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Nanocrystalline Bi_2Te_3 thin films synthesized by electrodeposition method for photoelectrochemical application

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ABSTRACT

Bismuth Telluride (Bi_2Te_3) thin films are prepared onto the stainless steel substrates by electrodeposition technique. Effects of varying deposition time on physico-chemical properties of Bi_2Te_3 thin films are studied. X-ray diffraction (XRD) analysis shows that all the Bi_2Te_3 films are polycrystalline in nature and it has Rhombohedral crystal structure. The results analyzed from FT-Raman and XRD analysis are well matched with each other and confirms the rhombohedral crystal structure. Scanning electron microscopy (SEM) images show that the variation in surface microstructure with respect to deposition time. Compositional elements (Bi and Te) distributions on the surface of Bi_2Te_3 film are estimated by EDX spectroscopy. Bi_2Te_3 thin films show the water contact angle in hydrophilic range. Photoconversion efficiency and fill factor of photoelectrochemical (PEC) cell formed with Bi_2Te_3 film are found to be 0.0987% and 0.3979 respectively.

1. Introduction

Nowadays, the research is focused toward the fabrication of cheap and eco-friendly energy conversion devices. Solar energy is enormous source of renewable energy which is clean and sustainable. It has been converted into harvesting energy to overcome the energy problems [1,2]. There are two ways: photovoltaic and thermoelectric technology that are used to directly convert solar radiation into electricity [3,4]. Semiconductor photoelectrodes have attracted much attention for direct conversion of solar radiation into electrical energy via photovoltaic process [5]. Bismuth telluride (Bi_2Te_3) is one metal chalcogenide. It has multiple applications such as solar cell [6], thermoelectric generator [7], photodetector [8], solar thermoelectric generator [3] and for ohmic back contact to CdTe solar cell [9], etc. Bi_2Te_3 is mostly used for its thermoelectric properties.

Song et al. [10] have investigated the effect of surfactants added into electrolyte solution on surface morphology and mechanical properties of electrodeposited Bi_2Te_3 thin films. They observed that Bi_2Te_3 thin films deposited with surfactants show smooth and denser surface as compared to those without surfactants. Vinoth et al. [11] synthesized hexagonal nanoplatelet Bi_2Te_3 thin films by solvothermal method. They observed that the films show n-type conductivity due to the excess presence of “Te”. It shows highest maximum absolute value of Seebeck coefficient ($-355\,\mu V/K$). Kaddouri et al. [12] prepared Bi_2Te_3 thin films on Si and SiO_2/Si substrates by hot wall epitaxy technique. They observed that the estimated band gap of Bi_2Te_3 are in good agreement with energy band gap calculated using density-functional theory which is 0.11 eV. They also reported that n-type film and p-type film have 1.7×10^{20} cm^{-3} and 2.4×10^{19} cm^{-3} carrier density respectively. Carrier concentration and mobility of Bi_2Te_3 film are 6.15×10^{20} cm^{-3} and 34.03 cm^2/ Vs, respectively reported by Singkaselit et al. [13]. Patil et al. synthesized fern shaped Bi_2Te_3 thin films by electrodeposition method for photoelectrochemical solar cell application. They studied the effect of different surfactants on the surface morphology, crystal orientation associated with the film growth and photoelectrochemical performance of Bi_2Te_3 thin films. They observed that higher crystalline films show better solar conversion efficiency [6].

Current efforts focused towards the synthesis of nanostructured Bi_2Te_3 thin film. Bi_2Te_3 thin films have been synthesized by various methods such as solvothermal [14], hydrothermal [15], pulsed laser deposition [16], thermal evaporation technique [17] and electrodeposition method [18] etc. Considering these approaches, the electrodeposition method is one of the promising technique used to prepare uniform nanostructure of different metal chalcogenides (Bi_2Te_3) film. It has several advantageous such as the operating at low temperature, no need of vacuum, high deposition rate, low cost and high flexibility to

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design uniform nanomaterial [6]. In this technique, growth rate can be easily controlled through electrical quantities such as current density and deposition potential [19,20]. Potentiostatic method of electrodeposition is a more assisted due to its better to control the properties of films by controlling deposition potential and electrochemical reactions [21]. The main prospective of this paper is to synthesis of highly crystalline and uniform nanostructure thin films. These films further employed for solar cell application. There are very few reports on study of Bi_2Te_3 thin films based solar cells.

In this paper, Bi_2Te_3 thin films synthesized onto the stainless steel (SS) substrates by cost effective electrodeposition method. Approaches of this work to prepare Bi_2Te_3 thin films without surfactant. The effect of thicknesses on structural, morphological, wettability, electrochemical properties and photoelectrochemical performances are studied.

2. Experimental details

2.1. Materials

Bismuth nitrate ($Bi(NO_3)_3{\cdot}5H_2O$) and sodium tellurite (Na_2TeO_3) as precursors were purchased from Alfa Aesar, Mumbai. Ethylene diamine tetra acetic acid (EDTA) was used as complexing agent. Nitric acid (HNO_3) and double distilled water were used as solvents. All chemicals were used without further purification.

2.2. Synthesis of Bi_2Te_3 thin films by electrodeposition method

Bi_2Te_3 thin films were deposited onto the stainless steel (SS) substrates by potentiostatic electrodeposition method. The substrate cleaning process was mentioned in recently published paper [22]. Bismuth nitrate and sodium tellurite were used as precursors for synthesis of Bi_2Te_3 thin films. Bismuth nitrate salts were dissolved into concentrated nitric acid and then diluted it by adding double distilled water into the concentrated nitric acid containing Bi^{3+} ions to form 0.05 M electrolyte solution. Sodium tellurite salts (0.05 M) were dissolved into the double distilled water. These two salts were dissolved separately in 100 ml beaker. The above two precursor solutions were mixed into together. The 10 ml EDTA solution was added by dropwise into the prepared precursor solution. The volumetric ratio of Bi:Te:EDTA was 5:5:1 in electrolyte solution which is used for the preparation of Bi_2Te_3 thin films onto the cleaned SS substrate by electrodeposition method. The deposition times were varied from 100 to 400 s at an interval of 100 s. The detail experimental preparative parameters for electrodeposition method to prepare Bi_2Te_3 thin films were noticed in Table 1. Synthesized thin films of Bi_2Te_3 by electrodeposition method were abbreviated as BT_1, BT_2, BT_3 and BT_4 for 100 s, 200 s, 300 s and 400 s respectively for a same volumetric ratio of Bi:Te:EDTA in electrolyte solution.

2.3. Characterization of Bi_2Te_3 thin films

XRD patterns of Bi_2Te_3 films were recorded by Bruker powder X-ray diffraction, Model D2: phaser with CuK_α radiation of wavelength 1.5406 Å. Identification of phase and crystalline nature of Bi_2Te_3 thin films were analyzed from XRD patterns using X′ Pert high score plus software. Fourier transform Raman (FT-Raman) spectrum was recorded using Bruker MultiRAM, Germany over the range of 200–600 cm^{-1} excited with Nd:YAG laser source (excitation wavelength is 1064 nm). Thicknesses of synthesized Bi_2Te_3 films were calculated by using weight difference method. The surface morphology of synthesized Bi_2Te_3 films were studied using field emission scanning electron microscopy (FE-SEM), (Model: MIRA 3 LMH). Elemental analysis of Bi_2Te_3 film was carried out using EDS techniques attached with FE-SEM techniques (NCA x-Act detector of Oxford instruments, USA). The interaction between liquid and surface of Bi_2Te_3 thin films were studied by measuring water contact angle between them using Rame-hart USA equipment with CCD camera. Electrochemical impedance spectroscopy (EIS) analysis of Bi_2Te_3 films was carried out using electrochemical workstation (AUT85804, Netherlands, frequency range from 10^6 Hz to 10^{-6} Hz in AC mode (100 mV)).

Table 1
Preparative parameters of electrodeposition method for preparation of Bi_2Te_3 thin films.

Sr. No.	Parameter	Value
1	Medium	Non-aqueous
2	Total quantity	25 ml
3	Bath Composition	0.05 M $Bi(NO_3)_3{\cdot}5H_2O$ + 0.05 M Na_2TeO_3
4	Concentration of EDTA	0.05 M
5	Applied potential	−0.170 V/SCE
6	Deposition temperature	297 K
7	Substrate	Stainless steel (SS)
8	pH	~2

2.4. Photoelectrochemical studies

Photoelectrochemical (PEC) cell was fabricated using two electrode configuration. The working electrode acts as Bi_2Te_3 thin films which are deposited onto the stainless steel (SS) substrate and counter electrode acts as graphite electrode. Distance between these two electrodes was 0.5 cm. The 0.2 M polysulfide electrolyte was used as redox electrolyte. PEC cell configuration was SS/Bi_2Te_3/0.2 M Polysulfide/Graphite. PEC cell was illuminated by 100 W tungsten filament lamp (intensity = 40 mW/cm^2) which was placed parallel to the PEC cell at 30 cm. The short circuit current (I_{sc}) and open circuit voltage (V_{oc}) of PEC cell formed with Bi_2Te_3 films were measured under dark and illumination.

3. Results and discussion

3.1. Film formation and reaction mechanism

The growth of Bi_2Te_3 thin films were studied by recording CV in two different electrolyte solution such as bismuth and tellurium which determined the electrode electrolyte interface and electrochemical reactions relevant. Thus, the reduction potential of a bismuth and tellurium are determined from the reduction peak which gives the appropriate deposition potential range. The estimated potential from CV is reduction potential of each species.

Fig. 1a illustrates the CV of the unitary Bi whose concentration is 0.05 M bismuth nitrate in electrolyte solution. It shows one oxidation peaks at 0.061 V and one cathodic peak at − 0.17 V which corresponds to the reductive deposition potential of Bi^{3+} in electrolyte solution. The weak value of reductive deposition potential indicates that slow deposition kinetics of Bi^{3+} ions in reaction [6]. Fig. 1b represents the CV of Te system whose concentration is 0.05 M sodium tellurite in electrolyte solution. It shows one oxidation peak at 0.611 V and one reduction peak at − 0.109 **V**. The reduction peak at − 0.109 V represents the consecutive reduction of $HTeO_2+$ to Te^{2-} in electrolyte solution. Fig. 1c represents the CV for mixed solutions of Bi and Te in same concentration to each other. Two anodic peaks for bismuth and tellurium are situated at approximately 0.238 V and 0.420 V respectively, while the two cathodic peaks at approximately − 0.094 V and − 0.217 V for bismuth and tellurium respectively which are in good agreement with literature [6]. Bi_2Te_3 thin films were deposited at − 170 mV/SCE.

3.2. X-ray diffraction (XRD) studies

Fig. 2 displays the XRD patterns of synthesized Bi_2Te_3 thin films deposited at various thicknesses by varying deposition time from 100 to 400 s at interval of 100 s. XRD patterns are recorded in 2θ range from