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Orientation-controlled synthesis and characterization of Bi_2Te_3 nanofilms, and nanowires via electrochemical co-deposition

İbrahim Y. Erdoğan[a,*], Ümit Demir[b]

[a] Bingol University, Faculty of Sciences and Arts, Department of Chemistry, 12000 Bingol, Turkey
[b] Atatürk University, Faculty of Sciences, Department of Chemistry, 25240 Erzurum, Turkey

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ABSTRACT

An electrochemical deposition technique based on co-deposition was used to deposit preferentially oriented Bi_2Te_3 nanostructures (nanofilm, and nanowire). The shared underpotential deposition (UPD) potentials for both Bi and Te co-deposition were determined by cyclic voltammetric measurements. The scanning probe microscopy (scanning tunneling microscopy (STM) and atomic force microscopy (AFM)) and the X-ray diffraction (XRD) data indicated that the electrodeposition of Bi_2Te_3 results in nanofilm-structured deposits with a preferential orientation at (0 1 5) and nanowired-structured deposits with a preferential orientation at (1 1 0) in acidic and basic (in the presence of ethylenediaminetetraacetic acid (EDTA)) medium, respectively. The results show that the nucleation and growth mechanism follows 3D mode in acidic solutions and 2D mode in basic solution containing EDTA additive. The optical characterization performed by reflection absorption Fourier transform infrared (RA-FTIR) spectroscopy showed that the band gap energy of Bi_2Te_3 nanostructures depends on the thickness, size, and shape of the nanostructures and the band gap increases as the deposition time decreases. Moreover, the quantum confinement is strengthened in the wire-like deposits relative to the film-like deposits. Energy dispersive X-ray spectroscopy (EDS) analysis demonstrated that Bi_2Te_3 nanostructures were always in 2:3 stoichiometry, and they were made up of only pure Bi and Te.

1. Introduction

Synthesis of nanomaterials with controlled size, shape, and crystallographic orientation has become an important issue in material science research. The properties of semiconductor nanocrystals, which possess many novel properties that differ considerably from those of the bulk [1,2], depend both on dimension and superlattice structure. Therefore, the development of synthetic methods that enable their precise control is expected to have a significant impact on progress. Bi_2Te_3 with a narrow band gap and other V–VI group semiconductors are the best-known materials for thermoelectric (TE) applications at room temperature and are widely used for biomedical and optoelectronic applications such as heat pumps, power generation, solid state refrigeration, cooling IC chips, infrared sensors, optoelectronic sensors, and photo detectors [3–6]. The performance of TE devices depends on the material's figure of merit, $ZT = (\alpha^2 T/(\kappa)$, where Z is a measure of a material's TE properties, α Seebeck coefficient, T temperature, (electrical resistivity, and κ thermal conductivity. To increase device efficiency, the figure of merit (ZT) of TE materials must be improved [5]. Research results indicate that the ZT value of certain nanoscale materials, due to the stronger quantum confinement, is higher compared to that of their bulk materials [5,6]. Therefore, the ZT value can be tailored through controlling the size or thickness of nanoscale TE materials, which will have much better potential applications in TE devices. It was reported that the ZT of Bi_2Te_3-based materials could be significantly improved if the materials were nanostructured, such as superlattices [7], nanofilms [8], nanowires [9], and nanorods [10]. These nanostructures are an important class of materials potentially useful as key building blocks in "bottom-up" manufacturing nanotechnology. Recently $ZT > 2$ has been observed in thin film superlattices or quantum well materials from TE nanomaterials [6,7]. The first significant result was reported by Venkatasubramanian et al. [6], who demonstrated $ZT($ 2.4 using p-type Bi_2Te_3/Sb_2Te_3 quantum well superlattices with 6 nm periodicity. The 3D bulk ZT value of Bi_2Te_3 is 0.8 at 300 K. For comparison the best calculated ZT values of Bi_2Te_3 for 2D quantum well of 0.5 nm thickness and 1D quantum wire of 0.5 nm diameter are ~5 and ~14, respectively [10,11]. These impressive results indicate that a significant increase in ZT can be achieved by going to lower dimension due to the change in the density of states and the quantum confinement effect. Various methods have been developed to grow Bi–Te films, such as molecular beam

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* Corresponding author. Tel.: +90 426 2132550 1185.
E-mail address: ibrahimyerdogan@gmail.com (İ.Y. Erdoğan).

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epitaxy [12], metal organic chemical-vapour deposition [13], magnetron sputtering [14], and electrochemical deposition [15]. Among these techniques, electrochemical deposition has been widely used because of its simplicity, high cost-effectiveness, and rapid deposition rate. Bi_2Te_3 nanowires and nanorods have been synthesized by electrodeposition into porous anodic alumina membrane (PAAM) templates [9,16], on highly oriented pyrolytic graphite (HOPG) surfaces [17] from acidic solution. Bi_2Te_3 films have been prepared electrochemically in acidic solution [18,19]. Furthermore, Bi_2Te_3 films [20] have been obtained via electrochemical atomic layer epitaxy (ECALE), which has been developed by Gregory and Stickney [21].

Recently, we developed a simple and convenient method [22] for the electrochemical deposition of compound semiconducting materials, which was based on the combination of co-deposition and the underpotential deposition (UPD). We showed that this method could be used for the growth of highly crystalline nanofilms of PbS [22], ZnS [23], CdS [24], PbTe [25], Sb_2Te_3 [26] and $(Bi_xSb_{1-x})_2Te_3$ [27].

In the present paper, we illustrate the detailed growth process and optical characterization of Bi_2Te_3 nanostructures electrodeposited on single crystalline Au (1 1 1) electrodes by using morphological, structural, optical, and compositional characterizations performed by atomic force microscopy (AFM), scanning tunneling microscopy (STM), X-ray diffraction (XRD), reflection absorption Fourier transform infrared (RA-FTIR) spectroscopy, and electron dispersive spectroscopy (EDS). We report that the shape, size, thickness, and band gap energy of Bi_2Te_3 nanostructures can be readily controlled by pH, composition of the solution, and the electrodeposition time.

2. Experimental

2.1. Chemicals

All solutions were prepared from reagent grade chemicals and deionized water (resistivity > 18 M(cm). Working solutions were deaerated by blowing purified N_2 gas through and over the solution for 15 min. Bi_2Te_3 electrodeposition in acidic solution was carried out from a 0.001 M TeO_2 (Merck) and 0.001 M $Bi(NO_3)_3$ solutions with a pH value of 1.5. Bi_2Te_3 electrodeposition in basic was realized from a 0.001 M TeO_2 (Merck), 0.002 M $Bi(NO_3)_3$ (Merck) and 0.01 M EDTA disodium salt ($C_{10}H_{14}N_2Na_2O_8{\cdot}2H_2O$, Merck) solutions with a pH value of 9.0. The pH values of all solutions were adjusted with $HClO_4$ and NH_3.

2.2. Electrochemistry

All electrochemical experiments were performed in a conventional three-electrode cell system (C3 Cell Stand, BAS) under an N_2 atmosphere, at room temperature with a BAS 100B/W Electrochemical Workstation. The working electrode was a (1 1 1)-oriented single-crystal gold (Johnson Matthey, 99.999%) prepared with a pure gold wire in hydrogen flame. A platinum wire was used as a counter electrode. All the potentials were referenced to a 3 M Ag/AgCl reference electrode.

2.3. Characterization of materials

The optical absorbance spectra of electrochemically synthesis Bi_2Te_3 nanostructures were measured using a variable angle reflection rig in conjunction with a Perkin–Elmer Spectrum One FT-IR spectrometer in the spectral range 1000–7000 cm^{-1} at room temperature. The each measure was obtained by an average of 100 scans and a resolution of 2 cm^{-1}. X-ray diffraction (XRD) experiments for nanofilms that were identified with the help of PDF-ICDD on Au (1 1 1) were done in a Rigaku Advance Powder X-ray Diffractometer instrument using Cu Kα radiation ((= 0.154 nm), operating at 30 kV and 30 mA over a 2θ range of 20°–70°. The elemental compositions (Bi/Te) of the Bi_2Te_3 deposits were determined by EDS with a JEOL-6400 system coupled to the SEM. The operating conditions for EDS analysis include an accelerating voltage of 15 kV, a beam current of 5 nA, a working distance of 15 mm an a live time of 70 s for each run. The surface morphologies of the films were inspected by non-contact mode NC-AFM and constant current mode STM (PicoSPM, Molecular Imaging Inc.). All images were taken in air. 225 μm length, 7 μm thickness and 38 μm width silicon nitride cantilevers with a 48 N/m force constant and 190 kHz resonant frequency for NC-AFM were used. Typical tunneling current and applied voltages to obtain good quality images were 0.5 nA and 1–2 V, at scan rates ranging 2 Hz. Tungsten and Pt–Ir tunneling probes were employed. AFM/STM images were taken at different zones of the films to check its homogeneity.

3. Results and discussion

3.1. Electrochemistry of Te and Bi on Au (1 1 1) in acidic and basic solutions

It is well known that Te is soluble in the form of ${HTeO_2}^+$ at pH < 1.9 and in the form of ${TeO_3}^{2-}$ at pH > 8.4 in concentrations of 0.1 mM and higher (Eqs. (1) and (2)). Tellurium precipitates as TeO_2 at pH between 1.9 and 8.4 (Eqs. (2) and (3)) [28,29].

$$Te^{4+} + 2H_2O \leftrightarrow {HTeO_2}^+ + 3H^+ \quad (1)$$

$$TeO_2 + H_2O \leftrightarrow {TeO_3}^{2-} + 2H^+ \quad (2)$$

$$HTeO_2^+ \leftrightarrow TeO_2 + H^+ \quad (3)$$

Bismuth is soluble as Bi^{3+} only at pH < 2 (Eq. (4)) in aqueous solutions. At pH higher than 5, Bi precipitates in the form of Bi_2O_3 at concentrations of 0.1 mM and higher (Eq. (5)). In the range of 2 < pH < 5 (Eqs. (4) and (5)), Bi is soluble as $BiOH^{2+}$ [28,29].

$$Bi^{3+} + H_2O \leftrightarrow BiOH^{2+} + H^+ \quad (4)$$

$$2BiOH^{2+} + H_2O \leftrightarrow Bi_2O_3 + 4H^+ \quad (5)$$

For the electrodeposition, the precursors are required to be water-soluble. Therefore, the pH value of the solutions containing Bi and Te precursors should be adjusted to lower than 2 for the electrodeposition of Bi_2Te_3. In addition, we could have Bi as a soluble form in the basic solution by converting bismuth into a complex form using a suitable complexing agent. Ethylenediaminetetraaceticacid (EDTA), as a complexing agent for Bi^{3+}, could be used to coordinate Bi^{3+} to form $BiEDTA^-$ (K = 22.8) [30,31]. Since Te and Bi will be present in the electrodeposition solution as ${TeO_3}^{2-}$ and $BiEDTA^-$ at pH higher than 8.5, Bi_2Te_3 could also be electrodeposited at pH > 8.5.

The cyclic voltammogram of Au (1 1 1) in an acidic solution containing 1 mM TeO_2 (pH: 1.5) in the UPD region of Te is shown in Fig. 1a. The reductive peaks (C_1: 345 and C_2: 90 mV) correspond to the surface-limited electrodeposition of $Te^{4+}({HTeO_2}^+)$. The bulk tellurium electrodeposition starts at −50 mV in the acidic solution. On the reverse scan, the oxidative peaks (A_2: 505 and A_1: 575 mV) are due to desorption of electrodeposited Te from the Au (1 1 1) surface. Fig. 1b shows the electrochemical behavior of Te in a basic solution containing 1 mM TeO_2 and 0.01 M EDTA (pH: 9.0) in the UPD region of Te. The broad anodic stripping peak, labeled A^* (around 295 mV), is associated with the two cathodic deposition peaks, labeled C_1^* and C_2^* (around −500 and −595 mV, respectively). Tellurium bulk electrodeposition does not occur until −700 mV in basic conditions, suggesting that the surface limited atomic layers of Te could be