# Effect of Deposition Time on Structural and Morphological Properties of Electrodeposited Bismuth Telluride (Bi2Te3) Thin Films

**Article** · December 2020

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International Journal of Disaster Recovery and Business Continuity
Vol.11, No. 3, (2020), pp. 1982–1988

# Effect of Deposition Time on Structural and Morphological Properties of Electrodeposited Bismuth Telluride ($Bi_2Te_3$) Thin Films

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## *Abstract*

*Present work deals with the temporal electrodeposition of $Bi_2Te_3$ thin films. Structural, elemental and surface morphological analysis of deposited films has been caused out using XRD and SEM with EDXs techniques. XRD contributes the formation of $Bi_2Te_3$ crystals with crystalline size in the range of 3 nm to 9 nm. EDXS is in agreement with X-ray diffractometer and confirms the qualitative formation of $Bi_2Te_3$ in the stoichiometry of 2:3. Scanning electron microscope reveals the influence of the deposition time over the evolution of spherical morphology with increasing diameters of the $Bi_2Te_3$ particles in the deposited films.*

**Keywords:** *Bismuth telluride; Crystal size; Electrodeposition; deposition time; Thin films;Seeback effect ; figure of merit;*

## 1- Introduction

Now-a-days Energy has become one of the most critical issues. In near future our fossil fuels resources will get exhausted. Hence, it is critical for the mankind's survival to look into the other possible sources of energy. Due to this, there is strong focus of researchers to find out alternative energy resources and different energy conversion technologies. At the present time, one of the types of technology that has caught attention of the researchers is thermoelectric energy conversion. The effect is used in thermocouples to measure the temperature using the current generated [1].Thermoelectric effect encompasses three differently identified effects.

When temperature gradient is applied between the two ends of the thermoelectric generator (TEG), it generates electric current, the effect is known as Seebeck effect [2], on the contrary, thermoelectric cooler (TEC) migrates the thermal energy when current passes through it, which ultimately heats or cool the TEC i.e. if one side of TEC is cooled then the other side of is heated, this effect is known as Peltier effect [1,2]. These effects are material properties. Hence, it is important to select a proper material in order to optimize the power output. An important parameter for selection of material is the figure of merit (ZT). It is a quantity used to characterize the performance of a material in a thermoelectric device. The conversion efficiency of material can be determined through this factor,

$$ZT = \alpha^2\sigma T/\kappa = \alpha^2 T/\rho\kappa \qquad (1)$$

Here, α is the Seebeck coefficient, σ is the electrical conductivity, k is the thermal conductivity, T is the absolute temperature, ρ is the electrical resistivity.

Using the formula for figure of merit it is clear that a thermoelectric material to be used in thermoelectric energy conversion should possess high Seebeck coefficient and electrical conductivity, whereas should have low thermal conductivity. These criteria are well satisfied by the semiconductors; hence they are considered as good thermoelectric materials for the purpose [3].

ISSN: 2005-4289 IJDRBC

The field of thermoelectric has been recognized as a potentially transformative energy generation technology, since, it can benefit us in two ways: one, by converting the heat to electricity in a clean way and two, the heat that they convert to electricity may come as wasted heat in other processes ex. Heat wasted by an IC engine may be used to obtain the electricity through this effect. This will not only increase the efficiency of the existing devices but also contribute in fighting the global warming [4]. They have capability to act as solid-state refrigerators (TEC) or heat pumps which do not involve any usage fluids which can harm environment [1-4]. However, a major problem involved in use of these devices is the power output from these devices is very low. This problem can be overcome through the use of nanomaterials and nanostrcutures such as super lattices, quantum dots, nanowires, and nanocomposites [5]. By exploiting nano-scale effects, these materials show enhancements in thermoelectric properties which cannot be achieved in traditional bulk materials. By using thermoelectric nanomaterials large increases in the thermoelectric figure of merit can be achieved [6]. Literature review indicates that, $Bi_2Te_3$ is one of the best thermoelectric materials. In recent years, many studies have been carried out to develop nanostructure of $Bi_2Te_3$ [7]. Bi2Te3 is compound of Bismuth (Bi) and Tellurium (Te). Bi behaves like metal but when it is alloyed with Te, the compound is a remarkable semiconductor and hence, ideal for thermoelectric applications as stated before [7-12]. The formula for ZT shows that the operating temperature is a key parameter on which the efficiency of thermoelectric material depends; the temperature range for $Bi_2Te_3$ is 200-400 K [8]. Several methods are reported for synthesis of $Bi_2Te_3$, such as spark plasma sintering (SPS), chemical vapour deposition (CVD), however, electrodeposition is extensively used method amongst all [9-15].

Present work deals with preparation of $Bi_2Te_3$ thin films using potentiostatic electrodeposition method. The structural and morphological properties of the films are studied. Preparative parameters like deposition time, thickness of films, deposition potential, are optimized. Thin films of $Bi_2Te_3$ deposited at optimized preparative parameters are characterized by XRD, SEM, EDAX, which revels the spherical morphology of the deposited films.

## 2- Experimental details

It is well know that the properties of a thin film vary significantly with the thickness of the film. Hence the first step towards the optimization of electrodeposited $Bi_2Te_3$ film for their thermoelectric properties was to vary the film thickness. This can be easily achieved by varying the deposition time. This section explains the methodology used for obtaining the films of varying thickness using electrodeposition.

### *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 $2cm^2$ used as working electrode and graphite plate as the counter electrode. $Bi_2Te_3$ thin films were 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) were dissolved in 1M HNO3 to prepare electrolyte of desire concentration of Bi and Te. In order to completely dissolve the $TeO_2$, concentrated $HNO_3$ 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 $Bi_2Te_3$ thin films. The electrodeposition was carried out at deposition potential -400 mV w.r.t. SCE at different deposition times ranging from 20 min to 60 min. When the deposition timing increased, there is progressive growth of film observed and films become thick out of the material from the substrate. Prior to deposition the substrate of stainless steel was 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 preparative parameters for $Bi_2Te_3$ thin film deposition are tabulated in Table1.

**Table 1. Preparative parameters for electrodeposition of $Bi_2Te_3$ thin films.**

| | |
|---|---|
| Bath Composition | 7.5 mM of Bi2(NO3)3 .5H2O, 10 mM of TeO2 , 0.1 M EDTA |
| Deposition Potentials | -400 mV/SCE |
| Bath Temp | 29.1(Room Temp) |
| pH value | 0.5 - 0.7 |
| Deposition time | 20, 30, 40, 50 and 60 min. |

### *2-2-Reaction Mechanism*

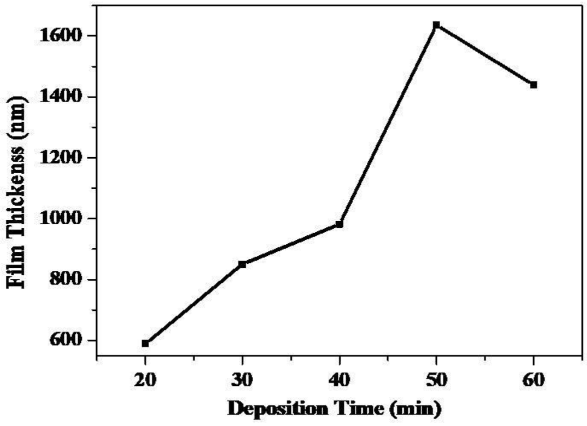
During potentiostatic electrodeposition processes, bismuth and tellurium compounds are dissolved into nitric acid to form the oxide cations BiO+ and $HTeO_2$+. Bismuth telluride is insoluble in dilute nitric acid; thus, reduction of $HTeO_2^+$ to $Te^{2-}$ at an electrode results in the precipitation of $Bi_2Te_3$ on the electrode surface. This takes place in a potentiostatic electrodeposition process, because $BiO^+$ requires a lower potential than $HTeO_2^+$ [16]. $Bi_2Te_3$ thin films electrodeposited at different deposition timings as 20 min, 30 min, 40 min, 50 min and 60 min at deposition potential -400 mV with reference to SCE. The overall reaction for the process is stated in equation 2 below

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

### *2-3-Thickness of the deposited films*

Indirect weighing (weighing by difference) method was used for measurement of the thickness of $Bi_2Te_3$ films.. The variation of thickness of the films with deposition time, deposited at deposition potentials of -400mV with SCE. From Figure 1, it is observed that thickness of the film was found to be increased with deposition time up to 50 min. and there after further increase in time leads to the decrease in the thickness. The film thickness increases with deposition time and reaches an outmost value of 1635 nm in 50 min. for the deposition potential -400 mV/SCE. Further increase in deposition time, film deposition adversely affected because of hydrogen evolution. Superior quality of $Bi_2Te_3$ film was obtained at deposition potential -400 mV/SCE at deposition time 50 min. X-ray diffraction pattern of electrodeposited Bi2Te3 thin films 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 SEM (model: JEOL-JSM 6360).

**Figure 1 Variation of film thickness with deposition time**



## 3-Results and discussions

### *3-1-XRD studies of $Bi_2Te_3$ thin films*

The X-ray diffraction pattern confirmed the rhombohedral crystal structure. Four peaks were observed at the $2\Theta$ angle 27.72˚, 41.16˚, 44.36˚ and 50.4˚corresponding to the hkl planes (015), (110), (0015), (205) respectively as shown in figure 2. It was observed that $Bi_2Te_3$ films showed sharp peaks with maximum intensity.

The crystallite size of $Bi_2Te_3$ thin films was evaluated using Debye–Scherer formula. The crystallite size (D), dislocation density (δ), and micro strain (ε) are given in the table.

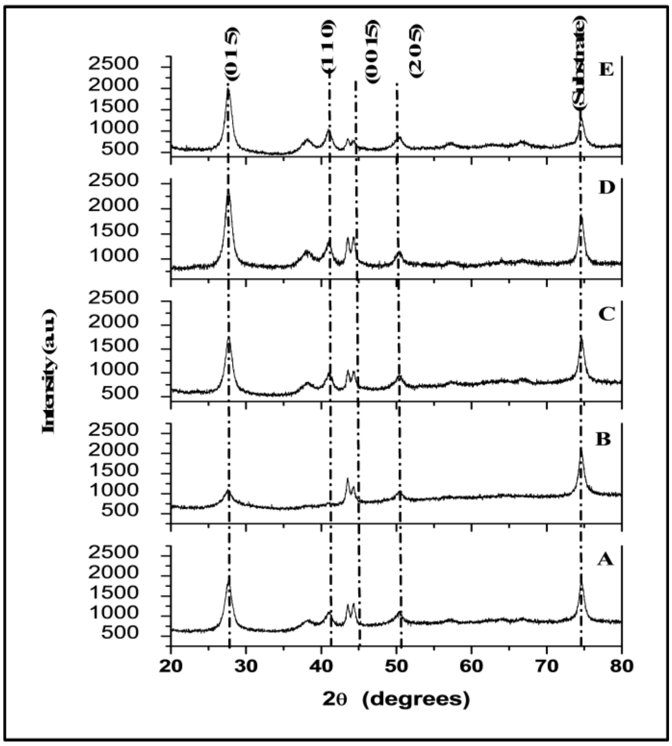


**Table 2. Induced micro strain and dislocation density measurements along (015) plane for samples (A-E)**

| Legend | Time [min] | d-spacing [˚A] | FWHM [˚] | Crystal size [nm] | Microstrain ($10^{-4}$ lin$^{-2}$ m$^{-4}$) | Dislocation density ($10^{14}$ lin/m$^2$) |
|---|---|---|---|---|---|---|
| A | 20 | 3.22 | 1.778 | 4.80 | 75.32 | 536.86 |
| B | 30 | 3.23 | 2.621 | 3.26 | 111.07 | 1167.33 |
| C | 40 | 3.22 | 1.654 | 5.16 | 70.07 | 464.63 |
| D | 50 | 3.24 | 1.681 | 5.08 | 71.24 | 480.21 |
| E | 60 | 3.21 | 1.384 | 6.17 | 58.64 | 325.43 |

### *3-2-SEM studies of $Bi_2Te_3$ thin films*

Morphology of $Bi_2Te_3$ thin films was investigated from SEM images, shown in figure 3. The surface morphology of shows formation of coagulated masses formed from dendrites (dendrites as per the previous studies) at t=20 min, further at t=30 min these masses turn into highly directional structures exhibiting the smallest crystal size as indicated in the X-ray diffractogram results table. Further the crystal size goes on increasing and this directional morphology turns to spherical structures at t=40min and t=50 min. There after it becomes a mass of coagulated spheres at t=60 with

**Figure 2 X-ray diffraction patterns of sample (A-E)**

highest crystal size.

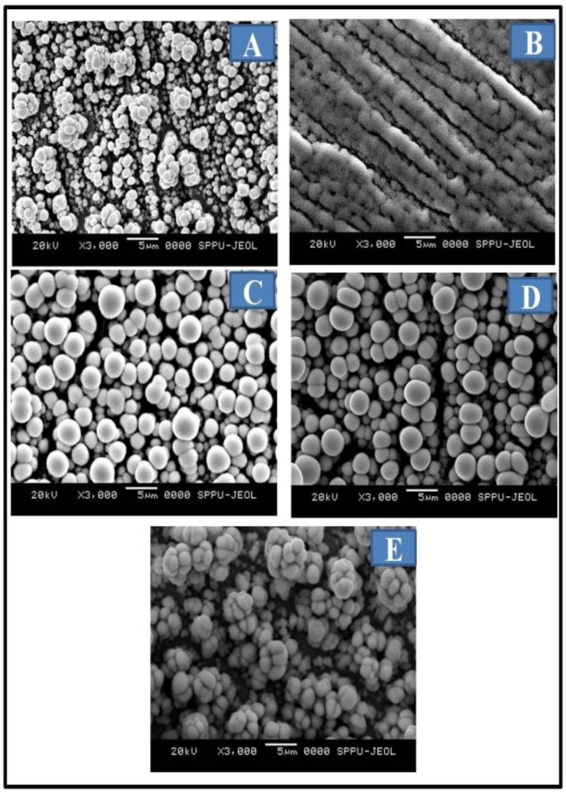


**Figure 3 Scanning Electron  Micrographs of samples (a-f)**

### ***3-3- EDAX studies of $Bi_2Te_3$ Thin films***

EDAX was used for investigation of the elemental composition of the $Bi_2Te_3$ film and as shown in fig.4. From EDAX analysis, film contains 42.79 percentage of Bi atoms and 57.21 percentage of Te atoms. EDAX result represents, deposited $Bi_2Te_3$ film having stoichiometry near to that of the expected ratio of 40:60 (Bi:Te).

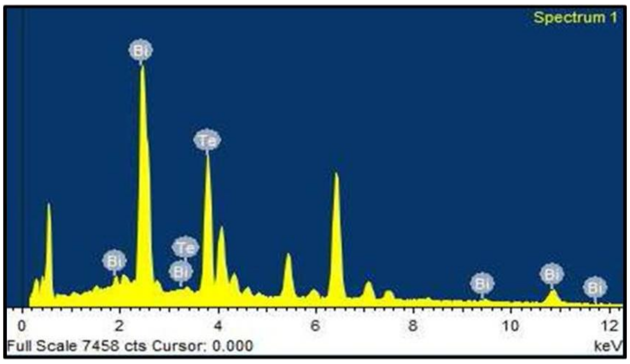


**Figure 4Typical EDXS spectra for $Bi_2Te_3$ film**

## 4- Thermoelectric properties

When it comes to the thermoelectric properties following factors contribute to the high figure of merit: low thermal conductivity, high Seebeck coefficient and high electrical conductivity. It is well known that the Seebeck coefficient for a polycrystalline bulk materials decreases with increase in grain size at room temperature; however the other factor i.e. electrical conductivity increases as well which increases the figure of merit. Hence, the thermoelectric properties were measured for film D only which shows moderate crystal size and highest thickness (for lesser electrical resistance when it comes to device fabrication). The results are shown in the table below.

| **Property** | **Unit** | **Value** |
|---|---|---|
| Sample | - | D |
| Deposition Time | Minutes | 50 |
| Bulk Concentration | / $cm^3$ | $-1 \times 10^{21}$ |
| Mobility | $cm^2$ / Vs | 419 |
| Resistivity | Ω cm | $1.49 \times 10^{-5}$ |
| Conductivity | 1/ Ω cm | $6.7 \times 10^4$ |
| Hall coefficient | $cm^3$/ C | -0.006 |
| Seebeck Coefficient | μ V/T | 45.81 |
| Power Factor | $\mu$ W $cm^{-1}$ $K^{-2}$ | 140.57 |
| Temperature | K | 300 |
| ZT | -- | 0.08598 |

## 5- 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 of 7.5 mM of $Bi_2(NO_3)_3$ $.5H_2O$ and 10 mM of $TeO_2$. X-ray diffraction analysis confirms that the $Bi_2Te_3$ 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 $Bi_2Te_3$ films. The presence of elemental constituents is confirmed from EDAX analysis. The average atomic percentage ratio of $Bi_2Te_3$ is found to be (40.00) Bi :( 60.00) Te. Further the study of the thermoelectric properties for the film with optimized thickness (for t=50 min) indicates the potential for thermoelectric micro-devices applications.

## 6- Acknowledgement

The present study does not receive any grants. VSK is thankful to Department of Physics, Vidya Bharati Mahavidalaya, Amravati and Department of Engineering Physics, MET's Institute of Engineering, Nasik for experimentation and lab support. VSK is also grateful to Prof. (Dr.) V. P. Wani, Principal, MET IOE BKC for encouragement.

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