Chapter 2

Experimental techniques

2.1 Introduction

This chapter covers the details on experimental techniques employed to accomplish the objectives of this thesis. The chapter would begin with an introduction to thin film deposition and various types of deposition techniques that have been used in this thesis. This is followed by description of characterization techniques viz. transmission electron microscopy (TEM), scanning electron microscopy (SEM), scanning transmission electron microscopy (STEM), focused ion beam (FIB), electron backscatter diffraction Technique (EBSD) and Rutherford backscattering spectrometry (RBS).

The gold and germanium nanostructures can be synthesized in several ways like thermal vapor deposition and molecular beam epitaxy (MBE) method, where the bulk metal is subjected to resistive heating under high vacuum/ultra high vacuum conditions. Depending on the rate of deposition, vacuum level and substrate condition, the gold nanostructure morphology varies. In this thesis work, deposition of gold nanostructures onto silicon substrates has been done using both vacuum coating method and molecular beam epitaxy (MBE) method and germanium deposition has been done using the MBE. The detailed will be discussed in the following sections.
2.2 Thin film Growth

Thin film growth is an essential part in modern device fabrication. It is desirable to have an ability to control morphology and microstructure to meet functional requirements of devices made by stacking thin film layers. Understanding of growth kinetics is, therefore, crucial in advancing the modern technology. Besides this practical purpose, it has been a challenging fundamental scientific subject and is still an active research area.

Thin film depositions can be either purely physical-like evaporative methods, or purely chemical-like gas and liquid phase chemical processes [66]. Some of the other techniques which involve glow discharge and reactive sputtering can be regarded as physical-chemical methods. In this thesis, only physical *viz.* vacuum coating method will be discussed.

### 2.2.1 Physical vapor deposition Method

Thermal evaporation (physical vapor deposition) is the vaporization of a material by heating to a temperature such that the vapor pressure becomes appreciable and atoms or molecules are lost from the surface in vacuum[68]. Physical Vapor Deposition (PVD) employs the atomic vapor cloud formed by the vaporization of metal in a vacuum environment to cover all the surfaces. It involves the following sequential steps: (i) Conversion of deposited material into vapour by heating, (ii) Transportation of material from source to the target substrate and (iii) Condensation of the vapour on the substrate and formation of thin film. Heating of the material in PVD can be done in several ways. The simplest one is the resistive heating, when a wire of tungsten or molybdenum is resistively heated, so that the metal being in thermal contact to the wire melts and evaporates (sublimation can occur as well). In electron beam evaporation, a beam of electrons is directed at the material, thus heating up and evaporating the material. A thermal evaporator uses an electric resistance heater to melt the material and raise its vapor pressure to a useful range. This is done in a high vacuum (generally $5 \times 10^{-5}$ to $1 \times 10^{-6}$ mbar) both to allow the vapor to reach the substrate without reacting with or scattering against other gas-phase atoms in the chamber and reduces the incorporation of impurities from the residual gas in the vacuum chamber. Obviously, only materials with a much higher vapor pressure than
the heating element can be deposited without contamination of the film. The principal requirement for successful thin film growth in this experiment is that the mean free path of the gold atoms must be greater than the distance between the source and substrate [69].

In this thesis work, we have used thermal evaporation technique to deposit the material. Au films of various thicknesses were deposited using Hind hivac made thermal evaporator (model 12A4-D). The deposited material was placed in a tantalum boat. A large current was passed through this boat, heated it up and melted the material to be deposited. The coating unit for this system consists of a cylindrical, stainless steel vacuum chamber, approximately 55 cm tall and 40 cm in diameter. This chamber is connected to double stage pumping system: 250 liter per min rotary pump and 280 liter per second oil diffusion pump. There is a stationary sample stage placed 12cm away from the boat at the top of the chamber for holding substrates, including a shutter for controlling film growth, and there is an evaporation boat at the bottom of the chamber. Pirani and Penning gauge are used to measure the vacuum level during deposition. Thickness of the thin film was controlled using thickness monitor with quartz crystal microbalance. The quartz crystal mechanically oscillates when ac voltage is applied to it (piezoelectric effect)[67]. The resonance frequency of oscillations is dependent on the mass of the film deposited onto it. Quartz monitors can measure thickness of about a single atomic layer with relatively high accuracy. The calibration is checked routinely with RBS experiment.

2.2.2 Molecular beam epitaxy

This is another vacuum deposition technique but carried out under ultra high vacuum (UHV). While characterizing a surface on an atomic level, basic requirement will be that the surface composition essentially remains unchanged over the duration of the experiment. This requires that the experimental chamber to be in ultra high vacuum. The concept of vacuum can be understood in terms of parameters such as molecular density, mean free path and the time constant to form a monolayer(ML), where one ML corresponds to $6.78 \times 10^{14}$ atoms cm$^{-2}$ for a Si(100) surface. At UHV, mean free path of atoms/molecules present in the chamber is of the order of kilo meters and the time required for the formation of a monolayer is almost a hour. Whereas in low vacuum ($\approx 10^{-2}$ mbar) it reduces to fraction of a centimeter and time required
for monolayer is fraction of milisecond [76]. Molecular beam epitaxy (MBE) is an advanced, sophisticated vacuum deposition process under UHV conditions, where in, significantly more precise control of beam fluxes and growth conditions are possible. The growth process is governed by mainly the kinetics of the surface processes occurring when the incident atomic/molecular beam interacts with a few surface atomic layers of the substrate crystal. As it is done in UHV, the growth process may be observed and controlled by in-situ surface sensitive methods such as reflection high energy electron diffraction (RHEED), Auger electron spectroscopy (AES) etc.

MBE was developed in the early 1970’s as a technology to grow high-purity epitaxial layers of compound semiconductors [70, 71]. Since then, it has evolved into a popular technique for growing compound semiconductors Si[72, 73, 74, 75] and Ge, as well as several other materials, such as oxides. MBE can produce high-quality single crystal layers with very abrupt interfaces, monolayer control of thickness, precise doping and compositional accuracy. Because of the high degree of control and flexibility using MBE, it is a valuable tool in the development of sophisticated electronic, magnetic and photonic devices. The operating principle behind MBE is conceptually very straightforward; a source material is heated up to a high enough temperature where a considerable vapor pressure is realized and the development of a directed vapor towards a substrate is accomplished by the process called effusion. Consider a container filled with gas molecules in equilibrium. If a small hole is made in the wall of the container, molecules with the right velocity components will effuse out of the container through the small hole, forming a molecular beam (after which MBE is named). When the hole is sufficiently small, only a tiny portion of the gas molecules effuses out of the container and the equilibrium state is disturbed to a negligible extent. Molecular-beam epitaxy (MBE) is a process of depositing epitaxial films from molecular beams on a heated crystalline substrate under ultra-high vacuum (UHV) conditions. UHV conditions are necessary in order to prevent the interference of impurities with the growth.

Growth Modes

The growth of deposited thin film can take any form during deposition depending upon the deposition conditions (viz. temperature and pressure during deposition,
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![Figure 2.1: Schematic illustration of the three equilibrium growth modes: (a) layer-by-layer (Frank-van der Merwe, FM) growth mode (b) layer-plus-island (Stranski-Krastanov, SK) growth mode (c) Island (Volmer-Weber, VW) growth mode [77].](image)

chemical bonding between the substrate and the material, surface energy of film and substrate). For the determination of the growth mode, the surface free energies of the substrate ($\gamma_{\text{sub}}$), interface ($\gamma_{\text{int}}$) and the film ($\gamma_{\text{film}}$) are important [76, 77]. The growth of thin film depends on the resultant free energy as follows:

$$\Delta \gamma = \gamma_{\text{film}} + \gamma_{\text{int}} - \gamma_{\text{sub}} \quad (2.1)$$

**Island growth mode (VW Growth)**

In this growth mode, the smallest stable clusters nucleate on the substrate and grow in three dimensions to form islands. This happens when the deposited atoms are more strongly bound to each other than to the substrate. Hence, adsorbate forms 3-dimensional islands instead of a complete layer. This type of growth is commonly known as Volmer-Weber growth (Fig. 2.1(c)). Here $\Delta \gamma > 0$. This growth mode is typical for metal on insulators.

**Layer Growth Mode (FM Growth)**

In this growth mode, the smallest stable clusters grow in two dimensions, resulting in the formation of planar sheets. This happens when the atoms are more strongly bound to the substrate than to each other. The adsorbate is forming a complete monolayer before a second layer starts on top of the first. This type of growth is commonly known as Frank-van der Merwe growth (Fig. 2.1(a)). Here $\Delta \gamma \leq 0$. An example of this growth mode is single crystal epitaxial growth of semiconductor films.
**Layer plus Island growth mode (SK Growth)**

This growth mode is considered as intermediate between the FM and VW growth modes. After forming the first few monolayer, subsequent growth is unfavourable and islands are formed on the top of the intermediate layer. This type of growth is commonly known as Stranski-Krastanov (Fig. 2.1(b)). It happens if $\Delta \gamma \leq 0$ and the materials have large lattice mismatch and strain associated. This is due to the influences of the surface and the interfaces and also the film structure, determined by the initial condensation process. First it tries to form an wetting layer and after a critical thickness when no more strain can be accommodated, then only island forms. In SK growth, islanding happens to relieve the misfit strain. The clusters grow in size and density until the islands begin to merge in what is known as the coalescence phenomenon. Coalescence decreases the island density allowing further nucleation to occur. The strain-assisted self assembly in the Ge/Si(100) system is a popular example of this growth mode.

**Relaxation and Reconstruction:** The atoms at solid surfaces have missing neighbors on one side. Driven by this asymmetry, the topmost atoms often assume a structure different from the bulk. They might form dimers or more complex structures to saturate dangling bonds. In the case of *surface relaxation*, the lateral or in-plane spacing of the surface atoms remains unchanged but the distance between the topmost atomic layers is altered. If the lateral distance of the atoms are changed, this is called the *surface reconstruction*. For example, semiconductor surfaces tend to exhibit surface reconstruction due to the directional character of the dangling bonds at the surface. Reconstruction can be readily detected by electron diffraction techniques, including low-energy electron diffraction (LEED) and reflection high-energy electron diffraction (RHEED).

A photograph of the MBE system used [78] for this thesis work is shown in Fig. 2.2. It is a custom-designed, compact MBE system along with the capability to transfer the MBE-grown samples to a UHV STM without breaking vacuum (Omicron, GmbH) (Fig. 2.2). It consists of a load-lock chamber and growth chamber which is connected to the STM chamber. Each chamber has an associated pumping system. The load-lock facilitates the introduction and removal of samples or wafers without
Figure 2.2: A custom-designed compact MBE system (MBE chamber diameter: 250 mm) and a UHV variable temperature scanning tunneling microscope (VTSTM) attached to it.
significantly influencing the growth chamber vacuum. Magnetic transfer rods are used to transfer the sample to main chamber and to STM chamber. The main elements of growth chamber are: sources of molecular beams (Three Knudsen cells and an electron beam evaporator); a manipulator for heating, translating and rotating the sample; shutters to occlude the molecular beams; gauge to measure chamber base pressure and molecular beam fluxes; a RHEED (reflection high energy electron diffraction) gun and screen to monitor film surface structure. Thickness is measured by a quartz microbalance. Sample cleaning is done by resistive heating followed by direct heating. It has an option for Ar sputtering as well. Three Knudsen cells contain Au, Ag and Ge sources. Electron beam evaporator is used for Si deposition. In STM chamber (VTSTM), the temperature range available is -248°C to 1227°C. The best base pressure achieved in the MBE chamber is $3 \times 10^{-11}$ mbar and that in the VTSTM chamber is $1 \times 10^{-10}$ mbar.

### 2.2.3 Low vacuum annealing setup

The low vacuum annealing setup used for this work is a tube furnace connected to a rotary pump. The vacuum inside the chamber is about $10^{-2}$ mbar and the maximum temperature it can go upto $1400^\circ$ C with heating rate $1^\circ$C to $10^\circ$C. The heating element used in this set up are SiC rods. The temperature is controlled by the honeywell DC-1040 temperature controller with 10 steps programmable and automatic control. The heating zone inside the tube is about 10 cm. The same chamber is used for the growth of oxides by connecting one end of the tube to the oxygen cylinder.

### 2.3 Characterization techniques

*In-situ* study of thermal behaviour of gold nanostructures has been done mainly by transmission electron microscope (TEM). Scanning transmission electron microscope (STEM) with its major accessories has also been used to do structural characterization at room temperature. Single tilt hot-stage holder was used in carrying out *in-situ* annealing studies. Characterization of samples was also done using SEM based EBSD. All the above tools will be discussed briefly in the following sections.
2.3.1 Transmission electron microscopy

In the advancement of materials science and engineering, it is necessary to observe, analyze and understand the phenomena occurring on a small size scale. The transmission electron microscope (TEM) is a powerful and versatile instrument which permits characterization of materials [80, 79, 81]. It offers variety of information obtained from different modes such as bright field (BF) and dark field (DF) imaging, selected area diffraction (SAD) and high resolution lattice imaging (HREM). BF and DF imaging are used to characterize defects and domain structures. SAD with combination of tilting of crystal in the microscope allows reconstructing the reciprocal space and in that way obtain information about the crystal structure and identifying different phases. HREM allows under certain conditions to directly visualize the projected crystal potential. The first TEM was built by two German scientists, M. Knoll and E. Ruska, in 1932 [82]. Nowadays, TEMs have become widely available.

In a TEM, a high-energy (∼ 200 keV) electron beam is transmitted through the specimen. During transmission, the electrons interact with the specimen, giving rise to signals containing information about the internal structure and chemistry of the specimen. Electron diffraction patterns and lattice images are two forms of data which give an insight of crystallographic information in TEM. Lattice images are interference patterns between the direct beam and diffracted beams, viewed in direct space, and are obtained by high-resolution TEM (HRTEM) imaging. In the images, the spacing of a set of fringes represents the lattice spacing. If one looks at as more details manner, then the image or diffraction phenomena are aspects related to the scattering of incident electrons from the specimen atomic potentials. For direct information of defect structure on the atomic scale, an HRTEM is particularly useful with low spherical aberration coefficient (or corrected aberration coefficients), given that this is the typical spacing between atoms in solids [80].

In selected area diffraction pattern (SAED), the sample is illuminated with a parallel electron beam to ensure the focusing of the transmitted and diffracted beam onto the back focal plane of the objective lens. A specific area of the sample is selected by an SAED aperture that is in an image plane conjugate with the sample in the electron optic system of the TEM. The inserted SAED aperture creates a virtual aperture in the sample plane, giving a selected area that is about 0.4 µm or greater, in diameter [79]. A few hundred nanometers is therefore the typical lateral size of the region sampled by SAED in TEM.
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**Instrumentation**

A transmission electron microscope consists of an illumination system, specimen stage and imaging system analogous to a conventional light microscope. A schematic diagram of illumination section, sample stage and imaging section is shown in Figure 2.3(a). An electrostatic lens in the form of Wehnelt cup is used after the filament to converge the maximum number of emitted electrons. Illumination section consists of electron source, acceleration column and condenser lenses. The role of the illumination system in TEM is to project an electron beam on the part of the specimen that is observed. In this thesis, most of the TEM measurements have been carried out using JEOL 2010 TEM operating at 200 keV with LaB$_6$ thermionic emission type gun. Here, high voltage is generated in a separated power supply unit using Cockcroft-Walton technique and is coupled to the acceleration column. Following the acceleration column, condenser lens system is available. Electrons are generated in the electron gun by thermionic emission. (Any material that is heated to a high enough temperature will emit electrons when they have enough energy to overcome the work function according to $J = AT^2e^{-\phi/kT}$, (where $\phi$ is the work function, $J$ is the current density at the tip and $A$ is the Richardson’s constant). After leaving the electron gun the electrons are accelerated towards the anode and enter the column. Since the velocity of the electrons close to the speed of light the wavelength of the electrons has to be corrected for relativistic effects:

$$\lambda = \frac{2m_0eE}{h^2} \sqrt{1 + \frac{eE}{2m_0c^2}}$$

For 200 keV electrons, $\lambda$ is equal to 0.0025 nm. It accelerates towards the anode at the top of the column and focuses at the specimen with the condenser lenses. The function of the condenser lens system is to provide a parallel or convergent beam of electrons at the specimen surface. In practice, this is not possible and the beam always possesses a certain kind of convergence when imaging at high resolution, usually in the range of 1 mrad for LaB$_6$ emitters (for our machine, it is $\sim 0.68$ mrad). Using different size of condenser aperture one can change the illuminated area on the specimen. Just below the sample (2-5 mm), Objective lens (OL) is situated. The combination of intermediate and projector lenses do the final image magnification. After the objective lens, objective aperture and selected area diffraction aperture are placed (shown in (Figure 2.3(b),(c)))). Finally the magnified image forms at phosphor screen. To record the image or diffraction pattern, photographic film and/or charge coupled
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Figure 2.3: A schematic diagram of (a) Filament and illumination part, (b) Diffraction pattern formation and (c) Image formation [79].

device (CCD) can be used. The light generated on the phosphor screen is channeled to the CCD through the optical fiber and the CCD output is connected to the computer using image processing system. As electron is very highly interacting particle, the vacuum maintained inside the column of TEM, is $10^{-8}$ mbar. Three parameters are important for the best TEM imaging: the brightness, source size and energy spread of the electrons. The brightness is defined as the current density per solid angle and is conserved when the beam passes an (ideal) electron lens. Accelerating the electrons results in a less diverging beam and increases the brightness. The source size is the area from where the electrons seem to originate. Due to some electron-optic effects the source size is not always equal to the actual emitting area on the tip and is then referred to as the virtual source size. High resolution TEM demands for a planar coherent electron wave, since high-resolution images are formed by phase contrast.

Interaction of electrons with the specimen

After entering the specimen most of the electrons are elastically scattered by the nuclei of the atoms in the specimen. Some electrons are inelastically scattered by the electrons in the specimen (figure 2.4). Compared to X-ray or neutron diffraction the interaction of electrons with the specimen is huge and multiple scattering events are common. For thick specimens at lower resolutions an incoherent particle model
can describe the interaction of the electrons with the specimen. However, with thin specimens at high resolution, this description fails because the wave character of the electrons is then predominant. The electrons passing the specimen near the nuclei are somewhat accelerated towards the nuclei causing small, local reductions in wavelength, resulting in a small phase change of the electrons. Information about the specimen structure is therefore transferred to the phase of the electrons. For the formation of high resolution images, only the elastically scattered electron are of importance. The inelastic scattered electrons contribute mostly to the background of the image. The energy loss spectrum of the inelastic scattered electrons contains valuable information of the chemical composition of the specimen. This information can be extracted by observing the electron energy loss spectrum (EELS). The details of EELS will be discussed later in this chapter. The inelastic scattered electrons also produce Kikuchi lines in the electron diffraction pattern that is helpful for accurate crystallographic alignment of the crystals in the specimen.
Imaging and Diffraction

The conventional TEM image formation for thick specimen is very similar to the projector principle. In this case, an incoherent particle model can describe the interaction of the electrons with the specimen. Specimen contains variation in thickness and density. So the electrons will loss more energy when it transmits through the thicker and denser region and hence it will appear as darker object. Same way, the thinner and rarer region will appear as brighter object. This is called thickness contrast imaging. Contrast in TEM also depends upon the crystallinity of the specimen known as diffraction contrast. However, for thin specimen at high resolution, this description fails because the wave nature of the electrons is then predominant. If the specimen is thin enough and crystalline, then elastic scattering is usually coherent and these electrons are now contribute to the image formation. After the exit of electrons (elastically transmitted coherent electron beams), the diffraction spots and image are used to form at back-focal plane and image plane of OL, respectively. The diffraction pattern can be understood by taking the fourier transformation (FFT) of the wave function of electron at the back focal plane of OL. One more time FFT of this wave function at back focal plane of OL gives the high resolution (HR) lattice image. The HR image will form due to interference between the direct and diffracted beams depending on the phase difference between these two. So the highly diffracted beams are used to cut down by the objective aperture. The resolution and the details of image formation are governed by the contrast transfer function (CTF).

To retrieve structural information of the specimen from the micrographs it is necessary to calculate the trajectory of the electron wave through the specimen. In the kinematical approximation, multiple scattering of the electrons in the sample is ignored resulting in an undisturbed central beam. This approach already fails at a small thickness or a single atom. In dynamical calculations all the scattered beams and their mutual exchange of intensity during the course of multiple scattering in the specimen are taken into account. It is possible to do full dynamical calculations but these are soon limited by the available computing power. Using the fact that the vast majority of the electrons are scattered in a forward direction with small diffraction angles Cowley and Moodie devised the multislice approximation[83].

In this thesis work, two kinds of TEM systems have been used. Majority of HRTEM and in situ has been carried out using JEOL 2010 TEM operating at 200 keV (Fig. 2.5). The OL pole piece is an ultra high resolution pole piece (UHR-URP22) with a
spherical aberration coefficient \( (C_s) \) of 0.5 mm, which helps to achieve a point-to-point resolution of 0.19 nm. For imaging as well as real-time studies, a charge-coupled-device (CCD) based detector with 40 ms time resolution and with 4008 × 2672 pixels (Model 832, Gatan Inc.) has been used. In this thesis work, STEM, Electron energy loss spectroscopy (EELS) and EDS were carried out with 300 keV electrons in the Cs-corrected FEI Titan 80/300 system at the University of Bremen, Germany. The probe diameter was 0.2 nm during HAADF and STEM-BF mode.

Sample preparation

Sample preparation is the most important part of the TEM characterization. As the electrons transmit through the specimen, the specimen has to thin down to the electron transparency \(< 100 \text{ nm}\) for conventional TEM and even lesser \(< 10 \text{ nm}\) for HRTEM. There are two types of samples to be prepared depending on the interest of study. Cross-sectional TEM (XTEM) sample is required to probe the interface and/or bulk solid while planar TEM specimen preparation is required to probe the surface morphology.

Figure 2.6 and 2.7 show the schematic diagrams of one of the methods to prepare both planar and cross sectional TEM sample preparation respectively.

Planar specimen

For Planar TEM sample preparation, we cut the sample into 3 mm disc using ultrasonic disc cutter and thin down to \( \sim 100 \text{ nm} \) using the South Bay Technology (SBT) made lapping and polishing system (LPS-Model-910). Here, the mechanical thinning starts with a rough emery paper with larger grit size and ends with an emery paper with finer grit size. Then the specimen is again thinned (down to 30-40 \( \mu \text{m} \)) and polished by diamond paste and alumina suspension in Gatan made dimple grinder (DG) system (model 656). In this process, the edge remains thicker but center part becomes dimpled. The final electron transparency is achieved by ion milling with the Gatan made precision ion polishing system (PIPS) (model 691). During PIPS, 3.5 keV Ar ion beam is used to sputter the material from the specimen in grazing incidence \( (4^\circ - 7^\circ) \) (Fig. 2.6).
Figure 2.5: 200 keV JEOL HRTEM installed at Institute of Physics, Bhubaneswar.
Figure 2.6: A schematic diagram of procedure to prepare a typical planar TEM specimen.

Figure 2.7: A schematic diagram of procedure to prepare a typical cross-sectional TEM specimen.
Cross-sectional specimen

For Cross-sectional TEM sample preparation, we cut the as deposited sample into two rectangular pieces of size \( (2.5 \times 3) \) mm\(^2\) each using SBT made Abrasive Slurry saw (model 850). Then the pieces were glued face to face using Gatan G1 epoxy as thin as possible. It will ensure an optimal ion milling rate i.e. if the glue quantity will be too high, the ion mill will remove it quicker than the sample resulting a sharp hole with a sharp edge, opaque to electron beam. Again the above assembly is glued with two silicon dummy pieces with similar dimensions. Then it was put in stainless steel tube having inner and outer diameter 2.5 mm and 3 mm respectively. Then we made a 1 mm slice out of it using SBT made Low speed diamond wheel saw (model 650). After that the mechanical thinning (using LPS and dimple grinder) was done followed by 3.5 keV Argon ion milling to make it electron transparent. We repeated the procedure for thinning as required for planar specimen. But in this case one needs to perform those steps for both sides of the sample excluding dimpling for one side. The procedure of cross-sectional specimen is depicted pictorially (Fig. 2.7).

Hot-stage holder

Many phenomena occur at elevated temperatures and they are of fundamental interest. The use of specimen heating during TEM observation allows the possibility to study direct phase transformations, such as nucleation and growth, dissolution processes etc. In-situ TEM is a powerful method to observe phase transformation, order-disorder phenomenon in nano materials by varying specimen temperature. In this thesis work, in-situ experiments have been done by using Model 628 UHR single tilt heating holder procured from Gatan. Inc. It is custom designed to fit small high resolution pole piece gaps. This is associated with a Model 901 smart set hot-stage controller. It is a side entry furnace type single tilt holder, where the specimen can be heated up to 1000\(^\circ\)C, accurate to a couple of degrees(Figure 2.8).

The furnace (made up of tantalum) is mounted on the spring loaded 3 insulating ceramic mounts which accommodate expansion or contraction during heating or cooling. Tantalum is used, because of its high temperature stability and resistance to solid state welding to most technical materials including silicon. The furnace contains a miniature encapsulated heater that is spot welded to two terminal posts in the specimen tip. Both sides of the heater circuit are connected via copper wires to a 5 pin
Figure 2.8: Single tilt hot stage holder installed at IOP, Bhubaneswar (Model 628, Gatan, Inc.).

vacuum feed-through, mounted at the end of the specimen rod. The temperature is measured by platinum-rhodium thermocouple, spot welded to the furnace body. The thermocouple leads are anchored by terminals in the specimen tip and are then fed along the axis of the specimen rod to the five pin vacuum feed through. Above 500°C, the water circulation automatically starts driven by the controller. Recirculation of distilled water from a stainless steel tank to the heating holder is performed through two polyurethane tubes of length 260 cm each. Water cooling basically helps in extending the operating range and to reduce the specimen drift by maintaining a local constant temperature heat sink.

2.3.2 FIB-SEM-Cross beam system

The combination of field emission scanning electron microscopy (FESEM) and focused ion beam (FIB) is a future key technology for semiconductor and material science related applications. A scanning electron microscope (SEM) is a microscope that uses electrons instead of light to form an image. Since their development in the early 1950’s, scanning electron microscopes have developed new areas of study in the medical and physical science communities. The focused ion beam (FIB) technique was mainly developed during the late 1970s and the early 1980s. Modern FIB systems are
becoming widely available in semiconductor research and processing environments, as well as in failure analysis and chip-design centers. The technology enables localized milling and deposition of conductors and insulators with high precision, hence its success in device modification, mask repair, process control and failure analysis and also the preparation of specimens for transmission electron microscopy (TEM).

The experimental setup used for this thesis work is a cross-beam system coupling a Carl Zeiss, Neon 40 scanning electron microscope (SEM, Gemini Column) and a Canion 31 focused ion beam (FIB, Orsay Physics), equipped with gas injection system (GIS, Orsay Physics), STEM detector, Four Quadrant Back scattered electron detector (Carl Zeiss ) and EDS detector (INCA, Oxford) [figure 2.9]. The two beams are focused on the same point of the sample. Both beams coincide at a crossover point 5 mm below the objective lens of the SEM. The working distance (WD) for the FIB in this coincidence point is 12 mm. The geometrical layout and arrangement of the two columns enables perpendicular tilt of the sample to the ion beam in the coincidence point. To provide full eucentric tilt at all operating conditions a 6-axis motorized eucentric specimen stage is used. This allows real time simultaneous FIB machining and non-destructive non-contaminating SEM imaging at high resolution. The sample may be tilted between 0° and 54° to face perpendicularly the ion or the electron beam. At 0° tilt, imaging at normal incidence with the electron beam is possible while at 54°, imaging and machining with the FIB is performed. Both imaging techniques are based on the collection of secondary electrons. The FIB column operates at an accelerating voltage of Ga+ ions ranging from 2 to 30 kV with a minimal Gaussian beam diameter around 7 nm. The beam current can be varied from 1 pA for the lowest current to 50 nA. Our FIB system can be used for imaging, milling and deposition (using Gas Injection System). One Kleindiek Micromanipulator is attached inside the specimen chamber for TEM lamella preparation (for lift out). The system is fitted with a computer controlled gas injection system that can handle up to five different gases for metal and insulator deposition or enhanced and selective etching The GIS (Gas injection system) is composed of five distinct lines for gas injection. Gas flows from a reservoir through a capillary. Temperature of reservoirs and capillaries are independently controlled. The needles at the end of the capillaries are mounted on a micro stage table. Thus they can be precisely positioned close to the working area (<100 µm) in order to create a local high gas pressure. A turbo molecular pump ensures
a dynamic pumping and the base pressure in the chamber is $10^{-6}$ mbar. To avoid damages and contamination by Ga$^+$ ions, all the tunings such as focus and alignment can be systematically performed in the neighborhood of the working area. Our cross beam system can also be used for both e-beam and ion beam lithography (ELPHY Quantum lithography system, Raith).

Now, we discuss the working principle of SEM and FIB individually.

![FIB-SEM Crossbeam System](image)

**Figure 2.9**: FIB-SEM crossbeam system installed at Institute of Physics, Bhubaneswar.

**Scanning Electron Microscopy (SEM)**

The microscope used in this work is a Zeiss Neon 40. This microscope is equipped with a field emission gun, GEMINI electron-optics, a lateral secondary electron (SE) detector (*Everhart-Thornley*), a backscatter detector, an in-lens SE detector. The
main characteristic of the GEMINI optics is the use of a beam booster and an objective lens which acts as a combined electrostatic/electromagnetic lens. The electrons generated at the gun tip are accelerated to the set acceleration voltage as they are accelerated towards the anode. However, the beam booster, which is installed directly after anode, is always at a potential of an extra 8 kV when the set acceleration voltage is \( \leq 20 \text{ kV} \). When low voltages are used, this arrangement will ensure that the energy of the electrons in the beam path will always be 8 kV higher than the set acceleration voltage and will reduce the influence of magnetic stray fields on the electron beam. Before the electron beam exits the objective lens, the electrostatic lens reduces the potential by an opposite applied 8 kV. The main advantage of this technique is that a stable beam is obtained even at low acceleration voltages. In addition to acting as a retardant towards the electrons ejected from the electron column, the electrostatic lens will act as a collector for the electrons generated at the sample surface. The sample electrons are accelerated and focused back up the beam path, where the in-lens SE detector is positioned (annular detector). The combination of the electrostatic lens and the in-lens detector results in a very high detection efficiency for the in-lens detector even at low (< 1 kV) acceleration voltages [88].

**Image Formation**

Image formation in the SEM is dependent on the acquisition of signals produced from the electron beam and specimen interactions. These interactions can be divided into two major categories: elastic interactions and inelastic interactions. Elastic scattering results from the deflection of the incident electron by the specimen atomic nuclei or by outer shell electrons of similar energy. This kind of interaction is characterized by negligible energy loss during the collision and by a wide-angle directional change of the scattered electrons. Incident electrons that are elastically scattered through an angle of more than 90° are called backscattered electrons (BSE), and yield a useful signal for imaging the sample. Inelastic scattering occurs through a variety of interactions between the incident electrons and the electrons and atoms of the sample, and results in the primary beam electrons transferring substantial energy to that atom. The amount of energy loss depends on whether the specimen electrons are excited singly or collectively and on the binding energy of the electron to the atom. As a result, the excitation of the specimen electrons during the ionization of specimen atoms leads to the generation of secondary electrons (SE). In addition to those signals
that are utilized to form an image, a number of other signals are produced when an electron beam strikes a sample, including the emission of characteristic x-rays, Auger electrons and cathodoluminescence (figure 2.10). Basically, when primary electrons interact with the sample, the primary electrons cause either secondary electrons (SE’s) or backscattered (BSE’s) to be emitted from the sample, which are mainly used for image formation. As a result of inelastic interactions of the primary electrons with the sample, the secondary electrons are emitted from the sample with energy less than 50eV [89]. The energy distribution of the backscattered electrons has a peak just below the primary electron energy and a tail towards zero. As the secondary electrons are lower in energy than the backscattered electrons, they can be separated from the high energy backscattered electrons with an electric field. Because of the low energy of the secondary electrons, they only escape from the topmost layers of the sample and hence carry information from these layers. A secondary electron image thus gives information about the topography of the sample. The higher energy backscattered electrons can escape from deeper in the sample. The number of backscattered electrons depends on the atomic number of the sample. Hence a backscatter electron image gives information about the composition of the sample. Most commonly an Everhart-Thornley detector (E-T detector) is used to detect the electron signals in the scanning electron microscope. The E-T detector consists of a Faraday cage covering a scintillator, a light guide and a photomultiplier. The Faraday cage is placed outside the detector and either a negative or a positive bias voltage can be applied to it. When a negative bias voltage is applied, all secondary electrons are rejected and hence only the backscatter signal is detected. When a positive bias voltage is applied to the Faraday cage, the secondary electrons are attracted to the detector. The positive bias voltage causes the trajectory of electrons emitted from the sample over a large solid angle to be deviated towards the detector. In the detector the electrons are accelerated to the scintillator where they induce light emission. The light is guided to the photomultiplier tube amplifying the signal and converting it into an electric current which can be read out on a screen.

**Focused Ion Beam (FIB)**

The structure of the column is similar to that of a scanning electron microscope, the major difference being the use of a gallium ion (Ga⁺) beam instead of an electron beam. A vacuum of about $1 \times 10^{-7}$ mbar is maintained inside the column. The basic
Figure 2.10: A schematic diagram of different processes taking place during electron—solid interaction.
components of a FIB system are normally an ion source, an ion optics column, a beam deflector and a substrate stage. The ion beam is generated from a liquid-metal ion source (LMIS) by the application of a strong electric field. This electric field causes the emission of positively charged ions from a liquid gallium cone, which is formed on the tip of a tungsten needle. A typical extraction voltage is 7000 V. The extraction current under normal operating conditions is 2µA. After a first refinement through the aperture, the ion beam is condensed in the first electrostatic lens. The upper octo pole then adjusts the beam stigmatism. The ion beam energy is typically between 2 and 30 keV, with beam currents varying between 1 pA and 50 nA. Using the variable aperture mechanism, the beam current can be varied, allowing both a fine beam for high-resolution imaging on sensitive samples and a heavy beam for fast and rough milling. Blanking of the beam is accomplished by the blanking deflector and aperture, while the lower octopole is used for raster scanning the beam over the sample in a user-defined pattern. In the second electrostatic lens, the beam is focused to a fine spot, enabling a best resolution in the sub 10 nm range. All operations such as manipulating the stage, controlling valves for gas delivery, turning on and off pumps and manipulating the ion beam are carried out via software. A system of vacuum pumps is needed to maintain the vacuum inside the column and the work chamber. A rotary pump is used in combination with a turbo pump for pumping the work chamber. The ion column is additionally provided with one or two ion pumps.

2.3.3 Electron Backscatter Diffraction Technique (EBSD)

The electron backscatter diffraction (EBSD) is an additional characterization technique to SEM which provides quantitative micro structural information about the crystallographic nature of the inorganic crystalline materials such as metals, minerals, semiconductors and ceramics. It reveals size and orientation of grains, grain boundary character, texture and phase identity of the sample under the beam.

EBSD patterns are generated on the phosphor screen by backscattered diffraction of stationary beam of electrons(with energy 10 - 30 Kev) from the crystalline material. When the primary beam interacts with the crystal lattice, low energy loss backscattered electrons are channeled and subjected to path differences which leads to form a diffraction pattern by constructive and destructive interference. The diffraction pattern consists of kikuchi bands in which the band width is related to many parameters such as electron energy, working distance etc. Electron backscattered pattern
(EBSP) is analyzed with a stationary beam on a point on the sample. It is uniquely defined by the parameters such as lattice parameters of the particular crystal, its orientation in space, the wavelength of the incident electron beam and the proximity of the EBSP detector to the sample. Specialized computer software analyzes the EBSP by detecting a number of Kikuchi bands using an optimized Hough transform [90]. The software determines all possible orientations with each phase and reports the best fit as the identified phase and orientation, which helps in indexing the EBSP. EBSD mapping can be performed by considering the phase and orientation at each pixel and the sampling step size between points with the use of basic RGB coloring scheme. For example, In inverse pole figure (IPF) for cubic phases, full red, green and blue are assigned to grains whose $\langle 100 \rangle$, $\langle 110 \rangle$ and $\langle 111 \rangle$ axes respectively, are parallel to the surface-normal direction, where as for intermediate orientations, colors are assigned by an RGB mixture of the primary components. EBSD data processing software can generate an enormous variety of additional visual and analytical information, including overall preferred orientation (texture), distribution of grains in specific orientations, phase distribution and distribution of grain boundaries. Details about various aspects of EBSD technique can be found in reference [91].

2.3.4 Scanning Transmission Electron Microscopy (STEM)

In STEM, the image formation process is completely different. The probe is sharply focused onto the specimen plane with a diameter in the sub-nanometer range. The signal on the (ring-shaped) high angle annular dark field (HAADF) detector comes from electrons scattered to large angles well above 30 mrad. Local information is finally retrieved by mapping the HAADF signal against the position of the probe. Therefore, the probe is rastered over the specimen. The single most important feature of a STEM instrument is its versatility: atomic resolution images, diffraction patterns from nanometer regions and nanometer scale spectroscopy data can be obtained either simultaneously or sequentially from the same region of the specimen [92, 93].

High Angle Annular Dark Field Imaging (HAADF)

The HAADF detector is an annular detector of scintillator material coupled to a photomultiplier tube. The main difference between TEM-DF mode and STEM-DF mode is that, in TEM case, only a fraction of scattered electrons are allowed to enter the objective aperture, where as in STEM, the images are formed by collecting most
Figure 2.11: Schematic diagram of detector geometry for a STEM [94].
Experimental techniques

of the electrons on the annular dark field (ADF) detector. In case of HAADF, the inner and outer radius are larger than the ADF which detects the electrons that are scattered to higher angles and contribution of incoherent Rutherford scattering makes the images less noisy. These radii can both vary over a large range, but typically the inner radius would be in the range of 30–100 mrad and the outer radius 100–200 mrad. Here, the contrast depends on $Z^2$ of the material. So, HADDF imaging is also called z-contrast imaging. As the scattering angle increases, the scattered intensity from an atom approaches the $Z^2$ dependence that would be expected for Rutherford scattering from an unscreened Coulomb potential. In practice, this limit is not reached and the $Z$ exponent falls to values typically around 1.7 [95] due to the screening effect of the atom core electrons. This sensitivity to atomic number results in images in which composition changes are more strongly visible in the image contrast than the high-resolution phase-contrast imaging. As the center of the detector is a hole, electrons below the inner radius can pass through the detector for use either to form a BF image or to form an electron energy-loss spectrum (figure 2.11).

X-ray Energy dispersive spectroscopy (XEDS)

An incident electron is inelastically scattered at an atom of the specimen and excites, say, a core electron. An electron from a higher orbital fills the empty states in lower orbital. The energy difference is released in form of photons (when the core level electron of high enough atomic number is knocked out, the emitted photons would be in the X-ray regime), whose energy is characteristic for the transition in the respective target atom. The X-rays are detected spectrally resolved (the number of counts in a given energy width of typically few eV/channel) with an appropriate energy dispersive detector, like Si(Li) or SDD (silicon drifted detector). To create an elemental map, an EDX spectrum is recorded for each scan point in STEM mode. The energy windows can be selected around certain spectral peaks, so that the respective peak intensity can be mapped against the position of the STEM probe. In this thesis, both the STEM based and SEM based energy dispersive spectrometry (EDS) measurements were used.

Electron energy loss spectroscopy (EELS)

Another method to investigate the chemical composition of a material is electron energy loss spectroscopy (EELS). It is the analysis of the energy distribution of the
electrons emanating from the sample. The principle of signal development is as follows: An incident electron is inelastically scattered by an atom of the specimen, for example, it excites a core electron of an atom in the specimen. This energy loss is characteristic for the scattering atom and can thus be used for elemental analysis. To measure the energy loss, an imaging filter such as, post-column Gatan Image Filter (GIF), has been used which works roughly as follows: Electrons transmitted through specimen will pass the magnetic prism, where they are dispersed according to their energy loss by the Lorentz force. Finally, a CCD camera detects the electrons. An energy-selecting slit may be inserted to select electrons that have suffered a certain energy loss (energy window). By applying a potential to the drift tube the energy window can be selected. A sequence of lenses is then used to form an image using these electrons in the so-called energy-filtered TEM (EFTEM) mode. In spectroscopy mode, the spectral energy distribution of the electrons can be visualized. It can provide information on the electronic structure, oxidation states and chemical composition on an atomic or sub nanometer scale (figure 2.11). The combination of XEDS and EELS with HAADF imaging technique can provide detailed information on the composition, chemistry and electronic and crystal structure of nano scale systems with atomic resolution and sensitivity.

In this thesis, STEM, Electron energy loss spectroscopy (EELS) and EDS were carried out with 300 keV electrons in the Cs-corrected FEI Titan 80/300 system at the University of Bremen, Germany. The probe diameter was 0.2 nm during HAADF and STEM-BF mode.

2.3.5 Rutherford Backscattering Spectrometry

Rutherford Backscattering Spectrometry (RBS) is an analytical technique used to determine the structural and compositional details of a material by analyzing the backscattered high energy ions. It is based on classical scattering in a central-force field. Aside from the accelerator, which provides a collimated beam of MeV particles (usually \( \text{He}^+ \) or \( \text{He}^{++} \) ions), the instrumentation is simple. Semiconductor nuclear particle detectors are used that have an output voltage pulse proportional to the energy of the particles scattered from the sample into the detector. The technique is also the most quantitative, as MeV Helium ions undergo close-impact scattering collisions that are governed by the well-known Coulomb repulsion between the positively
charged nuclei of the projectile and target atom. More about various aspects of RBS technique can be found in ref.[97].

**Kinematic factor**

![Figure 2.12: A schematic diagram of the interaction of two particles][97].

The ratio of the projectile energy after a collision to the projectile energy before a collision is defined as the kinematic factor ($K_{M_2}$). When a projectile with mass and energy $M_1$ and $E_0$ collides elastically with a stationary particle (target atoms) of mass $M_2$ ($M_2 > M_1$), energy will be transferred from the projectile to the target atoms. If the projectile energy ($E_0$) is much larger than the binding energy of the target atoms, but less than the energy required for nuclear reactions and resonances, then the kinematic factor for this system shown in figure 2.12 can be expressed as:

$$K_{M_2} = \frac{E_1}{E_0} = \left[ \frac{M_1 \cos \theta + (M_2^2 - M_2^2 \sin^2 \theta)^{1/2}}{M_1 + M_2} \right]^2$$

(2.3)

**Thickness analysis**

In a real experiment, instead of particle-particle collision, a beam of light positive ions (He ions or protons) are incident upon a target material. Relative number of backscattered ions from a target atom that are directed towards a certain solid angle $d\Omega$ is termed as differential scattering cross section.

$$\frac{d\sigma}{d\Omega} = \frac{1}{Nt} \frac{dQ/d\sigma}{Q}$$

(2.4)

where $N$ is the atomic density of the target atoms and $t$ is its thickness. $\sigma$ is called average differential scattering cross section and can be defined as,

$$\sigma = \frac{1}{\Omega} \int_{\Omega} \frac{d\sigma}{d\Omega} d\Omega$$

(2.5)
Experimental techniques

Figure 2.13: A schematic diagram of the RBS spectrum for a thin film [97].

and the differential scattering cross-section for an elastic collision between two atoms is given by Rutherford’s formula,

\[
\frac{d\sigma}{d\Omega} = \frac{Z_1 Z_2 e^2}{4E_0} \cdot \frac{4}{\sin^2 \theta} \cdot \frac{[1 - (\frac{M_1}{M_2} \sin \theta)^2]^{1/2} + \cos \theta]^2}{1 - (\frac{M_1}{M_2} \sin \theta)^2}^{1/2}
\]

(2.6)

where \(Z_1\) and \(Z_2\) are the atomic numbers of the projectile and target atom respectively. From the above equations, simple way get the thickness is dividing the term \(Nt\) by the atomic density \(N\). In other words, the total no of detected particles can be written in terms of the height of the spectrum as \(H_i = \sigma(E_i)QN.dt\), when the beam is falling normally onto the sample. Here, \(i\) denotes the number of equally smallest slabs for which backscattered energy can resolute, that means \(t = i.dt\) and \(\sigma(E_i)\) must be calculated at each backscattered energy \(E_i\). Now, the total number of counts (area under the curve) is \(A = \sum_i H_i\). In figure 2.13, \(H_0\) denotes the total number of counts at energy \(KE_0\). So total no of counts is given by,

\[
A = H = \sum_i H_i = \sum_i \sigma(E_i)\Omega QN.dt = \sigma\Omega QNt
\]

(2.7)

The value of \(A\) can be obtained by taking the area under the spectrum.
Instrumentation

RBS instrumentation can be broadly divided into three parts: accelerator, target chamber and energy analyzer. In the first part, H or He ions are generated through ionization process. Then, these ions are accelerated using the accelerator upto an energy of 1–3 MeV. Selection of the required isotope is done by passing the beam through a mass analyzer. Finally, the collimated beam falls on the sample (target chamber). In the target chamber, a surface barrier detector (SBD) is used to detect backscattered projectiles kept at a very high angle ($\geq 150^\circ$). The sample is connected with the current integrator to get the total number of incident ions (total charge accumulated on the target). The energy related output from SBD goes through the energy analyzer. It consists of preamplifier, amplifier, analog to digital converter and multi channel analyzer (MCA). Finally, the output of MCA can be fed to the computer, where the resulting RBS spectrum can be stored. For the present thesis work, we have used 45$^\circ$ degree beam line of the 3 MV tandem Pelletron accelerator (9SDH2, NEC, USA) facility at IOPB [98]. Surface barrier detector was placed at 160$^\circ$ at a distance of about 11 cm from the sample holder. For the RBS measurements, 1.35 MeV $He^+$ ions were used and RBS simulation was carried by SIMNRA software package [99].