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An aqueous synthesis and characterization of nanocrystalline $MoBi_2Te_5$ thin films

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Abstract

Using Arrested Precipitation Technique (APT) which is based on self organized growth process molybdenum bismuth telluride thin films have been prepared on clean glass substrate. Deposited $MoBi_2Te_5$ thin films were dried in constant temperature oven at 110°C and further characterized for their optical, structural, morphological, compositional and electrical analysis. Optical absorption spectra recorded in the wavelength range 300-800 nm showed band gap (Eg) 1.72 eV. X-ray diffraction pattern and scanning electron microscopic images showed that $MoBi_2Te_5$ thin films are nanocrystalline having rhombohedral structure. The compositional analysis showed close agreements in theoretical and experimental atomic percentages of Mo^{4+}, Bi^{3+} and Te^{2-} suggest that chemical formula $MoBi_2Te_5$ assigned to as deposited molybdenum bismuth telluride new material is confirm. The resistivity and thermoelectric power measurement showed that the films are semiconducting with n-type conduction.

Keywords: Thin films, APT, SEM, EDAX, XRD, TEP.

1. Introduction-

During recent years, thermoelectric materials aiming at thermoelectric devices applications have attracted much attention because the application of thermoelectric microcooling devices is very promising for thermal management of microelectronics & optoelectronics [1]. Transition metal chalcogenide represent an important family of materials that have been proven useful as thermoelectric materials in optoelectronic devices [2], magnetic superconductors [3], supercapacitors [4], quantum dots [5], sensors [6] and photovoltaics [7]. Bismuth chalcogenide compounds are considered to be the best candidates for thin film thermoelectric coolers due to their excellent figure of merit and thermoelectric properties near room temperature region [8]. The bismuth chalcogenides are applicable in optical and photosensitive devices in photoelectrochemical cells (PEC) in solar selective decorative coatings and in the fabrication of an ideal Hall effect magnetometer [9] Molybdenum dichalcogenides are indirect semiconductors with their optical band gap comparable to solar spectrum. Thus molybdenum dichalcogenide hold promise in photovoltaic applications such as photoelectrode in high efficiency photoelectrochemical solar cells. The main advantage of molybdenum dichalcogenide semiconductor is the prevention of electrolyte corrosion because of photo transition involving non bonding d-d orbital of Mo atoms [10]. Because of these characteristics of binary chalcogenides we have attempted to prepare ternary molybdenum bismuth telluride thin films.

Until now, different fabrication techniques such as spray pyrolysis [11], molecular beam epitaxy [12] including liquid phase epitaxy, bulk powder synthesis, thermal evaporation [13] and electrochemical deposition [14] has been employed for chalcogenide compounds. These commonly used methods are either costly or difficult to realize. Arrested precipitation technique provides an attractive alternative route to the fabrication of high quality thin films with promising properties offering several advantages over other methods. These include low cost, high controllability with silicon microfabrication processes as well as room temperature fabrication.

To the best of our knowledge this is the first reported synthesis of ternary nanocrystalline $MoBi_2Te_5$ thin films using self organized growth process popularly known as arrested precipitation technique [15-17]. The APT process based on Ostwald ripening law [18, 19]. In the present investigation we attempted to synthesize ternary $MoBi_2Te_5$ thin films by simple arrested precipitation technique. The purpose of present work is to establish and optimize the growth condition to produce nanocrystalline $MoBi_2Te_5$ thin films. The as grown films are then used for characterization study such as optostructural, optoelectronic, compositional and surface morphology. All these characteristics of nanocrystalline $MoBi_2Te_5$ thin films are used to check, its suitability as photoelectrode in PEC solar cell and thermo cooling behavior.

2.1. Experimental details

$MoBi_2Te_5$ thin films were deposited using Arrested Precipitation Technique (APT) on microglass slide substrates from aqueous bath. The deposition bath consisted of an aqueous solution of Mo-TEA, Bi-TEA complexes and sodium tellurosulphite for $MoBi_2Te_5$ thin film growth. Initially high purity precursors of ammonium molybdate and bismuth nitrate triturated separately in triethanolamine complexing agent to form clear solution of Mo-TEA, Bi-TEA complex. The concentrations of precursors, pH of bath solutions, temperature and rate of substrate rotation were finalized at the initial stages of the thin film formation. By obtaining proper conditions good quality and uniform films were obtained on substrate support. The film growth involves reaction of Mo^{4+}, Bi^{3+} & Te^{2-} ions in aqueous medium. At alkaline pH (9.25) and temperature 55^0 C. Mo-TEA, Bi-TEA arrested metal ions slowly dissociate from complex and reacts with chalcogen ion Te^{-2}. Ion by ion condensation took place which results in thin film formation on substrate surface. Ionic product K exceed the solubility product Ksp which results in condensation of metal ions and chalcogen ions [20] into quasi binary thin film formation $MoTe_2$, Bi_2Te_3 to ternary $MoBi_2Te_5$ thin films.

2.2. Characterization of sample

The thickness of the film was determined by surface profiler [AMBIOS XP-1]. The optical transmittance was measured using UV-Visible NIR- Spectrophotometer [Hitachi model 330 Japan] in wavelength range 300 to 800 nm. The structure of thin films was determined by X-ray Diffraction (XRD) analysis [Philips PW-1710 X-ray diffractrometer] with Cu Kα target having wavelength 1.540A^o for the 2θ ranging from 20^o to 80^o. The elemental composition of the as deposited thin film was determined by Energy Dispersive X-ray Analysis (EDAX) attached to Scanning Electron Microscopy (SEM) model [JEOL- JSM-6360 A]. DC electrical conductivity was measured by two probe method in the temperature range 350K to 475K. Thermoelectric power measurement was carried out under the condition of maximum temperature difference and minimum contact resistance.

3. Results and Discussion-

3.1. Optical studies-

The absorbance measurements have been taken out using an UV-Vis-NIR spectrophotometer in order to determine the band gap value of the material. The absorption coefficient (α) of the deposited films is calculated from the observed absorbance and transmittance values using the following equation [21].

$$\alpha = 1/t \ln (A/T) \qquad \ldots\ldots\ldots 1$$

Where, α is absorption coefficient in Cm^{-1}, t is film thickness, A is absorbance and T is transmittance. The nature of transmission is determined using the following equation [22].

$$\alpha h\upsilon = A\,(h\upsilon - Eg)^{n} \qquad \ldots\ldots\ldots 2$$

Where, A is Energy dependant constant, Eg is band gap energy of material, hυ is photon energy and n is index number (1/2, 3/2…..) depending upon mode of transition.

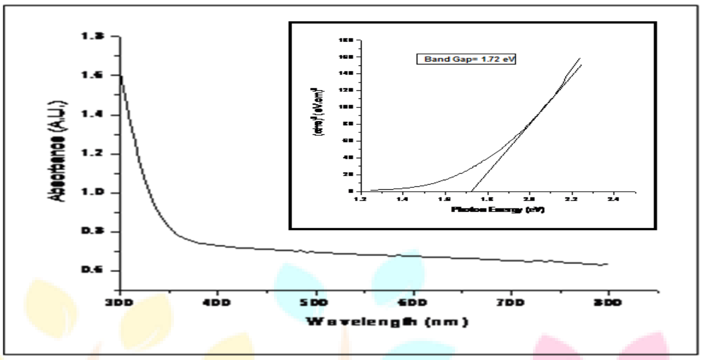

Figure 1. Determination of band gap $MoBi_2Te_5$ thin films.

The optical absorption spectra of $MoBi_2Te_5$thin films have been recorded as a function of wavelength in the range between 300 to 800 nm. The value of absorption coefficient (α) rises sharply owing to band transition & levels of later.

Figure 1 represents the plot of wavelength Vs absorption. The plot of (hυ) Vs $(\alpha h\upsilon)^2$ is shown in insert image which is linear at absorption edge, indicating a direct allowed transition. The straight line portion was extrapolated to the energy axis & when $(\alpha h\upsilon)^2=0$, the intercept gives the band gap energy. It is observed that the band gap of $MoBi_2Te_5$ thin film is 1.72 eV.

3.2. SEM Analysis-

The surface morphology of $MoBi_2Te_5$ thin films was investigated by using Scanning electron micrograph technique. SEM has been proved to be a unique, convenient and versatile method to analyze surface morphology of thin film and to determine the grain size. Scanning electron micrograph of $MoBi_2Te_5$ thin film in the as grown condition is as shown in figure 2 represents an image at magnification (× 6,000) of the $MoBi_2Te_5$ thin film.

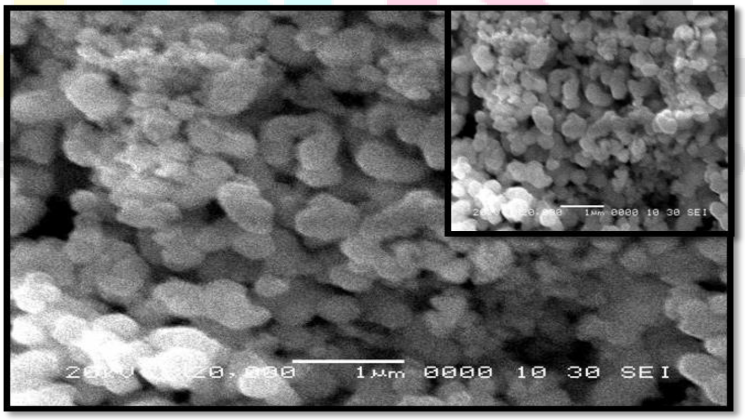

Figure 2. SEM micrograph of $MoBi_2Te_5$ thin films

The microstructure of the films observed by SEM shown that, on the surface of $MoBi_2Te_5$ film the agglomerate particles composed of nanoflakes were distributed on the substrate homogeneously, but many voids existed between particles in the film The smooth and uniform, adherent film surface without cracks feature observed in low magnification, so it has shown high mechanical stability of the films. The inset image represents the higher magnification (× 20,000) of the same sample. The spherical nature of the particle with average grain size in order to 400 nm is discernable from the image.

3.3. Compositional Characterization-

The composition of $MoBi_2Te_5$ is a topic of main importance since many cell properties are influenced by deviations from stoichiometry [23]. The typical EDAX spectrum of synthesized material is as shown in figure 3. This analysis shows that the atomic percentage of Mo, Bi and Te confirms the stoichiometry of synthesized compound. The EDAX data showed close agreements in theoretical and experimental values of Mo^{4+}, Bi^{3+}, Te^{2-} so atomic weight percent suggest the chemical formula $MoBi_2Te_5$ of as deposited molybdenum bismuth telluride thin films. The percentage of Mo and Bi in the film is higher than expected this is attributed to the fact that Mo in +4 state is more stable and reactive than in +6 state as well as bismuth is more metallic and its reactivity towards Te^{2-} is higher. Moreover molybdenum and bismuth forms antisite defects [20].

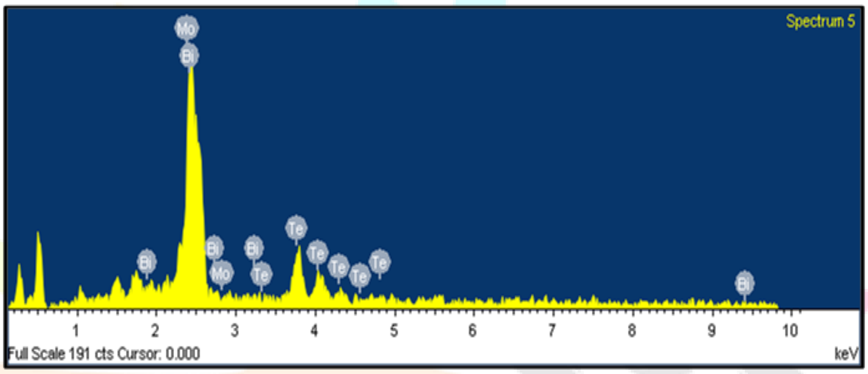

Figure 3. EDS spectrum of $MoBi_2Te_5$ thin films.

3.4. X-ray diffraction analysis-

The crystal structure of $MoBi_2Te_5$ thin films was studied by X-ray diffraction with CuKα radiation (λ=1.540A°). The of 2θ angle was from 20^0 to 80^0.

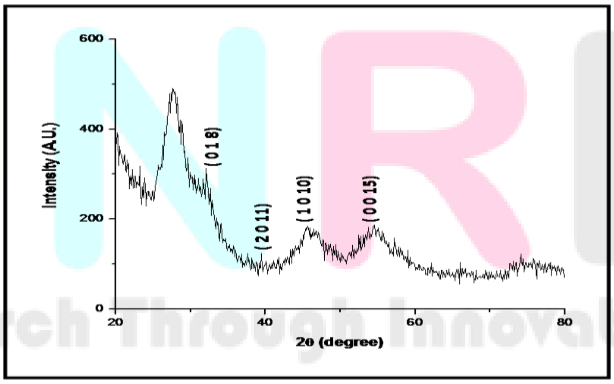

Figure 4. X-ray diffraction of $MoBi_2Te_5$ thin films.

Figure 4 shows typical X-ray diffraction of $MoBi_2Te_5$ thin films. X-ray diffraction pattern reveals that the deposited films posses polycrystalline nature with rhombohedral structure. The diffraction peaks of rhombohedral $MoBi_2Te_5$ are found at 2θ values of angles 32.1°, 38.2°, 45°, 53.1° corresponding to lattice planes (0 1 8), (1 0 10), (0 0 15), (2 0 11) respectively. The different peaks in difractogram are indexed and the corresponding values of interplaner spacing'd' are calculated and compared with standard values of JCPDS data (Card No. 08-0021 and 23-1257).

The crystallite size of the deposited films is calculated using FWHM data & Debye Scherer formula given below [8].

$$D = 0.9\,\lambda / \beta \cos\theta \qquad \ldots\ldots 3$$

Where, λ is wavelength of X-ray, θ is Bragg's diffraction angle at peak position in degrees and β is full width at half maximum of peak in radians. The crystalline size estimated for (0 1 8) peak is 43.6 nm.

3.5. Electrical Analysis-

The measurements of electrical resistivity of $MoBi_2Te_5$ thin films was carried out in temperature range 350 - 475 K on 1×1 cm shaped samples, using standard DC two point probe method under dark. A plot of inverse absolute Vs log (resistivity) for cooling cycle is shown in figure 5. The resistivity decreases with increase in temperature which is the indication of typical semiconductor characteristics [11].

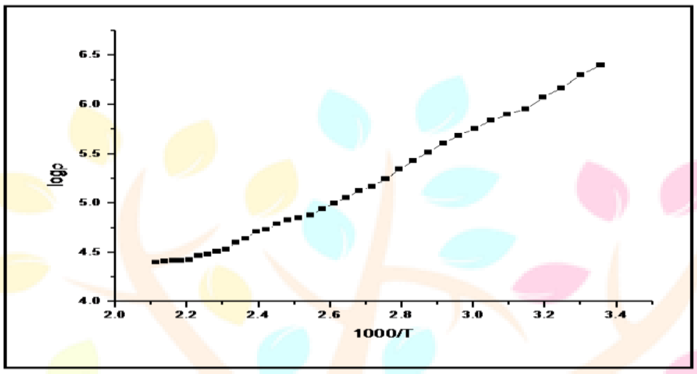

Figure 5. Temperature dependence of the DC conductivity for $MoBi_2Te_5$ thin films.

The activation energy Ea can be estimated from plot of ln σ against 1/T according to equation-

$$\sigma = \sigma_0 e^{(-Ea/kT)} \qquad \ldots\ldots..4$$

Where Ea is activation energy for electrical conduction, k is Boltzmann constant and σ is the temperature independent part of the conductivity and σ_o represents the pre-exponential factor. From the graph it indicates that in high temperature σ exhibits activated behavior. In low temperature region the slope of curve continuously decreases with increasing temperature indicates that σ in this region exhibits non-activated behavior. The activation energy for high temperature region is 0.003214 eV and activation energy for low temperature region is 0.001532 eV.

3.6. TEP Studies-

The TEP is most sensitive to any change or distortion of the Fermi level in the material. The temperature difference between the ends of sample causes transport of carriers from hot to cold end and thus creates electrical field which give rise to thermal voltage.

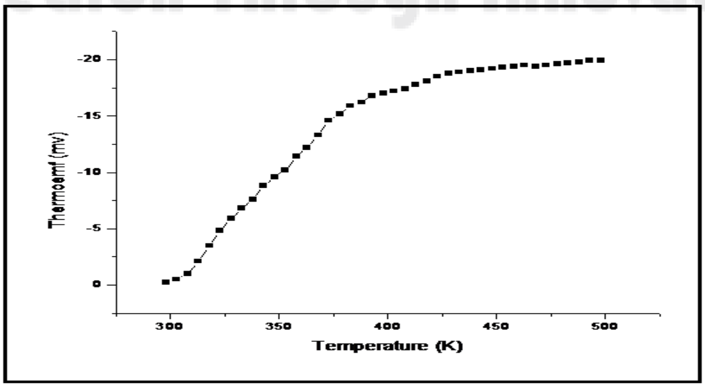

Figure 6. Temperature dependence of the TEP analysis for the $MoBi_2Te_5$ thin films.

This thermally generated voltage is directly proportional to the temperature difference created across the semiconductor. The type of conductivity of $MoBi_2Te_5$ thin film is determined from TEP measurement. Figure 6 shows variation of thermo voltage Vs temp difference for $MoBi_2Te_5$ thin films. The negative sign steams from dominance of n-type behavior of the $MoBi_2Te_5$ thin films [20].

4. Conclusions-

Arrested precipitation technique is applied successfully to deposit stoichiometric, adherent and uniform deposition of $MoBi_2Te_5$ material in thin film form. Optostructural and SEM results obtained shows material can be useful for device application such as a photo electrode in solar cell and thermocooling properties. X-ray diffraction confirms the proper phase formation of material. $MoBi_2Te_5$ exhibits an n-type semiconducting behavior with low electrical conductivity which is strongly suitable for fabricating a thin film solar cell.

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