

Electrochemical Deposition and Characterization of Lead Telluride Thin Films

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Abstract: Electrochemical deposition and characterization of Lead Telluride (PbTe) thin films onto indium doped tin oxide (ITO) coated conducting glass substrates from an aqueous acidic bath containing $Pb(NO_3)_2$ and TeO_2 is discussed in this paper. The effect of bath temperature on the properties of PbTe films have been studied. The films deposited in the bath temperature range from 30°C to 90°C are characterized by x-ray diffraction, scanning electron microscopy, energy dispersive analysis of x-rays and optical absorption techniques for their structural, morphological, compositional and optical properties. The effects of bath temperature on the above properties of the films are discussed in detail.

Keywords: Lead chalcogenides, electrodeposition, x-ray diffraction, texture coefficient, scanning electron microscopy.

1. INTRODUCTION

Lead chalcogenides are considered important technological materials because of their potential applications in IR detectors, laser diodes and thermo photovoltaic energy converters [1-4]. Among them, lead telluride (PbTe) is a narrow band gap semiconductor with an energy gap value of 0.27 eV which is utilized for the fabrication of thermo photovoltaic energy converters [5]. PbTe thin films are mainly crystallized in cubic structure. Several methods such as molecular beam epitaxy (MBE) [6], hot well technique [7] and pulsed laser evaporation [8] have been attempted to prepare PbTe thin films. Electrodeposition and chemical bath deposition are the alternative methods that are particularly utilized for the preparation of chalcogenide materials. Chemical deposition of chalcogenides is already used for producing interfacial layers in high efficiency thin film solar cells. The lead chalcogenide compounds have been the objects of numerous studies concerning thin film electrodeposition from aqueous solutions. Recently, electrodeposition has emerged as a simple, economical and viable technique to synthesize good quality films for device applications [9-10]. The attractive features of this method are: convenience for producing large area devices, low temperature growth and the possibility to control film thickness and morphology by readily adjusting the electrical parameters as well as the composition of

the electrolytic solution. Streltsov et al studied the mechanism of PbTe thin films coated on platinum (Pt) substrates [11]. Saloniemi et al [12] have studied the properties of PbTe thin films prepared on gold (Au) substrates. Beaunier et al [13] have prepared PbTe thin films on chromium (Cr) and indium phosphide (InP) substrates and studied their properties. All the above works are mainly focussed deposition mechanism of PbTe thin films on various substrates. No report is available for the preparation of PbTe thin films on indium doped tin oxide (ITO) coated conducting glass substrates. Hence, we have planned to prepare PbTe thin film on indium doped tin oxide coated conducting glass substrates and studied their properties.

In this work, we focused the preparation and characterization of PbTe thin films on ITO substrates with an emphasis of structural, morphological, compositional along with optical properties of the films. The effects of bath temperature on the above properties of the films are studied and discussed.

2. EXPERIMENTAL DETAILS

All the chemicals used in this work were of analytical grade (99 % Purity, E-Merck). PbTe thin films were deposited on ITO substrates from an aqueous electrolytic bath containing 0.05 M $Pb(NO_3)_2$ and 0.02 M TeO_2 . The electrochemical experiments were carried out using PAR scanning potentiostat (Model 362, EG & G, Princeton Applied Research, USA) employing three electrode

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configuration with indium doped tin oxide coated conducting glass substrate as cathode, graphite plate as anode and saturated calomel electrode (SCE) as reference electrode. Before use, ITO substrates were treated for 15 minutes with ultrasonic waves in a bath of isopropanol and then rinsed with acetone. The saturated calomel electrode was introduced into the solution by luggin capillary whose tip was placed as close as possible to the working electrode. All the experimental potentials are referred with respect to SCE. The deposition potential was fixed as -600 mV versus SCE for all depositions. The pH of the electrolytic solution was maintained at 3.0 ± 0.1 . The plating experiments were carried out at various bath temperatures from 30 °C to 90 °C with different intervals of time.

Thickness of the deposited films was measured using stylus profilometer (Mitutoyo, SJ-301, USA). X-ray diffraction data of prepared films was analyzed using an X-ray diffractometer (X'Pert PRO PANalytical, Netherlands) with $\text{CuK}\alpha$ radiation with $\lambda = 1.5418 \text{ \AA}$ by varying the diffraction angle 2θ with a step width of 0.02° . Surface morphology and film composition were analyzed using an energy dispersive x-ray analysis set up attached with scanning electron microscope (Philips Model XL30), respectively. Optical measurements was carried out using an IR spectrophotometer.

3. RESULTS AND DISCUSSION

3.1. Film thickness

The deposition of PbTe thin films was controlled by two independent variables such as (i) film thickness and its uniformity (ii) surface morphology [14]. Thickness of the deposited films was estimated using stylus profilometer. The average thickness of deposited layers can be directly controlled by controlling the plating current and the plating time. During deposition, it was observed that at higher bath temperatures (above 70°C) the film formation is hindered due to hydrogen evolution. At lower bath temperatures (below 50°C) an irregular growth with rough surface was obtained. Fig. 1.a,b,c shows the variation of film thickness with deposition time for films deposited at various bath temperatures from 30 to 70°C. It is observed from Fig. 1 that the film thickness increases

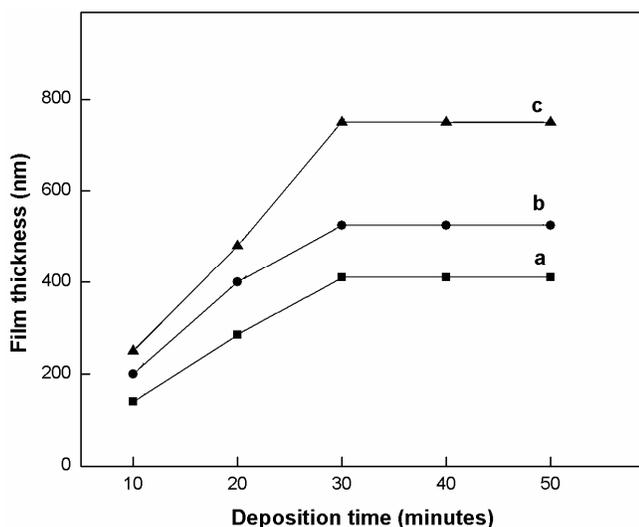


Figure 1. Variation of film thickness with deposition time for PbTe thin films electrodeposited at various bath temperatures (a) 30°C, (b) 50°C (c) 70°C.

linearly with deposition time and tend to attain saturation. The bath temperature is expected to influence the deposition rate by: (i) increase of precursor solubility and (ii) increase of the diffusion coefficient and the decrease of viscosity [14]. The solubility of TeO_2 increases exponentially with raising temperature and at pH 4.5 a 20-fold increase of solubility from room temperature to 99°C was observed by Cheng et al [15]. Due to the increase in solubility of TeO_2 with bath temperature, higher thicknesses were obtained for films deposited at higher bath temperature such as 70°C. It could be observed from Fig. 1 that maximum film thickness of PbTe was obtained from a single deposition within 30 minutes for bath temperatures from 30 to 70°C. Further, at lower pH (3.0 ± 0.1), free tellurium was deposited and at comparatively higher pH (4.0 ± 0.1), the solution became cloudy due to the precipitation of TeO_2 . Increasing the tellurium ion concentration in the solution by adding TeO_2 is limited by the solubility of TeO_2 at a given pH and bath temperature [16]. Since, tellurium is less electropositive than lead, the Te could be more likely to deposit as the element from its ions in an electrolytic bath than Pb from its ions. Hence, a very low concentration of Te in the electrolytic bath must be maintained when compared to Pb ions.

3.2. Structural studies

X-ray diffraction studies was carried out in order to identify crystallinity and phases of the deposited films. From x-ray diffraction data, the interplanar spacing d_{hkl} was calculated using the Bragg's relation [17]

$$d_{hkl} = n\lambda / 2\sin\theta \quad (1)$$

where λ is the wavelength of the x-rays used, d the interplanar spacing, n the order number and θ is the Bragg's diffraction angle. The factor "d" is related to (hkl) indices of the plane and the dimension of the unit cell.

$$1/d_{hkl}^2 = h^2 + k^2 + l^2 / a^2 \quad (2)$$

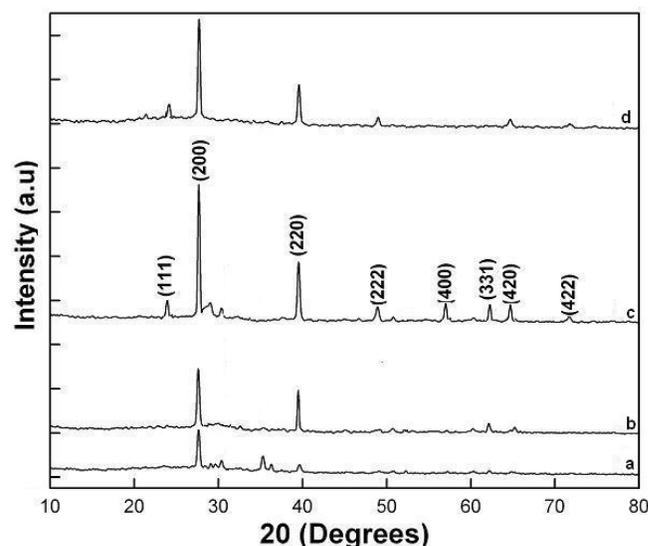


Figure 2. X-ray diffraction patterns of PbTe thin films electrodeposited at various bath temperatures (a) 30°C, (b) 50°C, (c) 70°C, (d) 90°C.

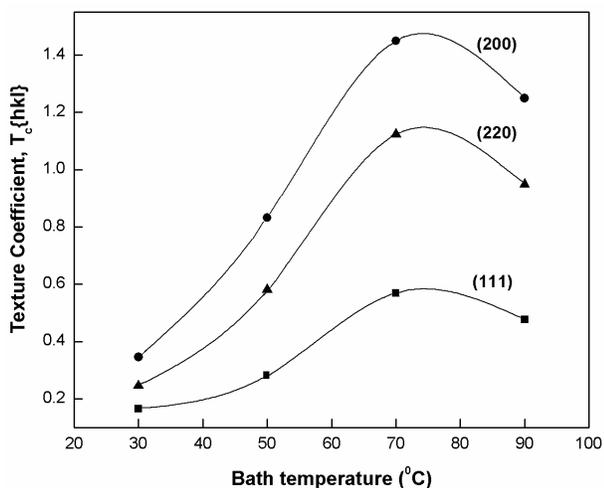


Figure 3. Variation of texture coefficient along (111), (200), (220) planes of PbTe thin films deposited at various bath temperatures from 30^o to 90^oC.

X-ray diffraction pattern of PbTe thin films electrodeposited on ITO substrates with bath composition of 0.05 M Pb(NO₃)₂ and 0.02 M TeO₂ at various bath temperatures from 30^oC to 90^oC is shown in Fig. 2.a,b,c,d. The XRD patterns revealed that the deposited films are found to be polycrystalline in nature with cubic structure with lattice constant (a= 6.454 Å). The observed diffraction peaks of PbTe are found at 2θ values of angles 23.86, 27.61, 39.47, 49.02, 57.10, 62.12, 64.53 and 71.60 corresponding to the lattice planes (111), (200), (220), (222), (400), (331), (420) and (422), respectively. The different peaks in the diffractograms were indexed and the corresponding values of interplanar spacing “d” were calculated and compared with standard values [18]. The bath temperature affects the nature of the films and higher temperatures are required to obtain good quality films. PbTe thin films deposited at bath temperature below 50^oC are found to be poorly crystallized indicated by broad XRD peaks as shown in Fig. 2a. However, these peaks are started to increase while increasing bath temperature above 40^oC indicates the presence of crystalline nature of PbTe thin films. It is found that higher deposition temperature led to the formation of well crystallized films. It is observed that higher deposition temperature resulted in good quality films with improved crystallinity as evidenced by intense diffraction peaks indicated in Fig. 2c. PbTe thin films deposited at 70^oC is found to be well crystalline in nature with a preferential orientation along (200) plane. It is observed that the height of the preferential peak increases and some new peaks of PbTe begins to appear while increasing bath temperature from 30^oC to 70^oC, thereafter the height of the preferential peak slightly decreases. At higher bath temperatures (above 70^oC) the current densities are found to be higher. These higher current densities led to the formation of PbTe films with rough surface with poor adhesion. The film thickness increases linearly with bath temperature and it is clear that the bath temperature affects the rate of release of ions. The height of (111) peak in x-ray diffraction pattern for PbTe thin films deposited at higher bath temperature (70^oC) has shown sharper peaks and small FWHM data resulted in the enhancement of crystallite size in the deposited

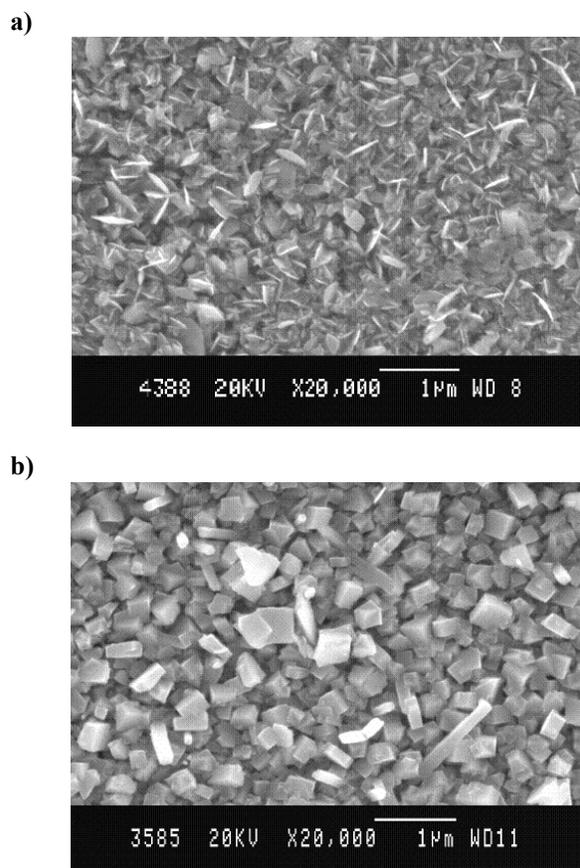


Figure 4. SEM picture of PbTe thin films deposited at different bath temperatures (a) 30^oC, (b) 70^oC.

films at higher temperatures. Similar behaviour exhibited for ZnHgTe thin films have been reported earlier [17]. The effect of bath temperature on the orientation of the polycrystalline films are investigated by evaluating the texture coefficient T_c{hkl} using the following relation [19].

$$T_c \{hkl\} = \frac{I \{hkl\} / \{I_0 \{hkl\}\}}{(1/N) [\sum_N I \{hkl\} / I_0 \{hkl\}]} \quad (3)$$

where T_c{hkl} is the texture coefficient of the {hkl} plane, I is the measured intensity, I₀ is the JCPDS standard intensity and N is the number of diffraction peaks. From the above equation (3) it is seen that, the value of texture coefficient approaches unity for a randomly distributed powder sample, while T_c is larger than unity when the {hkl} plane is preferentially oriented. Fig. 3. shows the variation of texture coefficient with bath temperature for PbTe films prepared at various bath temperatures from 30 to 90^oC and at a deposition potential – 600 mV versus SCE. The increase in preferential orientation is attributed with increased number of crystallites along the plane. The lower value of texture coefficient reveals that the films have poor crystallinity and the crystallinity may be improved by increasing bath temperature from 30^oC to 70^oC, thereafter it slightly decreases. Hence, PbTe films deposited at bath temperature 70^oC has good crystallinity and well adherent to the substrate. The crystallite sizes of the deposited films are calculated using FWHM data and Debye-Scherrer formula [10].

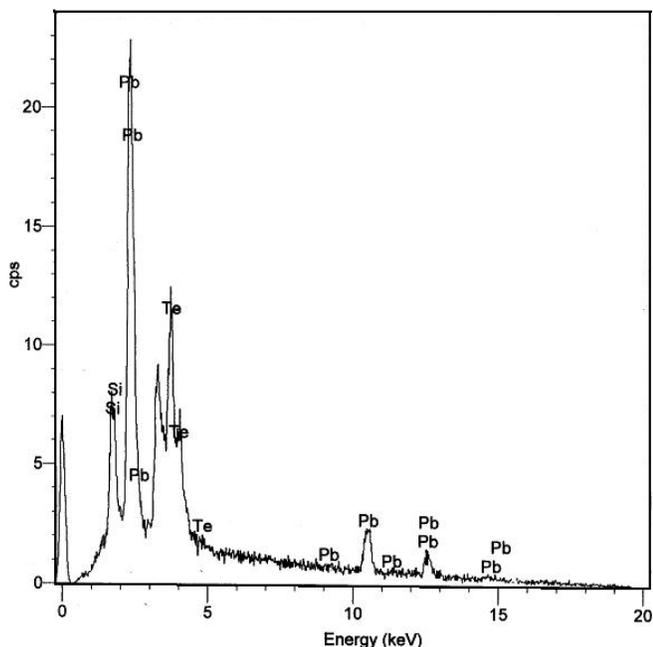


Figure 5. Typical EDAX spectrum of PbTe thin film deposited at bath temperature of 70°C and at deposition potential of -600 mV versus SCE.

$$P=0.9\lambda/\beta\cos\theta_B \quad (4)$$

where λ is the wavelength of CuK α target ($\lambda=0.15418$ nm), β is Full Width at Half Maximum of the peak in radians, θ_B is Bragg's diffraction angle at peak position in degrees. The sizes of the crystallites are found to be in the range between 24 and 42 nm.

3.3. Morphological and compositional analysis

The surface morphology of PbTe thin films was analyzed using scanning electron microscopy. The SEM picture of PbTe thin films deposited at bath temperature 30°C is shown in Fig. 4a. It is observed from Fig. 4a. that the films deposited at bath temperature of 30°C is found to exhibit mosaic like structure. The surface is not uniform and covered with unshaped grains. The surface morphology of PbTe thin film deposited at bath temperature 70°C is shown in Fig. 4b. The film surface is observed to be smooth, and covered with cubic shaped grains. The grains are distributed uniformly over the entire surface of the films. The sizes of the grains are found to be in the range between 0.18 and 0.41 μm . The average size of the grains is found to be 0.28 μm .

The film composition was estimated using EDAX microanalytic unit attached with scanning electron microscope. A typical EDAX spectrum of PbTe electrodeposits with Pb²⁺ concentration of 0.05 M and TeO₂ concentration of 0.02 M deposited at bath temperature of 70 °C and at a deposition potential of -600 mV versus SCE at solution pH value of 2.0 \pm 0.1 is shown in Fig. 5. It is observed that the emission lines of Pb and Te was present in the investigated energy range indicate the formation of PbTe thin films. The atomic molar ratio of Pb:Te for film deposited at bath temperature of 70°C is found to be 44.07:55.93 indicating the stoichiometric formation of PbTe thin films. This result is consistent with x-ray diffraction

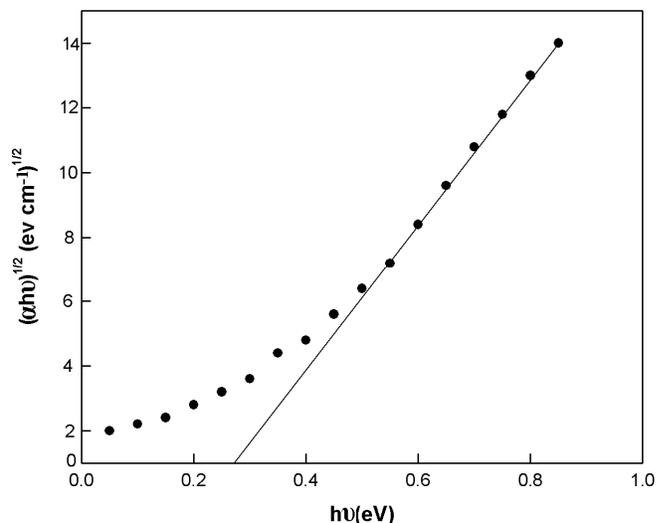


Figure 6. $(\alpha h\nu)^{1/2}$ versus $h\nu$ plot for PbTe thin film electrodeposited at bath temperature of 70°C.

analysis of the sample (i.e.) the sample phase is PbTe. This value is quite closer to the value reported earlier [20].

3.4. Optical band gap studies

Optical constant such as absorption coefficient play an important role in understanding the opto-electronic properties of semiconducting materials. The absorption coefficient of the strong absorption region of thin film is calculated from their optical transmittance and reflectance values using the formula [9].

$$\alpha = \frac{\ln[T/(1-R)^2]}{d} \quad (4)$$

where α is the absorption coefficient is T the transmittance (%), R is the reflectance (%) and d thickness of the film. The type of band gap is identified using the absorption coefficient values from the following equation.

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

where E_g band gap of the material, $h\nu$ photon energy and A is an energy dependent constant, substituting the value of n as 1/2, 2, 3/2 and 3 for direct allowed, indirect allowed, forbidden direct and forbidden indirect transitions, respectively. The plots drawn for $(\alpha h\nu)^2$ versus $h\nu$, $(\alpha h\nu)^{1/2}$ versus $h\nu$, $(\alpha h\nu)^{2/3}$ versus $h\nu$, $(\alpha h\nu)^{1/3}$ versus $h\nu$ give an intercept with $h\nu$ (energy axis) which directly gives band gap energy of the respective transition. A plot of $(\alpha h\nu)^{1/2}$ versus $h\nu$, for PbTe thin film electrodeposited at bath temperature 70°C is shown in Fig. 6. The band gap value of the film deposited at 70°C has been calculated from the linear fit of $(\alpha h\nu)^{1/2}$ versus $h\nu$ (Tauc's plot) and the band gap value is found to be 0.27 eV. This value is in good agreement with the value reported earlier [5].

4. CONCLUSIONS

Electrochemical deposition was carried out potentiostatically in order to prepare polycrystalline PbTe thin films by single step elec-

trodeposition process from an aqueous solution mixture of $\text{Pb}(\text{NO}_3)_2$ and TeO_2 . The structural studies revealed cubic structure with preferential orientation along (200) plane and the variation of texture coefficient with bath temperature of the films were studied. The degree of crystallinity of the films increased while increasing bath temperature from 30°C to 70°C, thereafter it slightly decreases. Surface morphology exhibits smooth surface with cubic shaped grains for films deposited at 70°C than those deposited at 30°C. EDAX results shows that stoichiometric films of PbTe could be obtained at a bath temperature of 70°C. The band gap value of the films obtained in this work is found to be 0.27 eV which is in close agreement with the value reported earlier (0.27 eV).

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