Chapter IV

Structural Studies
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4.1 Introduction

The term structure encompasses a variety of concepts, which describe, on various scales, the arrangement of the building blocks of a material. On an atomic scale, one deals with the crystal structure, this is defined by the crystallographic data of the unit cell. Even today x-ray diffraction is considered to be a very powerful tool by crystallographers for the study of crystal structure and crystal imperfections. Indeed, it would have been the best if the atoms in the crystal could have been made visible directly like images of objects using an optical microscope. However, we know that this is not possible with visible light which must be used to see an object through an microscope. It can easily be shown using Rayleigh's criterion that the highest limit of resolution attainable with visible light is of the order of 1000 Å which is far greater than the interatomic distance in any crystal. Obviously one has to look for some radiations whose wavelengths are of the same order as the interatomic distances in crystal. In fact, there are several such radiations whose wavelengths are quite small and can be used to study the structural properties of solids to different extents, depending upon their relative properties.
In the power method determining crystal structure, the intensity of reflected beam can also be recorded in a diffractometer which uses a counter in the place of film to measure intensities. The counter moved along the periphery of the cylinder and records the reflected intensities against 2θ. Peaks in the diffractometer recording correspond to positions where the Bragg conditions is satisfied. There is an optimum specimen thickness for the transmission method, because the diffracted beams will be very weak or entirely absent if the specimen is either too thin (insufficient volume of diffracting material) or too thick (excessive absorption). The specimen thickness which produces the maximum diffracted intensity is given by $l/\mu$, where $\mu$ is the linear absorption coefficient of the specimen.

4.2 X-ray diffraction studies

Thin films have been prepared increasingly with complex structures in view of their applications in wide variety of spheres demanding tailor made properties. Sophisticated characterization techniques have emerged to understand the multifaceted properties of thin films. X-ray diffraction method is adjusted as the best method for the estimation of crystallographic parameters. The instrument used in this work is JEOL JDX- 8030 employing Cu $K_\alpha$ radiation with a scan rate of 0.1°/sec and with 2θ ranging from 10 to 80°. The diffraction peaks are identified using American Society for Testing Materials (ASTM) standards to study the
crystallographic nature and structure of the films [1]. The determination of an unknown structure proceeds in three major steps:

(i) The shape and size of the unit cell are deduced from the angular positions of the diffraction lines. An assumption is first made as to which of the seven crystal systems the unknown structure belongs to, and then, on the basis of this assumption, the correct Miller indices are assigned to each reflection. This step is called 'indexing the pattern' and possible only when the correct choice of crystal system has been made. Once this is done, the shape of the unit cell is known (from the crystal system), and its size is calculable from the positions and Miller indices of the diffraction lines.

(ii) The number of atoms per unit cell is then computed from the shape and size of unit cell, the chemical composition of the specimen, and its measured density.

(iii) Finally, the positions of the atoms within the unit cell are deduced from the relative intensities of the diffraction lines.

4.3 Review of earlier work on structure of ZnTe

Zinc telluride, one of the II-VI compound semiconductors, has found a wide range of applications in switching devices and solar cells [2, 3]. These applications make ZnTe a material worthy of study. ZnTe has a direct optical band
gap of 2.26 eV at room temperature [4]. Polycrystalline ZnTe thin films are usually p-type with a low electron affinity [5] and a high absorption coefficient in the order of $10^4 \text{ cm}^{-1}$ [6]. However, two main problems encountered in II-VI wide band gap compounds have prevented until now the extended use of these materials. Nearly all wide band gap semi-conductors exhibit a marked preference for one type of conductivity, and other type is usually difficult to achieve. The strong self-compensation mechanisms which are mainly responsible for this behaviour are not fully understood, but it is widely accepted that the presence of defects, which introduce localized electronic levels in the band gap, may play an important role in the compensation mechanisms [7, 8]. The second problem which has hindered the fabrication of optoelectronic device is the rapid degradation observed in these devices during operation. The short lifetime may be caused by the presence of dislocations at densities as low as $10^3 \text{ cm}^{-2}$ [9]. The photoelectronic properties of ZnTe thin films are greatly influenced by both native and foreign imperfections. Native defects such as vacancies, interstitial atoms can cause a considerable change in electrical and optical properties of semiconductor films without causing a major change in crystal structure [10].

Unlike other semiconducting compounds belonging to the II-VI group, the crystalline structure of zinc telluride has been studied in a small number of papers only. The authors studied the crystalline structure of ZnTe thin films arrived
at the conclusion that this substance crystallizes in the cubic system only. Kashyout et al [11] studied the x-ray diffraction analysis and showed that polycrystalline ZnTe films were produced by annealing the deposits at 375 and 400°C. Neumann-Spallart et al [12] reported the XRD pattern, and a single phase cubic ZnTe was obtained. Chaure et al [13] characterized the XRD peaks and reported that the ZnTe is known to possess either a closed packed cubic or hexagonal structure like ZnS with marginal difference in corresponding d values. Mondal et al [14] established the formation of a highly oriented cubic phase along with ITO peaks. Arico et al [15] has reported the hexagonal structure and they are characterized by good homogeneity.

Bozzini et al [16] obtained the relationship between the relationship between electrochemical growth conditions and the crystalline structure of as-deposited ZnTe were disclosed and correlated to the cathode chemistry during the growth process. Chaure et al [17] have shown that a mixed cubic as well as hexagonal ZnTe film was obtained even at a potential lower than the equilibrium potential of Zn electrodeposition. Basol et al [18] obtained the XRD patterns along with ITO peaks and the a values for the measured films were graphically determined. Lin et al [19] reported the annealing effect of the x-ray diffraction on ZnTe films prepared by molten salts. Pistone et al [5] characterized ZnCuTe films and the formation of ternary compound, having the cubic structure of ZnTe, was obtained upon annealing at 400°C.
Our aim is to investigate the crystalline structure of ZnTe thin films obtained under very different conditions and to establish how the crystalline structure of the thin films depends on the conditions of preparation and on further annealing treatment. In the present work, ZnTe thin films are prepared by an electrodeposition process cathodically. In order to understand the effects of deposition parameters, films are prepared under various concentrations of Zn\(^{2+}\), deposition potentials, bath temperatures and pH values.

4.4 Potentiostatically deposited ZnTe thin films

The description regarding the preparation conditions of ZnTe by potentiostatic cathodic deposition technique has been explained in chapter III. The asdeposited and annealed films are characterized by x-ray diffraction. The observed \(d\) values are compared with data available in JCPDS files. The various peaks corresponding to reflections from different set of planes according to Bragg’s law, 
\[2d \sin \theta = n\lambda\] are indexed.

4.4.1 Structural studies

Structure of ZnTe deposits are analysed using x-ray diffraction patterns. XRD studies showed that the deposits are polycrystalline with a cubic structure. Diffraction peaks of the films under different deposition conditions are recorded and the role of deposition parameters on the surface texture is analysed.
In the present work, ZnTe thin films are prepared under the following conditions and their XRD patterns are analysed.

(i) Various deposition potentials (-0.8V, -0.95V and -1.1V versus SCE)
(ii) Various Zn\(^{2+}\) concentrations (0.05 M, 0.10 M, 0.15 M, 0.20 M)
(iii) Various bath temperatures (30\(^\circ\) C, 50\(^\circ\) C, 70\(^\circ\) C, and 90\(^\circ\) C)
(iv) Various pH values.

A number of films are prepared under the above conditions and good quality, pin hole free thick films are used for x-ray diffraction studies. The preferential orientation and dominant orientation types are studied using the method given by Janda and Kubovy [20]. The values of G, the degree of crystallinity for the films are estimated using the same method. The grain size of the films is determined using the Debye-Sherrer formula.

4.4.2 Effect of deposition potential

The structure of the electrodeposited ZnTe films is investigated by x-ray diffraction analysis with CuK\(_\alpha\) radiation. Three samples fabricated under different plating potentials are analysed by XRD and their diffraction patterns are shown in Fig.4.1. The patterns revealed that the films are of polycrystalline in nature with cubic structure and exhibited preferential orientation along (111) direction. Examination of the peaks exhibits that electrodeposits are not formed from two separate elements but correspond to a single alloy phase. It is seen from the Fig.4.1
Fig. 4.1 XRD spectra of typical ZnTe layers deposited at (a) -0.8 V versus SCE, (b) -0.95 V versus SCE, (c) -1.1 V versus SCE.
that the degree of crystallinity increased with decreasing deposition potential. The preferred orientation of ZnTe films are weakened with the decrease in cathodic potential from -1.1 to -0.8 V versus SCE, and was lost for the films prepared under -0.8 V versus SCE or comparatively positive plating potentials. The relative intensities of the diffracted x-ray lines for sample prepared at -1.1 V (SCE) exactly resembles with those tabulated in JCPDS files. The films deposited above -1.1 V versus SCE, the XRD peak height decreases due to the interference of hydrogen evolution.

In electrodeposition process, hydrogen is the second element produced at the cathode: in some cases it is ignored, in some other cases it cannot be ignored. It is produced electrochemically but its consequences are metallurgical. This hydrogen evolution apparently reduces the plating efficiency by ejecting already deposited material into the solution, and/or by further reduction of Te to Te$^2\text{-}$. Oxygen reduction is, in principle, possible but can be neglected as, even with air agitation replenishment, its contribution is usually very small. Other cathode reactions are in practice neglectable, because either the kinetics or thermodynamics are insufficiently favorable (e.g., hydride formation) or are dependent upon a special combination of chemical and physical conditions (e.g., cathode film formation). The well crystallized phase was present in deposits from a solution with lower HTeO$_2^+$ concentration. Deposits prepared in a solution with higher concentration of HTeO$_2^+$

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Fig. 4.2 A plot between deposition potential and intensity of cubic (111) plane for typical ZnTe film at deposition potential -1.1 V versus SCE.
are less crystalline. Samples deposited at 90°C show narrower peaks than that deposited at 25°C.

The XRD peaks are found to depend on the deposition potential as shown in Fig.4.2. It is observed that the intensity of cubic (111) peak increases with more negative potentials and reaches a maximum value for deposition potential of -1.1 V versus SCE. The (111) peak intensity further decreases with more negative potential (-1.2 V versus SCE). The reduction of peak height at more negative potentials (< -1.1 V versus SCE) may be due to the hydrogen evolution which suppresses the growth of (111) oriented cubic phase. ZnTe films deposited at -1.1 V versus SCE exhibited a stoichiometric composition of Zn/Te in the ratio 49:51 atomic %. It is estimated from EDAX studies that films deposited at more negative potentials (< -1.2 V versus SCE) exhibited zinc rich phase whereas films deposited towards positive potentials (> -0.8 V versus SCE) revealed Te rich films. Fig.4.3 shows the variation of FWHM for the most prominent (111) peak of ZnTe as a function of deposition potential. It is obvious that the deposition potential -1.1 V (SCE) favours polycrystalline ZnTe morphology. The sharp increase in FWHM for potential between -0.95 to -1.05 V (SCE) suggests formation of microcrystalline ZnTe.
Fig. 4.3  Variation of full width at half maximum (FWHM) for (111) peak of ZnTe as a function of deposition potential.
4.4.3 Effect of zinc concentration

According to theory and results reported on the electrodeposition of CdTe [21, 22] the precursor of the less noble constituent of the alloy can be present in the bath at quite high concentrations (up to 2M for Cd\(^{2+}\)) and influences very little the result of the plating. In contrast and surprisingly, we found that the plating of ZnTe is very sensitive to the Zn\(^{2+}\) concentrations which must be comparatively low to obtain ZnTe at all. A concentration range of 0.05 - 0.25 M is investigated for TCO substrates. We found the optimum plating conditions for ZnTe at relatively low Zn\(^{2+}\) concentrations (Fig. 4.4).

The XRD signal of (111) cubic ZnTe (intensity normalized to charge per area) increases with decreasing Zn\(^{2+}\) concentrations. At 0.15 M a preferential (111) orientation of the deposited layer \([I (111) = 90, I (200) = 10, I (220) = 70, I (311) = 35, I (331) = 14\) shown in Fig. 4.5\] and comparatively low plating currents \((\approx 100 \ \mu A cm^{-2})\) are observed. From these facts, we can conclude that crystal growth surpasses nucleation at low Zn\(^{2+}\) concentrations. Film deposited on TCO at higher Zn\(^{2+}\) concentrations, with the other deposition parameters remaining unchanged, gave lower XRD signal. Moreover, at concentrations \(\geq 0.25\) M an excess Te was found in the XRD diagram. An increase of the current density was observed with raising Zn\(^{2+}\) concentration \((\text{from } \approx 100 \ \mu A \ cm^{-2} \text{ at } Zn^{2+} 0.15 \ M \text{ up to } 300 \ \mu A \ cm^{-2} \text{ at } Zn^{2+} 0.25 \ M)\). Again, as with the increase of plating currents due to temperature
Fig. 4.4  Intensity (normalized to charge per area) of the XRD signal of the ZnTe (111) peak as a function of Zn$^{2+}$ concentration: (a) -1.1 V versus SCE, (b) -0.95 V versus SCE.
Fig. 4.5 XRD patterns of ZnTe films deposited at -1.1 V versus SCE, for various Zn\(^{2+}\) concentrations. (a) 0.05 M, (b) 0.15 M, (c) 0.25 M.
increase, the increase in current density is accompanied by a change of the optical properties. Whereas films deposited at high Zn\(^{2+}\) concentrations (high current densities) were grayish brown and had a rough surface, those plated at low Zn\(^{2+}\) concentrations (\(\leq 0.15\) M) gave films well adherent on the TCO substrate with a reddish brown aspect. The increase of the plating currents with Zn\(^{2+}\) concentration and the tellurium excess for high Zn concentrations is unexpected on the basis of Kroger's theory [21, 22]. Moreover, growth control by leveling via an absorbed species (Zn\(^{2+}\)) of the bath seems to be absent. Table 4.1 shows the variation of (111) peak height of the cubic phase of ZnTe films deposited at various Zn\(^{2+}\) concentrations with bath temperature 90°C. It is observed from the table that as the Zn\(^{2+}\) concentration decreases, the (111) peak height increases which indicates the formation of single phase cubic ZnTe films at low Zn\(^{2+}\) concentrations.

4.4.4 Effect of bath temperature

The X-ray diffraction studies are carried out on ZnTe thin films prepared at various bath temperatures. The films usually showed a shiny reddish brown appearance (Zn is bluish white and Te is brownish black). The more blackish colour of films deposited from baths with more TeO\(_2\) (0.7 mM) could be ascribed to an excess of unbound Te. All the films are strongly adhering to the substrates, and could not be lifted off. The XRD patterns of ZnTe thin films deposited at various
Table 4.1

Variation of (111) peak height of ZnTe films deposited at different Zn$^{2+}$ concentrations at 90°C.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Zn$^{2+}$ Concentration</th>
<th>Height of (111) peak (a.u)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.05 M</td>
<td>1630</td>
</tr>
<tr>
<td>2</td>
<td>0.10 M</td>
<td>1530</td>
</tr>
<tr>
<td>3</td>
<td>0.15 M</td>
<td>1400</td>
</tr>
<tr>
<td>4</td>
<td>0.20 M</td>
<td>1320</td>
</tr>
<tr>
<td>5</td>
<td>0.25 M</td>
<td>1150</td>
</tr>
</tbody>
</table>
temperatures are shown in Fig.4.6. The sharp peak reveals that the films are polycrystalline in nature and the crystal structure is identified to be cubic. All XRD peaks show the presence of well crystallized compound of cubic symmetry with crystallite size of the order of 0.6 µm, which is estimated by Full Width at Half Maximum studies and using Debye–Scherrer formula [23]. The value of the lattice constant for all the four samples are in good agreement with the standard value of a = 6.07 Å. In the case of the as-deposited films, the most prominent reflection is corresponding to (111) phase.

It was found that plating of ZnTe is very sensitive to the Zn$^{2+}$ concentration and it may be maintained at comparatively low to obtain ZnTe films. The XRD signal of (111) cubic ZnTe increases with decreasing Zn$^{2+}$ concentration. The films deposited at higher Zn$^{2+}$ concentration with high current densities are dark brown in colour and has a rough surface. The experiments showed that the preferential orientation and dimensions of the crystallites contained in ZnTe thin films as well as other structural properties change as a function of the preparation conditions. Because of the texture and dimensions of the crystallites in ZnTe thin films have been investigated in tight correlation with other structural characteristics.

4.4.5 Effect of solution pH

The influence of pH is one hand that of controlling of the freely diffusing species, $HTeO_2^+$, via the protonation equilibrium of $TeO_2$[24] which in
Fig. 4.6 XRD patterns of ZnTe thin films deposited at various bath temperatures: (a) 30°C, (b) 50°C, (c) 70°C, (d) 90°C.
our experiments is always added in excess (as stock solution) to the plating bath. Lowering the pH increases the effective concentration of $HTeO_2^+$ (for constant TeO$_2$ activity of 1) at 25°C: $\log [HTeO_2^+] = -2.07 - pH$ (The effective concentrations of $HTeO_2^+$ at temperatures used for plating, up to 100°C, may be considerably higher [25]). Furthermore, lower pH results in a more positive redox potential of $HTeO_2^+/Te$:

$$E(HTeO_2^+/Te) = E^0(HTeO_2^+/Te) + \frac{RT}{4F} \ln \frac{a(HTeO_2^+)}{a(Te)} + \frac{3RF}{4F} \ln a_H.$$ 

On the other hand, further reduction of Te to $H_2Te$, or 6 e$^-$ reduction of $HTeO_2^+$ to $H_2Te$, and reduction of $H^+$ to $H_2$ are reactions occurring in addition to ZnTe formation more easily at low pH (and deposition potential). This might be what is also indicated by the data in Fig.4.7, if the intensity of the (111) peak is to be taken as a rough measure for the effective rate of ZnTe plating. Lower pH increases the concentration of $HTeO_2^+$ and facilitates its reduction at a given potential (leading to higher current densities), but the side reactions (reductions leading to $H_2Te$ to $H_2$) diminish the Faradaic efficiency of ZnTe formation. The pH of the plating solutions affected also the composition of electrodeposited thin films. A pH range of 2.3 to 4.1 was investigated. While at $pH < 3.0$ as well as ZnTe crystalline Te was also found, at higher $pH (> 3.0)$ XRD signals of thin films gave only the characteristic diffraction peaks of cubic ZnTe. The fact that at lower pH, besides ZnTe, crystalline Te was
Fig. 4.7 Intensity of the XRD signal of ZnTe (111) plane as a function of deposition potential, normalized to charge per area (Q/A).
also found could be explained by the more rapid crystallization of tellurium compared with that of ZnTe.

4.4.6 Effect of annealing

One of the key steps during the process of a heterojunction based on polycrystalline semiconductors is the annealing treatment of the entire film. During this step, the modifications occurring in chemical composition structure and morphology influence the optoelectronic characteristics of the material which, in turn, determine the heterojunction properties. The as grown ZnTe films are usually less crystalline. It has been observed in the present work that the films deposited at all temperatures between 30 and 90°C are found to be cubic with the preferential orientation of (111). However, a thermal treatment of annealing is to be carried out on the films on account of the following reasons:

(i) Electrodeposited ZnTe films are usually weakly crystallized and contain less Zn ion vacancies.

(ii) Annealing treatment increases the grain sizes of the crystallites and thereby the grain boundary scattering is reduced in the films.

(iii) The asdeposited semiconducting ZnTe films always posses a very high resistivity. Thermal treatment can reduce the resistivity drastically and make the films useful for optoelectronic applications.
The x-ray diffraction patterns of typical as-deposited and annealed ZnTe films deposited at 70°C are shown in Fig.4.8. All the major peaks are associated with ZnTe and no major Zn or Te peaks are observed. The sharp (111) peak at $2\theta$ around 25.2° for as-deposited and annealed films establishes the formation of a highly oriented cubic phase ZnTe films, which is in close agreement with the reported values [14]. It is observed from Fig.4.8b that the peak height of predominant lines of ZnTe film annealed at 350°C is larger than those of as-deposited films. The Full Width at Half Maximum (FWHM) values of prominent lines are observed to be lower for annealed films indicating an increase of grain size which may be ascribed to regrowth through diffusion. The grain size of annealed ZnTe films along (111), (220) and (311) are estimated to be 0.57 μm, 0.43 μm and 0.33 μm respectively.

**Annealing with temperature and time**

The influence of annealing temperature and time on the ZnTe properties was investigated. When the samples were annealed for 1 h, it was found that the characteristic XRD peaks of cubic ZnTe became stronger (Fig.4.9) as the annealing temperature was increased from 150 to 250°C, and reached a maximum at 350°C. Further increase in the annealing temperature to 450°C significantly weakens the ZnTe reflection peaks. EDS analysis of the annealed deposits showed that the atomic fraction of zinc in the deposits annealed at 450°C was higher than that found
Fig. 4.8 X-ray diffraction patterns of ZnTe films:
(a) asdeposited at 70°C and (b) annealed at 350°C for 1 hour
(Deposition temperature: 70°C).
Fig. 4.9 XRD spectra of ZnTe films for different annealing temperatures: (a) 150°C 1 hour, (b) 250°C 1 hour, (c) 350°C 1 hour, (d) 450°C 1 hour.
in the deposits annealed at 350°C, indicating that part of the tellurium may have escaped from the deposits during annealing due to volatility of tellurium at higher temperatures. When the ZnTe electrodeposits were annealed at 350°C, the XRD peaks of cubic ZnTe became sharper (Fig. 4.10) as the annealing time was increased from 30 to 45, and 60 minutes. At even longer annealing times (90 minutes), however, the ZnTe peaks diminished. In summary, at a lower annealing temperature, a longer annealing time was required for the formation of cubic ZnTe, whereas at a higher annealing temperature tellurium may escape faster from the deposits.

**Nelson - Riley plot**

The absorption of XRD signal in ZnTe thin film causes a fractional error in \( d \) and is directly proportional to \( \cos^2 \theta \). For our cubic system, if the value of \( a \) computed for each line on the pattern is plotted against \( \cos^2 \theta \), a straight line should result and \( a_0 \), the true value of \( a \) can be found by extrapolating this line to \( \cos^2 \theta = 0 \) (or, since \( \sin^2 \theta = 1 - \cos^2 \theta \), the various values of \( a \) may be plotted against \( \sin^2 \theta = 1 \)). Nelson and Riley analyzed the various sources of error, particularly absorption, more rigorously than we have done and showed the relation,

\[
\Delta d/d = K \left( \cos^2 \theta / \sin \theta + \cos^2 \theta / \theta \right)
\]

to estimate the lattice constants more accurately. The bracketed terms are sometimes called the Nelson - Riley function. The value of \( a_0 \) can be found out by
Fig. 4.10 X-ray diffraction patterns of ZnTe films annealed at 350°C for different annealing time: (a) 30 minutes, (b) 45 minutes, (c) 60 minutes, (d) 90 minutes.
plotting $a$ against the N-R function, which approaches zero as $\theta$ approaches 90°.

Although it is doubtful whether any advantage results from using the N-R function instead of $\cos^2 \theta$ in the back-reflection region, the greater range of linearity of the N-R function is an advantage when there are only a few lines in the high angle region.

A cubic crystal gives diffraction lines whose $\sin^2 \theta$ values satisfy the following equation, obtained by combining the Bragg law with the plane spacing equation for the cubic system,

$$\frac{\sin^2 \theta}{(h^2 + k^2 + l^2)} = \frac{\sin^2 \theta}{S} = \frac{\lambda^2}{4a^2}$$

The systematic error in $\sin^2 \theta$ shows up as a gradual decrease in the value of $\lambda^2 / 4a^2$, and a gradual increase in the value of $a$ as $\theta$ increases. It is found that the systematic error in $a$ decreases as $\theta$ increases. Nelson – Riley plot [25] for ZnTe film prepared at 70°C in the as-deposited and annealed conditions (350°C) are shown in Fig.4.11. The lattice constants are estimated to be 0.611 and 0.608 nm for as-deposited and annealed samples respectively. It is observed that the lattice constant value of annealed ZnTe film is near to the ASTM data value of 0.607 nm [26].

4.5 Structural studies on galvanostatically deposited ZnTe thin films

Structural studies on galvanostatically deposited ZnTe films are carried out using the above said process by x-ray diffractometry. Polycrystalline
Fig. 4.11 Nelson-Riley plots for typical ZnTe films deposited at 70°C (a) as-deposited and (b) annealed at 350°C, 1 hour, Deposition potential: -1.1 V versus SCE.

\[ f(\theta) = \frac{1}{2} \left( \frac{\cos^2 \theta}{\sin \theta} + \frac{\cos^2 \theta}{\theta} \right) \]
ZnTe films are also deposited galvanostatically at various bath temperatures in the range between 30°C and 90°C. The current density for the deposition is maintained at 1.6 mAcm⁻². The preferential orientation, structure and composition of the films are determined by recording the x-ray diffraction patterns using JEOL JDX-8030 x-ray diffractometer.

Films with different compositions, grain size and preferential orientation are deposited under various deposition conditions and the effects of deposition parameters on the surface structure are studied. It is found that the structure strongly affects the appearance of the films. The film appearance may be either matt or shiny. Each of these characteristics is related to a certain structure of the film surface. Films with smaller grain size produce shiny appearance, whereas films with larger grain size produce matt appearance. To study the effect of deposition parameters on the structure of ZnTe films, ZnTe films are deposited under the following conditions.

(i) Various current densities (1.4, 1.5, 1.6, 1.7 mAcm⁻²)
(ii) Various Zn²⁺ concentrations (0.05 M, 0.10 M, 0.15 M, 0.20 M)
(iii) Various bath temperatures (30°C, 50°C, 70°C and 90°C)
(iv) Various pH values (2.5 to 6).

4.5.1 Effect of current density

Galvanostatic deposition of ZnTe films on F: SnO₂ substrates yielded dark brown ZnTe films with good adherence. Fig.4.12 shows the x-ray diffractogram...
Fig. 4.12 XRD spectra of ZnTe films deposited at various current densities: (a) 1.4 mA cm$^{-2}$, (b) 1.5 mA cm$^{-2}$, (c) 1.6 mA cm$^{-2}$, (d) 1.7 mA cm$^{-2}$.
Fig. 4.13 A plot between cathodic current density and intensity of cubic (111) plane for ZnTe films.
Fig. 4.14 Variation of grain size with rate of deposition.  
Current density: 1.6 mAcm$^2$. Deposition time: 60 minutes.  
Deposition temperature: 80°C. Solution pH: 3.6 ± 0.1.
of the ZnTe films deposited at various cathodic current densities from 1.4 to 1.7 mAcm\(^{-2}\). All the films are found to be polycrystalline with cubic structure and exhibited a preferential orientation of (111). No change in crystal structure is noted as the current density varies. But some small intensity Te peaks are appeared for the films prepared at 1.4 and 1.5 mAcm\(^{-2}\). The presence of Te in samples deposited under these conditions is a surface effect, probably related to the chemical attack brought about by the acidic bath on the top layers of the coating. This provides a sort of dezincification, a typical corrosion form of Zn alloys with more noble elements. The intensity of the peak for the film prepared at 1.7 mAcm\(^{-2}\) is reduced and the films prepared at 1.6 mAcm\(^{-2}\) have maximum peak intensity.

The XRD peak intensities are found to depend on the cathodic current density as shown in Fig.4.13. It is observed that the intensity of cubic (111) peak increases with cathodic current density and reaches a maximum value at 1.6 mAcm\(^{-2}\) and after that decreases. The reduction in peak height at higher current density (1.7 mAcm\(^{-2}\) and above) is due to the effect of hydrogen evolution and dezincification. Fig.4.14 shows an increase in grain size up to the rate of 1.6 mAcm\(^{-2}\), and then it begins to decrease. The more increase in rate of deposition causes the production of films with lower grain size at a current density than 1.6 mAcm\(^{-2}\).
4.5.2 Effect of bath temperature

Zinc telluride thin films are deposited galvanostatically at different temperatures between 30 and 90°C using an aqueous electrolyte at pH 3.6 ± 0.1. The structural characteristics of ZnTe deposits are greatly influenced by the bath temperature. Fig.4.15 shows the diffractogram of the ZnTe films prepared at different bath temperatures. X-ray diffraction studies revealed that the films deposited at lower bath temperatures (below 50°C) yielded poor deposits with pale brown colour. The x-ray diffraction patterns of the films deposited at higher temperatures (> 50°C) exhibited a good crystalline nature with brown appearances and the quality of the crystallites increases with temperatures. From the figure (Fig.4.15) it is found that, all the films are preferentially oriented along the (111) plane. No change in crystal structure and preferential orientation is recorded under different bath temperatures, whereas the peak height and the crystal quality increase with temperatures. These investigations reveal that the optimum temperature to deposit ZnTe thin films with higher crystalline quality is 90°C.

4.5.3 Effect of solution pH

The variation in pH in the vicinity of the cathode surface is monitored over a wide range of current densities. An important effect is the increase in the magnitude of the transition current density as the bath becomes more acidic. This indicates that an increase in bath acidity can significantly reduce the current range
Fig. 4.15 XRD spectra of ZnTe films deposited at various bath temperatures. (a) 30°C, (b) 50°C, (c) 70°C, (d) 90°C.
over which anomalous co-deposition is obtained. Also the increase in acidity lowered the current efficiency with which the alloys are deposited. In electrodeposition of metallic films, the type of surface structure depends upon the rate of deposition which, in turn, is proportional to the deposition current. In galvanostatic deposition, the rate of deposition remains constant during deposition. The growth rate could be changed by changing the $pH$ of the solution. XRD spectra of ZnTe films deposited at different pH values are recorded and analysed.

The XRD spectrum of the sample deposited at different $pH$ values are shown in Fig.4.16. The XRD spectrum of a sample deposited at $pH$ 3.5 ± 0.1 (Fig.4.16c) shows a strong (111) peak and it is revealed that the film is preferentially oriented along (111) plane parallel to the substrate surface with cubic structure. The colour of the film is found to be dark brown. The same result with decrease in peak height is observed at $pH$ 3.0 ± 0.1 (Fig.4.16b). Fig.4.16d shows the x-ray diffraction pattern of a film prepared at $pH$ 4.0 ± 0.1. The resultant XRD spectrum reveals that the materials is ZnTe with cubic structure, but instead of getting five peaks two peaks missed. The colour of the films is found to be pale brown. The film deposited at $pH$ 2.5 ± 0.1 shows only Te peaks (Fig.4.16a), no ZnTe peaks are observed. Since Te is noble it can deposit even at lower $pH$ values.

All these results revealed that the deposition of ZnTe under various $pH$ values causes no change in crystal structure, whereas the film composition and the
Fig. 4.16 XRD spectra of ZnTe films deposited at various pH values: (a) 2.5 ± 0.1, (b) 3.0 ± 0.1, (c) 3.5 ± 0.1, (d) 4.0 ± 0.1. Current density: 1.6 mAcm⁻². Deposition time: 5 minutes. Deposition temperature: 90°C.
material to be deposited vary. Due to variation in pH, rate of deposition and the deposition potential (cell potential) changes. This change in cell potential with pH causes films of various species to be deposited during deposition at fixed current density. These studies revealed that the deposition of ZnTe films at pH 3.5 ± 0.1 with current density of 1.6 mA cm⁻² (rate of deposition of 0.1 μm min⁻¹) is preferred to obtain ZnTe films with higher crystallinity.

4.5.4 Annealing studies (Galvanostatic deposition)

Structural studies reveal that most of the as-grown electrodeposited ZnTe films are cubic and weakly crystallized. A careful annealing treatment must be applied to increase the grain size and to increase the concentration of Zn ion vacancies. In the present study, a number of ZnTe thin films are prepared under galvanostatic deposition with various bath conditions. The as-grown films are subjected to annealing in air at various temperatures (150 to 450°C) with various duration 30 to 90 minutes.

XRD spectra of ZnTe films annealed at various temperatures are recorded as shown in Fig.4.17. XRD studies showed the same cubic structure for both annealed and un-annealed films and no significant change except the change in peak heights are observed. Increasing in annealing temperature increases the peak heights and hence caused improvement in the crystallinity of the films. The pattern of ZnTe films annealed below 350°C is found to be similar except the variation in
Fig. 4.17 XRD spectra of ZnTe thin films for different annealing temperatures: (a) 150°C, (b) 250°C, (c) 350°C, (d) 450°C. Annealing time: 1 hour.
Fig. 4.18 X-ray diffraction patterns of ZnTe films annealed at 300°C for different annealing time: (a) 30 minutes, (b) 45 minutes, (c) 60 minutes, (d) 90 minutes.
peak height with annealing temperature. However, annealing temperature above 350°C the peak height is reduced. Again if we increased the annealing temperature (above 450°C), peeling off the film from the substrate is obtained.

The spectra obtained for different annealing time as shown in Fig.4.18. The same nature is appeared from the spectra. Annealing studies revealed that annealing not only causes crystallinity improvement but also increasing the grain size of the films. The grain size of annealed ZnTe films along (111), (220) and (311) are estimated to be 0.63 μm, 0.48 μm and 0.37 μm respectively.

4.6 Conclusion

The structural studies were carried out on electrodeposited ZnTe thin films. The studies revealed that, stoichiometric films with well defined composition were obtained by adjusting the deposition parameters. The structure of the ZnTe thin films were found to be cubic with preferential orientation along (111) plane. The effects of zinc concentration, deposition potential, bath temperature, solution pH and annealing with different durations were analyzed. The precise measurement of lattice constant was found out using Nelson-Riley plot. It was observed that annealing enhances the crystallinity of the samples through diffusion and regrowth.
References


