CHAPTER 111
STRUCTURE AND COMPOSITION

3.1. Introduction

The knowledge of the structure of as-deposited film is essential to understand its nature and for interpreting different physical properties which can be used for device applications. The structure exhibited by as-deposited films depends on an array of factors so depressingly large that only rather broad generalizations are possible. In the case of films deposited by thermal evaporation [1], the most important of such factors are: pressure and nature of residual gas in the deposition chamber, temperature of evaporation source, rate of deposition of condensing atoms or molecules, temperature of substrate surface, mobility of atoms or molecules on substrate, nature of substrate, presence of electric and/or magnetic field(s) at the substrate surface, occurrence of chemical reactions between deposit and substrates, etc.,

Structural and compositional studies on thin films could be made precisely using sophisticated techniques such as X-ray diffraction (XRD), scanning electron microscopy (SEM), transmission electron microscopy (TEM), scanning tunneling electron microscopy (STEM), energy dispersive analysis using X-rays (EDAX), electron spectroscopy for chemical analysis (ESCA), electron probe micro analysis (EPMA), Rutherford Backscattering spectrometry (RBS), etc. Each method has got its own advantages and disadvantages. X-ray diffraction method is one of the accurate methods of structural studies and it offers many benefits over other methods. It requires small amount of sample and it is non-destructive. However, this method assumes a lateral homogeneity in composition; therefore compositional changes due to the diffusion along the film surface or interface cannot be studied by this technique.

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X-ray diffraction method has been used by many workers for the structural investigations of the films [2 - 9]. In the present work, the structure of Te and Se$_x$Te$_{1-x}$ thin film samples have been analysed by XRD and the composition of Se$_x$Te$_{1-x}$ films have been determined using RBS technique.

3.2. X-ray diffraction technique

X-ray diffractometer consists of three parts, a basic diffraction unit, a counter goniometer and an electronic circuit panel with automatic recorder. Diffraction angles and intensity of lines are measured with greater accuracy. Possible directions in which a crystal can diffract a beam of monochromatic X-rays are simply determined by the Bragg's condition,

$$n\lambda = 2d \sin \theta$$  \hspace{1cm} (3.1)

where $n$ is the order of reflection, $\lambda$ is the wavelength of the incident X-rays, $d$ is the distance between atomic planes parallel to the axis of the incident beam, and $\theta$ is the angle of the incidence relative to the planes in question. The factor $d$ is related to the (hkl) indices of the planes and the dimensions of the unit cells. It is therefore seen that the diffraction directions are solely determined by structure and size of the unit cell.

The intensities of the diffracted beams depends on the possible diffraction directions and the lattice parameters such as 'a' and 'c' in the case of hexagonal symmetry and 'a', 'b' and 'c' in the case of orthorhombic symmetry can be expressed by the relation [10],

$$\frac{1}{d(hkl)} = \frac{1}{[(4/3a^2)(h^2+k^2+hk)+(l^2/c^2)]]^{1/2}}$$  \hspace{1cm} (Hexagonal) ---(3.2)
The crystallite size \( t \) in the films can be determined using the Scherrer's formula \[11\],

\[
0.94 \frac{\lambda}{t} = \frac{0.94 \lambda}{\beta \cos \theta}
\]

(3.4)

where \( \beta \) is the full width half maximum (FWHM) in radians.

The R.M.S. strain \( \eta \) in the films is calculated using the formula \[12\],

\[
\beta \cos \theta = \frac{\lambda}{t - \eta \sin \theta}
\]

(3.5)

A plot of \( \beta \cos \theta \) Vs \( \sin \theta \) is a straight line whose intercept gives \( \lambda \) \( / \) \( t \) and the slope gives the strain. The dislocation density \( \rho_d \) is determined from the crystallite size using the relation,

\[
\rho_d = \frac{1}{t^2}
\]

(3.6)

### 3.2.1. Measurements

X-ray diffraction (XRD) measurements were made using a Philips vertical goniometer and controller system with rotating Cu-anode, X-ray generator and tungsten filament. The characteristic \( K_{\alpha} \) radiation for Cu lines are at \( K_{\alpha_1} = 0.15405 \) and \( K_{\alpha} = 0.15443 \) nm. A graphite monochromator was used in the diffracted beam to remove CuK\( \beta \) as well as fluorescence and incoherent sample radiation. A weighed average of \( K_{\alpha_1} \) (2/3) and \( K_{\alpha_2} \) (1/3),
Kα = 0.15418 nm was used at 2θ for accurate d-spacing calculations. The operating conditions for all the samples were 40 kV and 20 mA. Films for analysis were mounted on suitable holders to eliminate substrate thickness effects on the position of the diffraction plane. Thin film samples coated on glass substrates of sizes approximately 1 cm x 1 cm were used for XRD studies. Taking into account the systematic errors, such as, peak position determination of the test sample, data shifting and substrate thickness effects, the accuracy of the d spacing determination is of the order of ± (0.001 - 0.003) nm.

3.2.2. Results and discussions

3.2.2.1. Tellurium thin films

Fig. 3.1. (a and b) shows the diffraction patterns obtained for tellurium thin films of two different thickness viz., 151nm and 176nm respectively and in both crystalline structure is observed. The X-ray diffractogram of a Te film of thickness 176nm deposited at room temperature reveals a hexagonal structure with a = 0.4459 nm and c = 0.5929 nm. From the observed 2θ values, corresponding to the peaks, the 'd X' values have been calculated.

The crystallite size [11] of the films were calculated by following the Sherrer and Williamson formulae and it is found that the crystallite increases as the film thickness increases. The dX values calculated using the above formulae are in good agreement with each other.

Graphs are drawn between β Cosθ and Sinθ of Te films of different thicknesses Fig. 3.2. (a and b). The slope values give the strain in the films, while the intercepts give the crystallite sizes.
FIG. 3.1 (a,b). XRD PATTERNS OF Te THIN FILMS OF DIFFERENT THICKNESSES 151 and 176 nm RESPECTIVELY.
FIG. 3.2 (a,b) VARIATION OF $\beta \cos \theta$ Vs $\sin \theta$ OF Te FILMS OF DIFFERENT THICKNESSES 151 and 176 nm RESPECTIVELY.
A decrease in strain values is noticed with the increase of film thickness. Similarly, the dislocation density also decreases with increase of film thickness. These values are tabulated in Table 3.1.

### 3.2.2.2 Se$_{0.7}$ Te$_{0.3}$ thin films.

Fig. 3.3. (a and b) shows the diffraction patterns obtained for Se$_{0.7}$ Te$_{0.3}$ thin films of different thicknesses viz., 76nm and 129nm respectively. The XRD patterns of the films reveal that they are amorphous in nature.

### 3.2.2.3. Se$_{0.5}$Te$_{0.5}$ thin films

Fig. 3.5 (a and b) shows the X-ray diffraction patterns of Se$_{0.5}$Te$_{0.5}$ thin films of thicknesses 67nm and 110nm respectively. Crystallite sizes are calculated by using both the Scherrer and Williamson formulae and the results are compared. The strain values are calculated from the $\beta \cos \theta$ and $\sin \theta$ plot (Fig. 3.6. a and b). It is seen that the strain and dislocation density decrease with the increase of crystallite size (Table 3.3). The lattice parameters were also calculated as $a = 0.396$ nm and $c = 0.529$ nm respectively for a typical film of thickness 110 nm.

### 3.2.2.4. Se$_{0.3}$ Te$_{0.7}$ thin films.

Fig. 3.7. (a and b) depicts the diffraction patterns of Se$_{0.3}$ Te$_{0.7}$ thin films of thicknesses 81nm and 138 nm respectively. The 'd$_x$' spacing values are calculated. The graph connecting $\beta \cos \theta$ and $\sin \theta$ (Fig. 3.8. a and b) is used to calculate the crystallite size and strain and it is found that the crystallite size increases while strain and dislocation density decrease with the increase of film thickness (Table 3.4.). The lattice parameters were calculated as $a = 0.428$ nm and $c = 0.546$ nm respectively.
FIG. 3.3 (a,b) XRD PATTERNS OF $\text{Se}_{0.7}\text{Te}_{0.3}$ THIN FILMS OF DIFFERENT THICKNESSES 76 and 129 nm RESPECTIVELY.
FIG. 3.5 (a,b) XRD PATTERNS OF Se$_{0.5}$Te$_{0.5}$ THIN FILMS OF DIFFERENT THICKNESSES 67 and 110 nm RESPECTIVELY.
FIG. 3.6. (a,b). VARIATION OF $\beta \cos \theta$ Vs $\sin \theta$ OF Se$_{0.5}$ Te$_{0.5}$ FILMS OF DIFFERENT THICKNESSES 67 and 110 nm RESPECTIVELY.
3.3 Electron Beam Technique (SEM)

3.3.1. Introduction

SEM (Scanning electron microscope) is becoming more useful for the direct observation of surfaces because they offer better resolution and depth of the field than optical microscopes. In addition, in-situ observation of surface morphology changes during heat treatment of specimens is possible.

3.3.2. Experimental

A beam of very small diameter (order of 10nm) is produced by the electron gun and electron lenses. The scanning coils deflect this beam and sweep it over the specimen surface. A cathode ray display tube is scanned synchronously with the electron beam. The brightness of the display tube is modulated by the signal which arises from the interaction of the beam with the surface element which is being probed. The yield of the collected electrons liberated from the specimen depends on the nature of the specimen surface and on its inclination with respect to the probing beam. Consequently one obtain pictures with a highly perspective appearance. JEOL scanning electron microscope was used in the present study to analyse the surface morphology of the thin film samples.

3.3.3. Surface Morphology

SEM of as-deposited Te films is shown in figure 3.9. (a and b). The films deposited show crystalline particles. The nucleation of the crystallite grains has been so initiated that they look like pebbles.
FIG. 3.7. (a,b). XRD PATTERNS OF $\text{Se}_{0.3}\text{Te}_{0.7}$ THIN FILMS OF DIFFERENT THICKNESSES 81 and 138 nm RESPECTIVELY.
FIG. 3.8 (a,b). VARIATION OF $\beta \cos \theta$ Vs $\sin \theta$ OF Se$_{0.3}$ Te$_{0.7}$ FILMS OF DIFFERENT THICKNESSES 81 and 138 nm RESPECTIVELY.
Figs. 3.10. (a and b) show the SEM patterns of vacuum deposited $\text{Se}_{0.7} \text{Te}_{0.3}$ thin films, which indicates the higher degree of amorphousity of the films.

The $\text{Se}_{0.5} \text{Te}_{0.5}$ films appear to possess more smooth surfaces. This is clearly visible in Fig. 3.11 (a and b). The disappearance of high agglomerates may be due to the diffusion of Selenium in the Te matrix. In contrast to the above observations, $\text{Se}_{0.3} \text{Te}_{0.7}$ films exhibit microcrystallinity as shown in Fig. 3.12 (a and b).

3.4 Ion Beam Technique (RBS).

3.4.1 Introduction

Rutherford backscattering spectrometry (RBS) is one of the most important technique adopted for the analysis of thin film composition. Several books and review articles are available on RBS analysis of materials [13-16]. In RBS, one is concerned with the fact that the projectiles moving through a target, lose energy along their path and are scattered by collision with the target atom. The four basic physical concepts such as scattering cross section, kinematic factor, stopping cross section and energy straggling form the basis of RBS.

The present work involves the studies by RBS technique using a Tandem Pelletron Accelerator which is available at the Institute of Physics, Bhubaneswar, India. Two types of ion sources are present. One (Alphatross) is for providing $\text{He}^{+}$ and $\text{H}^{+}$ ions and the other (SNICS) for almost all elements in the periodic table except inert gas ions. One beam line is dedicated to
FIG. 3.9. (a,b) SEM PATTERNS OF VACUUM DEPOSITED Te FILMS OF DIFFERENT MAGNIFICATIONS.
FIG. 3.10. (a,b). SEM PATTERNS OF VACUUM DEPOSITED Se_{0.7}Te_{0.3} FILMS OF DIFFERENT MAGNIFICATIONS.
FIG. 3.11. (a,b). SEM PATTERNS OF VACUUM DEPOSITED Se$_{0.5}$Te$_{0.5}$ FILMS OF DIFFERENT MAGNIFICATIONS.
FIG. 3.12. (a,b). SEM PATTERNS OF VACUUM DEPOSITED Se$_{0.3}$Te$_{0.7}$ FILMS OF DIFFERENT MAGNIFICATIONS.
condensed matter and material science research. A multipurpose scattering chamber, designated to carry out RBS, channeling NRA and PIXE studies is attached to the 45° beam line. A Si(Li) detector for X-ray detection and a NaI detector for γ rays detection are provided with the systems. Two surface barrier detectors (SBD) can be placed inside the vacuum chamber. The chamber has two view points and several other ports for various feedthroughs. The scattering chamber is provided with Blazors DIF-set pumping station with liquid nitrogen trap and a chilled water cooling facility. The vacuum attained by this pumping is of the order of 1.3 x 10^-5 Pa. The scattered particles are detected by SBD. The detected signal is shaped, amplified and finally with a pulse height analyzer the energy spectrum is stored and displayed in a multichannel analyzer (MCA). The block diagram of the RBS experimental set-up is shown in Fig.3.13.

3.4.2 Experimental

High energy ion scattering (HEIS) with He++ beams of 3.045 MeV energy at a scattering angle of θ =164° is used for the RBS spectra from which composition and thickness of the film are determined. In HEIS, the ions can penetrate deeper into the sample and hence, under channeling condition the technique becomes very surface sensitive which enables to study the composition of the films.

The scattered ion yields and energies can be measured with detectors. If A and B are two different elements present in the film, then the composition of the film (N_A and N_B) can be calculated using the expression[17]

\[
\frac{N_A}{N_B} = \left( \frac{H_A}{H_B} \right) \times \left( \frac{Z_B^2}{Z_A^2} \right) \tag{3.7}
\]
FIG. 3.13. EXPERIMENTAL ARRANGEMENT FOR RBS MEASUREMENTS.
where $H_A$ and $H_B$ represent the signal heights and the symbols $Z_A$ and $Z_B$ represent the atomic number of $A$ and $B$ respectively. The thickness of the film can be determined by using the relation [18].

\[
\delta_E = \frac{\delta_X}{N\left[K\varepsilon(E_0)/\cos\theta_1 + \varepsilon(KE_0)/\cos\theta_2\right]}
\]

where $\delta_X$ is the thickness of each channel, $\delta_E$ is the energy per channel, $N$ is the number of atoms per $m^3$, $K$ is the kinematic factor, $\varepsilon$ is the stopping cross-section and $E_0$ is the incident energy, $\theta_1$ is the angle of incidence and $\theta_2 = \pi - \theta_s$ where $\theta_s$ is the scattering angle. The total thickness can be computed as the number of channels multiplied by the thickness of each channel.

3.4.3 Composition and thickness

The RBS spectra of the films of three compositions of the present study with thicknesses 243, 110 and 81 nm respectively are shown in Figs.3.14 to 3.16.

The compositions are calculated using the formula 3.7 and the values are compared with the bulk sample values (Table 3.5). Ignoring the slight deviation of the compositions, throughout the forthcoming chapters, the compositions of the films are taken as $Se_{0.7}Te_{0.3}$, $Se_{0.5}Te_{0.5}$ and $Se_{0.3}Te_{0.7}$.

Thicknesses of the films are evaluated using formula 3.8. The thicknesses of the films evaluated by this technique are compared with those obtained from MBI method (Table 3.6). A close agreement between the thickness values obtained from the two methods is observed.
FIG. 3.14. RBS SPECTRUM FOR $\text{Se}_{0.7}\text{Te}_{0.3}$ THIN FILM OF THICKNESS 243 nm.
FIG. 3.16. RBS SPECTRUM FOR Se_{0.3}Te_{0.7} THIN FILM OF THICKNESS 81 nm.
### Table 3.1 Microstructural Parameters for Te films.

<table>
<thead>
<tr>
<th>Thickness (nm)</th>
<th>(d_x)</th>
<th>hkl Plane</th>
<th>(t) (nm)</th>
<th>(n_x \times 10^4)</th>
<th>(\rho_D \times 10^{15}) lines/m²</th>
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<tr>
<td>151</td>
<td>3.867</td>
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<td></td>
<td>3.209</td>
<td>101</td>
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<td></td>
<td>2.184</td>
<td>1110</td>
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### Table 3.3 Microstructural Parameters for Se₀.₅Te₀.₅ thin films.

<table>
<thead>
<tr>
<th>Thickness (nm)</th>
<th>(d_x)</th>
<th>hkl Plane</th>
<th>(t) (nm)</th>
<th>(n_x \times 10^4)</th>
<th>(\rho_D \times 10^{15}) lines/m²</th>
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<td>67</td>
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<td>3.812</td>
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<td>10.08</td>
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<td></td>
<td>3.119</td>
<td>101</td>
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<td>11.41</td>
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Table 3.4 Microstructural Parameters for Se$_{0.3}$Te$_{0.7}$ thin films.

<table>
<thead>
<tr>
<th>Thickness (nm)</th>
<th>d$_x$</th>
<th>hkl plane</th>
<th>t (nm)</th>
<th>$\eta_x \times 10^{-4}$</th>
<th>$\rho_{\eta} \times 10^{15}$ lines/m$^2$</th>
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<tr>
<td>81</td>
<td>3.902</td>
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<td></td>
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Table 3.5 Composition of Se$_x$Te$_{1-x}$ bulk and thin film samples

<table>
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<tr>
<th>Composition</th>
<th>Bulk Se : Te</th>
<th>Thin film Se : Te</th>
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<tr>
<td>0.7 : 0.3</td>
<td>0.68 : 0.32</td>
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</tr>
<tr>
<td>0.5 : 0.5</td>
<td>0.50 : 0.50</td>
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</tr>
<tr>
<td>0.3 : 0.7</td>
<td>0.31 : 0.69</td>
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Table 3.6 Comparison of thicknesses of Se$_x$Te$_{1-x}$ bulk and thin film samples

<table>
<thead>
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<th>Composition</th>
<th>Thickness (nm)</th>
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<td>RBS</td>
<td>MBI</td>
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<tr>
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<tr>
<td>Se$_0.5$Te$_0.5$</td>
<td>115</td>
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<tr>
<td>Se$_0.3$Te$_0.7$</td>
<td>85</td>
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</tbody>
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REFERENCES