

The Influence of Deposition Potential on Properties of Electrodeposited Bi₂Te₃ Thin Films

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Abstract: Bismuth Telluride (Bi₂Te₃) thin films successfully prepared by the potentiostatic electro-deposition technique on stainless steel substrate from the aqueous bath of bismuth nitrate and tellurium dioxide. The deposited films are characterized by X-ray diffraction (XRD), Scanning Electron Microscope (SEM), Energy Dispersive Analysis by X-rays (EDAX), Electrical conductivity, resistivity and band gap energies are measured. The XRD showed polycrystalline nature of deposited films with rhombohedral crystalline structure. The parameters such as crystallite size, micro strain and dislocation density evaluated. SEM study showed growth of uniformly distributed grains in the form of dendrites sphere over the surface of substrate. The presence of indirect direct transition band gap energies is determined by four probe methods and showing semiconducting nature of the film and the electrical resistivity of the thin films prepared at different potential recur the same.

Keywords: Band gap energy, Crystallite size, Electrical Resistivity, Electrodeposition, SEM

I. Introduction

Bismuth telluride nanostructure is attractive material due its efficiency of conversion of heat into electricity [1]. Currently, bunch of research is going on to improve the efficiency thermoelectric materials by the development of Bi₂Te₃ nanostructure [2-5]. Bi₂Te₃ basically considered as a compound element of Bismuth (Bi) and Tellurium (Te), when Bi is alloyed with Te, then it behaves like a well-organized semiconductor thermoelectric type material [6]. It is used for some applications like as cooler thermoelectric refrigeration, thermal Sensor, TEG etc. [7-9].

The efficiency of a thermoelectric device is highly dependent on the performance of the "leg" materials used in the device, through the well-established figure of merit, zT [1,10]. It is a dimensionless quantity defined as $zT = S^2\sigma T/\kappa$, where S is the Seebeck coefficient, σ is the electrical conductivity, T is the temperature in absolute range, and κ is the thermal conductivity. Operating temperatures is key parameter on which the efficiency of thermoelectric materials depends. One of the recognized binary thermoelectric materials is bismuth telluride (Bi₂Te₃) at 200–400° K temperature range [11]. There several methods are reported for Bi₂Te₃ preparation, like spark plasma sintering (SPS) [12], Chemical vapour deposition (CVD) [13], but among all of these electrodeposition were extensively used [14-19]. M. Saleemi et al fabricated bulk Bi₂Te₃ with zT 1.1 at 340° K using SPS [12]. Obtained a super lattice thin film composed of Sb₂Te₃/ Bi₂Te₃ with zT 2.4 at 300° K using CVD by R. Venkatasubramanian et al.[13]. P. Heo et al. prepared an electrodeposited film with power factor 740 $\mu\text{W}/\text{m}\cdot\text{K}^2$ [15]. Among all these different techniques for preparation of thermo electric materials, electrodeposition has the advantages like it have lower equipment cost, organize growth rates, higher deposition rate, ability to be performed at room temperature and atmospheric pressure [14,20-22]. Large scale Industrial implementation is also possible, because, electrodeposition method operate either at constant potential/current or by potential/current pulses. This method has already been applied in several studies for the growth of thin films [16, 23-24] and nano wires [25-27]. Martin-Gonzalez et al. has performed a wide study on the potentiostatic deposition of Bi₂Te₃ deposition, by changing the bath pH and studying the most stable chemical species for a given pH and applied potential [16]. By addition of ethylene glycol in the electrolyte Li et al. studied the fabrication of highly homogeneous thicker films for future applications, reporting an improved morphology and thicker films of the order of 300 μm [28]. Even though the potentiostatic method is a simple and more rapid process, it still required optimization as most reported results present highly granular nano wires, reducing electric conductivity. In this sense in present work attempt is made for preparation of Bi₂Te₃ thin films by potentiostatic electrodeposition method. Preparative parameters like deposition time, thickness of films, deposition potential, are optimized. Thin films of Bi₂Te₃ deposited at optimized preparative parameters are characterized by XRD, SEM, EDAX, electrical resistivity measurements are carried out to study the electrical

nature of deposited films.

II. Experimental Details

2.1 Bath preparation

Electrodeposition experiments were performed at room temperature using a conventional three electrode cell comprising of saturated calomel electrode (SCE) as the reference electrode, stainless steel (ASTM 304-type) substrate of area 2 cm² used as working electrode and graphite plate as the counter electrode. Bi₂Te₃ thin films were cathodically deposited using aqueous bath of 7.5 mM of Bi₂(NO₃)₃ · 5H₂O (A.R., S.D. Fine chemicals Ltd) and 10 mM of TeO₂ (A.R., Alfa Aesar) were dissolved in 1M HNO₃ to prepare electrolyte of desired concentration of Bi and Te. In order to completely dissolve the TeO₂, concentrated HNO₃ was used and electrolyte finally diluted to 0.5 pH - 0.7 pH. Ethylene Diamine tetra acetic acid disodium salt (EDTA) of 0.1M was used as a complexing agent to complex Bi ions. Each of 13.5 ml of above two solutions was mixed with 3 ml of EDTA to form electrolyte solution for electro deposition of Bi₂Te₃ thin films. The electrodeposition was carried out for various applied potentials ranging from -350 mV to -500 mV w.r.t. SCE with an interval of 50 mV/SCE. When the potential is increased above -400 mV/SCE, there is progressive growth of film observed and peeling out of the material from the substrate. Prior to deposition the substrate of stainless steel were mirror polished by zero grade polish paper and degreased by acetone, rinsed with double distilled water, treated with ethanol and subsequently dried in hot air. The optimized preparative parameters for Bi₂Te₃ thin film deposition are tabulated in **TABLE 1**.

Table 1. Preparative parameter for electrodeposition of Bi₂Te₃ thin films.

| | |
|-----------------------|---|
| Bath Composition | 7.5 mM of Bi ₂ (NO ₃) ₃ · 5H ₂ O, 10 mM of TeO ₂ , 0.1 M EDTA |
| Deposition Potentials | -350 mV to -500mV/SCE with difference of 50 mV |
| Bath Temp | 29.1(Room Temp) |
| pH value | 0.5 - 0.7 |
| Deposition time | 50 min. |

2.2 Reaction mechanism

During potentiostatic electrodeposition processes, bismuth and tellurium compounds are dissolved into nitric acid to form the oxide cations BiO⁺ and HTeO₂⁺. Bismuth telluride is insoluble in dilute nitric acid; thus, reduction of HTeO₂⁺ to Te₂⁻ at an electrode results in the precipitation of Bi₂Te₃ on the electrode surface. This takes place in a potentiostatic electrodeposition process, because BiO⁺ requires a lower potential than HTeO₂⁺ [16]. Bi₂Te₃ thin films electrodeposited at different potentials -350mV, -400mV, -450mV, and -500 mV with SCE, the overall reaction for the process is shown in ("equation 1)

$$13\text{H}^+ + 18\text{e}^- + 2\text{BiO}^+ + 3\text{HTeO}_2^+ \rightarrow \text{Bi}_2\text{Te}_3\downarrow + 8\text{H}_2\text{O} \quad (1)$$

2.3 Thickness measurements of Bi₂Te₃ thin films

Indirect weighing difference method was used for measurement of the thickness of Bi₂Te₃ films. The deposition of Bi₂Te₃ films was controlled by variables as; film thickness, its uniformity and surface morphology [16]. The variation of film thickness with deposition time for Bi₂Te₃ films prepared at various deposition potentials -350mV, -400mV, -450mV, and -500 mV with SCE are shown in figure 1. From the graph it is observed that thickness of the film was found to be increased with deposition time and deposition potential up to -400 mV/SCE, and there after further increase in potential leads to the decrease the thickness. The rate of deposition increases progressively with potential and attains a maximum at deposition potential -400 mV /SCE. The film thickness increases with deposition time and reaches an utmost value of 1635 nm in 50 min. for the deposition potential -400 mV/SCE. Further increase in deposition potential, film deposition adversely affected because of hydrogen evolution becomes high. Superior quality of Bi₂Te₃ film was obtained at deposition potential -400 mV/SCE.

X-ray diffraction pattern of electrodeposited Bi₂Te₃ thin films were recorded with the help of Panalytical Xpert PRO X Ray Diffractometer with Cu K α radiation ($\lambda = 1.5405 \text{ \AA}$). Surface morphology and compositional analysis were carried out using a SEM (model: JEOL-JSM 6360). Electrical conductivity, resistivity and band gap energy studies were carried out using a four probe method.

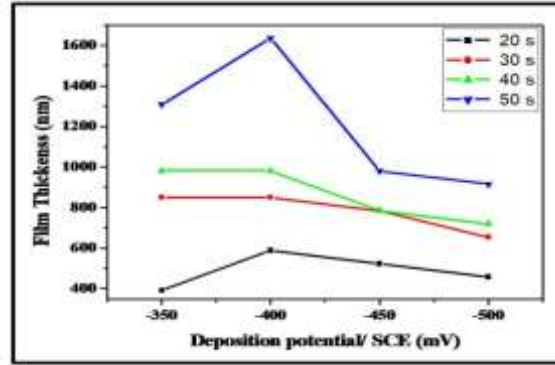


Figure 1. Variation of films thickness with deposition time for Bi₂Te₃ thin films prepared at potentials -350 mV to -500 mV/SCE

III. Results And Discussions

3.1 XRD studies of Bi₂Te₃ thin films

The X-ray diffraction patterns of Bi₂Te₃ thin film prepared at various potentials ranging from -350 to -500 mV/SCE are shown in figure 2 (a-d). The X-ray diffraction patterns showed the deposited films exhibited rhombohedral crystal structure. Five peaks were observed at 2θ angles 27.66°, 38.83°, 41.14°, 44.57°, and 50.31° corresponding to the hkl planes (015), (1010), (110), (0015) and (205) respectively. The observed peaks were compared with standard diffraction values of JCPDS (card no. 15-0863). From Figure 2 (b), it is observed that Bi₂Te₃ films showed sharp peaks with maximum intensity. It is concluded that the deposition potential -400 mV/SCE is suitable potential for the formation of well-crystallized films of Bi₂Te₃.

The crystallite size of Bi₂Te₃ thin films was evaluated using Debye–Scherer formula,

$$D = \frac{0.9\lambda}{\beta \cos\theta} \quad (2)$$

Where, D is the mean crystallite size, β is the full width at half maxima of the diffraction line, θ is diffraction angle and λ is the wavelength of the X-ray radiation.

The dislocation density (δ) is evaluated from Williamson and Smallman’s formula,

$$\delta = \frac{15\epsilon}{aD} \text{ lines/m}^2 \quad (3)$$

The micro strain (ε) is calculated using the relation

$$\epsilon = \frac{\beta \cos\theta}{4} \quad (4)$$

The crystallite size (D), dislocation density (δ) and micro strain (ε) are calculated from (“equations 2–4”), the variation of crystallite size and micro strain with deposition potential for Bi₂Te₃ film deposited at potentials ranging from -350 to -500 mV/SCE is shown in fig. 3, it shows the crystallite size decreases with deposition potential, it may be due to the fast release of ions and the film deposited at -350 mV/SCE is found to have the maximum value of crystallite size. Fig. 4, represents the variation of dislocation density with deposition potential for Bi₂Te₃ films. It is observed that the dislocation density is found to increase when the deposition potential is increased up to -400 mV versus SCE. Thereafter the dislocation density slightly decreases and further increases. Bi₂Te₃ films with lower micro strain and dislocation density improves the stoichiometry of the films, which in turn causes the volumetric expansion of the films.

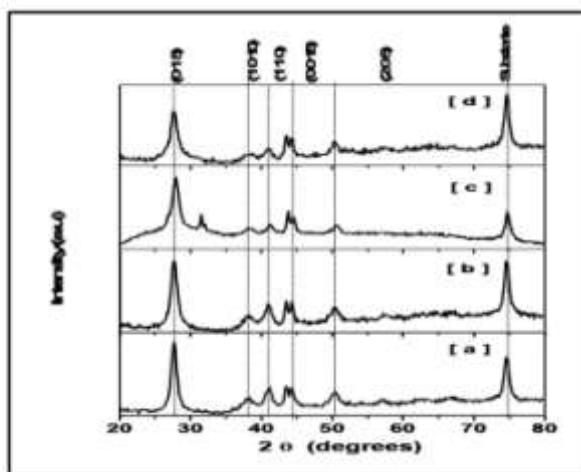


Figure 2. X-ray diffraction patterns of Bi_2Te_3 thin film prepared at potentials (a) -350 mV, (b) -400 mV, (c) -450 mV and (d) -500 mV /SCE

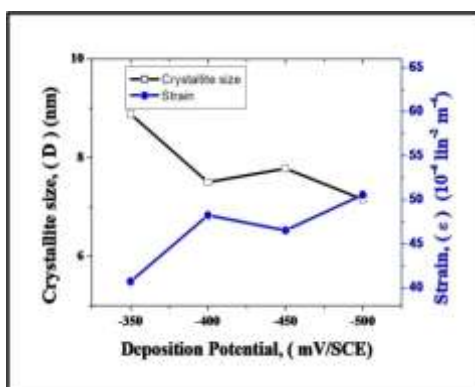


Figure 3. Variation of crystallite size, strain with deposition potential for Bi_2Te_3 thin films.

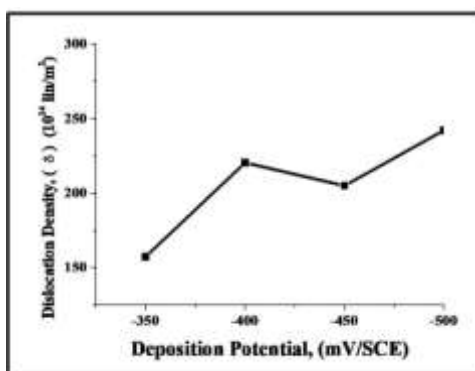


Figure 4. Variation of dislocation density with deposition potential for Bi_2Te_3 thin films.

3.2 SEM studies of Bi_2Te_3 thin films

Morphology of Bi_2Te_3 thin film with deposition potentials -350mV,-400mV,-450mV and -500 mV/SCE was investigated by SEM as shown in fig. 5 (a-d). The surface morphology of deposited film at -350 mV/SCE shows formation of dendrites and with increasing potential up to -400 mV/ SCE dendrites come together and forms a spherical shapes. By further increasing potential up to -450 mv/SCE these spherical shapes comes together and forms marigold / cauliflower morphology. And there after it becomes dense at -500 mV/SCE.

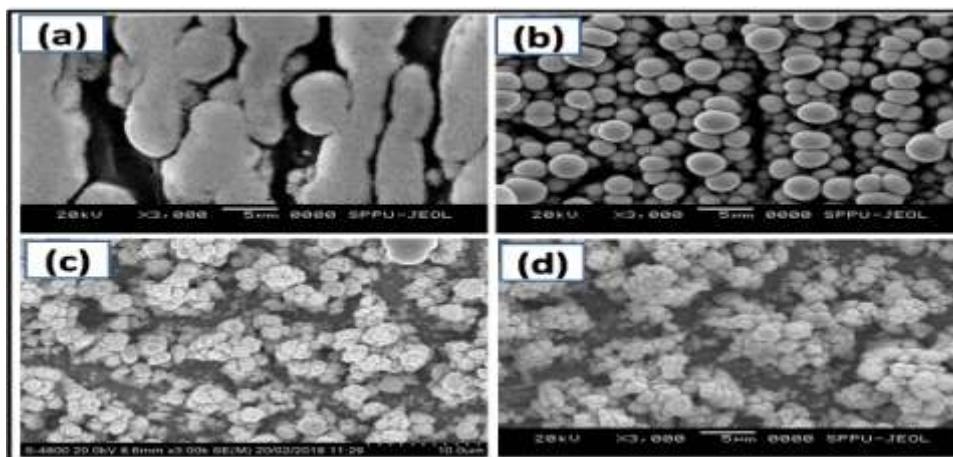


Figure 5. Scanning Electron Micrographs of the deposited Bi_2Te_3 thin film with 3000x magnifications at potentials (a) -350 mV, (b) -400 mV, (c) -450 mV, (d)-500 mV/SCE

3.3 EDAX studies of Bi_2Te_3 thin films

The composition of the Bi_2Te_3 film was investigated using an energy dispersive analysis by X-rays (EDAX) as shown in fig. 6. From the EDAX analysis, atomic percentage of Bi and Te is changing with deposition potentials, at potentials -350 mV and -400 mV/SCE, deposited Bi_2Te_3 thin film showing almost stoichiometry. Further increasing in potential, there is rising of Bi atomic percentage and falling of Te atomic percentage.

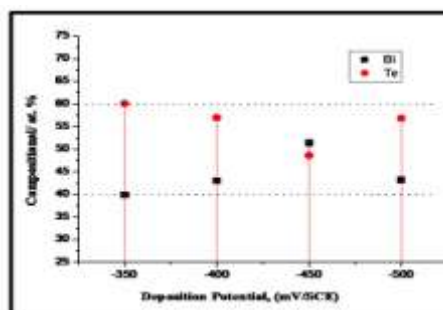


Figure 6. Variation of atomic % of Bismuth and telluride for Bi_2Te_3 thin film prepared at potentials -350 mV to -500 mV/SCE

3.4 Electrical resistivity studies of Bi_2Te_3 films

The electrical resistivity of Bi_2Te_3 film were calculated using a four-probe method in the temperature range from 308– 373° K and is shown in fig. 7. It is observed that the resistivity decreases non-linearly with temperature. This shows the semiconducting nature of the prepared Bi_2Te_3 film. Fig. 8 shows variation of band gap energy with deposition potential, from fig. it is observed band gap energy decreasing with increasing deposition potential, it also reveals that the prepared films were semiconductor in nature having narrow band gap in the range of 0.19 eV to 0.05 eV.

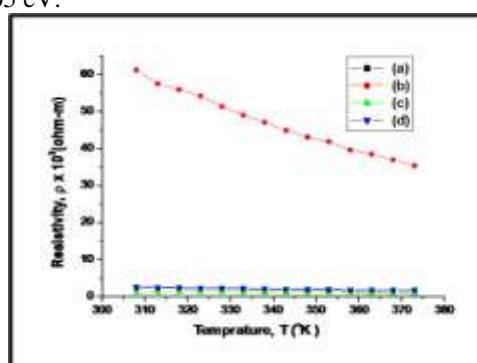


Figure 7. Variation of electrical resistivity with temperature for the Bi_2Te_3 film prepared at Potentials (a) -350 mV, (b) -400 mV, (c) -450 mV, (d)-500 mV /SCE

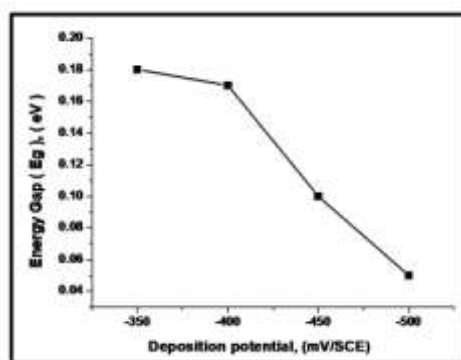


Figure 8. Variation of band gap energy with deposition potentials for Bi₂Te₃ thin film prepared at -350 mV to -500 mV/SCE

IV. Conclusion

Bismuth Tellurium (Bi₂Te₃) thin films were prepared by electrodeposition at potentiostatic mode on stainless steel substrates from aqueous solutions using aqueous bath of 7.5 mM of Bi₂(NO₃)₃ · 5H₂O and 10 mM of TeO₂ at various potentials, -350mV to -500 mV/SCE. X-ray diffraction analysis confirms that the Bi₂Te₃ films are crystalline in nature with rhombohedral structure. Various structural parameters crystallite size, micro strain and dislocation density were also calculated analytically. SEM studies show the uniform distribution of grains over the entire surface of the substrate of the Bi₂Te₃ films. The presence of elemental constituents is confirmed from EDAX analysis. The average atomic percentage ratio of Bi₂Te₃ is found to be (40.00) Bi : (60.00) Te with stoichiometry. Four probe analyses confirm the presence of indirect transition with band gap energy of 0.19 eV to 0.05 eV for the film deposited at various potentials. Bi₂Te₃ thin film prepared at deposition potential -400mV/SCE showing optimize in nature, which get confirm from X-ray diffraction pattern, SEM and EDAX analysis in addition to this thin film having band gap value 0.18eV and resistivity found in order of 4.96 ohm cm which supporting semiconducting nature.

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