

STRUCTURAL AND OPTICAL CHARACTERIZATION OF SiGe THIN FILM GROWN ON GLASS

Submitted in partial fulfillment of the requirements for the award of

Master of Science degree in Physics

By

J. KAVITHA

(41590009)



DEPARTMENT OF PHYSICS

SCHOOL OF SCIENCE AND HUMANITIES

SATHYABAMA

**INSTITUTE OF SCIENCE AND TECHNOLOGY
(DEEMED TO BE UNIVERSITY)**

**Accredited with "A" grade by NAAC I 12B Status by
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BONAFIDE CERTIFICATE

This is to certify that this Project Report is the bonafide work of J.Kavitha (41590009) who carried out the project entitled "STRUCTURAL AND OPTICAL CHARACTERIZATION OF SiGe THIN FILM GROWN ON GLASS" under my supervision from November 2022 to May 2023.

Internal Guide
(Dr. Twisha Sain)

Head of the Department
(Dr.S. Ravichandran)

Submitted for Viva voce Examination held on 9.5.2023 2023

INTERNAL EXAMINER

EXTERNAL EXAMINER

Dr.D. DINESH KUMAR

Associate Professor (Research)

DECLARATION

I J. Kavitha hereby declare that the Project Report entitled STRUCTURAL AND OPTICAL CHARACTERIZATION OF SiGe THIN FILM GROWN ON GLASS done by me under the guidance of Dr. Twisha Sain (Internal), Department of Physics, Sathyabama Institute of Science and Technology, Chennai is submitted in partial fulfilment of the requirements for the award of Master of Science Degree in Physics.

A handwritten signature in black ink, reading "J. Kavitha", with a long horizontal flourish extending to the right.

DATE: 09-05-2023

PLACE: CHENNAI

SIGNATURE OF THE CANDIDATE

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ABSTRACT

In the present work, the effect of annealing on the structural and optical properties of Ge-rich SiGe thin films at temperature 450°C have been studied. SiGe thin films of thickness ≈ 100 nm were deposited on glass substrates by electron beam evaporation techniques. The as-deposited film is amorphous in nature. Upon carrying out vacuum annealing at 450 °C significant changes in structural properties were observed. Upon annealing at 450 °C, the crystallinity increased further. The transition from amorphous to crystalline nature was also confirmed using Raman spectra with the presence of SiGe peak around 400 cm^{-1} . The optical response of the as-deposited and the annealed films was studied. The reflectance and transmitted spectra of the as-deposited films were measured. The energy band gap of the films was analyzed. The as-deposited film has a band gap value of 0.845 eV, for the annealed film, the band gap decreased to 0.826 eV. The polycrystalline SiGe thin film with a band gap in the NIR region could be a highly promising candidate for green energy applications like solar photovoltaic cells.

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LIST OF ABBREVIATIONS

TFT	- Thin Film Transistors
AFM	- Atomic Force Microscope
PVD	- Physical Vapor Deposition
CVD	- Chemical vapor deposition
XRD	- X-Ray diffraction
GIXRD	- Grazing incidence X-ray diffraction
UV-VIS	- Ultraviolet-Visible
NIR	- Near infrared
CMOS	- Complementary Metal-Oxide-Semiconductor
LPCVD	- Low-Pressure Chemical Vapor Deposition
IC	- Intergrated Circuit
EDX	- Energy Dispersive X-ray Spectroscopy
MC	- Main Chamber
LLC	- Load Lock Chamber
RMS	- Root mean square

Chapter 1

INTRODUCTION

We are living in a world that is rapidly getting smaller and smaller, in no small part thanks to the contribution of semiconductor thin film industry. The transistor and integrated circuit (IC) serve as the cornerstone of these remarkable capabilities, which are built on digital and analogue electronic systems. With thousands of technical papers published annually and many new electronic devices being created, the semiconductor electronics industry is still undergoing rapid change [1].

1.1 SILICON GERMANIUM (SiGe)

Silicon (Si) & Germanium(Ge) is obviously the most well-known semiconductor material. Si and Ge share the same solid structure as diamond fcc [2]. Group IV metals include lead, germanium, tin, silicon, and carbon. In this Carbon is a non-metal, Si and Ge are metalloids and tin is typically a metal. Due to its high mobility and comparatively low bandgap, silicon germanium $\text{Si}_{1-x}\text{Ge}_x$ is a desirable material for the bottom sub-cell of a multi-junction solar cell [3]. In the area of photovoltaic and microelectronic devices, $\text{Si}_{1-x}\text{Ge}_x$ alloy is a potentially good substitute for Si. The $\text{Si}_{1-x}\text{Ge}_x$ alloy's stoichiometry-dependent tunable properties make it possible. This allows for tailoring of the optical and electrical properties from Si-like (1.12 eV) to Ge-like (0.66 eV) [4, 5, 6].

1.1.1 History of SiGe

Chemists - Jons Jacob Berzelius and Clemens A. Winkler, respectively, discovered Si and Ge, two crucial components of the semiconductor industry, in 1824 and 1869, respectively. The real practical application, though, didn't occur until much later. At Bell Labs in December 1947, John Bardeen, Walter Brattain, and William Shockley created the first iteration of transistors using Ge [7 8] and the fig (1.1) shows it. $\text{Si}_{1-x}\text{Ge}_x$, a material structure made up of the two elemental semiconductors Si and Ge, is a member of the group IV-IV alloy family.

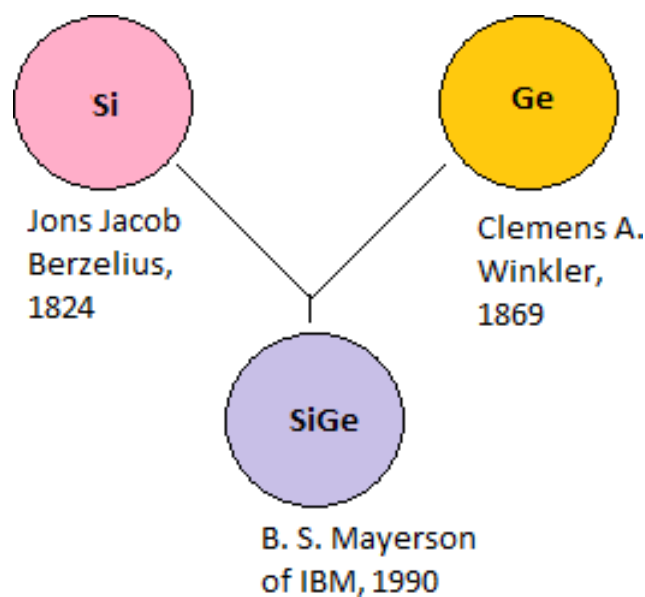


Figure 1.1: SiGe

1.1.2 Phase Diagram of SiGe

The phase diagram fig(1.2) demonstrates how over the full composition range, they are completely miscible and form a solid solution of $\text{Si}_{1-x}\text{Ge}_x$, where x is the fraction of germanium in the alloy [9].

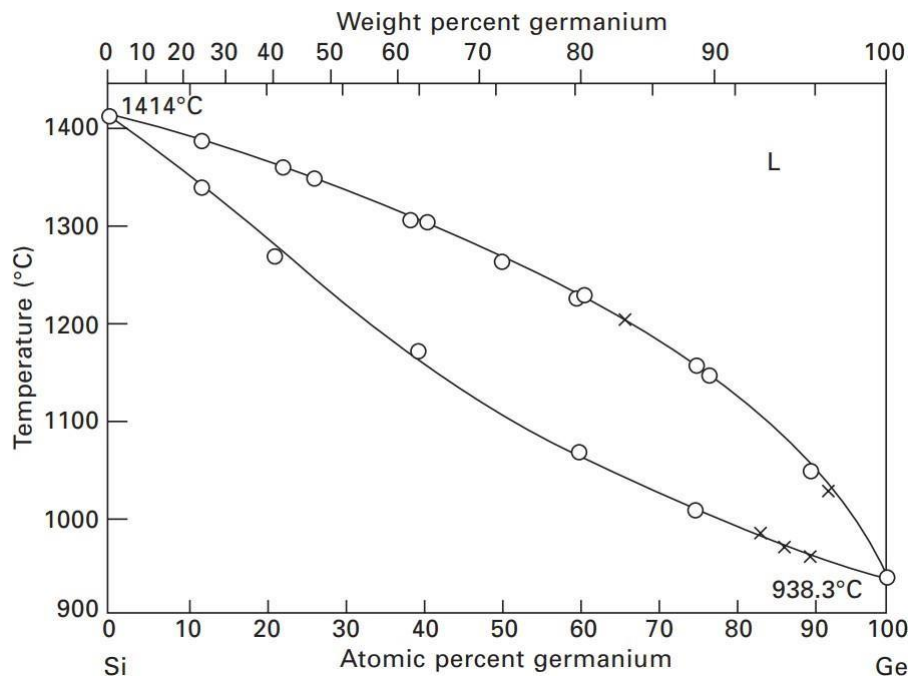


Figure 1.2: Phase diagram of SiGe

1.1.3 Properties of SiGe

The chemical, electrical, thermal, and mechanical, optical properties of SiGe.

Chemical Properties

Chemical Formula	SiGe
Molecular Weight	100.7265
Group	Silicon – 4; Germanium - 4
Crystal Structure	Diamond
Symmetry Group	Oh7-Fd3m

Table 1.1: Chemical Properties

Electrical Properties

Breakdown Field	$< 3 \times 10^5$ V/cm
Electron Mobility (at 300 K, $0 \leq x \leq 0.3$)	$\approx (1396-4315x)$ cm ² /Vs
Hole Mobility (at 300 K, $0 \leq x \leq 0.3$)	$\approx (450-865x)$ cm ² /Vs

Table 1.2: Electrical Properties

Thermal Properties

Density	$(2.329 + 3.493x - 0.499x^2) \text{ g cm}^{-3}$
Surface Micro-hardness	$(1150 - 350x) \text{ kg mm}^{-2}$

Table 1.3: Thermal Properties

Mechanical Properties

Linear Thermal Expansion Coefficient (at 300 K, $x < 0.85$)	$(2.6 + 2.55x) \times 10^{-6} \text{ K}^{-1}$
Thermal Conductivity (at 300 K, $0.2 < x < 0.85$)	$\approx (0.046 + 0.084x) \text{ W cm}^{-1} \text{ K}^{-1}$

Table 1.4: Mechanical Properties

Optical Properties

Infrared Refractive Index (at 300K)	$3.42 + 0.37x + 0.22x^2$
-------------------------------------	--------------------------

Table 1.5: Optical Properties

1.1.4 Crystal Structure of SiGe

Si and Ge both have diamond face-centered cubic (fcc) crystal structures. The alloy likewise displays a diamond fcc crystal structure. Each of the identical atoms in a diamond lattice is surrounded by its four equally spaced nearest neighbours which is shown in fig (1.3). This forms the four corners of a tetrahedron. The diamond space lattice is made up of two fcc lattices that are interpenetrating, with one lattice spaced out from the other along the space or body diagonal by a quarter. The figure given below represents the crystal structure of SiGe. Vegard's law is a rough empirical rule that states there is a linear relationship between an alloy's crystal lattice constant and the concentrations of its component elements at constant temperature [10]. Vegard's law for alloyed materials is a linear function:

$$E_{\text{alloy}} = xE_A + (1 - x)E_B,$$

where E_A , E_B , and E_{alloy} are the respective properties of pure A, pure B, and the alloy A_xB_{1-x} , and x is the fraction of one ingredient in a material point [11].

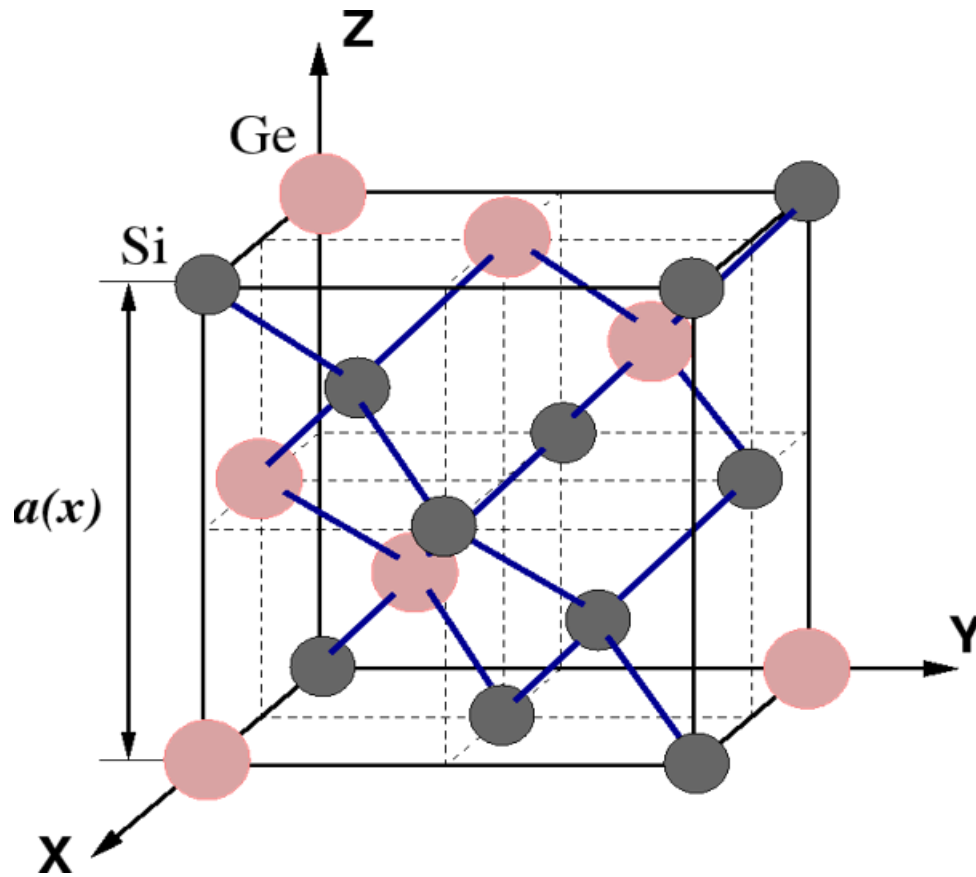


Figure 1.3: Structure of SiGe

1.2 APPLICATIONS OF THE SiGe THIN FILMS

Currently due to cost effectiveness, SiGe in its thin film form finds applications in thin film solar cells, hetero junction bipolar transistor. It is also used as strain inducing layer in CMOS transistors. It is used in IC fabrication [12].

1.2.1 Thin Film Solar Cell

Thin film solar cell is designed to convert light energy to electrical energy (through the photovoltaic effect) and is composed of micron thick photon absorbing material deposited over a flexible substrate which is shown in fig(1.4). Photon absorbing layer is called active layer. Thin film solar cells are cost effective, require less raw materials, don't have any harmful ingredients, produce less waste, and are quite simple to make. They are superior to the other varieties in terms of flexibility and weight, making them ideal for use in portable devices.

1.2.2 Thin Film Transistors

Thin film transistors, usually referred to as TFTs, are a class of field-effect transistors that are most frequently employed in liquid crystal displays (LCDs). With LCD technology, each pixel in a flat-panel display has its own thin-film transistor, which essentially serves as an on/off switch for each pixel. A semiconductor and a dielectric layer are deposited over a non-conducting substrate, such as glass, to create TFTs. The core of active-matrix displays are thin-film transistors, which are arrayed in flat-panel displays in a matrix pattern which is shown in fig (1.5). TFTs, however, also have numerous industrial applications, from head-up displays to digital radiography detectors.

The components that make up TFT:

- Substrate: Commonly glass or plastic
- Semiconductor: Silicon, cadmium selenide, or metal oxides
- Dielectric: Inorganic materials such as silicon oxide or silicon nitride
- Gate electrode: Commonly polysilicon, TiN, TaN, or WN
- Drain/source metal: Commonly metal silicides [13]

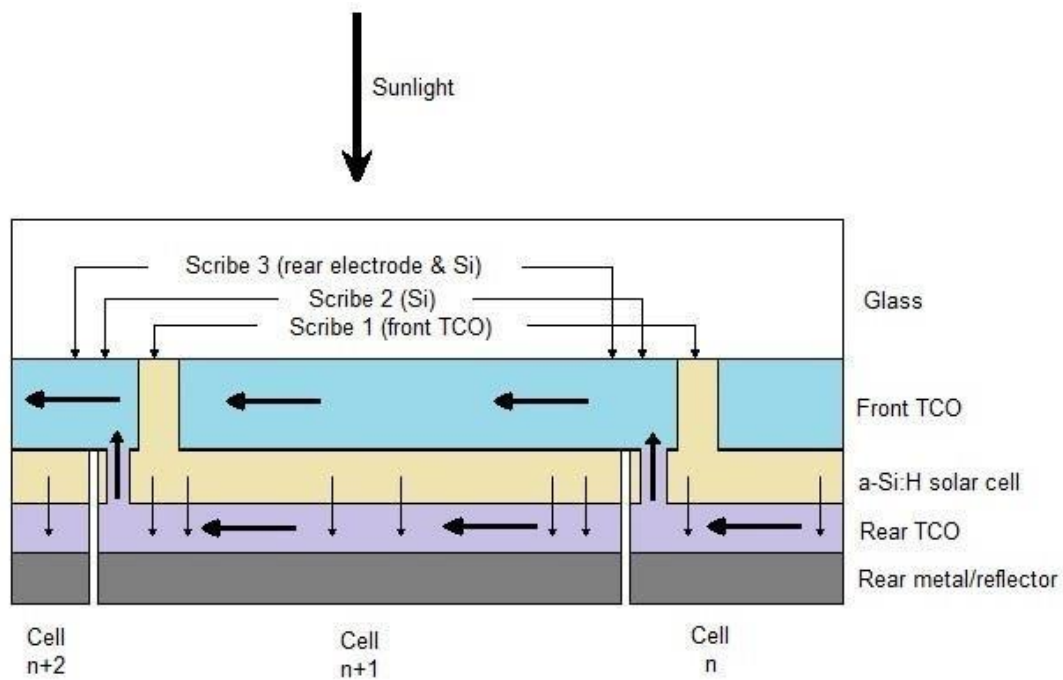


Figure 1.4: Thin Film Solar Cell

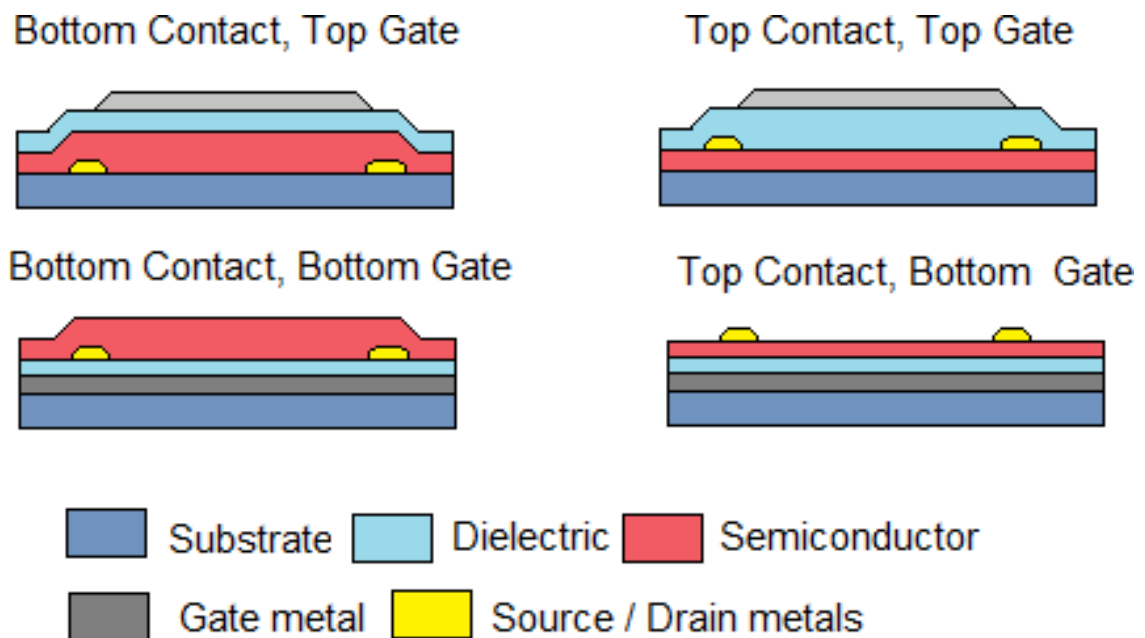


Figure 1.5: Thin Film Transistors

Chapter 2

LITERATURE SURVEY

2.1 DEPOSITION AND CRYSTALLIZATION OF SiGe

2.1.1 In-situ formation of Ge-rich SiGe alloy by electron beam evaporation and the effect of post deposition annealing on the energy band gap

This article describes how polycrystalline (poly)- SiGe alloy is achieved at low temperature of 500°C through solid state reaction of Si/Ge multilayer thin film on Si and glass substrates . Utilizing improved in-situ heating and electron beam evaporation, the pure thin layer were deposited. Results demonstrate that in the pure thin film, the amorphous Si (a-Si) phase and the poly-SiGe phase coexist. It was discovered that after post-deposition annealing in the 600–800 °C range, the a-Si phase dissolved into the SiGe phase. The optical characteristics of the annealed poly-SiGe thin films also revealed dual energy band gaps. On the basis of diffusion of Si in poly-SiGe, the stoichiometric evolution of the pristine thin film and its subsequent impact on the band gap after annealing has been explored [14].

2.1.2 Solid-phase crystallization of amorphous SiGe films deposited by LPCVD on SiO₂ and glass

In-depth research has been done on the crystallization kinetics and film microstructure of poly-SiGe layers produced by solid-phase crystallization (SPC) of amorphous SiGe with Ge fractions (x) between 0 and 0.42. Using Si₂H₆ and GeH₄ as gas sources, amorphous SiGe films 100 nm thick were formed by LPCVD at 450°C on thermally oxidized Si wafers and 7059 Corning glasses. The samples crystallized

under low pressure and at 550°C (below 9 Pa). X-ray diffractometry and transmission electron microscopy were used to study the process of crystallization and the final film microstructure. The growth kinetics was evaluated. The characteristic crystallization time declines with x , more sharply for higher values of x and more slowly for $x < 0.3$. In the fully crystalline layers, the grain size gets smaller as x gets larger.[15].

2.1.3 Ge-rich SiGe thin film deposition by co-sputtering in in-situ and ex-situ solid phase crystallization for photovoltaic applications.

This paper focuses the in-situ and ex-situ solid phase crystallization of high Ge content SiGe Thin films on glass substrate deposited by RF magnetron co - sputtering. By carefully controlling the growth temperature, the structural and optical properties of SiGe films have been studied. EDX analysis was used to assess the stoichiometry of the films, and it revealed up to at 77% of Ge. XRD was used to analyze the structural characteristics of the samples, which showed that all of them were amorphous in nature. The characteristics of amorphous films improved at 450 °C in both in-situ and ex-situ SPC procedures, according to the results of Raman and UV-VIS-IR transmittance measurements. Additionally, the introduction of oxygen during ex-situ the $\text{Si}_{0.23}\text{Ge}_{0.77}$ thermal annealing revealed a benefit of in-situ procedure over ex-situ using EDX. These films may have a significant future as components in thin film Si-based solar cells due to the possibility of deposition at low substrate temperatures[16].

2.2 PROPERTIES & APPLICATION OF SiGe

2.2.1 Efficiency enhancements in crystalline silicon solar cells by alloying with germanium.

The promise of low-cost photovoltaic cells with good performance comes from thin-film crystalline silicon (c-Si). A thin-film c-Si cell can improve its near infrared responsiveness by including a germanium-alloyed zone because of smaller bandgap. This claim is supported by theoretical investigations and computer device modelling, which demonstrate that realistic surface introduction of narrow bandgap Ge in Si matrix can lead to considerable increases in cell efficiency[17].

2.2.2 Thickness effect on the structural and electrical properties of poly-SiGe films.

The influence of thickness on Young's modulus, residual stress, resistivity, and Hall mobility of ultrathin poly-Si₁₁Ge₈₉ films formed by low pressure chemical vapor deposition is examined in depth in this research. It is found that with increase in film thickness, the resistivity decreases and mobility improves. Thus, the existing literature shows that the crystalline temperature, crystal quality, surface morphology affects the optical and electrical properties of the SiGe thin films and thier applications. thus improvement in crystalline quality directly affects the application of the material. further research towards achieving high quality polycrystalline SiGe is desirable[18].

Chapter 3

AIM & SCOPE

3.1 AIM

- This work is aimed towards achieving good quality polycrystalline SiGe thin film on cost effective glass substrate and to analyse their optical response.
- Amorphous films deposited using e beam evaporation are annealed at appropriate temperature for crystallization.
- The reflectance and transmittance of the amorphous and crystalline films are measured.
- To transform the amorphous $\text{Si}_{1-x}\text{Ge}_x$ thin film to crystalline by annealing it and reducing the defects and dislocations.

3.2 SCOPE

Amorphous thin films are non-crystalline materials and lack any sort of clear shape, form, or structure. Optical and electrical properties are function of alloy structure and stoichiometry. Thus, a good crystalline alloy will have improved optical and electrical properties. The scope of this work lies in the fact of improving crystalline quality of the SiGe film thereby achieving better optical properties.

Chapter 4

EXPERIMENTAL AND CHARACTERIZATION METHODS

4.1 PHYSICAL VAPOR DEPOSITION

In physical vapour deposition (PVD), material is vaporised from a solid or liquid source in the form of atoms or molecules, transported in the form of a vapour through a vacuum or low pressure gaseous (or plasma) environment to the substrate where it condenses. PVD methods can be used to create multilayer coatings, graded composition deposits, extremely thick deposits, and freestanding structures in addition to depositing films with thicknesses ranging from a few nanometers to thousands of nanometers. PVD deposition speeds typically range from 10 to 100 (1 to 10 nanometers) per second. Reactive deposition techniques can be employed in PVD procedures to deposit films of elements, alloys, and compounds. High vacuum (between 10^{-3} and 10^{-7} mbar) and extremely high vacuum (above 10^{-7} mbar) are the conditions under which these procedures are performed. They can also be utilised to create freestanding structures, graded composition deposits, very thick deposits, and multilayer coatings.

4.1.1 Advantages of PVD

- Environment friendly than paint & electroplating
- Good strength and durability
- Absence of toxic by products this is more safer than CVD
- Atomic level control of Chemical composition
- Energy required ranges from 0.5eV to 2eV

4.1.2 Disadvantages of PVD

- High vacuum required
- Cooling system is required
- Low deposition rate
- Production of thin coating layers

4.1.3 Electron beam Evaporation

Electron beam (e-beam) evaporation is a deposition technology for producing dense, high purity coatings. During an e-beam evaporation process, current is first passed through a tungsten filament which leads to joule heating and electron emission and to evaporate the source by resistive heating or electron beam in a vacuum chamber below 10^{-6} torr and condensation of evaporated vapor on surface (cold substrate). The source material, or the material to be deposited, is put within a water-cooled crucible. The material is heated to the vaporization temperature using a focused, high-energy electron beam with a few tens of kV in energy. The heated filament (often W or Ta) that is protected from the direct line of sight of both the evaporant and the substrate is where the electrons are thermionically released. Between the filament and the hearth, on which the crucible is set, a high voltage is applied. The flux of electrons released from the filament under this high voltage is accelerated and bent in the direction (by 270°) of the source material using magnetic field. Compared to other vaporization techniques, the thermal vaporisation rate can be relatively high. The composition of the substance that is vaporised from the source is proportional to the relative vapour pressures of the substance in the molten data sources. Thermal evaporation is often carried out using thermally heated sources, such as tungsten wire coils, or by heating the source material directly using high-energy electron beams. In order to decrease radiant heating of the substrate by the vaporisation source, the substrates are often positioned at a significant distance from the evaporation source. Energy required ranges from 0.5 eV to 2 eV [19]. A schematic of Electron beam evaporation system is shown in fig (4.1). The chamber is vented with the combination of scroll pump and turbomolecular pump to a base pressure nearly upto 10^{-8} mbar. This main chamber consists of 3 pocket electron gun, water cooled

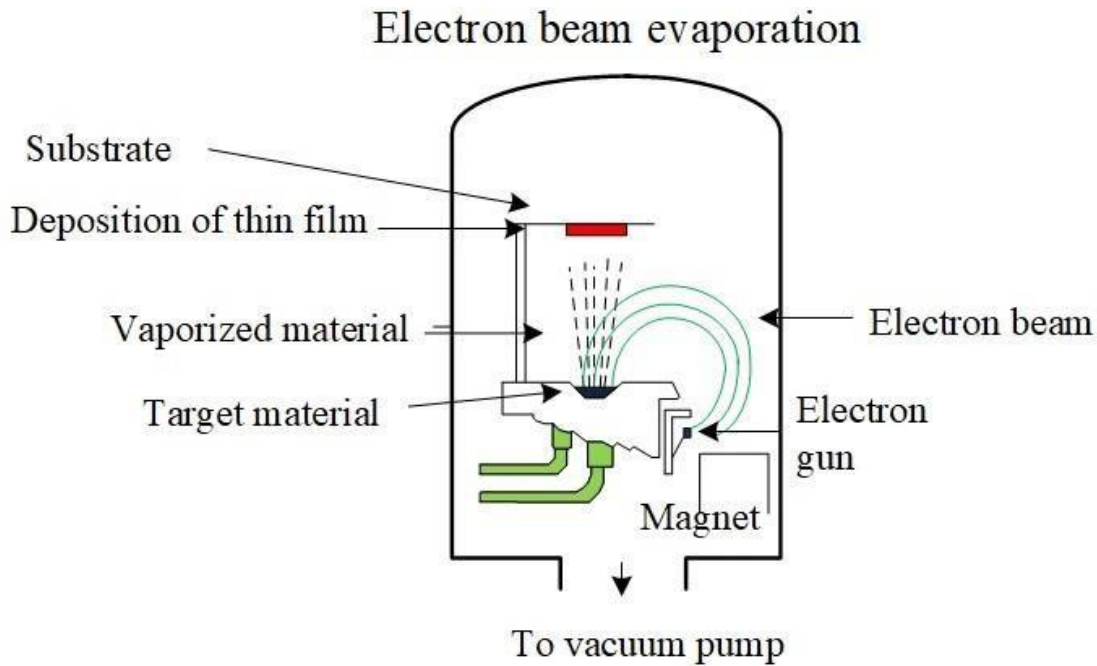


Figure 4.1: Electron Beam Evaporation System
Image source : Google

crucible, electron beam trajectory, single pocket electron gun, substrate holder and heater, Residual Gas Analyser, substrate manipulator, pressure gauge, vent valve, view port, quartz crystal monitor. This is isolated from the Load Lock chamber by a isolation valve. The load lock chamber Consists of Argon ion etching, Linear Transporter, pump, view port, vent valve and a pressure gauge. The substrate holder with a substrate manipulator has a vertical and rotational motion. The substrate is kept in the LLC and then is pumped with scroll pump and turbomolecular pump to get a desired base pressure near 10^{-8} mbar. Then the sample is transferred to the MC with the linear transporter. The sample is assembled near the heater. The heater is turned on at 450°C for 4 hours and the sample kept is annealed to make it crystalline from the amorphous as deposited. The MC and LLC is isolated seperately by a isolation valve. Residual Gas Analyzer monitors any presence of gas. The argon ion etching is to etch the surface oxides which is formed on the substrate for the deposition to be done. The Proportional Integral Derivative (PID) controller calculates an error in the system. After annealing the sample is brought back to the LLC and when the sample is not hot anymore, the LLC is vented and the sample is removed to do the desired characterization.

4.1.4 Deposition Parameters

Parameter	Corresponding Value
Current (I)	20-40 mA
Power (P)	3.84 kW
High Voltage (H.V)	9.6 kV
Annealed Temperature	450°C
Pressure	25×10^{-7} mbar
Deposition Rate	0.1 - 0.3 Å/sec

Table 4.1: Deposition parameters

4.2 STRUCTURAL DETERMINATION

4.2.1 X-Ray Diffraction

It is a technique to study the crystal structure of a material. when X-ray is incident on a material then the electron cloud interact with the X-ray and scatter it. Diffraction can happen if the X-rays' wavelength is of the order of interatomic spacing of the material. A schematic of XRD is shown in fig (4.2). In this thesis most of the diffraction patterns have been acquired from a Bruker D8 Discover four circle diffractometer with Mo radiation ($\lambda = 0.709 \text{ \AA}$).

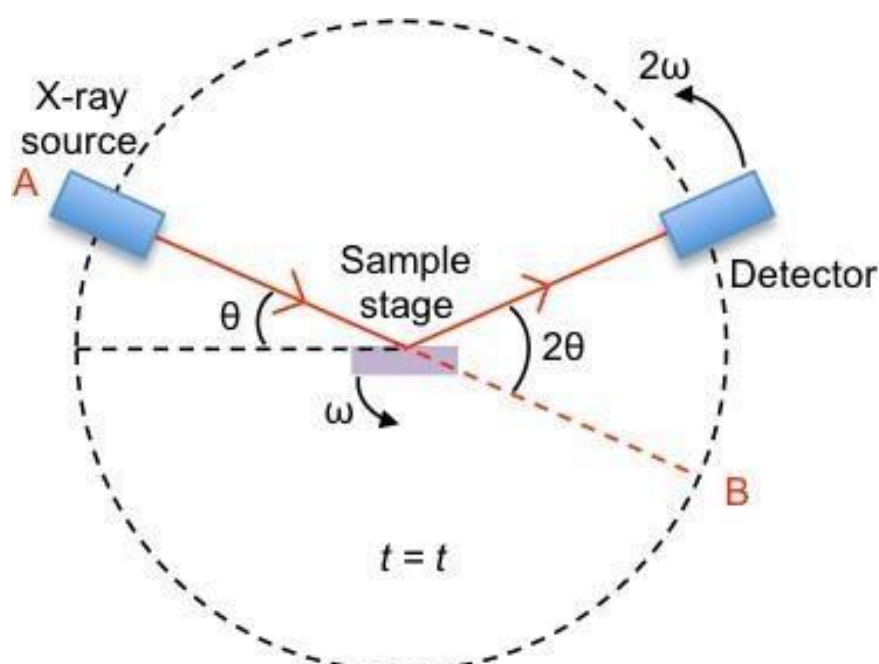


Figure 4.2: X-Ray Diffractometer
Image source : Google

The Bragg's Equation

According to Bragg's law, a crystal can be divided into different groups of parallel planes. The constructive interference will occur when path difference 'd' is equal to the whole number 'n' of the wavelength [20]. The diffraction pattern is shown in fig (4.3).

$$n\lambda = 2d\sin\theta$$

where,

d_{hkl} is the path difference is dependent on both the lattice spacing,

and the angle of incidence of the X-ray beam ϑ ,

n - order of diffraction (integer),

λ - wavelength of X-ray

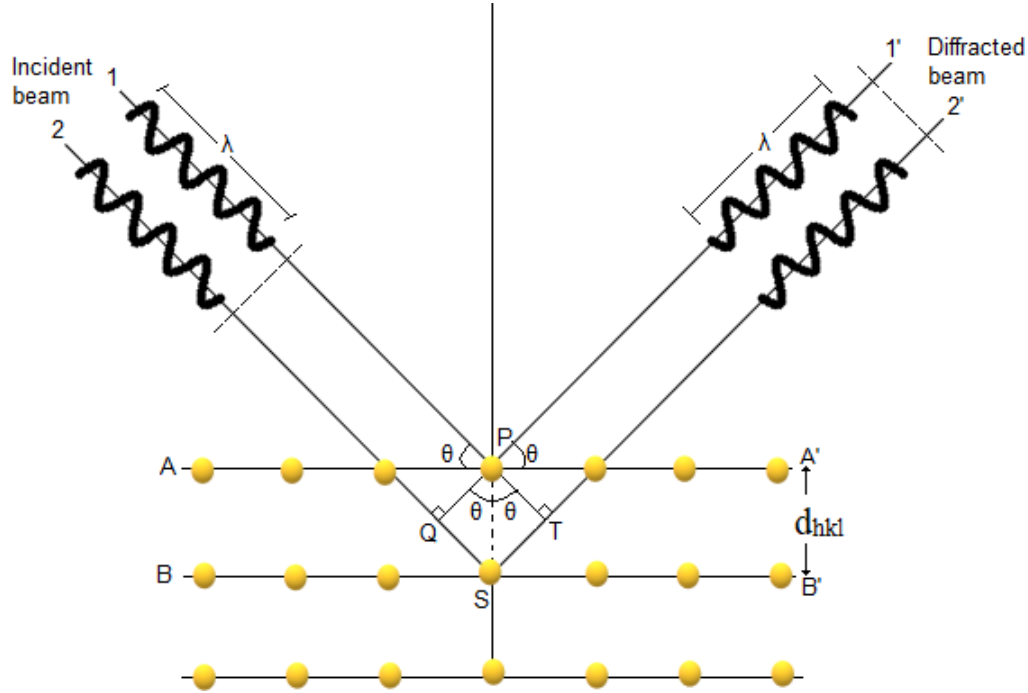


Figure 4.3: Bragg's Law for Diffraction

Debye–Scherrer equation

The broadening of XRD peak arises from crystallite size and strain effects due to presence of defects and dislocation in the sample. Along with this, the instrumental effect is also present which is called instrumental broadening. Thus total peak broadening is given by the formula in the equation (4.1) in this work the instrumental broadening part is taken care by acquiring data with LaB_6 sample. Next for the SiGe film the XRD pattern is acquired and using the famous Debye Scherrer formula (4.2) the crystallite size is evaluated. D represents the average crystallite size, K is the Scherrer constant, which depends on the shape of the crystallite ($K = 0.94$ or 1), λ denotes the wavelength of the X-rays (Molybdenum $\lambda = 0.71 \text{ \AA}$), β represents the full width at half maximum (FWHM) of the peak in radians, ϑ is the Bragg

angle at which the peak is observed[21].

$$b_{hkl} = \frac{\sqrt{(b^2)_{\text{Measured}} + (b^2)_{\text{Instrumental}}}}{K\lambda} \quad (4.1)$$

$$D = \frac{K\lambda}{\beta \cos(\vartheta)} \quad (4.2)$$

D represents the average crystallite size, K is the Scherrer constant, which depends on the shape of the crystallite ($k = 0.94$ or 1), λ denotes the wavelength of the X-rays (Molybdenum $\lambda = 0.71 \text{ \AA}$), β represents the full width at half maximum (FWHM) of the peak in radians, ϑ is the Bragg angle at which the peak is observed.

Grazing Incidence X-ray Diffraction (GIXRD)

For many years, researchers have studied thin films using the commonly used technique known as GIXRD. However, there is an inherent issue with GIXRD trials. The incident x-rays only travel $50 \text{ \AA}$ into the sample at angles below the sample's critical angle. Only a small fraction of the incident x-rays are scattered by the sample, which results in a low intensity of scattered x-rays. The vast majority of the x-rays incident on the sample are reflected. In turn, this leads to low signal-to-noise ratios and the requirement for lengthy exposure times in order to detect a significant enough quantity of dispersed x-rays for analysis[22]. (Fig 4.4) shows the schematic of a GIXRD set up. In the present work for the structural characterization GIXRD has been performed. The GIXRD was taken with Powder XRD with a Molybdenum wavelength source of 0.71 nm .

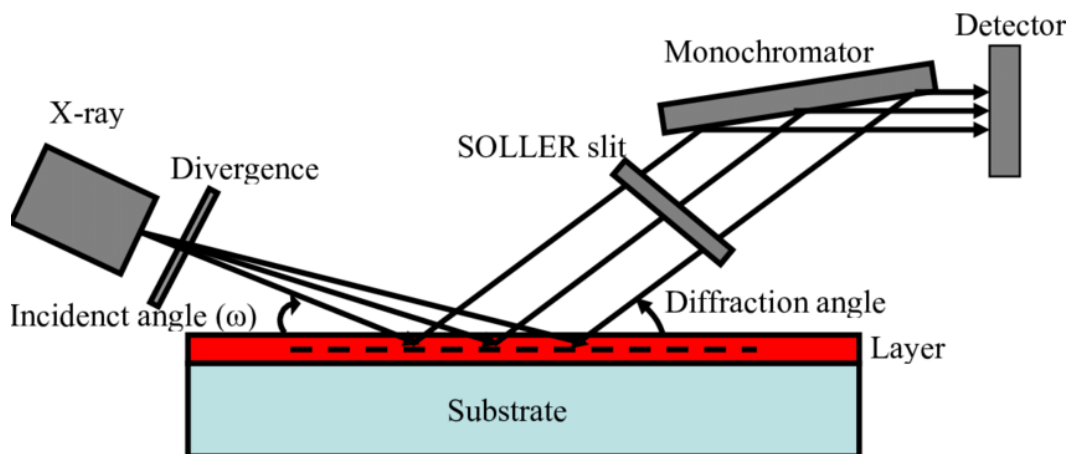


Figure 4.4: GIXRD
Image source : Google

Ewald Sphere

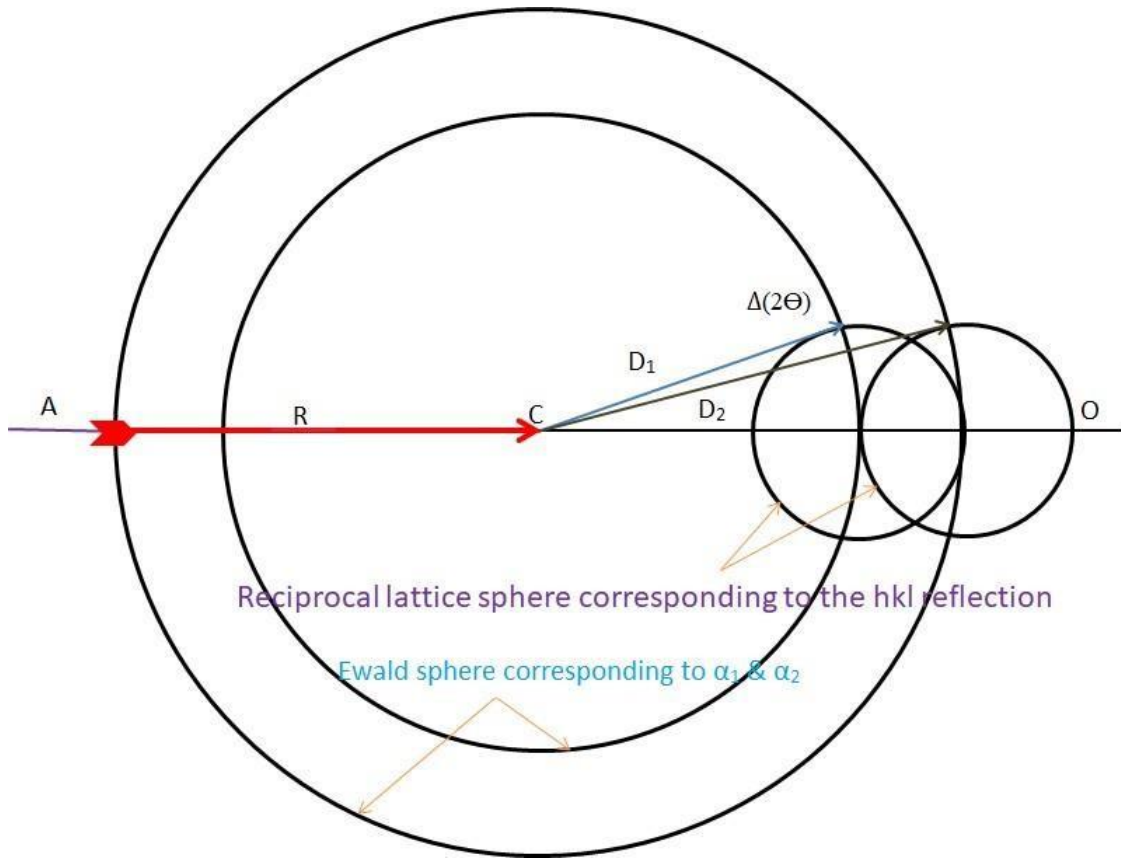


Figure 4.5: Ewald Sphere

In electron, neutron, and x-ray diffraction, a pattern of geometry known as the Ewald sphere is employed to illustrate the link between: a given reflection's diffraction angle, the wavevector of the incident and diffracted beams, the crystal's reciprocal lattice.

Equation (4.3) provided a method for determining the separation between the members of the set of parallel planes given by the Miller indices, which describe the orientation of planes. When the indices are not small and the coordinate system established by the unit cell edges is oblique, it can be challenging to see the orientations of these planes.

$$hkl = \frac{1}{u'} \frac{1}{v'} \frac{1}{w'} \quad (4.3)$$

where h , k , and l are integers that represent the intercepts of the crystal plane with the x , y , and z axes respectively, and u , v , and w are the smallest integers that satisfy the relationship ($uh+vk+wl = 0$). We

will define one point for each combination of planes since it is simpler to visualise where a point is in space. We create a line from the origin that is parallel to the planes. We mark a point along this line at a distance of $1/d$ from the origin, where d is the interplanar spacing. The reciprocal lattice point for the set of planes is this point. A lattice is made up of all of these points, one for each set of parallel planes identified by a triplet of integral Miller indices. Bragg's law in the form can help us understand the benefit of employing reciprocal distances.

$$\frac{1}{d} = \frac{2 \sin \vartheta}{\lambda} \quad (4.4)$$

We derive ϑ values from our films; the higher the ϑ value, the lower the associated d value. Thus, our diffraction patterns can be thought of as sine-distorted images of the reciprocal lattice. Ewald demonstrates how this theory can be used to X-ray diffraction issues to make them simpler. [23]

4.2.2 Raman Spectroscopy

The experimental set up of Raman Spectrometer is shown in (Fig 4.6). Using Raman spectroscopy the structural analysis of a material is done. In Raman spectroscopy, the sample is exposed to a powerful laser beam in the UV-Visible region (ν_0), and the scattered light is often seen in the direction opposite to the incident beam. There are two different types of scattered light: one, known as Rayleigh scattering, is powerful and has a frequency that is the same as the incident beam (ν_0), and the other, known as Raman scattering and has frequencies that are $\nu_0 + \nu_m$, where ν_m is the vibrational frequency of a molecule, they are called Stokes and anti Stokes lines.[24]

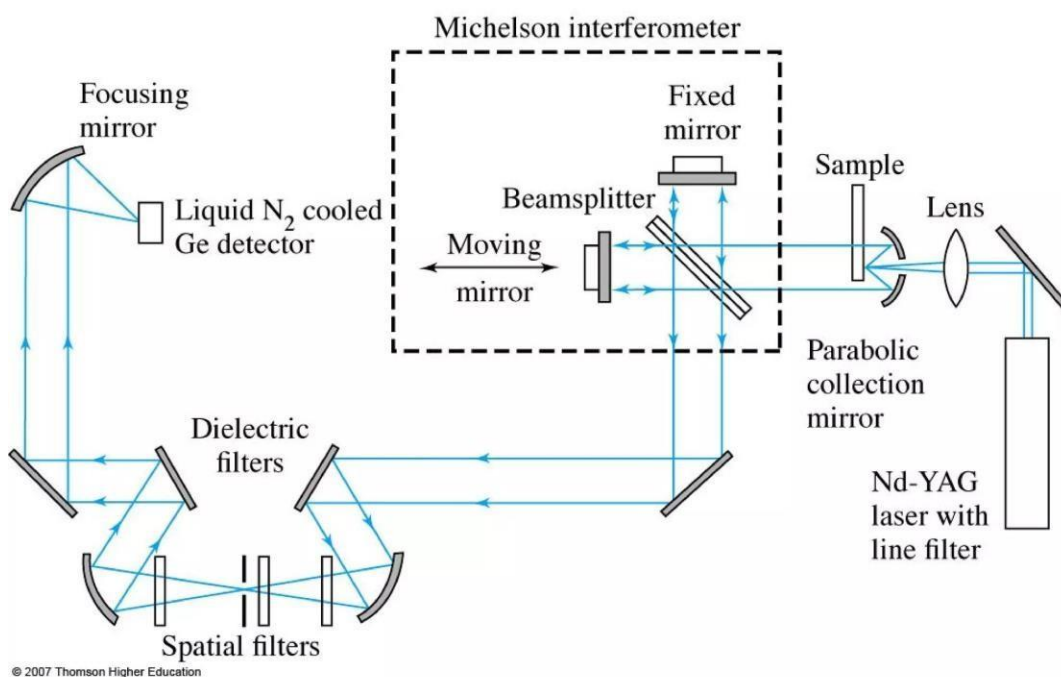


Figure 4.6: Schematic of Raman Spectrometer
Image source : Google

As a result, in Raman spectroscopy, we determine the vibrational frequency (ν_m) as a difference from the frequency of the incident beam (ν_0). All the films are characterized using a raman microscope of, UK make micro Raman "Renishaw" instrument using a green light laser (514.5 nm) as the excitation source. Using a Leica microscope with 10x, 20x, 50x, and 100x objective lenses, the sample is lit. The scattered signal is monochromatized using a diffraction grating with 1800

grooves per millimetre, and a thermoelectrically cooled charge coupled detector (CCD) is used to detect the signal when it is backscattered. The Stokes and anti-Stokes lines are denoted by the symbols $\nu_0 - \nu_m$ and $\nu_0 + \nu_m$, respectively which is shown in fig (4.7).

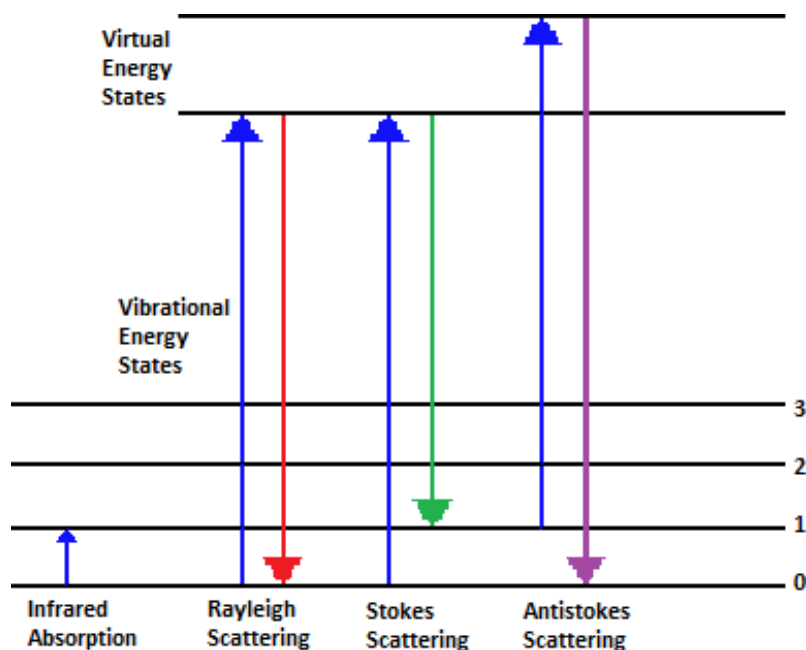


Figure 4.7: Raman Scattering

4.3 SURFACE MORPHOLOGY & OPTICAL DETERMINATION

4.3.1 Atomic Force Microscope

The fundamental working principle of a conventional AFM system with optical feedback is scanning a sample surface with an AFM probe. Near the free end of a flexible AFM cantilever, the silicon or silicon nitride AFM tip is integrated. The lateral and vertical positions of the AFM probe with respect to the surface are controlled by a piezoelectric ceramic scanner. The deflection of the AFM cantilever varies when

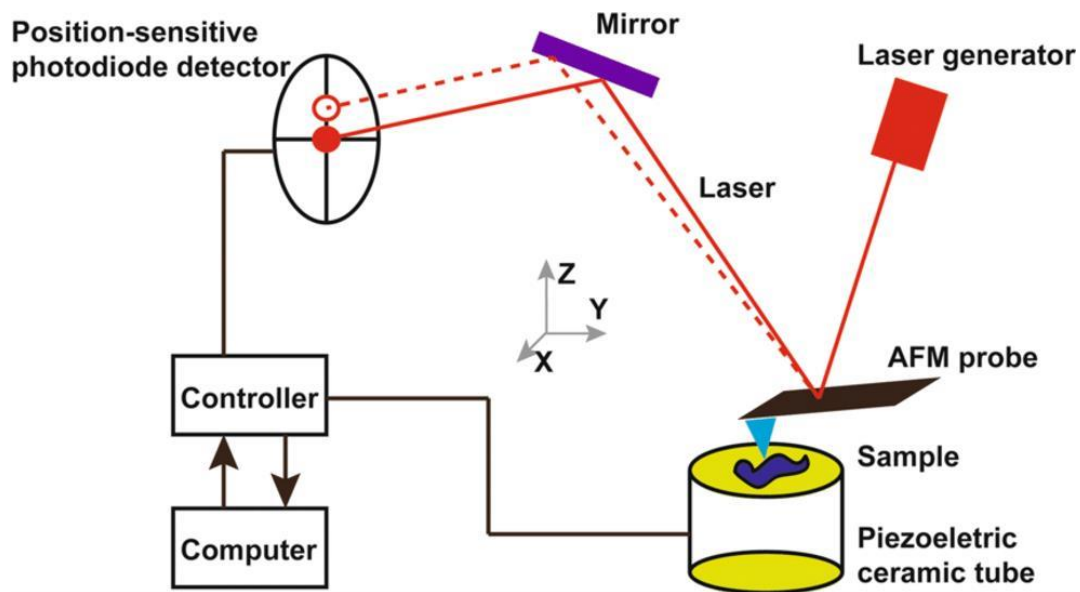


Figure 4.8: Atomic Force Microscope
Image source : Google

the AFM tip passes over different surface features. A laser beam is reflected from the rear of the AFM cantilever and directed into a position-sensitive photodetector in order to measure this deflection. In order to keep the AFM cantilever deflection almost constant and hence the contact force constant, a feedback loop regulates the scanner's vertical extension. A three-dimensional topographic representation of the surface is created by combining the coordinates that the AFM tip tracks throughout the scan. (Fig 4.8) shows schematic of AFM.

Modes of AFM Operation

With an atomic force microscope, there are two primary modes for imaging surface topography: static or contact mode and dynamic mode.

Depending on the forces that interplay between the AFM tip and the surface, Tapping or Intermittent Contact and Non-Contact Mode are further divisions of Dynamic Mode which are shown in fig (4.9).

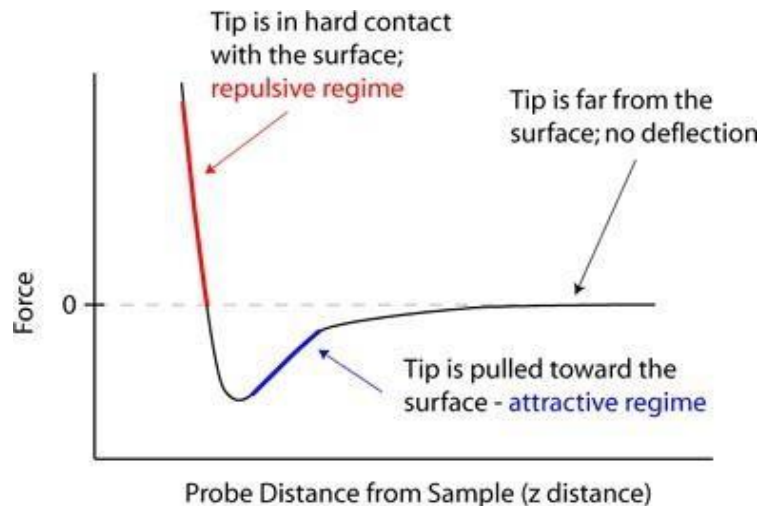


Figure 4.9: Atomic Force Microscope
Image source : Google

- **Contact Mode** : In this mode, the cantilever deflection brought on by surface interactions is detected while the AFM probe remains in continual touch with the sample surface. Although this mode is good for studying relatively smooth and flat surfaces, the constant contact between the probe and the sample can damage the surface. In this work the surface morphology of the SiGe thin films are evaluated using AFM in contact mode .
- **Non-Contact Mode** : This mode involves moving the AFM probe towards the sample surface but away from it. The amplitude of the probe oscillation is changed while the probe oscillation frequency is maintained at or near its resonant frequency. It measures the cantilever's bending caused by the van der Waals forces acting between the probe and the sample. Since it doesn't damage the sample surface, this imaging mode is appropriate for imaging non-conductive and delicate samples.
- **Tapping Mode** : This mode is a variation of non-contact mode AFM, where the AFM probe is oscillated close to the sample surface, but intermittently taps the surface during each oscillation cycle. The tapping motion of the probe reduces the interaction

forces between the probe and the sample, and it reduces the amount of sample damage compared to contact mode AFM. This mode is commonly used to image a wide range of samples, including biological samples and soft materials.

In the current study, every AFM topograph was taken using an NT-MDT system in semi-contact mode. Additionally, the surface roughness of various samples under various annealing conditions has been assessed [25].

4.3.2 UV- Vis Spectrophotometer

When light is incident on a thin film sample several phenomenon takes place. A part of the beam is specular reflected, a part is diffused reflected and another part is transmitted after being absorbed by the sample . The amount of light absorbed depends on the absorption coefficient of the sample. The information about the reflectance, transmittance and absorbance of thin film samples can be obtained using a spectrophotometer. The important parts of a spectrophotometer are light source, mirror arrangements, detector. Comparing with a standard reference the data for sample reflectance and transmittance is acquired and absorption coefficient is calculated. Thereafter by Kulbeka munk formula (put the formula) the bandgap of the material can be evaluated. In this work the spectral response of the samples have been acquired in the wavelength range (put it) in a system (name of the system). Then the band gap of the sample upon annealing is evaluated. In the current thesis, the reflectance and transmittance of SiGe alloy thin films has been measured using UH4150 Htachi Spectrophotometer[26]. The schematic of UV-Vis is shown in fig (4.10).

Tauc Plot

Tauc suggested utilising optical absorption spectra to determine the band gap energy of amorphous semiconductors. The Tauc approach is predicated on the assumption that the following equation can adequately represent the energy dependent absorption coefficient:

$$(\alpha \cdot h\nu)^{\frac{1}{n}} = B(h\nu - E_g) \quad (4.5)$$

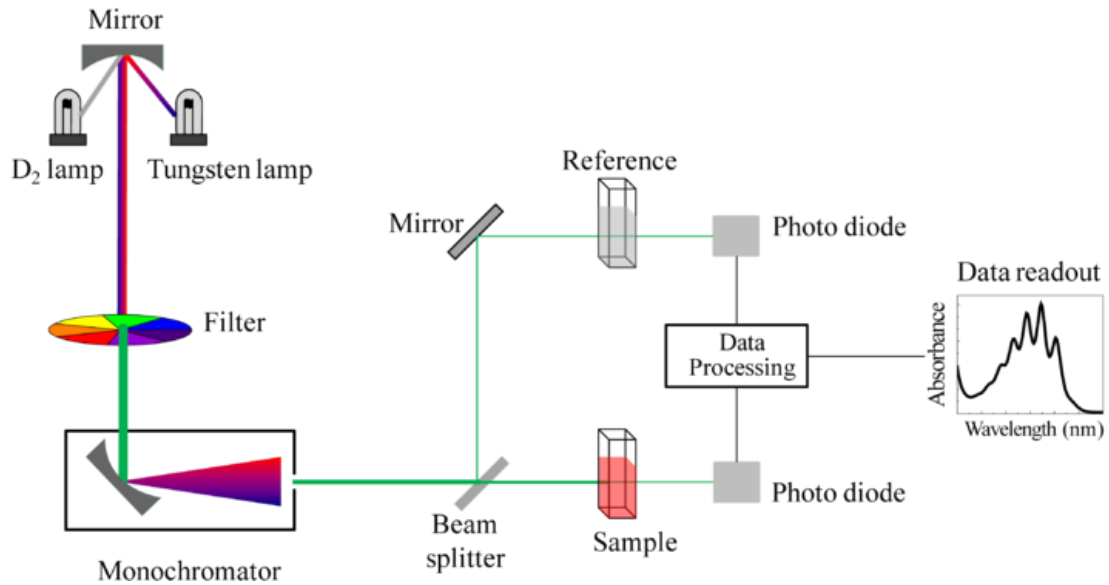


Figure 4.10: UV- Vis Spectrophotometer
Image source : Google

α represents a constant value, $h\nu$ denotes the energy of a photon, γ is another constant value, B represents a coefficient, E_g denotes the energy bandgap[27].

Kubelka Munk Theory

Light incident upon a surface can be reflected, transmitted, or absorbed by a film of material covered on a surface. The characteristics of the film have a significant impact on how light is modified. On the other hand, it might be a technique for characterising the "materials" in the movie. Light is absorbed or scattered differently by various materials. It can be considered that each coloured substance behaves differently when it comes to scattering or absorbing light. Of course, these parameters are influenced by the binder's characteristics. However, in an effort to keep things simple, it is assumed that the coloured materials alone are to blame for the absorption or scattering. Kubelka and Munk made the assumption that light that hits a surface is diffuse and is only thought to be scattered in the downward and upward directions. The film's thickness, the scattering and absorption properties of the coloured materials, and the background's reflectance all affect

how much light is reflected off the material's surface.

$$\alpha = \frac{(1 - R_{\infty})^2}{2R_{\infty}} \quad (4.6)$$

$$\alpha = \frac{(1 - R_0)^2}{2R_0(1 - R_0) + R_{\infty}(1 - R_0)} \quad (4.7)$$

Here, R_{∞} and R_0 are the reflectances at infinite thickness and zero thickness, respectively [28].

4.3.3 Optical Microscope

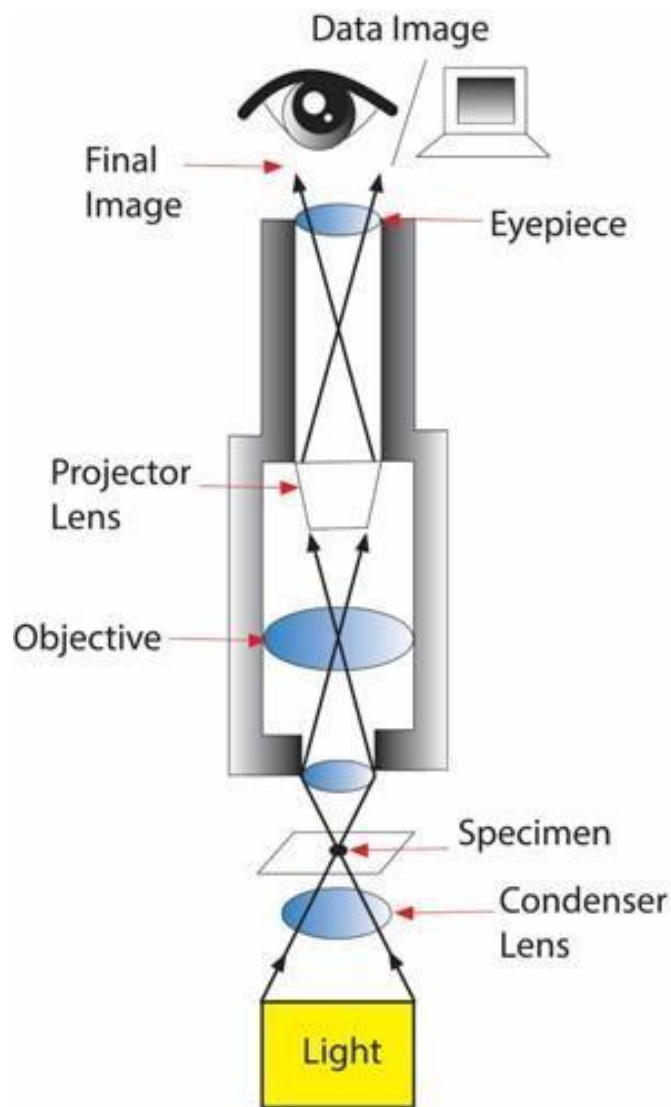


Figure 4.11: Optical Microscope
Image source : Google

Optical Microscope help us to observe the features of a sample which cant be seen by bare eyes. Optical Microscope first illuminate the sample and then create a magnified image of the sample features. The main parts of an optical microscope are light source, eyepiece, objective, nosepiece, focus wheel, condenser and stage. The schematic of Optical Microscope is shwown in fig (4.11). Initially, a magnified image is formed using an objective lens and then the formed image is further magnified by an eyepiece. In this work the microscopic fetaures of the sample are observed using a axio vert inverted optical microscope in refelction mode. In this work, an inverted optical microscope (Axio Vert.1) in reflection mode has been used to visualize the features of the sample upon annealing[29].

Chapter 5

RESULTS & DISCUSSION

In this chapter the structural characteristics of the as deposited thin film and its evolution with annealing has been studied using GIXRD.

5.1 STRUCTURAL ANALYSIS

5.1.1 X-Ray Diffraction Studies

The XRD done with molybdenum source for the as deposited (pristine) & annealed at 450°C for 4 hours are shown in the graph below. XRD plot shows that the pristine sample is amorphous in nature. The small intensity peak in the diffraction pattern appears from the substrate. Upon annealing the sample at 450 deg c for 4 hrs , crystallization process started. This is evident through the appearance of several peaks. Strong peaks at 12.61°, 20.71° corresponds to the diffracton plane (111) and (220) respectively. Thus upon annealing sige thin film has transformed to polycrystalline form. Along with the strong peaks two low intensity peaks arising from 311 and 400 planes are present at 24.16°and 29.08°respectively. The peak position indicates that the formed sige alloy thin film is Ge rich.

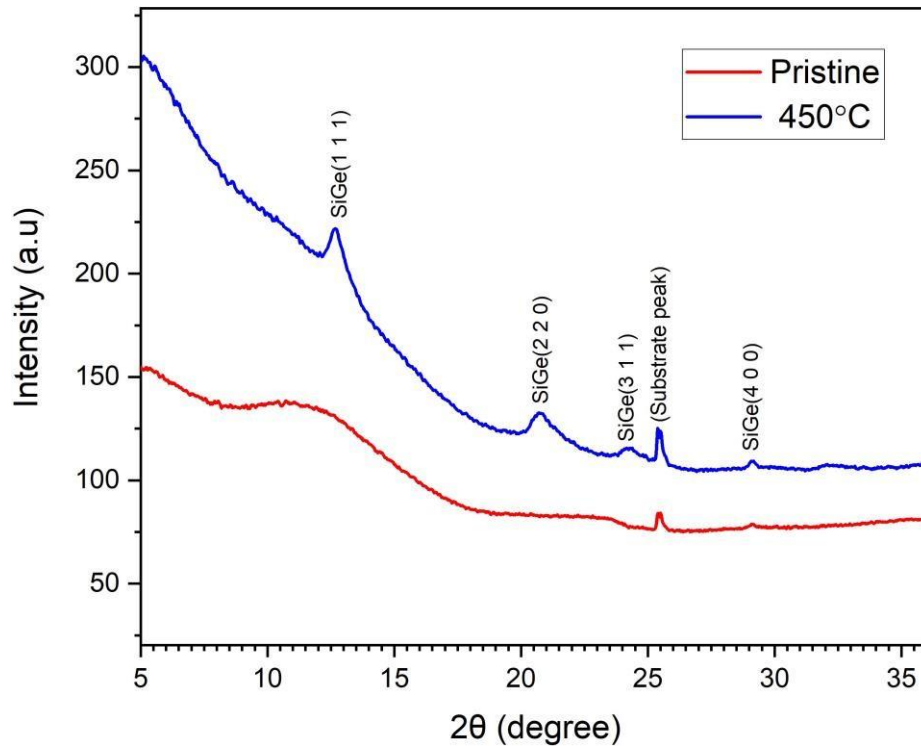


Figure 5.1: XRD data for pristine & annealed SiGe

Calculation of particle size:

We can now calculate the particle size by subtracting the background the 450°C annealed SiGe with the help of Debye - Scherrer equation.

$$D = \frac{K\lambda}{\beta \cos(\vartheta)} \quad (5.1)$$

The FWHM of the peak (β Sample) = 0.69376 (in degree)

The is instrumental broadening calculated from the polynomial fit of the LaB₆ XRD data , (β Instrumental) = 0.2 (in degree)

$$\beta = (\beta \text{ Sample}) - (\beta \text{ Instrumental})$$

$$\beta = 0.69376 - 0.2$$

$$\beta = 0.49376 \text{ (in degree)}$$

$$\beta = 0.008617 \text{ (in radian)}$$

$$2\vartheta = 12.630^\circ$$

$$\vartheta = 6.315^\circ$$

$$\cos\vartheta = 0.9939$$

$$\lambda = 0.071 \text{ nm}$$

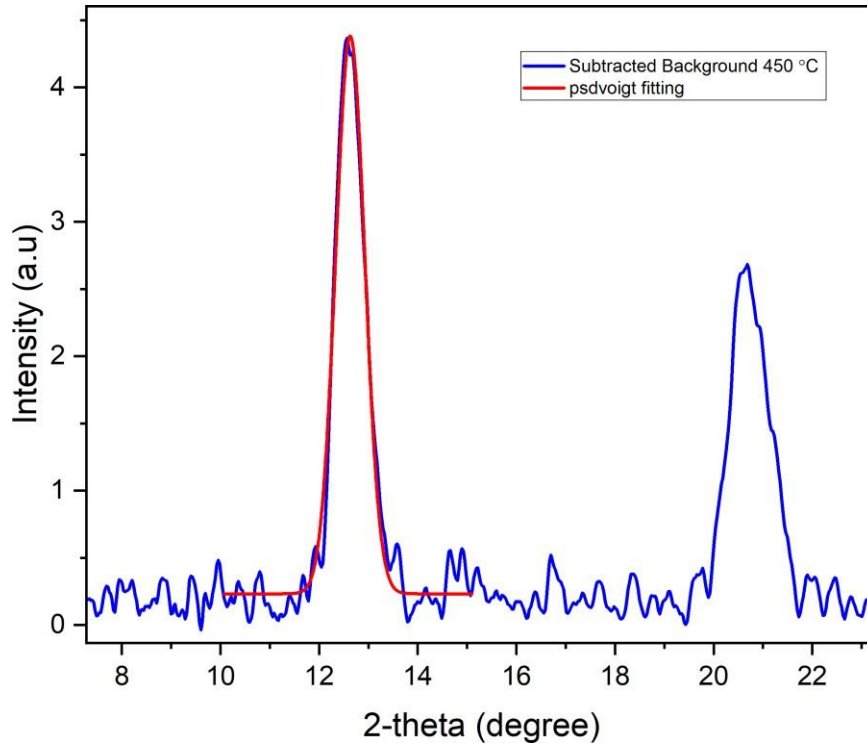


Figure 5.2: XRD background subtracted data of annealed SiGe

Substituting the above values in equation (5.1) taking the value of $K=1$, we get:

$$D = \frac{1 \times 0.071}{0.49376 \times \cos(6.315^\circ)}$$

$$D = \frac{0.071}{0.008617 \times 0.9939}$$

$$D = \frac{0.071}{0.008565}$$

$$D = 8.289 \text{ nm}$$

The particle size is found to be 8.289 nm.

5.1.2 Raman Studies

The Structural determination is done with Raman Spectroscopy to find whether the sample is crystalline or not. At first the pristine was found to be amorphous using Raman Spectroscopy. Then the annealed sample at 450°C is found to have a crystalline SiGe Peak. The Ge-Ge peak at 296.79 cm^{-1} and Si-Ge peak at 389.30 cm^{-1} is found. The raman shift is noted for both the samples. The peak position for SiGe shows that the alloy is Ge rich. Thus, the findings from the XRD is validated.

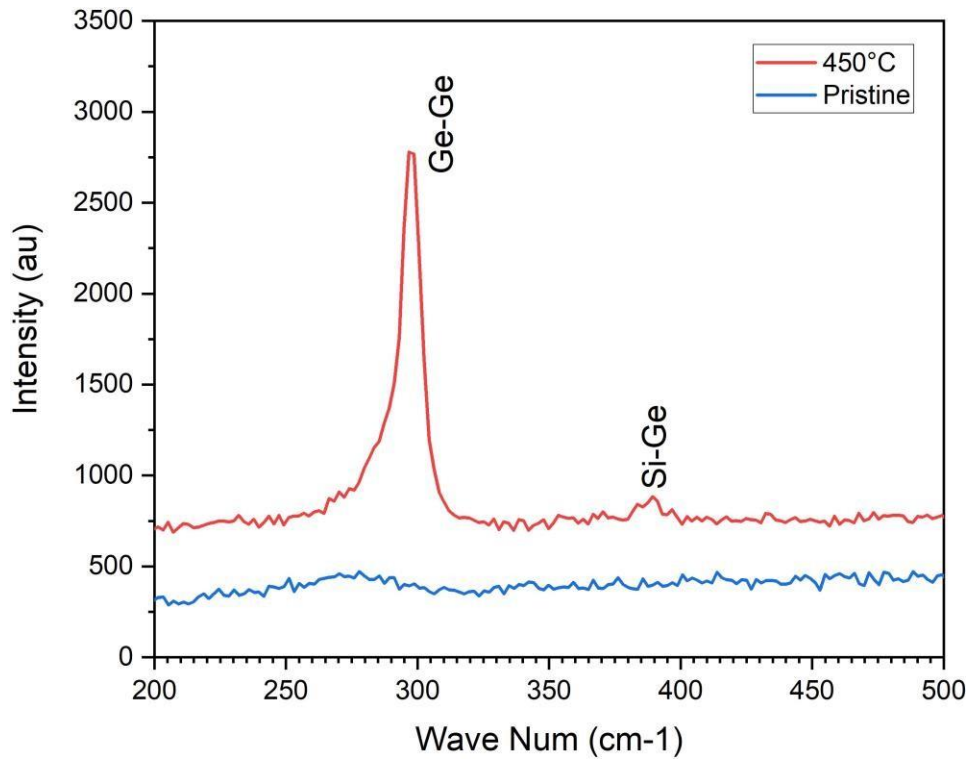


Figure 5.3: Raman data for pristine & annealed SiGe

5.2 SURFACE MORPHOLOGY AND OPTICAL CHARACTERIZATION

5.2.1 Atomic Force Microscopy Studies

The surface morphology of annealed sample is visualized under AFM. The 2D morphology is shown in (Fig 5.3 & Fig 5.4). It shows presence of grainy features with dimension of 0.1 μm . The RMS roughness of the sample is evaluated and it is 1.8 nm.

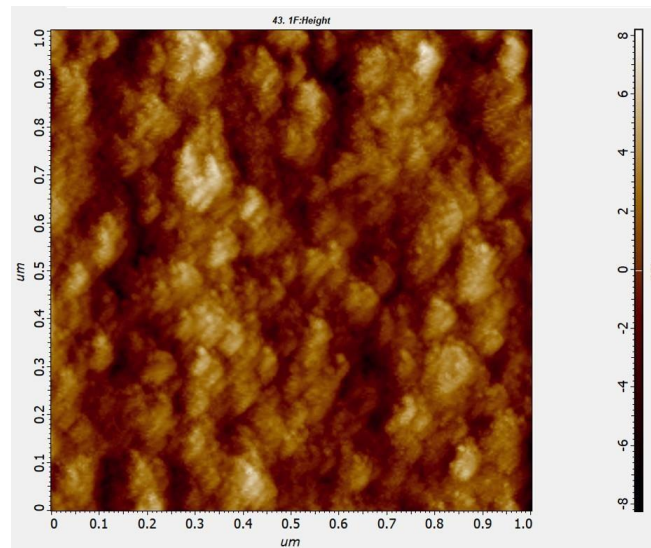


Figure 5.4: AFM data for annealed SiGe

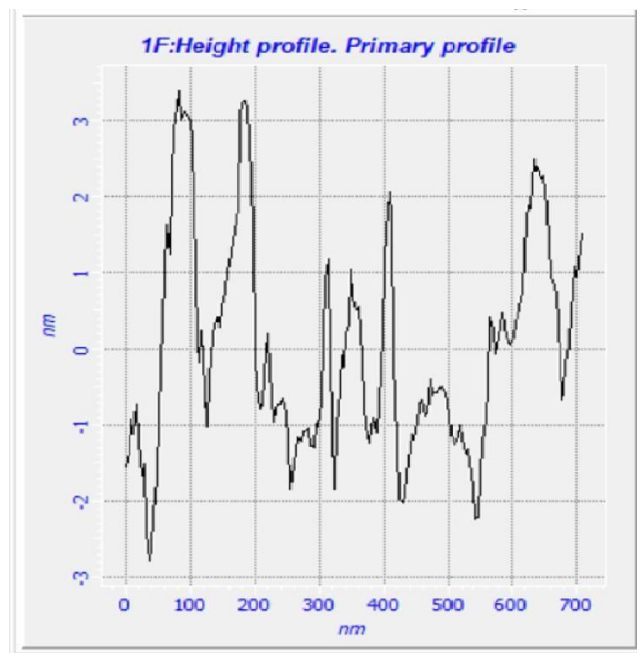


Figure 5.5: AFM graph for annealed SiGe

5.2.2 UV- Vis Spectroscopy Studies

The plotting of transmittance & Reflectance against the wavelength for both pristine & annealed sample.

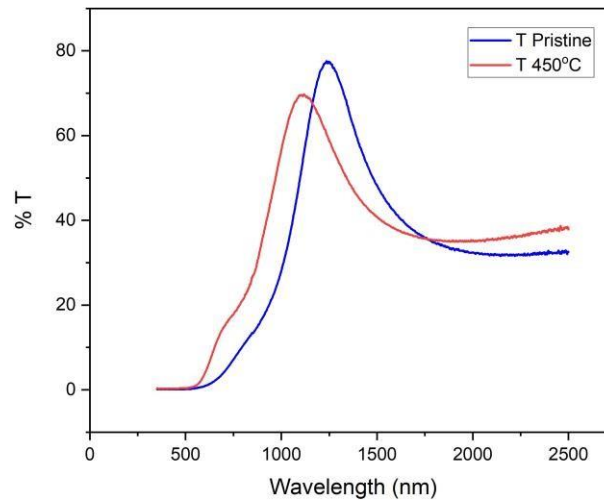


Figure 5.6: Transmittance for pristine & annealed SiGe

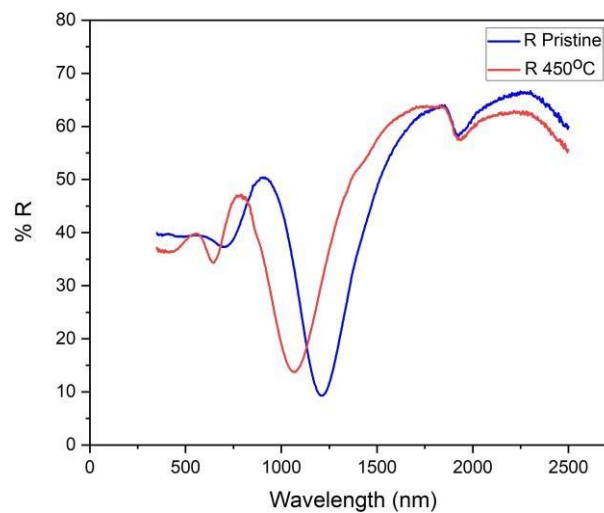


Figure 5.7: Reflectance for pristine & annealed SiGe

The optical response of the thin films are acquired using a spectrophotometer in the wavelength range 370-2500 nm. The reflectance and transmittance is shown in the (Fig 5.5 & Fig 5.6). From the graph it is found that upon annealing there is change in the reflectance and the transmittance of the samples. In order to understand the effect of annealing from the reflectance and transmittance data the absorption coefficient is found through the formula

$$\alpha = \frac{1}{d} \log \frac{100 - T}{R} \quad (5.2)$$

$$\alpha(h\nu) = A(h\nu - E_g)^n \quad (5.3)$$

$$\alpha(h\nu) = \frac{4\pi k}{\lambda} (h\nu - E_g)^n \quad (5.4)$$

[27]

where $h\nu$ is the photon energy, α is the absorption coefficient, k is the absorption index or absorbance, λ is the wavelength, E_g is the band gap energy, and n is an exponent.

The energy band gap of the films was analyzed. The as-deposited film has a band gap value of **0.845 eV**, for the annealed film, the band gap decreased to **0.826 eV**.

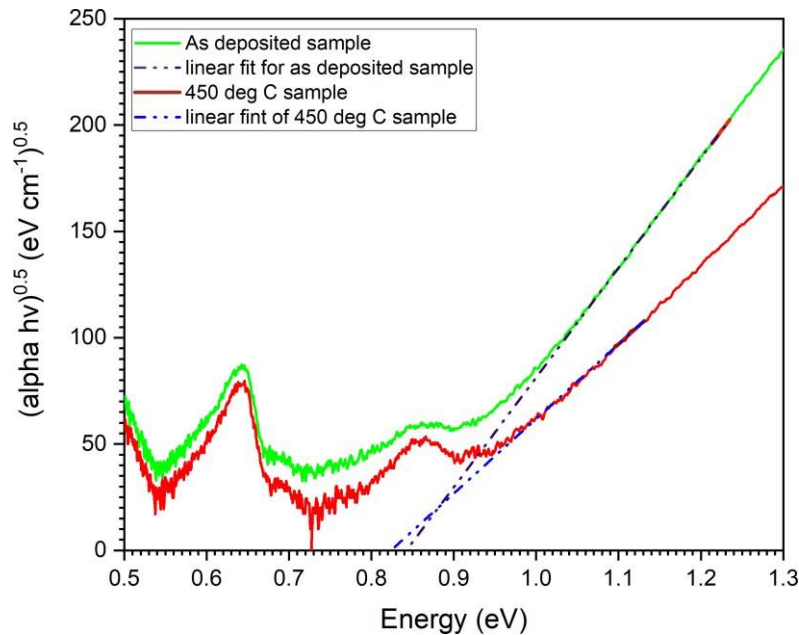


Figure 5.8: Indirect Band gap for pristine & annealed SiGe

5.2.3 Optical Microscope Studies

The samples are visualized under optical microscope to find the changes in the microstructural features upon annealing. The optical micrograph of the as deposited sample shows uniform illumination. (Fig 5.7) shows the optical microscpic image for as deposited sample. But upon annealing few microscopic features appear (dots) (Fig 5.8) . The light contrast in the micrograph arises from different types of atomic ordering & the amount of light reflected from them. Thus the appearance of the dots show that crystallinity has started upon annealing.

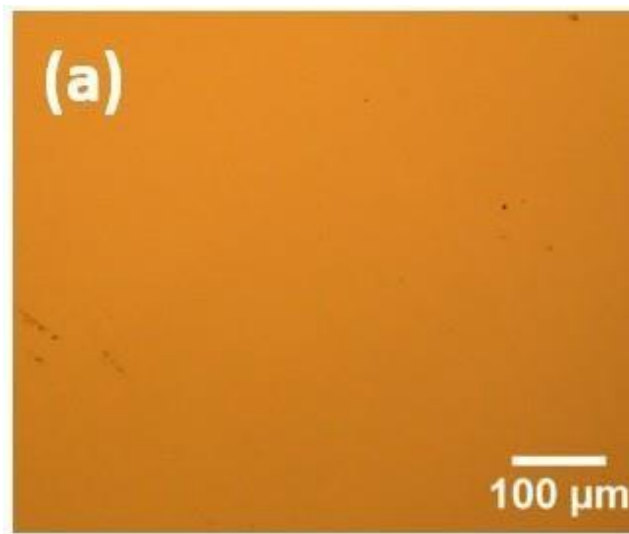


Figure 5.9: Optical Micrograph pristine SiGe

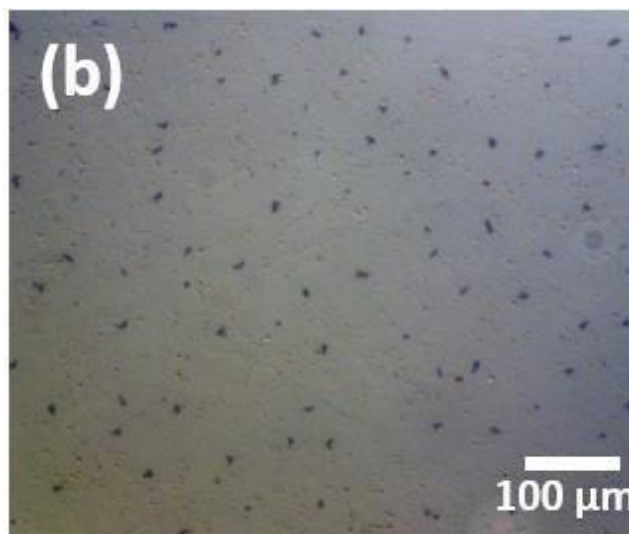


Figure 5.10: Optical Micrograph annealed SiGe

Chapter 6

CONCLUSION

The current thesis presents the results of synthesis of polycrystalline (poly)-SiGe via solid phase crystallization of amorphous SiGe upon annealing. In addition, an investigation on the structural and optical properties of the films upon annealing has been made to summarize

1. Poly SiGe is achieved at 450°C through vacuum annealing.
2. Grown poly SiGe is Ge rich in composition.
3. The optical band gap shows transition from 0.85eV to 0.8eV upon annealing.
4. The band gap evolution shows that crystallinity has improved with annealing.
5. Direct visualization of amorphous to crystalline phase change has been made through optical microscopic studies.

Thus, the grown Ge rich high quality polycrystalline SiGe thin films with band gap in NIR region shows the path for the material to be a potential candidate for application in NIR region of the solar spectra.

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