \ 0 \ 1)} = 0.5481 nm$</td>
<td></td>
</tr>
<tr>
<td>$-1670.4 \ b_{(1 \ 1 \ 0)} + 745.46 \ @ c_{(0 \ 0 \ 1)} = 0.5531 nm$</td>
<td></td>
</tr>
<tr>
<td>$-1631.5 \ b_{(1 \ 1 \ 0)} + 741.85 \ @ c_{(0 \ 0 \ 1)} = 0.5581 nm$</td>
<td></td>
</tr>
<tr>
<td>$-1632.9 \ b_{(1 \ 1 \ 0)} + 753.17 \ @ c_{(0 \ 0 \ 1)} = 0.5631 nm$</td>
<td></td>
</tr>
<tr>
<td>$-1646.0 \ b_{(1 \ 1 \ 0)} + 769.48 \ @ c_{(0 \ 0 \ 1)} = 0.5681 nm$</td>
<td></td>
</tr>
</tbody>
</table>

Table 4.3 Variation of (5 – 7) and (5 – 8) distances in simulated HOLZ line patterns
It can be observed from Table 4.3 that the variation of the considered distances such as (5 – 7) and (5 – 8) distances are linear over the varied lattice parameter range in the simulated patterns. Hence they were used as fitting curves for the lattice parameter evaluation from the experimental pattern. Figure 4-24 represents the plot of the (5 – 8) distance variation in several calculated patterns for different values of \( b_{(1\ 1\ 0)} \) lattice parameter. The solid horizontal line corresponds to the (5 – 8) distance which was measured as 116.81 pixels from a 512 x 512 pixel experimental pattern (Figure 4-23(b)). From the intersection of the solid line with the linear variation of the simulated (5 – 8) distance curve, \( b_{(1\ 1\ 0)} \) lattice parameter was determined to be:

\[
b_{(1\ 1\ 0)} = 0.38404 \text{ nm}
\]

(4.16)

From Figure 4-22(d, e), it was observed that with the change in the \( c_{(0\ 0\ 1)} \) lattice parameter, both the HOLZ lines that are oriented parallel and perpendicular to Si\(_{1-x}\)Ge\(_x\) interface appears to be shifted. However, according to Akaogi et al. [48-50] it was indicated that an indexed HOLZ line intersection pair having larger difference in ‘l’ indices compared to ‘h’ and ‘k’ possesses maximum impact on the lattice parameter that is oriented perpendicular to the interface. In the current case, it is the \( c_{(0\ 0\ 1)} \) lattice parameter. Thus, among 8 different HOLZ line intersection points in the considered [3 4 0] orientation shown in Table 4.2, the HOLZ lines \((7\ 5\ 1), (7\ 5\ 1)\) and \((6\ 4\ 10), (6\ 4\ 10)\) meet the requirement. Therefore, the distance between the corresponding (5 – 7) HOLZ line intersection points was used for the evaluation of \( c_{(0\ 0\ 1)} \) lattice parameter.
4.8 Shift of HOLZ lines

As mentioned earlier, the $c_{(0 \ 0 \ 1)}$ lattice parameter was determined by adopting a bilinear interpolation method using the previously determined $b_{(1 \ 1 \ 0)}$ lattice parameter value and experimental distance between the (5 – 7) HOLZ lines intersection points. Figure 4-25 shows the variation of (5 – 7) distance in simulated patterns with respect to $b_{(1 \ 1 \ 0)}$ and $c_{(0 \ 0 \ 1)}$ lattice parameters. From the observation of the array of (5 – 7) distance in different simulated patterns, it can be seen that the determined $b_{(1 \ 1 \ 0)}$ lattice parameter from Figure 4-24 (i.e. 0.38404 nm), and the experimental (5 – 7) distance (i.e. 

---

Figure 4-24 Plot of (5 – 8) distance variation in simulated patterns with respect to the change in $b_{(1 \ 1 \ 0)}$ lattice parameter and the legend at the bottom indicates the $R^2$ value of the variation
85.76 pixels) is positioned between $c_{(0 \ 0 \ 1)} = 0.5431\text{nm}$ and $0.5481\text{nm}$. In the coordinate form it can be understood as the data point $c_{(0 \ 0 \ 1)}$ lattice parameter which is $(0.38404, 85.76, \ )$ lies in-between $(0.38402, 80.22, 0.5431)$ and $(0.38702, 93.92, 0.5481)$. In Figure 4-25, the required data point location was represented by a dark solid triangle which is positioned between simulated $(5 – 7)$ distances of two different $c_{(0 \ 0 \ 1)}$ lattice parameter values.

The missing value in the data point $(0.38404, 85.76, \ )$ was evaluated by performing an initial interpolation along $0.38404$ and later in $85.76$ directions. After performing the first step of the interpolation, the coordinates $(0.38404, 79.75, 0.5431)$ and $(0.38404, 92.99, 0.5481)$ were obtained as an output. As the first component of the two sets of coordinates is same i.e. both the coordinates lie in $0.38404$ plane after interpolating in the respective direction, the remaining components can be expressed as two different quadratic equations such as: $0.5431 = 79.75m + c; 0.5481 = 92.99m + c$. By solving these two equations, the unknown values ‘$m$’ and ‘$c$’ were yielded as $0.51298 \text{nm}$ and $0.00037 \text{nm}$ respectively. Finally, by performing second step of interpolation in the $85.76$ pixel direction with ‘$m$’ and ‘$c$’ values, the required lattice parameter was determined as:

\[ c_{(0 \ 0 \ 1)} = 0.54537 \text{nm} \tag{4.17} \]
4.8 Shift of HOLZ lines

The accuracy of the entire analysis is mainly dependent upon the level of tracing HOLZ line positions from an experimental pattern. As Hough transformation is adopted in the current analysis for detecting the HOLZ line positions, the error in tracing an HOLZ line is influenced by the resolution of transformed space. As indicated earlier, the HOLZ line positions were extracted with an accuracy of 0.51 pixels from a 512 x 512

Figure 4-25 Plot of (5 – 7) distance and \( b_{(1 \, 1 \, 0)} \) lattice parameter for different values of \( c_{(0 \, 0 \, 1)} \) lattice parameter

![Graph showing the relationship between (5-7) distance and lattice parameter for different values of lattice parameter.](image-url)
4. Interfacial Strain analysis in $Si_{1-x}Ge_x$-Si Strained Layer Superlattice structure

experimental transformed micrograph. Hence this results in a measurement error of 0.0002nm and 0.0004nm in determined $b_{(1 \ 1 \ 0)}$ and $c_{(0 \ 0 \ 1)}$ lattice parameters respectively.

4.9 Strain variation in an individual SLS nanostructure

![STEM Bright Field micrograph](image)

**Figure 4-26 STEM Bright Field micrograph showing 9 alternative $Si_{1-x}Ge_x$ and Si layers of an individual SLS structure**

Using the quantification methodology described in 4.8.5, based on the shift of HOLZ line positions, the lattice strain variation inside an individual SLS structure has been studied further. As it was seen in section 4.7, the surface relaxation in a thinned TEM specimen possesses a strong impact upon the appearance of the HOLZ lines in CBED patterns. Hence the present investigation was performed based on the quantitatively
determined specimen thickness along the electron beam direction near the evaluated lattice strain region of interest of the SLS structure. Figure 4-26 shows the STEM bright field micrograph of an individual SLS structure representing Si$_{1-x}$Ge$_x$ and Si layers with darker and brighter contrasts respectively. To differentiate the layers of the SLS structure, the Si$_{1-x}$Ge$_x$ and Si bands were indexed sequentially using i – ix symbols.

Around 150 to 170 CBED patterns were recorded from all the 9 different bands of SLS structure using STEM probe, operating in spot mode of illumination performed along the line scan parallel to the (0 0 1) crystallographic plane. The specimen drifting during the acquisition of CBED patterns was avoided by selecting the piezo option on the stabilised goniometer and assigning a STEM micrograph that was recorded at a medium range magnification say 400 – 500k for performing the spectrum imaging (i.e. STEM probe operating along a defined line scan over the specimen). To investigate the strain variation between ≈ 10nm wide bands, correct selection of beam conditions is crucial. Hence, initially the effect of a converged beam on a particular interface is discussed schematically and experimentally adopted conditions for the analysis were reported further.

4.9.1 Focused electron beam characteristics

From Figure 4-27, it can be observed that the resolution with which a particular interface can be examined depends upon the basic characteristics of the focused electron probe such as convergence angle (2α) and beam diameter (d). Due to the non-convergence of the electron beam, its diameter continuously changes along the sampling volume.
Due to this artefact, at the interface the intensity change can no longer be a sharp step variation as shown in Figure 4-27(b). It should be noted that with the change in the probe size, HOLZ lines do not move but the selected beam diameter determines the resolution of the analysed region.

In STEM-CBED mode, the convergence angle of the focused electron probe is fixed by the chosen size of condenser aperture of the illumination system. The JEOL 2100F TEM used in the present work is equipped with 4 different sized condenser apertures namely 10, 40, 100 and 200 µm. As the 10 µm aperture is very small and produces
weak beam intensity, a 40 µm condenser aperture was preferred and used for the entire strain evaluation.

Based on the width of the central disc (0 0 0) and the distance between the discs of a known reflection i.e. (4 0 0) reflection, the total convergence angle \(2\alpha\) was directly measured from the CBED pattern that was recorded from the silicon substrate. From small angle approximation as indicated in equation (2.12), the Bragg angle \(\theta_B\) of the (4 0 0) plane was calculated to be 18.48 mrad for a 200kv accelerating beam voltage. As the ratio of the (0 0 0) disc convergence angle to the (4 0 0) plane’s Bragg angle is equal to the ratio of (0 0 0) disc diameter ‘a’ to the distance between (0 0 0) and (4 0 0) discs ‘b’, the total convergence angle can be written as:

\[
2\alpha = 18.48 \times \left(\frac{a}{b}\right)
\] (4.18)

By substituting the values of ‘a’ and ‘b’ that was measured over the micrograph into equation(4.18), the half convergence angle was determined to be:

\[
\alpha = 14.33 \text{ mrad.}
\] (4.19)

This particular value was given as an input for all the simulated CBED patterns using the JEMS software. Depending upon the excitation current in the first condenser lens and the size of condenser aperture, both the convergence angle and the probe size of the analysis were defined.

Though there exists no universally accepted definition for the beam diameter, due to the involvement of the condenser aperture, it was understood that the focused electron probe possesses a Gaussian intensity distribution [52]. From the Full Width Half Maximum (FWHM) or Full Width Tenth Maximum (FWTM) that consists of 75% or
4. Interfacial Strain analysis in $Si_{1-x}Ge_x-Si$ Strained Layer Superlattice structure

90% respectively of the total Gaussian intensity is generally considered as a reasonable value of the beam diameter.

![Gaussian intensity profile of focused electron probe](image)

**Figure 4-28 Gaussian intensity profile of focused electron probe**

By imaging the probe in vacuum and from its intensity profile, it is possible to measure the beam diameter. However, direct imaging of the probe in STEM mode of JEOL 2100F TEM is not possible due to the unavailability of controls to the post specimen lenses. However, in JEOL TEMs’ the Scanning TEM mode is identical to TEM-CBED mode having alpha angle set to 9. With the same excitation currents of C1 condenser lens in both the modes, it is possible to establish similar specimen illumination conditions. Hence, by adjusting the C1 condenser lens currents of TEM-CBED mode equivalent to the value that was used for line scan in STEM mode, the highly magnified image of the focused electron probe was acquired with the CCD camera. Figure 4-28 shows the intensity profile of the recorded probe image that was performed for a length
4.9 Strain variation in an individual SLS nanostructure

of 5.51 nm. From the FWHM of the Gaussian intensity distribution of the profile, the beam diameter was determined to be:

\[
d = \text{1.018 nm}
\]  

(4.20)

Due to the spherical aberration in the determined beam diameter, it is apparent that all the incident beam directions in the converged beam do not exhibit a common focal point (i.e. disc of least confusion). Though there is no way to determine the exact lateral shape of an electron probe, from the theoretical work of Chuvilin et al. [53], it was predicted that the main probe intensity is concentrated in the middle of the beam diameter and a weak scattered intensity is surrounded around it. This again imposes an effect on the CBED patterns that were recorded from the interface. In Figure 4-27(a), it was shown that due to the convergence of the electron probe, the intensity change is no longer a step variation but rather a gradient variation as shown in Figure 4-27(b). Beside this, the non uniform intensity distribution of the focused electron beam adds as an additional effect for the loss of step variation of intensity at the interface.

4.9.2 Specimen thickness effects

In section 4.6.2, from the HOLZ line patterns that were simulated with strain-free parameters, it was observed that with the increase in specimen thickness, the contrast of the patterns was increased and HOLZ lines tend to appear sharper. In the current section, the experimental HOLZ line patterns that were obtained from strained regions of an individual SLS structure are discussed further.
Figure 4-29 (a) CBED patterns obtained from the centres of 9 different bands of an individual SLS structure at a specimen thickness of 130 nm
4.9 Strain variation in an individual SLS nanostructure

Figure 4-30 (b) CBED patterns obtained from the centres of 9 different bands of an individual SLS structure at a specimen thickness of 258 nm
Figure 4-31 (c) CBED patterns obtained from the centres of 9 different bands of an individual SLS structure at a specimen thickness of 474 nm
The considered Si$_{1-x}$Ge$_x$-Si SLS structure was studied at various specimen thicknesses by recording CBED patterns using a probe & step sizes of 1nm each along different line scans performed across Si$_{1-x}$Ge$_x$ and Si bands of the Superlattice. Figure 4-29(a – c) shows the HOLZ line patterns that were obtained from the centres of 9 different bands of the SLS structure at thicknesses of 130 nm, 258 nm, 474 nm respectively. The patterns that were obtained from the respective bands were numbered according to the symbolized bands of an individual SLS structure shown in Figure 4-26.

As discussed in section 4.7, the surface relaxation is dependent upon the ratio of specimen thickness ($t$) to the wavelength ($\Lambda = 24$) of the considered SLS structure. With $t/\Lambda$ ratio equal to 5.45, the CBED patterns shown in Figure 4-29(a) were most affected due to the surface relaxation and no analysable HOLZ line patterns were obtained from the bands i, ii, viii, ix of the SLS. Beside this, the HOLZ line patterns corresponding to the bands iii, iv and vi, vii were exhibiting split behaviour which makes it impossible for quantifying the shift in the HOLZ lines positions.

With the increase in the $t/\Lambda$ ratio to 10.76, the appearance of the HOLZ line patterns was improved as shown in Figure 4-30(b). However, due to the impact of surface relaxation, the HOLZ lines continue to exhibit split nature or no visibility in the patterns corresponding to the bands iii, vii and i, ii, viii, ix respectively. However as the appearance of the HOLZ lines obtained between the bands v and vi was comparatively better, the patterns were quantified for the shift of HOLZ line positions.

Figure 4-31(c) represents the patterns that were obtained at $t/\Lambda$ ratio equal to 19.78. At this particular ratio, it was possible to see all the HOLZ line patterns obtained from the
bands located on either ends of the SLS. As a few HOLZ lines that were inclined parallel to the Si$_{1-x}$Ge$_x$-Si interface appear broader, it can be understood that the impact of surface relaxation still exists. It can be observed that the variation in the HOLZ line positions is quite symmetrical in all the bands of the SLS structure. Hence, the patterns obtained from bands i and ii were chosen and quantified as discussed further.

### 4.9.3 Lattice parameters/strain variation plots

![Plot of measured $b_{(110)}$ and $c_{(001)}$ lattice parameters from the SLS at the specimen thickness of 258 nm](image)

Figure 4-32 Plot of measured $b_{(110)}$, $c_{(001)}$ lattice parameters from the SLS at the specimen thickness of 258 nm

Figure 4-32 shows the lattice parameters variation that was evaluated based on the shift of HOLZ line positions obtained from the CBED patterns acquired along the line scan from bands v and vi of an individual SLS structure at a specimen thickness of 258 nm.
As there was no observable shift in \((5 – 8)\) distance of the HOLZ line intersection points in the recorded CBED images, the variation along \(b_{(1\ 1\ 0)}\) lattice parameter tends to be constant and its value is quite close to the bulk silicon value (0.38404 nm) at room temperature. However, as there was continuous variation along the measured \((5 – 7)\) distance in the experimental HOLZ lines positions, the \(c_{(0\ 0\ 1)}\) lattice parameter illustrates compressive and tensile natures in the regions of \(\text{Si}_{1-x}\text{Ge}_x\) and Si bands of the SLS. Generally, \(\text{Si}_{1-x}\text{Ge}_x\) material tends to be more elastic than Si. Hence, large compressive strain in \(\text{Si}_{1-x}\text{Ge}_x\) bands compensates the minimum tensile strain in Si bands to maintain the lattice matching with the rigid silicon substrate [10].

Figure 4-33 shows the experimental HOLZ line patterns obtained at the end of the band – vi at a specimen thickness of 258 nm. As the FOLZ lines \((7 -5 \pm 1), (-9\ 7 \pm 1)\) are inclined nearly perpendicular \((83°, 85°)\) to the \(\{1\ 1\ 0\}\) plane, the influence of the surface relaxation over them was negligible. Due to this, the identification of the corresponding intersection points of the HOLZ lines i.e. 5 and 8 intersection points were found easily and the determined \(b_{(1\ 1\ 0)}\) lattice parameter value was quite reliable.

Nevertheless, this was not the case in identifying the intersection point 7 in some of the CBED patterns. As the corresponding SOLZ lines \((6 -4 \pm 10)\) were nearly parallel \((35.5°)\) to \(\{1\ 1\ 0\}\) plane, they were affected due to the surface relaxation along the thinning direction and the contrast of lines was deteriorated as shown in Figure 4-33(a), (b). To identify the respective point of intersection (i.e. HOLZ lines intersection No. 7), the automatically determined HOLZ lines positions in Hough transformation were carefully readjusted based on the un-split region of the \((6 -4 \pm 10)\) HOLZ line. Then
from the distance between the intersections 5 & 7 and determined $b_{(1\ 1\ 0)}$ value, the lattice parameter $c_{(0\ 0\ 1)}$ was determined to be 0.54233nm, 0.54329nm in experimental patterns 82, 84 respectively.

Figure 4-33 Experimental CBED pattern (a) 82, (b) 84 obtained from the silicon band no. 6 of the SLS at a specimen thickness of 258 nm
Figure 4-34 Plot of measured lattice strain distribution along \(b_{(110)}\) and \(c_{(001)}\) directions as a function of distance along the line scan over bands \(\nu\) and \(\nu_1\) of the individual SLS structure at a specimen thickness of 258 nm.

Based on the evaluated lattice parameters in bands \(\nu\) and \(\nu_1\) as shown in Figure 4-32, the lattice strain was determined along \(b_{(110)}\) and \(c_{(001)}\) directions using the following expression: \((x - a_s)/a_s\) where \(x\) is the determined \(b_{(110)}\) or \(c_{(001)}\) and \(a_s\) is the substrate lattice constant. Figure 4-34 illustrates the strain variations in the considered bands of the individual SLS structure. As the evaluated \(b_{(110)}\) lattice parameters are close to the unstrained value, it was observed that there exists no strain along that particular direction in both bands analysed. However, due to the larger unit cell of Si\(_1-x\)Ge\(_x\) alloy, a compressive strain was observed along \(c_{(001)}\) direction in band \(\nu\) of the
SLS structure. Moreover, as the widths of both Si_{1-x}Ge_x and Si bands are almost equal to each other, the silicon bands possess tensile strain as observed along c_{(0 0 1)} direction in band vi of the considered individual SLS structure.

Figure 4-35 Plot of measured \( b_{(1 1 0)} \), \( c_{(0 0 1)} \) lattice parameters from the SLS at the specimen thickness of 474 nm

Due to the large surface relaxation effect at a specimen thickness of 258 nm, very faint HOLZ lines were observed in the CBED patterns obtained from the bands i and ii of an individual SLS structure. However, with the increase in specimen thickness resulting in a t/\( \Lambda \) ratio equal to 19.78, the impact of relaxation was reduced and HOLZ lines started to appear in bands i, ii of the SLS structure. Figure 4-35 illustrates the evaluated \( b_{(1 1 0)} \)
& \( c_{(0 \ 0 \ 1)} \) lattice parameters based on the shifts in HOLZ line positions acquired from the line scan across bands i and ii of an individual SLS structure at a specimen thickness of 474 nm. The \( b_{(1 \ 1 \ 0)} \) lattice parameter appears to be constant in both the bands and its value is nearly equal to the bulk silicon values at room temperature (i.e. 0.38404nm) as there were no detectable shifts observed between 5 and 8 HOLZ lines intersection points. However, due to the continuous change in the distance between (5 – 7) HOLZ lines intersection points in the recorded CBED patterns, a constant variation was observed along the evaluated \( c_{(0 \ 0 \ 1)} \) lattice parameters in both the bands.

Figure 4-36 shows the experimental CBED patterns that were obtained from the middle of bands i, ii of the SLS at a specimen thickness of 474 nm. From the appearance of the HOLZ lines, it can be understood that there exists no split HOLZ lines at this particular thickness but some of the HOLZ lines appear broader as highlighted with red dotted lines in Figure 4-36. This clearly indicates that even at \( t/\Lambda \) ratio equal to 19.78, the influence of surface relaxation does exist.

Due to the negligible effect of surface relaxation on the HOLZ lines that are oriented perpendicular to the \( (1 \ \bar{1} \ 0) \) plane, the identification of \((7 \ -5 \ \pm 1), (9 \ 7 \ \pm 1)\) FOLZ lines intersection points was very apparent. Thus the determined \( b_{(1 \ 1 \ 0)} \) lattice parameter values based on 5 and 8 HOLZ lines intersection points were quite reliable in all of the CBED patterns. However, as the SOLZ lines \((6 \ -4 \ \pm 10)\) were nearly parallel \((35.5^\circ)\) to the \( (1 \ \bar{1} \ 0) \) plane, they were affected due to the thinning along the \([1 \ \bar{1} \ 0]\) direction.
Due to this in some CBED patterns, the lines that possess parallel inclination to \((1 \bar{1} 0)\) plane tend to appear broader.

Figure 4-36 Experimental CBED pattern (a) 23, (b) 39 obtained from the centre of the bands i, ii of the SLS at a specimen thickness of 474 nm
4.9 Strain variation in an individual SLS nanostructure

Determining the intersection point 7 which is composed of broad (6 -4 ±10) SOLZ lines and large inelastic scattering in some of the CBED patterns was found very complex. In such cases, the corresponding point of intersection was identified by carefully adjusting the automatically detected HOLZ lines in the Hough transformation to the middle of the broad HOLZ line. Then based on the distance between 5 & 7 HOLZ lines intersection points and the evaluated \( b_{\{1,1,0\}} \) lattice parameter of the experimental CBED pattern, the \( c_{\{0,0,1\}} \) lattice parameter was determined.

![Diagram](image)

**Figure 4-37** Plot of measured lattice strain distribution along \( b_{\{1,1,0\}} \) and \( c_{\{0,0,1\}} \) directions as a function of distance along the line scan over bands i and ii of the individual SLS structure at a specimen thickness of 474 nm
Based on the evaluated lattice parameters shown in Figure 4-36, the lattice strains along $b_{(1 \ 1 \ 0)}$ and $c_{(0 \ 0 \ 1)}$ directions were calculated using the equations $\left( \frac{(b_{(1 \ 1 \ 0)} - a_s)}{a_s} \right)$ and $\left( \frac{(c_{(0 \ 0 \ 1)} - a_s)}{a_s} \right)$ respectively where $a_s$ being the strain-free silicon lattice parameter, and the corresponding variation plots were presented in Figure 4-37. As observed in Figure 4-34, there was a minimal or no strain variation along $b_{(1 \ 1 \ 0)}$ direction but the strain along $c_{(0 \ 0 \ 1)}$ direction exhibit compressive and tensile natures in Si$_{1-x}$Ge$_x$ and Si bands of the individual SLS respectively.

Due to the distinct surface relaxation effects at various specimen thicknesses (i.e. $t =$ 258 nm, 474 nm), the general appearance of CBED patterns from the bands of the considered SLS were significantly different. At $t =$ 258 nm, the analysable HOLZ line patterns were only obtained from the bands located in the middle of the SLS structure (i.e. bands v, vi) whereas, when the specimen thickness is equal to 474 nm, the quantifiable HOLZ line patterns were acquired from all the bands of the SLS structure. However, in either case, by comparing the strain profile shown in Figure 4-34 with Figure 4-37, it can be observed that the strain variation across different bands of the SLS maintains similar variation along $b_{(1 \ 1 \ 0)}$ and $c_{(0 \ 0 \ 1)}$ directions regardless of the change in specimen thickness along the electron beam direction. In order to verify the quantified strain profiles obtained using CBED technique, the bands of the individual SLS structure were mechanically modelled using finite element simulations and the results were compared to the experimental profiles and discussed further.
4.10 Comparison with Finite Element simulations

By implementing Finite Element Modelling, it is possible to understand the spatially varying stress and strain states in complex geometries that are composed of different materials. In the present thesis, the required Finite Element models of the considered individual SLS geometry were performed by Dr. David Tanner [54] and was used for the quantitative comparison of the experimental bending angle and strain variation plots. By considering the surface relaxation effects, different elastic models were generated in ABAQUS software package to representing 90nm, 200nm and 400nm thin TEM lamellae.

As the evaluated SLS structure consists of pseudomorphic growth condition, in the constructed FE models, it was assumed that the strains between its layers are caused only due to the difference in lattice constants of the Si$_{1-x}$Ge$_x$ and Si lattice parameters. Thus, based on the thermal expansion coefficient\(^3\) values of Si [55] and Si$_{0.81}$Ge$_{0.19}$ [56], the misfit parameters in both materials were calculated and from which the strain values between the layers were predicted. In the constructed models, the orientation coordinates $X_{(0 \ 0 \ 1)}$, $Y_{(-1 \ -1 \ 0)}$ and $Z_{(1 \ 1 \ 0)}$ were treated as growth direction, electron beam/thinning direction and in-plane direction respectively.

In order to reduce the computation time and increase the efficiency of the finite element analysis, the structures were modelled by applying the symmetrical boundary condition to the upper half of the structure and Figure 4-38 represents the three dimensional anisotropic elastic model of 90nm deformed TEM foil.

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\(^3\) Thermal expansion coefficient is a material property that indicates the expansion of a material upon heating. In the present work, the residual strains and displacements are predicted based on thermal coefficients of Si and Si$_{0.81}$Ge$_{0.19}$. 

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Figure 4-38 Finite Element model representing deformed TEM thin foil of Si$_{0.81}$Ge$_{0.19}$-Si SLS structure with contour legend of strain values provided on the left side of the image. The displacements are enhanced by factor of 100 to provide better visualisation.
4.10 Comparison with Finite Element simulations

As the assembly of nodes, generally referred to as “mesh” of the constructed models corresponds to the crystal lattice of the real structure, it is possible to compare the evaluated CBED results to the finite element models. The deformations at the free surface of the model were magnified by a factor of 100 to aid visualisation of the effect of surface relaxation. As the t/Λ ratio of the constructed SLS structure is equal to the value of 3.75, the model shown in Figure 4-38 is expected to undergo large surface relaxation and it can be observed that the lattice planes parallel to the (1 -1 0) plane are strongly bent on top & bottom surfaces. Thus, as the electron beam passes through [1 1 0] direction, it samples differently oriented unit cells near the interface and as discussed in section 4.7, split HOLZ lines were recorded in experimental CBED patterns. Therefore, based on the averaged displacements of each node along the [1 1 0] direction, the deformation or the lattice plane bending angles at different thickness outside the SLS of the constructed FE models were quantified and compared to the experimentally evaluated bending angle plots.

In Figure 4-15, based on the outer width of the experimental split HOLZ lines that are inclined nearly parallel to the (1 -1 0) plane, the lattice plane bending angles were evaluated with respect to the distance from Si\textsubscript{1-x}Ge\textsubscript{x}-Si interface and plotted for different specimen thickness values. In Figure 4-39 and Figure 4-40, the measured bending angles from the experimental split HOLZ lines obtained at specimen thicknesses 188 nm, 387 nm were compared to the calculated bending angles obtained from 200nm and 400nm thick finite element models respectively. From both the plots, it can be observed that there is a good agreement between the experimental and calculated bending angle profiles obtained from the region outside the individual SLS layers.
4. Interfacial Strain analysis in Si$_{1-x}$Ge$_x$-Si Strained Layer Superlattice structure

Figure 4-39 Comparison of measured lattice plane bending angle at a specimen thickness of 188 nm with calculated bending angle from 200nm thick finite element model

This confirms that the assumptions related to the HOLZ lines splitting i.e. a bent lattice plane can be considered as, different interacting volumes for obtaining split HOLZ lines is valid. However, in the plots of Figures 4-39 & 4-40, due to the implementation of kinematical approximation of split HOLZ lines, only the outer magnitude of the HOLZ line is determined and compared to Finite Element model. To compare the inner fringes of the experimental split HOLZ line, dynamical simulation needs to be adopted.

As indicated earlier in section 4.7, at a particular specimen thickness from the regions very close to the outer interface of SLS structure, the experimental HOLZ lines were too distorted and cannot reveal any information. In such regions, using the Finite Element
models of the corresponding specimen thicknesses, it is possible to determine the lattice plane bending angles from the displaced nodes along the [1 1 0] direction.

Figure 4-40 Comparison of measured lattice plane bending angle at a specimen thickness of 387 nm with calculated bending angle from a 400nm thick finite element model

To compare the measured strain profiles obtained along the line scan across the bands of the individual SLS structure, the 400nm thick Finite Element model was taken and the displacement of nodes parallel to the \( \chi_{(\theta, \phi, \iota)} \) direction were considered to maintain similar line scan direction used for the experimental CBED patterns.
4. Interfacial Strain analysis in Si$_{1-x}$Ge$_x$-Si Strained Layer Superlattice structure

Figure 4-41 Comparison of measured lattice strain along $b_{(1 1 0)}$ direction at a specimen thickness of 474 nm with calculated lattice strain along $z_{(1 1 0)}$ direction of 400nm thick Finite Element model

From Figure 4-41, it can be observed that both calculated and measured lattice strains along [1 1 0] direction exhibit similar trend of variation across the bands i and ii of the considered individual SLS structure. However, there exists a constant difference of $\approx 2 \times 10^{-3}$ in the magnitudes of the calculated and measured lattice strain values across Si$_{1-x}$Ge$_x$ and Si bands of the superlattice. To understand this difference, a different Finite Element model that represents a bulk specimen with no surface relaxation is constructed and the strain variation along $\varepsilon_{(1 1 0)}$ direction is examined. In Si and Si$_{1-x}$Ge$_x$ layers of the bulk model, it was interesting to observe that the strain along $\varepsilon_{(1 1 0)}$ direction is
This mainly infers that the strain variation profile $\varepsilon_{(0 \ 0 \ 1)}$ obtained from FEM simulation is strongly influenced by surface relaxation and its variation gradually approaches to zero in a situation where there is no relaxation present such as a bulk case. Hence the small discrepancy that was observed in the magnitudes of experimental $\varepsilon_{(0 \ 0 \ 1)}$ and FE simulated $\varepsilon_{(0 \ 0 \ 1)}$ strain profiles obtained at 474nm and 400nm thicknesses respectively of Figure 4-41, may be explained based on the surface relaxations that can occur at different thicknesses.

![Figure 4-42 Comparison of measured lattice strain along $c_{(0 \ 0 \ 1)}$ direction at a specimen thickness of 474 nm with calculated lattice strain along $x_{(1 \ 1 \ 0)}$ direction of 400nm thick Finite Element model](image)

Based on the displacement of nodes averaged over the entire specimen thickness and oriented parallel to the $(0 \ 0 \ 1)$ plane in the 400nm Finite Element model, the $\varepsilon_{(0 \ 0 \ 1)}$...
strains across bands i and ii of the SLS were calculated and compared to the experimental $\varepsilon_{(001)}$ strains obtained at specimen thickness of 474 nm as shown in Figure 4-42. From the calculated $\varepsilon_{(001)}$ strain variations, it can be observed that there exists a step change across the bands of the considered SLS.

In order to obtain a step variation in the experimental HOLZ line patterns acquired from the bands, there should be sudden shift only in the HOLZ line positions obtained from $\approx 2$ nm on either side of $\text{Si}_{1-x}\text{Ge}_x$ (band i) and Si (band ii) interface of SLS. Here, the approximate value of 2 nm is considered based upon the sudden change observed at the interface of calculated $\varepsilon_{(001)}$ strain variation in Figure 4-42. There should be no shift in the HOLZ line positions that are obtained away from the band’s interface of the considered SLS. However, this phenomenon was never observed in any set of CBED patterns that were recorded across the bands of the SLS at different specimen thicknesses. The reason for this discrepancy may possibly be explained due to the non-convergence of the focused electron probe that changes its diameter continuously along the interface volume of $\text{Si}_{1-x}\text{Ge}_x$ and Si bands as discussed in section 4.9.1. Due to this, the evaluated $\varepsilon_{(001)}$ strain profiles using CBED technique cannot possess a step variation as observed in FEM simulation.

Moreover, the multiple Bragg diffractions that could occur along the sampling volume of a 474 nm thick specimen by the converged beam could be another possible reason for this discrepancy. Based on an observation from an experiment performed by Chuvilin et al. [53] using the multi-slice algorithm, it was shown that when a strained interface of a particular specimen is illuminated by a converged beam, the HOLZ lines inside the
central CBED disc do consist of structural information from the regions apart from the beam illuminated area. Therefore, excluding the gradient effect that appears at the interface between the Si and SiGe layers due to the artefact of a converged incident beam, the magnitudes of the calculated and measured strain profiles along $x_{(0 \ 0 \ 1)}$ and $c_{(0 \ 0 \ 1)}$ directions respectively at the middle of both Si$_{1-x}$Ge$_x$ and Si bands of the considered SLS are in good accordance. Thus, it can be finally affirmed that the both evaluated bending angle plots and strain variations between the bands of SLS are in good agreement with the calculated profile of Finite Element models.

**Discussion:**

To determine the mismatch strain between Si and SiGe layers which are approximately 10nm wide of an individual SLS structure, initially TEM accelerating voltage is calibrated to an accuracy of 40 volts. However due to the high voltage instabilities, the determined effective accelerating voltage value appeared to be fluctuating between 100 to 200 volts. To minimise its influence over the determined strain components, the accelerating voltage is calibrated regularly at the beginning of the TEM session based on the CBED pattern obtained from strain-free silicon substrate and further the HOLZ lines are acquired from strained regions of SLS structure for the analysis.

From the experimental CBED, LACBED & simulated CBED patterns, it was observed that the HOLZ lines that are inclined parallel to the SLS interface exhibit different characteristics to lattice distortions compared to the HOLZ lines positioned normal to the interface. Considering this observation and examining different low symmetry zone axes, [340] zone axis is found to be an ideal option for the strain evaluation. With the absence of grain boundaries or defects at the interface, it was assumed that the continuous bending of lattice planes occurred due to surface relaxation along the beam
4. Interfacial Strain analysis in Si$_{1-x}$Ge$_x$-Si Strained Layer Superlattice structure
direction is resulting in the split HOLZ lines at the outer interface of the SLS. From the appearance of the split HOLZ lines, it is inferred that there exists mirror symmetry in the CBED patterns but the intensity of the split HOLZ lines exhibit asymmetry. In a split HOLZ line pattern that consists of no intermediate fringes which is referred to as a doublet in the present research, the intensity of one set of HOLZ lines is dark while other appears to be brighter. This could be due to the planes that are oriented exactly to the Bragg diffraction may give rise to darker contrast HOLZ lines and the brighter contrast HOLZ lines could be from the planes that are nearer to the Bragg condition. Based on kinematical model of surface relaxation, the lattice plane bending angle is determined and compared successfully to the Finite Element simulations. However, due to the adoption of kinematical model, the subsidiary fringes seen inside the experimental split HOLZ lines cannot be well reproduced. To observe the more details of the experimental split HOLZ line, dynamical calculations based on multi-slice [57] or perturbation [37] methods needs to be performed which are generally more time consuming.

As mentioned in section 1.2.1, the shift in the sharp HOLZ lines is quantified by number of groups in different materials consisting of various geometries [38, 49, 58-64]. Specific to Si-SiGe strained layers [65-68], the strain distribution in experimental CBED patterns was performed using $\chi^2$ minimisation procedural matching with respect to the simulated patterns or through dedicated routines such as ASAC® software [69] developed in the framework of European project STREAM [70]. In the present research, based on the assumptions related to the TEM specimen geometry and distortion present between the SLS layers, a unique set of strained lattice parameters are evaluated and related strain distribution across the layers is investigated which has not been performed earlier. By the independent variation of the evaluated lattice parameters in JEMS
software, similar geometry of HOLZ line patterns were not been able to be produced. This confirms that the ambiguity issues related to the non-uniqueness of the obtained solution from the CBED patterns is eliminated. Moreover, due to tracing of HOLZ lines using the Hough Transformation, the lattice parameters evaluated using this approach are been able to achieve an accuracy of $2 - 4 \times 10^{-4}$ nm, which is comparatively good for unfiltered CBED patterns [71]. The quantification approach has been implemented for different TEM specimen thicknesses and as observed in shimotara et al. [40] theoretical elastic relaxation plot, considerable surface relaxation impact is found even at a thickness of 474nm.

In brief, it can be stated that a general procedure has been outlined for quantifying both split and shift of HOLZ lines which occurs commonly in CBED patterns when the electron beam scans dislocation free interfacial region of SLS and successfully compared the evaluated bending angle and strain profiles with respect to Finite Element simulations. The main results of the current chapter can be summarised as follows,

- From low resolution STEM bright field images and high resolution HAADF imaging of Si$_{1-x}$Ge$_x$-Si SLS layers, it was confirmed that the layers do not possess any noticeable planar or misfit dislocations at the interface and the growth is coherent in nature resulting in elastically strained SLS layers.

- From LACBED analysis, it was revealed that HOLZ lines tend to behave differently depending upon their orientation with respect to Si$_{1-x}$Ge$_x$-Si interface. Based on this observation, different high index zone axes were investigated that include large number of HOLZ lines which are oriented nearly parallel and perpendicular to the interface. Among various zone axes studied along <004> kikuchi line, [340] zone axis appeared to be the optimum choice that consists of
weak dynamical effects including no shift in the HOLZ line positions due to the thickness change.

- As the electron beam scans the regions outside the SLS structure, split HOLZ lines are observed. The inhomogeneous strain fields caused by crystal bending that result in split HOLZ lines are related to the surface relaxations which occur due to the thinning of TEM lamella. Moreover, the crystal bending effect is explained based on the kinematical CBED patterns that possess different CLC’s to represent electron beam sampling different regions of the bent lattice planes. From the bending angle plots, it is revealed that even at $t/\Lambda$ ratio equal to 19.58, there exists a considerable impact of surface relaxation in the TEM specimen.

- The ambiguity of multiple solutions of evaluated CBED lattice parameters is eliminated by making physical assumptions regarding the crystal lattice symmetry and demonstrated a methodology for determining a unique set of lattice parameters of Si and Si$_{1-x}$Ge$_x$ layers of SLS nanostructures.

- Shifts in the HOLZ line positions are quantified for different lattice strain variations for various $t/\Lambda$ ratios of individual SLS structures. The appearance of HOLZ lines inside the bands of the SLS is strongly dependent upon the surface relaxation present inside the nanostructures. From the evaluated lattice parameters/strain inside the SLS layers, it has been observed that significant change does occur along growth direction compared to any other directions.
Both the quantified split and shift of HOLZ line profiles are verified by comparing them to the finite element simulations. As the magnitude of the bending angle profiles calculated from split HOLZ lines is in same order of finite element simulations, it is confirmed that the HOLZ lines splitting is due to bent lattice planes near the interface. By excluding the gradient effect caused due to the non convergence of focused electron probe, the evaluated strains based on shift of HOLZ lines are in good accordance with the finite element simulations.
4.11 References


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Chapter 5

Crystal polarity evaluation of Cadmium Sulfide (CdS) Nanostructures

Crystal polarity is an intrinsic property of non-centrosymmetric crystal structures. In this chapter the main aim is to determine the polarity of wurtzite Cadmium Sulphide (CdS) nanostructures that were hydrothermally synthesised parallel to the $c = [0001]$ direction. The breakdown of Friedel’s law in the CdS crystal structure is discussed by plotting many-beam Bloch waves simulated intensity profiles among the Bijvoet related pairs in the $[1 \bar{1} 0 0]$ zone axis. Further, at a thickness less than the extinction distance of $\{0002\}$ beams, by adopting the concept of double diffraction among ZOLZ reflections, the asymmetric intensity distribution among $\{0002\}$ planes is theoretically shown. Finally based on comparing the diffraction intensities in a zone axis CBED pattern obtained from CdS nanostructure with the calculated pattern, the polarity of the nanostructure is determined. As the evaluated CdS nanostructure is a well defined shape, based on the orientation geometry of the shape, the thickness along the electron beam direction is determined and compared to the thickness that was used for calculating the zone axis CBED pattern.
5. Crystal polarity evaluation of Cadmium Sulfide (CdS) nanostructures

5.1 Introduction

Cadmium Sulphide (CdS), in its wurtzite form with band gap energy of 2.42eV is a promising II-VI semiconductor material in the fabrication of high performance Opto-electronic devices such as Light Emitting Diodes (LEDs) and Laser Diodes [1]. One of its important characteristic features is, lack of a centre of symmetry resulting in surface polarity in its crystal structure being the main cause for the formation of asymmetric crystal growth on the opposite surfaces of the same lattice [2]. Hence, to understand its growth process, surface morphology and electronic properties it is crucial to analyse the crystal polarity of the synthesised material. Adopting various techniques such as selective etching [3], X-ray Diffraction [4] and ion channelling, [5] it is possible to analyse the polarity of the bulk material. However, to investigate nanostructures with a high spatial resolution, microscopic techniques should be implemented in Transmission Electron Microscope (TEM). In the present work, using well established Convergent Beam Electron Diffraction (CBED) technique based on its asymmetric intensity distribution in the diffraction discs, the polarity of single crystal CdS structures are analysed.

Using the inorganic hydrothermal synthesis process, the Cadmium Sulphide (CdS) crystals were grown by Armstrong et al. [6]. The growth process mainly involves the aqueous mixture of Thioacetamide and Cadmium Sulphate treated at a temperature of 150°C for a synthesis time of 10 hours and by cooling down the process to room temperature and filtering the aqueous mixture run off, the final product has been obtained. By means of drop cast method as discussed in section 3.3.1, the TEM samples were prepared using holey carbon TEM grids and further used for the electron microscopy characterisations. All the required CBED patterns were acquired in TEM-CBED mode by increasing the excitation current of C1 condenser lens and limiting the
beam convergence angle by choosing the 40µm C2 aperture to produce Kossel-Möllenstedt CBED patterns i.e. the CBED patterns with no overlap.

5.2 Material properties

Generally the CdS crystals are available in both wurtzite and zinc-blende phases. Apart from its stacking order, both the phases are identical to each other.

Figure 5-1 Cadmium Sulphide with (a) wurtzite structural model and (b) [1 1 -2 0] projection exhibiting stacking order along c-axis
In the present work, the crystals that were exhibiting the wurtzite phase were considered and Figure 5-1(a) shows its schematic diagram. The wurtzite CdS form consists of a hexagonal unit cell (space group p63mc) with the atom positions located at Cd: \((1/3 \ 2/3 \ 0), \ (2/3 \ 1/3 \ 1/2), \ S: \ (1/3 \ 2/3 \ 3/8)\) \((2/3 \ 1/3 \ 7/8)\) and the lattice parameters ‘a’, ‘c’ as 4.136 Å, 6.713 Å respectively. Due to the absence of a centre of symmetry and tetragonal coordination between atoms in the structure, <0001> directions are polar in nature and exhibits stacking order of form ABAB as shown in Figure 5-1(b). Based on this, it is possible to determine the absolute crystal orientation using electron diffraction.

**Background**

As discussed in section 1.2.2, due to the limitations imposed by Tafto-Spence technique [7] such as specimen tilt requirement and its inability towards the large acentric crystals, in the chapter, the crystal polarity of CdS structures was evaluated using the high spatial resolution CBED technique in an exact zone axis orientation. The applicability of the considered technique is mainly influenced by specimen thickness, selected zone axis orientation and incident beam direction. By careful comparison between experimental CBED patterns and dynamical simulations, the specimen thickness is determined and the c-axis orientation \([1 \ 1 \ 0 \ 0]\) is considered for investigating \((0002)\) systematic row of reflections. Moreover, the incident beam direction is precisely adjusted using Kikuchi map and the symmetry between the higher order non-systematic reflections in spot diffraction pattern. The intensity of \((0002)\) reflections is calculated analytically by incorporating double diffraction scattering process among ZOLZ reflections and the validity of Friedel’s law is investigated.
5.3 Failure of Friedel’s law

Friedel’s law states that for centrosymmetric crystals, the diffraction patterns always possess inversion symmetry and the intensity of $hkl$ reflection is equal to the intensity in its opposite reflection $\overline{h\overline{k}\overline{l}}$. However, due to the multiple scattering in non-centrosymmetrical crystals, it may be violated [8]. Thus, initially by plotting the thickness dependent intensity variations across the Friedel pairs in $[1 \overline{1} 0 0]$ orientation of CdS crystal is investigated.

![Figure 5-2 Simulated CdS electron diffraction pattern in $[1 \overline{1} 0 0]$ orientation](image)

In the diffraction pattern shown in Figure 5-2, the reflections $(0002)$ and $(000\overline{2})$ are generally referred to as a Friedel pair and the reflections $(\overline{1}\overline{1}22)$ and $(\overline{1}\overline{1}2\overline{2})$ are referred to as Bijvoet pair. Typically both Friedel and Bijvoet pairs point to the same thing but however in three indices form, the Friedel pairs are strictly limited to $F(hkl)$ and $F(\overline{h}\overline{k}\overline{l})$ whereas Bijvoet pairs can be a symmetrical equivalent of $F(hkl)$ and $F(\overline{h}\overline{k}\overline{l})$.
reflections. In the present case $\mathbf{F}(l)$ and any mate that is symmetrically related to $\mathbf{F}(-l)$ are incorporated as Bijvoet pairs.

Figure 5-3 shows the calculated Pendellössung curves (i.e. beam intensity versus thickness) for the beams $\{0002\}$ and $\{\overline{1}122\}$ plotted at 200kv accelerating voltage using Bloch wave method in JEMS software. From the intensity plots it can be clearly observed that due to the breakdown of Friedel’s law, there exists asymmetric intensity distribution among the beams that have identical structure factors. Moreover, the asymmetric distribution can be observed from a very thin region (< 25nm) and the intensity difference from $\{0002\}$ beams is relatively greater than $\{\overline{1}122\}$ beams. The main cause for Friedel’s law violation in thin crystals that is resulting in asymmetric intensity distribution among Bijvoet/Friedel pairs can sufficiently be explained due to the multiple scattering among the ZOLZ interactions [9-10].

To confirm the effect of multiple scattering, the complex amplitudes of $\{0002\}$ beams were calculated based on the sum of direct and double diffraction amplitudes in $[1 \overline{1} 0 0]$ zone axis of CdS crystal and plotted further.

The extinction distance of $\{0002\}$ beams of CdS crystal at 200kv operating voltage is 61nm. In order to apply the kinematical approximation, the thickness which is less than half of its extinction distance needs to be considered. In that particular thickness range, the simplest case of a dynamical diffraction process can be understood as two kinematical scattering processes [9].
Figure 5-3 Simulated specimen thickness dependent intensity variations for \{0002\}, \{\bar{1}122\} beams of \([1 \bar{1} 0 0]\) oriented CdS crystal at accelerating voltage of 200kv
5. Crystal polarity evaluation of Cadmium Sulfide (CdS) nanostructures

If $\phi_0$ represents the wave function of an incident beam propagating along the z direction in a crystal of total thickness $t = 2\Delta z$, based on the Howie-Whelan equations, the change in amplitude and phase of the scattered wave $\phi_g$ in terms of structure factor $F_g$ and unit cell volume $V_0$ is given by [11],

$$\frac{d\phi_g(z)}{dz} = \frac{i\lambda F_g}{V_0 \cos \theta} \exp \left( -2\pi is_g z \right) \phi_0$$

(5.1)

By extending equation (5.1) to n-beam case [9, 12];

$$\frac{d\phi_g(z)}{dz} = \frac{i\lambda}{V_0} \sum_{h} F_{g-h} \exp \left( -2\pi is_{g-h} z \right) \phi_h \quad (g = g_1, g_2, \ldots, g_n; g_1 = 0)$$

(5.2)

Where $V_0$ is the volume of the unit cell, $\lambda$ the electron wavelength, $F_{g-h}$ the structure factor amplitude of the reflection $g-h$, $s_{g-h} = s_g - s_h$ the deviation parameter and $i$ is the imaginary term reflecting the phase difference of $\pi/2$ from the incidence beam.

As the total thickness of the considered crystal is $2\Delta z$, by subdividing the crystal into 2 layers as I and II, the thickness of an individual layer is treated as $\Delta z$. By considering the incident beam ($h = 0$) as the only contributor in equation(5.2), the scattered amplitude $\phi_g(\Delta z)$ after passing through layer-I is obtained as [9]:

$$\phi_g(\Delta z) = d\phi_g(\Delta z) = \frac{i\lambda \Delta z}{V_0} F_g \exp \left( -2\pi is_g \Delta z \right) \phi_0$$

(5.3)

In general, the total n-beams leaving the layer-I are written as a linear combination of all the beams $\phi_0 + \sum_{h} \phi_h$. These waves will be diffracted again in layer-II below. In this
double diffraction process, each beam acts as an incident beam in layer-II. By employing (5.2) and reassigning \( g = h \), the final wave function \( \phi_{g}(t) \) with \( z = t = 2\Delta z \) at the exit surface of the layer II can be written as:

\[
\phi_{g}(t) = \left\{ F_{g} + \frac{i\lambda t}{2V_{0}} \sum_{s\neq g} F_{s-h}F_{h} \right\} \frac{i\lambda t}{2V_{0}} \exp\left(-\pi i\varepsilon_{g}t\right)\phi_{0} \tag{5.4}
\]

In appendix B, the derivation of Equation (5.4) is discussed more in detail. The first term of the Equation (5.4) represents the direct scattering of the plane wave by the lattice plane \( g \) which is written as Equation(5.3). The sum in the second term, on the other hand, expresses the double diffraction. The double diffraction in the present scenario is described by two steps. The first step illustrates scattering into any direction \( h \) and the second step indicates scattering back into \( g \) by the lattice planes \( g - h \). It is important to note that the final diffracted wave \( \phi_{g} \) only depends on its own deviation parameter \( s_{g} \) but is not a function of other beams’ deviation parameter [9]. Assuming that the incident wave is propagating exactly along the zone axis i.e. \( s_{g} = s_{\bar{g}} \) the parameter \( \phi_{s_{g}} \) can be expressed as:

\[
\phi_{s_{g}}(t) = \left\{ F_{s_{g}} + \frac{i\lambda t}{2V_{0}} \sum_{s\neq g} F_{s-g}F_{h} \right\} \frac{i\lambda t}{2V_{0}} \exp\left(-\pi i\varepsilon_{s_{g}}t\right)\phi_{0} \tag{5.5}
\]

On comparing equations (5.4) and (5.5), the only difference that can be observed between \( \phi_{g} \) and \( \phi_{s_{g}} \) expressions is, the term in the curly bracket. Thus the wave function \( \phi_{g} \) was further simplified based on new constants \( C \), \( Z_{g} \) and \( A_{g} \) as:
\[ \phi_g \propto F_g + iC \sum_{h \neq 0} F_{g-h}^* F_h = F_g + Z_g = A_g \] \hspace{1cm} (5.6)

Where
\[ C = \frac{\lambda t}{2V_0} \] \hspace{1cm} (5.7)

\[ Z_g = i \frac{\lambda t}{2V_0} \sum_{h \neq 0} F_{g-h}^* F_h = iC \sum_{h \neq 0} F_{g-h} F_h \] \hspace{1cm} (5.8)

Based on the equations (5.6) – (5.8), the complex amplitudes of \{0002\} beams in [1 1 0 0] zone axis of CdS crystal were plotted as follows:

Figure 5-4 shows the considered double diffraction paths for \( g_{(0002)} \) and \( g_{(0002)} \) reflections. Here the scattering paths were chosen in such a way that the contributing beams i.e. \( h_1 - h_4 \) remain symmetrically same for both \( \pm g \) reflections around the considered zone axis. The structure factors of the relevant lattice planes for 200kv electron beam are listed in Table 5.1 and in appendix A, its calculation is illustrated more in detail.

**Table 5.1 Structure factors of CdS lattice planes at 200kv accelerating voltage [13]**

<table>
<thead>
<tr>
<th></th>
<th>( F_{1120} )</th>
<th>( F_{1120} )</th>
<th>( F_{1122} )</th>
<th>( F_{1122} )</th>
<th>( F_{0002} )</th>
<th>( F_{0002} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>Re (nm)</td>
<td>1.3241</td>
<td>0.6737</td>
<td>0.6737</td>
<td>1.2975</td>
<td>1.2975</td>
<td></td>
</tr>
<tr>
<td>Im (nm)</td>
<td>0</td>
<td>-0.3304</td>
<td>0.3304</td>
<td>-0.73</td>
<td>0.73</td>
<td></td>
</tr>
</tbody>
</table>
5.3 Failure of Friedel’s law

Figure 5-4 Schematic illustration of four double diffraction paths along $h$ and $g-h$ contributing to (a) $g_{(002)}$ (b) $g_{(003)}$ reflections in $[1 \bar{1} 0 0]$ zone axis of CdS crystal

For a crystal thickness of $\approx 16\text{nm}$ using Equation(5.7), the value of $C$ is determined as $0.2019 \text{ nm}^{-1}$ and based on Equation(5.8), $Z_{0002}$, $Z_{000-2}$ is calculated as:

$$Z_{0002} = (0.3533 + 0.7205) \text{nm}$$

$$Z_{000-2} = (-0.3533 + 0.7205i) \text{nm}$$ (5.9)

Finally from Equation(5.6), the complex amplitudes $A_{0002}$, $A_{000-2}$ were worked out and the results were plotted in Figure 5-5. It can be observed that after the considered double diffraction process in a thin CdS crystal regime, the plotted amplitudes are no longer equal to each other. As the intensities are proportional to the square of the calculated amplitudes, the intensities of $g_{(002)}$ and $g_{(003)}$ beams are determined as
5. Crystal polarity evaluation of Cadmium Sulfide (CdS) nanostructures

\[
I_{0002} = 2.725 \quad \text{(AU)}
\]

\[
I_{0002} = 2.995 \quad \text{(AU)}
\]  
(5.10)

Figure 5-5 Argand diagram representing the complex amplitudes of \( g_{(0002)} \) and \( g_{(0002)} \) beams in \([1 \bar{1} 0 0]\) zone axis of CdS crystal after the considered two-step scattering process.

From the values presented in (5.10), it is clear that after the two elastic scattering events among the ZOLZ reflections, the intensity of \( g_{(0002)} \) beam is no longer equal to \( g_{(0002)} \) beam which supports the violation of Friedel’s law in CdS crystal. From the plots shown in Figure 5-3, it can be understood that, for a specimen thickness less than 25nm, \( 0002 \) CBED disc tends to appears brighter compared to \( 0002 \) disc. However, the intensity values calculated from the considered two step scattering method does not
reveal it. The ambiguity could have occurred due to the inclusion of fewer number of \( h_1 - h_4 \) contributing beams in the determined intensities. Moreover, as the lattice spacing along c direction is about 0.6nm, along a specimen thickness of 16nm, around 26 scattering events could have taken place. Therefore, it is not possible to directly compare the intensity calculated based on two step scattering process by including fewer number of beams with the intensity profile obtained from many beam Bloch-wave simulation.

### 5.4 Analysis of single crystal CdS nanostructures

Crystal polarity analysis using CBED can be performed using off-axis [7, 14] or zone-axis [15-16] CBED patterns. Both these methods require a focused electron probe to produce electron diffraction patterns in the back focal plane of the TEM. In the case of the off-axis method, the crystal is tilted away from the [110] or [001] orientation towards a four-beam CBED condition and based on the constructive or destructive interference in the diffraction discs, the crystal polarity can be determined. Performing the analysis without any complex simulation is the primary advantage of this method. However, as indicated in section 1.2.2, tilting a particular CdS nanostructure to the necessary four-beam condition requires great effort and also the off-axis method is not favourable for compound with large degree of non-centrosymmetry [14, 17] such as CdS (atomic numbers, Z = 48 and 16).

Hence in the current work, based on the asymmetric intensity differences along the systematic row of reflections in \( [1\bar{1}00] \) zone axis, the crystal polarity is analysed.

Figure 5-6 shows the bright field TEM micrograph of a particular nanostructure that has been tilted to the \( [1\bar{1}00] \) orientation. The inset SAED pattern reveals that the crystal branch is single crystalline throughout its length.
5. Crystal polarity evaluation of Cadmium Sulfide (CdS) nanostructures

Figure 5-6 (a) Bright Field TEM image of a particular CdS nanostructure with inset spot diffraction pattern illustrating crystal orientation as [1 1 0 0] (b) Experimental CBED pattern obtained from the electron beam position indicated with red dot in (a). (c) Corresponding dynamically simulated CBED at a thickness of 16nm
In this particular orientation of the grown crystals, it was possible to distinguish the triangular face such as pyramids and flat edge sides of the nanostructures.

Figure 5-6(b) is the experimental CBED pattern that has been obtained from the electron beam positioned at the pyramidal tip as indicated in Figure 5-6(a). As noted earlier, asymmetric intensity distribution is apparently observed in \( \pm \mathbf{g} = \mathbf{0002} \) discs due to the non-centrosymmetric nature of the CdS nanostructures. The corresponding calculated pattern is shown in Figure 5-6(c) and by comparing the relative intensities in both images the crystal thickness is determined to be 16nm. The good agreement between experimental and dynamically simulated patterns confirms that crystal branch pyramids are Cadmium rich surfaces.

5.5 Geometrical evaluation of nanostructure thickness

*Figure 5-7 SEM micrograph of CdS nanostructures [6]*
5. Crystal polarity evaluation of Cadmium Sulfide (CdS) nanostructures

Figure 5-8 (a) Schematic diagram of an individual pyramidal CdS nanostructure viewed along top-down orientation (Not to scale) (b) Experimental micrograph of an individual CdS nanostructure tilted to $[1 \bar{1} 0 0]$ zone axis and representing the electron beam position with a red dot.
Figure 5-9 Simulated CBED patterns at a thickness of 16nm along $[\bar{1} 1 \bar{0} 0]$ zone axis with Centre of Laue Circle oriented at (a) (0, 0, 0) and (b) (-0.1818, -0.1818, 0.2146)
From the SEM micrograph of the synthesized nanostructures shown in Figure 5-7, it can be observed that the growth morphology consists of pyramids grown on one side of the platelets. Moreover, they are of regular three sided tetrahedral structures grown from the surface of the platelets. The SEM micrograph was acquired by Eileen Armstrong [6]. Based on the morphology of the synthesized material shown in the SEM micrograph, the shape of an individual CdS structure is considered to be a regular tetragonal shape and in Figure 5-8(a), the electron beam direction with respect to the pyramidal face is schematically shown. Depending upon the experimental CBED pattern acquisition position represented in Figure 5-8(b), the edge length of the pyramidal tip is determined to be 25nm. From this value, the thickness along the electron beam direction is calculated to be 21.65nm. However, there exists a slight difference of about 5nm from the value that was used for dynamically simulating the CBED pattern in Figure 5-6(C).

The discrepancy in the thickness values that was determined based on comparing the intensities of simulated pattern with respect to experimental pattern and geometrically predicted one may be explained due to variations in Centre of Laue Circle (CLC) orientation. Theory behind CLC concept was discussed more in Chapter-2, section 2.3.5. For the geometrical prediction of thickness, it was assumed that when an individual tetragonal pyramid with triangular base is seen from a top-down orientation, the angle between each of its sides remains to be 60°. The calculated CBED pattern that was matched to the experimental pattern in Figure 5-6 was simulated at a CLC of (-0.1818, -0.1818, 0.2146). This shows that there exists a small misorientation in the position of the tetragonal pyramid base. The difference in the contrast levels inside the CBED discs that were simulated with and without any misorientation in CLC can be observed in Figure 5-9. Due to the small misorientation in CLC, the difference in the determined thickness levels could have occurred.
5.5 Geometrical evaluation of nanostructure thickness

Discussion:

The polarity of various non-centrosymmetric crystals such as GaN, GaAs, InN, ZnO, ZnSe was primarily determined using CBED technique by several groups [2, 7, 14-16, 18-22]. In addition to this, by implementing the variant CBED technique such as LACBED [23] or using the bent contours in conventional TEM images [24], it was demonstrated that it is possible to evaluate the crystal polarity more efficiently. Every method has got its own advantages & disadvantages and generally becomes an ideal choice depending upon the experimental situation. In the present chapter, based upon the asymmetric intensity distribution observed inside the CBED discs combined with dynamical simulation, the crystal polarity of highly acentric wurtzite CdS (Z = 48, 15) compound has been determined unambiguously. Due to the well defined shape of pyramidal tip and flat edge surface on either sides of the crystal in \( [1 \bar{1} 0 0] \) orientation, it was considered to be an appropriate orientation for the electron beam direction to investigate the \( 0002 \) systematic row of reflections. The crystal was tilted accurately to the required zone axis orientation using the Kikuchi map that was obtained from the thicker region of the specimen. In a thin crystal regime (thickness less than one extinction distance), the breakdown of Friedel’s law is illustrated analytically based on the two step scattering among the ZOLZ reflections. However, to compare the evaluated intensities to the many beam Bloch wave simulations, just two step scattering process is not enough and more number of scattering processes needs to be considered. Moreover, the double diffraction paths shown in Figure 5-4 may be more realistic if \( 0002 \) systematic row routes are considered in the scattering process.
In conclusion, the CBED technique has been successfully implemented on novel single crystalline CdS nanostructures. Due to absence of a centre of symmetry in CdS structures, the variable growth rates of Cadmium and Sulphur elements resulted in pyramidal tips and flat edge platelets in the synthesized nanostructures. Based on the asymmetric intensity distribution in a zone axis CBED patterns, the absolute polarity of the nanostructures is determined.
5.6 References


6. Armstrong, E.: Materials and Surface Science Institute, University of Limerick, Ireland.


Chapter 6

Conclusions

In the present work, the Convergent Beam Electron Diffraction (CBED) technique has successfully applied for quantitative evaluation of lattice strains in Si$_{1-x}$Ge$_x$-Si Strained Layer Superlattice (SLS) structures and the crystal polarity in wurtzite Cadmium Sulfide (CdS) nanostructures. Based on the analysis performed in Chapters 4 and 5, the following major conclusions are derived:

6.1 Lattice strain variations in Si$_{1-x}$Ge$_x$-Si SLS structure

From high resolution High Angle Annular Dark Field (HAADF) imaging, the interfaces of SiGe bands with respect to a Si substrate is examined and observed that the interfaces do not possess any dislocations. Due to this, it was understood that the growth rate of the thin film is coherent in nature that is resulting in elastically strained SLS layers. Based on HOLZ lines intersection positions in a high index zone axis CBED pattern that consists of weak dynamical effects, the beam voltage was estimated to an accuracy of ± 0.037kV and used for the subsequent strain calculations. As the specimen thickness influences the appearance of HOLZ lines in CBED patterns, all the evaluated strain results are presented related to the thickness along the electron beam direction. The split HOLZ lines that are obtained from the outer interfaces of the considered individual SLS
structure were shown to result from the surface relaxation in the thinning direction. The experimental width of the split HOLZ lines was quantified by fitting various sets of HOLZ line patterns that differ in their Centre of Laue Circle (CLC). The lattice plane bending angle plots that are determined from split HOLZ lines have shown that the magnitude of bending angle was reduced and tends to zero with the increase in distance from the interface and specimen thickness levels.

The observed shifts in the HOLZ line positions of the CBED patterns that are obtained from the bands present inside the SLS structure are quantified for a unique set of lattice parameters. The quantification methodology is illustrated by considering an experimental HOLZ line pattern and the lattice parameters \( b_{[1 1 0]} \), \( c_{[0 0 1]} \) were determined to an accuracy of \( \pm 0.0002 \text{nm} \) and \( \pm 0.0004 \text{nm} \) respectively. The distances between the HOLZ lines intersections in the energy-unfiltered CBED patterns are obtained using Hough transformation.

By performing a spectrum-imaging line scans at different specimen thicknesses, several CBED patterns are recorded from the bands of an individual SLS structure and the shifts in HOLZ line positions are quantified for lattice strain using the described methodology. At a \( t/\Lambda \) ratio equal to 5.45 (where \( t = 130 \text{ nm} \)), due to the dominant surface relaxation effect, HOLZ line patterns with good contrast cannot be acquired from the bands of the SLS structure. With the \( t/\Lambda \) ratio equal to 10.76 (\( t = 258 \text{ nm} \)) and 19.78 (\( t = 474 \text{ nm} \)), better HOLZ line patterns were able to record and the strain variation in bands \( v, vi \) and \( i, ii \) respectively of the considered SLS was evaluated. From the measured strain variation profiles in the bands of the considered SLS, it is observed that most of the lattice strain is confined in the growth direction compared to the other directions.
On comparing the evaluated bending angle plots obtained from experimental CBED patterns with finite element simulations, there exists a good agreement between both the profiles. Moreover, on discarding the artefacts such as surface relaxation, gradient effect caused by beam convergence at the interface, the determined strain profiles along $h \langle 1 \ 1 \ 0 \rangle$ and $c \langle 0 \ 0 \ 1 \rangle$ directions are in good accordance with the calculated profiles obtained from finite element models.

6.2 Crystal polarity analysis of CdS nanostructures

The crystal polarity of the single crystalline wurtzite Cadmium Sulfide nanostructures is determined based on a low index zone axis CBED pattern obtained from a very thin region which is less than half of the extinction distance. By plotting many-beam Bloch wave intensities of Friedel & Bijvoet pair of reflections in $\langle 1 \ 1 \ 0 \ 0 \rangle$ zone axis, the asymmetric intensity distribution due to the violation of Friedel’s law in CdS crystal structure is shown. In a thin crystal regime, the multiple scattering among ZOLZ reflections is the main cause for the breakdown of Friedel’s law in non centrosymmetric crystals. By considering the concept of double diffraction among ZOLZ reflections in the $\langle 1 \ 1 \ 0 \ 0 \rangle$ zone axis, the complex amplitudes and the corresponding intensities of $\{0002\}$ beams is theoretically calculated.

Violation of Friedel’s law in CdS crystal is well supported by the asymmetric values obtained from the calculated $\{0002\}$ beam intensities. Based on the comparison of intensities in a zone axis CBED pattern obtained from the CdS nanostructure with the calculated CBED pattern, the absolute polarity of the nanostructure is determined. From the geometry of the nanostructure, the thickness along the electron beam direction at which the experimental CBED pattern acquired is determined as 21.65 nm. However,
due to the misorientation in Centre of Laue Circle (CLC) of the simulated CBED pattern, there exists a small error $\approx 5\text{nm}$ with respect to the geometrically determined thickness value.
Appendix A

Cadmium Sulphide structure factor calculation

As discussed in section 2.2.2, structure factor describes the amplitude of the electron scattering from a particular (hkl) set of crystallographic planes and is defined as:

\[ F(\theta) = \sum_i f_i \rho \sum_i f_i e^{2\pi i (h_1 + k_1 + l_1)} \]  

(A.1)

Where \( f_i \) represents the atomic scattering factor from \( i \) atoms with coordinates \( x_i, y_i, z_i \) and \( e^{2\pi i (h_1 + k_1 + l_1)} \), \((h, k, l)\) represents the phase of the electron wave, miller indices respectively. The exponential form of equation (A.1) in complex form can be written as

\[ F(\theta) = \sum_i f_i \cos\left\{2\pi \left( h x_i + k y_i + l z_i \right) \right\} + i \sum_i f_i \sin\left\{2\pi \left( h x_i + k y_i + l z_i \right) \right\} \]  

(A.2)

The structure factor calculation is shown for (0002) reflection and similar calculation was performed for other reflections in \([1 \bar{1} 0 0]\) zone axis of CdS crystal.

**Step-1:** Determination of \( \sin \theta / \lambda \) value

For the simplicity reason, the 4 indices of hexagonal crystal lattice i.e. \((h, k, -(h+k), l)\) are converted as 3 indices \((h, k, l)\) and discussed further. The interplanar spacing distance \( d_{hkl} \) in a hexagonal crystal for a set of \( \{hkl\} \) lattice planes is given as
\[
\frac{1}{d^2} = \frac{4}{3} \left( \frac{h^2 + hk + k^2}{a^2} \right) + \frac{l^2}{c^2}
\]  
(A.3)

For \( hkl = 002 \)

\[
d_{002} = 0.033565 \text{ Å} \]  
(A.4)

From Bragg’s law,

\[
\sin \frac{\theta}{\lambda} = \frac{1}{2} d_{002} = 0.14896 \text{ Å} \]  
(A.5)

**Step-2:** Atomic scattering factors of \( \text{Cd}^{2+} \) and \( \text{S}^{2-} \) ions

The atomic scattering factors of Cd and S atoms were obtained from International Crystallography Tables for \( \sin \frac{\theta}{\lambda} \) range equal to 0.14 to 0.15 and based on interpolation, the required values of \( \sin \frac{\theta}{\lambda} = 0.14896 \) were determined as shown in Table A.1.

<table>
<thead>
<tr>
<th>( \sin \frac{\theta}{\lambda} )</th>
<th>0.14</th>
<th>0.14896</th>
<th>0.15</th>
</tr>
</thead>
<tbody>
<tr>
<td>( f_{\text{Cd}} )</td>
<td>6.695</td>
<td>6.48791</td>
<td>6.464</td>
</tr>
<tr>
<td>( f_{\text{S}} )</td>
<td>3.783</td>
<td>3.65032</td>
<td>3.635</td>
</tr>
</tbody>
</table>

**Step-3:** Working out \( F_{002} \) value

Based on the four atom positions (i.e. 2 Cadmium, 2 Sulphur atoms) present inside the CdS crystal lattice and using the appropriate \( f_i \) values shown in Table A.1, for (002)
plane, the cosine and sine terms of equation (A.2) are evaluated to be 12.975Å, -7.3Å respectively.

Finally as $F_{002}$ is a complex value, it is written as

$$F_{002} = 12.975 - 7.3i$$  \hspace{1cm} (A.6)
Appendix B

Final wave function $\phi_g(t)$ at exit surface $z = t = 2\Delta z$

If $\phi_0$ represents the wave-function of an incident beam that is propagating along the $z$ direction in a crystal of total thickness $t = 2\Delta z$, based on the Howie-Whelan equations extended to the $n$-beam case, the change in amplitude and phase of the scattered wave $\phi_g$ is given by:

$$\frac{d\phi_g(z)}{dz} = \frac{i\lambda}{V_0} \sum_{h \in g} F_{g-h} \exp(-2\pi i s_{g-h} z) \phi_h \quad (g = g_1, g_2, ..., g_n; g_1 = 0)$$

(B.1)

Equation (B.1) states that the change in amplitude and phase of the scattered wave $\phi_g$ is expressed in the form of a linear combination of $n$ beams $g_1, g_2, ..., g_n; g_1 = 0$.

In a typical 5-beam condition i.e. one transmitted beam and 4 diffracted beams, as $\phi_0$ is considered as virtually unchanged, the electron wave $\phi_0 + \sum_{h \in g_1} \phi_h$ leaving crystal-I will be diffracted again in crystal-II. Thus based on equation (B.1) and reassigning $h = g_1, g_2, ..., g_5$, the wave function of each wave at the exit surface of crystal-II can be calculated as:

(1) $h = g_1 = 0; \quad \frac{i\lambda\Delta z}{V_0} F_g \exp(-2\pi i s_{g} \Delta z) \phi_0$

(B.2)
(2) \( h = g_2; \quad \frac{i \lambda \Delta z}{V_0} F_{g-g_2} \exp(-2\pi i s_{g-g_2} \Delta z) \phi_{g_2} \) \hfill (B.3)

(The beam \( g_2 \) generated in layer-I is assumed to act as an incident beam for layer-II. Due to this, the beam generates 5 scattered beams including itself in layer-II.)

\[
= \frac{i \lambda \Delta z}{V_0} F_{g-g_2} \exp(-2\pi i s_{g} \Delta z) \exp(2\pi i s_{g_2} \Delta z) \phi_{g_2}
\]

\[
= \frac{i \lambda \Delta z}{V_0} F_{g-g_2} \exp(-2\pi i s_{g} \Delta z) \exp(2\pi i s_{g_2} \Delta z) \frac{i \lambda \Delta z}{V_0} F_{g_2} \exp(-2\pi i s_{g_2} \Delta z) \phi_0 \hfill (B.4)
\]

\[
\left( \therefore \phi_{g_2}(\Delta z) = \frac{i \lambda \Delta z}{V_0} F_{g_2} \exp(-2\pi i s_{g_2} \Delta z) \phi_0 \right)
\]

\[
= \frac{i \lambda \Delta z}{V_0} F_{g-g_2} F_{g_2} \exp(-2\pi i s_{g} \Delta z) \frac{i \lambda \Delta z}{V_0} \phi_0
\]

Similarly,

(3) \( h = g_3; \quad \frac{i \lambda \Delta z}{V_0} F_{g-g_3} F_{g_3} \exp(-2\pi i s_{g} \Delta z) \frac{i \lambda \Delta z}{V_0} \phi_0 \) \hfill (B.7)

(4) \( h = g_4; \quad \frac{i \lambda \Delta z}{V_0} F_{g-g_4} F_{g_4} \exp(-2\pi i s_{g} \Delta z) \frac{i \lambda \Delta z}{V_0} \phi_0 \) \hfill (B.8)

(5) \( h = g_5; \quad \frac{i \lambda \Delta z}{V_0} F_{g-g_5} F_{g_5} \exp(-2\pi i s_{g} \Delta z) \frac{i \lambda \Delta z}{V_0} \phi_0 \) \hfill (B.9)

Finally, the total wave function \( \phi_h(\Delta z) \) of the considered 5-beam case is a linear combination of all the 5-beams which is written as:

\[
\phi_h(\Delta z) = \frac{i \lambda \Delta z}{V_0} F_g \exp(-2\pi i s_{g} \Delta z) \phi_0 + \frac{i \lambda \Delta z}{V_0} \sum_{h=g_2}^{g_5} F_{g-h} F_h \exp(-2\pi i s_{g} \Delta z) \frac{i \lambda \Delta z}{V_0} \phi_0
\]  

(B.10)
Moreover for n-beam case,

$$\phi_g(\Delta z) = \frac{i \lambda \Delta z}{V_0} F_g \exp\left(-2\pi is_g \Delta z\right) \phi_0 + \frac{i \lambda \Delta z}{V_0} \left(\sum_{l \neq 0} F_{g-h} F_h \right) \frac{i \lambda \Delta z}{V_0} \exp\left(-2\pi is_g \Delta z\right) \phi_0$$  \hspace{1cm} (B.11)$$

$$\phi_g(\Delta z) = \left( F_g + \frac{i \lambda \Delta z}{V_0} \sum_{i \neq 0} F_{g-h} F_h \right) \frac{i \lambda \Delta z}{V_0} \exp\left(-2\pi is_g \Delta z\right) \phi_0$$  \hspace{1cm} (B.12)$$

$$\phi_g(t) = \left( F_g + \frac{i \lambda t}{2V_0} \sum_{i \neq 0} F_{g-h} F_h \right) \frac{i \lambda t}{2V_0} \exp\left(-\pi is_g t\right) \phi_0$$  \hspace{1cm} (B.13)$$
Appendix C

List of Publications

Journal articles


Conference Proceedings


Conference Presentations


[2] **N.V.V. Mogili, D.A. Tanner**: “CBED & FE study of strain relaxation in cross-sectional Si, Si$_{0.81}$Ge$_{0.19}$ Strained Layer Superlattice structure”


Presented at *EM 50 (International Conference on Electron Nanoscopy)*, Hyderabad, India, July 6–8, 2011 (Invited oral).


Presented at *UL - NUI Galway Alliance Annual Engineering & Informatics Annual Research Day*, Galway, Ireland, April 7, 2011.


