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## Abstract

In the present studies thin film of Bismuth Telluride ($Bi_2Te_3$) is successfully prepared by the electro-deposition technique on stainless steel substrate from the aqueous bath of bismuth nitrate and tellurium dioxide. The deposited film is characterized by X-ray diffraction (XRD), Scanning Electron Microscope (SEM), Energy Dispersive Analysis by X-rays (EDAX), Electrical conductivity and resistivity measurements. The XRD showed polycrystalline nature of deposited films with rhombohedral crystalline structure. The parameters such as crystallite size and micro strain are evaluated. SEM study showed growth of uniformly distributed grains over the surface of substrate. The band gap of the deposited films obtained from the Four Probe studies were found in the range 0.17 eV.

## Keyword

XRD, SEM, EDAX, Electrical conductivity, Band gap energy

# Preparation and characterization of $Bi_2Te_3$ Thin Film by Electrochemical method.

## INTRODUCTION

As the thermoelectric devices directly convert waste heat into electrical energy so that it attracted a considerable amount of interest, also they are playing a vital role in energy harvesting and thermal management and can also be used for cooling using electrical power [1]. Automotive exhaust, home heating and industrial processes generate a huge amount of unused waste heat that could be converted to electricity by using thermoelectric devices [2]. As thermoelectric generators are solid-state devices with no moving parts, they are silent, reliable and scalable; making them ideal for small, distributed power generation [3]. Recent studies are starved for achieving additional efficiency of thermoelectric materials through the development of $Bi_2Te_3$ nanostructure ([4]-[11]). The structure of $Bi_2Te_3$ is a compound element of both Bismuth (Bi) and Tellurium (Te). Normally the behaviour of Bi is like a simple metal, when it forms an alloy with Te, then it turns in to well-organized semiconductor thermoelectric type material. Hence it can be considered for variety of applications like thermoelectric refrigeration, TEG, TEC and other segments of material science like thermal sensor ([12]-[19]).

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],[20]). 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 temperature is considered as one of the important factor for efficiency of the thermoelectric materials. The bismuth telluride ($Bi_2Te_3$) is accepted as the excellent binary thermoelectric material in temperature range from 200–400 K [21]] none of the methods restricted to spark plasma sintering (SPS) amongst several methods recognized for $Bi_2Te_3$ preparation [22]. Two most popular methods are Chemical vapour deposition (CVD) [23], and electrodeposition ([24]-[27]). M. Saleemi et al., proposed Bulk $Bi_2Te_3$ fabrication by using SPS [22]. Super lattice thin film composed of $Sb_2Te_3$/ $Bi_2Te_3$ by CVD is discovered by R. Venkatasubramanian et al. [23] An electrodeposited film with power factor 740 μW/m·K$^2$ is developed by P. Heo et al [28].

Electrodeposition method is found suitable for industrial applications due to its certain advantages over other methods like, lower equipment cost, high growth rates, higher deposition rate, ability to be performed at room temperature and atmospheric pressure ([25]-[27]). The work carried out in this paper allowed a better understanding of the chemical deposition processes of Bi and Te. Even though the potentiostatic approach is simple and fast but, it still requires optimization and reducing the thermal conductivity. Considering all the factors, efforts are put in the improvement of the potentiostatic methods, for producing highly quality thin films.

In the present work attempt is made for preparation of $Bi_2Te_3$ thin films by Electrodeposition method. Preparative parameters like deposition time, thickness of films, deposition potential, are considered. Thin films of $Bi_2Te_3$ deposited at -350 mV are characterized by XRD, SEM, EDAX, electrical conductivity, resistivity measurements are made to examine the electrical nature of as deposited films by four probe methods.

## 2. Experimental Details:

### 2.1 Bath preparation:

Experiment was performed at room temperature using a conventional three electrode cell comprising of saturated calomel electrode (SCE) as the reference electrode, stainless steel used as working electrode and graphite plate as the counter electrode. $Bi_2Te_3$ thin film was catholically deposited using aqueous bath of 7.5 mM of $Bi_2(NO_3)_3$ .$5H_2O$

(A.R., S.D. Fine chemicals Ltd) and 10 mM of $TeO_2$ (A.R., Alfa Aesar) be dissolved in 1M $HNO_3$ to prepare electrolyte of desire concentration of Bi and Te and pH of solution was kept at 0.5. Ethylene Diamine tetra acetic acid disodium salt (EDTA) of 0.1M was used as a complexing agent to complex Bi ions. The electrodeposition was carried out at potential -350 mV w.r.t. SCE. Before deposition, the substrate of stainless steel were mirror polished with zero grade polish paper and degreased by acetone, rinsed with double distilled water, treated with ethanol and subsequently dried in hot air.

### 2.2 Reaction mechanism:

Potentiostatic electrodeposition is carried out by dissolving bismuth and tellurium compounds in to nitric acid to form the oxide cations $BiO^+$ and $HTeO_2^{+}$. Reduction of $HTeO_2^+$ to $Te_2^-$ at an electrode results in the precipitation of $Bi_2Te_3$ on the electrode surface. In potentiostatic electrodeposition process, $BiO^+$ requires a lower potential than $HTeO_2^+$[29]. $Bi_2Te_3$ thin films electrodeposited at potential -350 mV with SCE, the general reaction for the process is described as,

$$13H^+ + 18e^- + 2BiO^+ + 3HTeO_2^+ \rightarrow Bi_2Te_3\downarrow + 8H_2O \qquad (1)$$

### 2.3 Thickness measurements of $Bi_2Te_3$ thin film:

The indirect weight difference method is used for measurement of thickness of $Bi_2Te_3$ film. The film thickness with its uniformity and surface morphology [30] are considered for deposition of $Bi_2Te_3$ films. The film thickness increases along with deposition time and reaches up to its maximum value of 1308 nm in 50 min. for the deposition potential -350 mV/SCE. In the deposition process, film thickness illustrates an increasing trend for the first 40 minutes and then maintains the saturation state up to 50 minutes. Further increase of time i.e. up to 60 minutes, the film thickness slightly decreases. Good quality of $Bi_2Te_3$ film was obtained at deposition potential -350 mV/SCE.

X-ray diffraction pattern of electrodeposited $Bi_2Te_3$ thin film were recorded with the help of Panalytical xpert pro X-ray diffractometer with cu kα radiation (λ = 1.5405 a°). Surface morphology and compositional analysis were carried out using a scanning electron microscope and an energy dispersive x-ray analysis setup (EDXS) attached with SEM **(model: JEOL-JSM 6360)** respectively. Wetability and electrical resistivity studies were carried out using a four probe method.

## 3. Results And Discussions:

### 3.1 XRD studies of $Bi_2Te_3$ thin films:

Fig.1 depicts the X-ray diffraction pattern of $Bi_2Te_3$ thin film prepared at potential -350 mV/SCE. The X-ray diffraction patterns demonstrate the deposited films exhibited rhombohedral crystal structure. Almost five peaks are being observed at 2θ angles 27.66°, 38.32°, 41.19°, 44.25°, and 50.27° corresponding to the hkl planes (015), (1010), (0111), and (0015) and (205) respectively. The comparison of the observed peaks is done with standard diffraction values of JCPDS (card no. 15-0863). Observations from fig. 1, cleared that $Bi_2Te_3$ films has shown sharp peaks with maximum intensity confirms that the formation of $Bi_2Te_3$ material at deposition potential -350 mV/SCE, further confirmed by EDXS studies.

Debye–Scherer formula is used for evaluation of the crystallite size of $Bi_2Te_3$ thin film,

Where, D signifies 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.

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

Where D signifies the main crystallite size, ß is the full width at half maxima of the diffraction line, θ is diffraction angle and ʎ is the wavelength of the X-ray radiation .

Williamson and Smallman's formula is used for dislocation density (δ),

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

The micro strain (ε) is calculated using the relation,

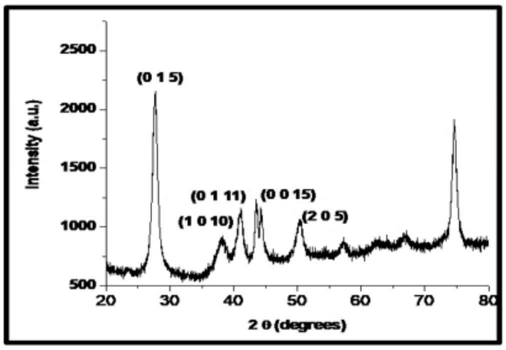
$$\varepsilon = \frac{\beta\cos\theta}{4} \qquad (4)$$

Equations (2)–(4) are used for calculating crystallite

**Table 1. XRD Parameters Of $Bi_2Te_3$ Thin Film.**

| Sample | Crystallite size | Dislocation density | Microstrain ($lin^{-2}$ $m^{-4}$) |
|---|---|---|---|
| $Bi_2Te_3$ | 8.88 nm | 157 x $10^{14}$ ( $line/m^2$) | 40.75 x $10^{-4}$ |

size (D), dislocation density (δ) and micro strain (ε) and obtained the values are tabulated in table no. I



**igure 1: X-ray diffraction pattern of Bi2Te3 thin film repared at -350 mV/ SCE**

### 3.2 Wetability study studies of $Bi_2Te_3$ thin films:

The information about the surface wetting capacity of the deposited material is acquired from the water contact angle measurement process carried for the films of bismuth telluride. The syringe is used for pouring the water droplet onto the surface of -deposited films of $Bi_2Te_3$ and the images of the drop were captured as illustrated in figure 2. It has been observed that the angle of contact for films of bismuth telluride with water is just about 60° and the acute angle of contact shows the hydrophilic nature of the prepared $Bi_2Te_3$ thin film.

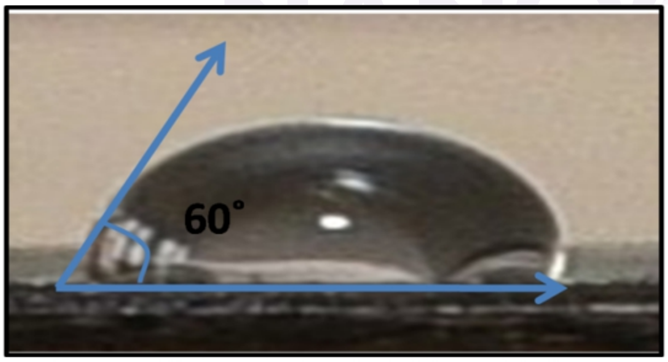


**Figure 2: Water contact angle for Bi2Te3 thin film**

### 3.3 SEM studies of $Bi_2Te_3$ thin films:

Morphology of $Bi_2Te_3$ with deposition potential -350 mV/SCE are investigated by SEM with magnification 10,000 and 30,000 as shown in fig.3 (a) and (b) respectively the surface morphology of deposited film confirm uniform distribution of dendrites over total expose area of the substrate with dense and fined grained morphology.

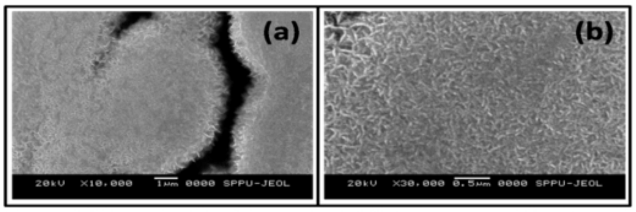


**Figure 3Figure 3: SEM image of Bi2Te3 at magnification (a) 10,000 and (b) 30,000**

### 3.4 EDAX studies of $Bi_2Te_3$ thin films:

The energy dispersive analysis by X-rays (EDAX) is used for investigation of the composition of the $Bi_2Te_3$ film and as shown in fig.4. From the EDAX analysis, the atomic percentage of Bi and Te is found to be 39.89 and 59.11, showing that the electrodeposited $Bi_2Te_3$ film is having stoichiometry.

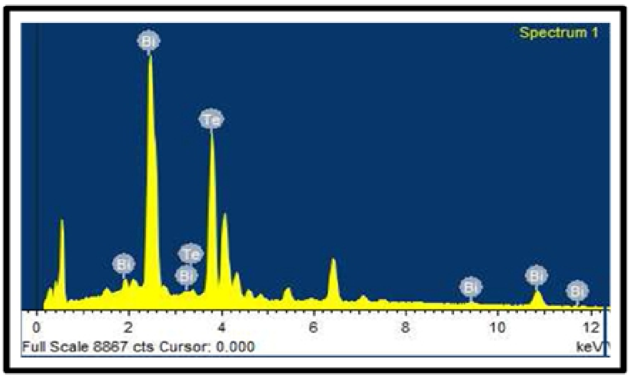


**Figure 4: The typical EDXS spectrum for Bi2Te3 deposited at -350 mV/SCE**

### 3.5 Electrical conductivity and resistivity studies of $Bi_2Te_3$ films:

Using four probe method the electrical resistivity of $Bi_2Te_3$ film deposited at -350 mV with SCE calculated in between the temperature ranges from 308– 373 K and is depicted in fig.5. The electrical resistivity of electrodeposited $Bi_2Te_3$ thin film found to be 0.051 ohm cm. From the observations it is concluded that the resistivity decreases non-linearly with temperature. This shows the semiconducting nature of the prepared $Bi_2Te_3$ films having energy gap 0.17 eV.

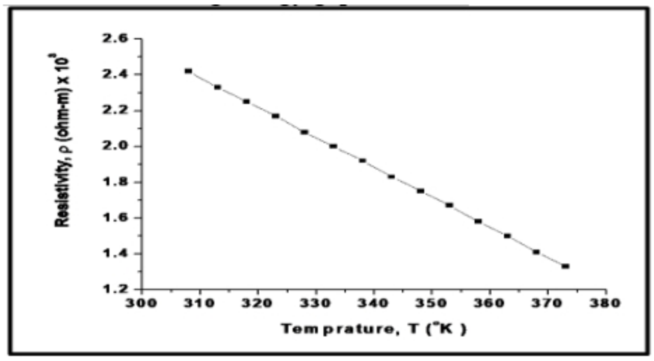


**Figure 5: The Variation of electrical resistance with temperature of Bi2Te3 film.**

## 4. Conclusion:

Bismuth Tellurium ($Bi_2Te_3$) thin films were prepared by electrodeposition at potentiostatic mode on stainless steel substrates from aqueous solutions using aqueous bath $Bi_2(NO_3)_3 .5H_2O$ and $TeO_2$ at potentials - 350 /SCE. X-ray diffraction analysis confirms that the $Bi_2Te_3$ films are crystalline in nature with rhombohedral structure. Different structural parameters like, crystallite size, micro strain, dislocation density are calculated analytically. SEM studies confirm the uniform distribution of dendrites grains over the entire surface of the substrate of the $Bi_2Te_3$ films. The presence of elemental constituents is confirmed from EDAX analysis. The atomic percentage ratio of $Bi_2Te_3$ is found to (39.89) Bi :( 59.11) Te with stoichiometry. It is beloved that the four probe analyses confirm the presence of indirect transition with band gap energy of 0.17 eV for the film deposited at optimized preparative parameter. Finally it is concluded that the semiconductor characteristics of the $Bi_2Te_3$ thin films with a resistivity found in order of 0.05 ohm cm which supported the semiconducting nature.

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