Orientation-controlled synthesis and characterization of Bi$_2$Te$_3$ nanofilms, and nanowires via electrochemical co-deposition

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A B S T R A C T

An electrochemical deposition technique based on co-deposition was used to deposit preferentially oriented Bi$_2$Te$_3$ 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$_2$Te$_3$ results in nanofilm-structured deposits with a preferential orientation at (0 1 5) and nanowire-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$_2$Te$_3$ 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$_2$Te$_3$ nanostructures were always in 2:3 stoichiometry, and they were made up of only pure Bi and Te.

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1. Introduction

Synthesis of nanomaterials with controlled size, shape, and crystalline 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$_2$Te$_3$ 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, $ZT=(\alpha^2T)/(\kappa)$, where $Z$ is a measure of a material’s TE properties, $\alpha$ Seebeck coefficient, $T$ temperature, $\kappa$ electrical resistivity, and $\kappa$ thermal conductivity. To increase device efficiency, the figure of merit ($ZT$) of TE materials must be improved [5]. 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$_2$Te$_3$-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$_2$Te$_3$/Sb$_2$Te$_3$ quantum well superlattices with 6 nm periodicity. The 3D bulk $ZT$ value of Bi$_2$Te$_3$ is 0.8 at 300 K. For comparison the best calculated $ZT$ values of Bi$_2$Te$_3$ for 2D quantum well of 0.5 nm thickness and 1D quantum wire of 0.5 nm diameter are $\sim 5$ and $\sim 14$, 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...
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$_2$Te$_3$ 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$_2$Te$_3$ films have been prepared electrochemically in acidic solution [18,19]. Furthermore, Bi$_2$Te$_3$ 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$_2$Te$_3$ [26] and (Bi$_x$Sb$_{1-x}$)$_2$Te$_3$ [27].

In the present paper, we illustrate the detailed growth process and optical characterization of Bi$_2$Te$_3$ nanostructures electrodeposited on single-crystalline Au (111) 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$_2$Te$_3$ 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 MΩ cm). Working solutions were deaerated by blowing purified N$_2$ gas through and over the solution for 15 min. Bi$_2$Te$_3$ 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$_2$Te$_3$ electrodeposition in basic was realized from a 0.001 M TeO$_2$ at pH between 1.9 and 8.4 (Eqs. (1) and (2)). Tellurium precipitates as TeO$_2$ at pH between 1.9 and 8.4 (Eqs. (2) and (3)) [28,29].

Te$_4^{4+}$ + 2H$_2$O ↔ HTeO$_2^{2-}$ + 3H$^+$ (1)

TeO$_2$ + H$_2$O ↔ TeO$_2^{2-}$ + 2H$^+$ (2)

HTeO$_2^{-}$ ↔ TeO$_2$ + H$^+$ (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$_2$O$_3$ (Eq. (5)). In the range of 2 < pH < 5 (Eqs. (4) and (5)), Bi is soluble as BiOH$_2^{2+}$ in aqueous solutions.

Bi$^{3+}$ + H$_2$O ↔ BiOH$_2^{2+}$ + H$^+$ (4)

2BiOH$_2^{2+}$ + H$_2$O ↔ Bi$_2$O$_3$ + 4H$^+$ (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$_2$Te$_3$. 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. Ethylenediaminetetraacetic acid (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$_2^{2-}$ and BiEDTA$^{-}$ at pH higher than 8.5, Bi$_2$Te$_3$ could also be electrodeposited at pH > 8.5.

The cyclic voltammogram of Au (111) 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–limitation electrodeposition of Te$^{4+}$ (HTeO$_2^{2-}$). The bulk tellurium electrodeposition starts at ~50 mV in the acidic solution. On the reverse scan, the oxidative peaks (A$_1$: 505 and A$_2$: 575 mV) are due to desorption of electrodeposited Te from the Au (111) 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$_1$ (around 295 mV), is associated with the two cathodic deposition peaks, labeled C$_1$ and C$_2$ (around ~500 and ~550 mV, respectively). Tellurium bulk electrodeposition does not occur until ~700 mV in basic conditions.

3. Results and discussion

3.1. Electrochemistry of Te and Bi on Au (111) in acidic and basic solutions

It is well known that Te is soluble in the form of HTeO$_2^{2-}$ at pH < 1.9 and in the form of TeO$_2^{2-}$ 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$_4^{4+}$ + 2H$_2$O ↔ HTeO$_2^{2-}$ + 3H$^+$ (1)

TeO$_2$ + H$_2$O ↔ TeO$_2^{2-}$ + 2H$^+$ (2)

HTeO$_2^{-}$ ↔ TeO$_2$ + H$^+$ (3)

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$_2$Te$_3$. 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. Ethylenediaminetetraacetic acid (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$_2^{2-}$ and BiEDTA$^{-}$ at pH higher than 8.5, Bi$_2$Te$_3$ could also be electrodeposited at pH > 8.5.
formed at potentials more positive than $-700 \text{ mV}$. These observations agreed well with those obtained in acidic solutions by us \[32\] and in basic solution by others \[33\].

Fig. 2a demonstrates a cyclic voltammogram obtained in an acidic solution (pH: 1.5) of 1 mM Bi$^{3+}$ on the Au substrate in the UPD region of Bi. The cyclic voltammogram shows a reductive peak C (235 mV) and an oxidative peak A (255 mV), corresponding to an atomic layer deposition and stripping of Bi. Bi multilayer (bulk) formation starts at $-25 \text{ mV}$ in these conditions. Similar UPD behavior for Bi in acidic solution has previously been reported \[34\]. The underpotential deposition of 2 mM Bi$^{3+}$ was also performed on the Au (1 1 1) in basic solutions (pH: 9.0) containing 0.01 M EDTA (Fig. 2b). The cyclic voltammogram in these conditions contains a redox couple corresponding to deposition (C*: $-330 \text{ mV}$) and stripping (A*: $-145 \text{ mV}$) peaks of Bi atomic layers. The difference between cathodic and anodic peak potentials (($E_p$) in the basic solution (Fig. 2b) is quite different from those obtained on Au (1 1 1) electrodes in aqueous acidic solution (Fig. 2a). Both the cathodic wave and anodic wave were shifted negatively, so that ($E_p$) was more than 180 mV. The potential shift for the cathodic wave is larger than that for the anodic wave. We have previously reported similar shifts for UPD deposition of Pb on an Au (1 1 1) electrode in the presence of EDTA \[25\].

3.2. Electrodeposition of Bi$_2$Te$_3$ on Au (1 1 1) in acidic and basic solutions

In order to determine a shared (joined) UPD potential in acidic medium (pH: 1.5), we overlapped both cyclic voltammograms of Te UPD and Bi UPD obtained in the same conditions (Fig. 3a). Since UPD is a surface-limited phenomenon, the resulting deposit is generally limited to an atomic layer. Atomic layer formation of Bi starts at 235 mV, while the multilayer formation of Bi does not begin until the bulk deposition potential of Bi ($-25 \text{ mV}$). In other words, if we keep the electrode potential between 235 and $-25 \text{ mV}$, we will have an atomic layer of Bi on the electrode surface. Based on the same idea, Te UPD deposition starts at 345 mV and ends at $-50 \text{ mV}$. Fig. 3a shows that the UPD waves of both Bi and Te coincide at potentials between 235 and $-25 \text{ mV}$. If the potential of the working electrode is kept constant between these potentials (shown with dotted lines), Bi and Te are deposited underpotentially at the Au electrode surface. Based on the same idea, Te UPD deposition starts at 345 mV and ends at $-50 \text{ mV}$. Fig. 3b shows that shared UPD potentials are between $-500 \text{ and } -650 \text{ mV}$ for basic solutions containing 0.01 M EDTA. Fig. 4 corrected to show that the potential range chosen is still in the UPD region of both Bi$^{3+}$ and Te$^{4+}$. As shown in the Fig. 4, the bulk Bi deposition does not occur until $-25 \text{ mV}$ and $-650 \text{ mV}$ in acidic and basic conditions, respectively. Fig. 5 shows the bulk
deposition potentials of Bi and Te on the Bi₂Te₃-covered Au electrode. As can be seen from the cyclic voltammograms in Fig. 5, the bulk deposition potentials of Bi and Te are never reached even on the Bi₂Te₃-covered Au electrode surface if the potential of electrode set to a potential which is in the range of co-deposition region. Since the potentials in the co-deposition region shown in Fig. 3 is limited for the UPD deposition of Bi and Te atomic layers but not for their bulk deposition. These underpotentially deposited Bi and Te atoms react with each other in both acidic and basic conditions and form the Bi₂Te₃ compound on the electrode surface, it should promote the electrochemical growth of Bi₂Te₃ at the substrate surface. This simple and one-pot electrochemical co-deposition method, based on the shared UPD potentials of Bi and Te, allows us to synthesize Bi₂Te₃ nanostructures with various thicknesses and sizes by simply using different deposition times with the same solution.

3.3. Morphological and structural characterization

Fig. 6 shows STM images of the initial stages of potential controlled electrodeposition of Bi₂Te₃ obtained after 1, 3, and 5 min at +50 mV in acidic solution (pH: 1.5). Randomly distributed nanodots 25 ± 5 nm in diameter and 0.3 nm in height on the flat Au (1 1 1) terraces can be seen in Fig. 6a. This image suggests that the Bi₂Te₃ nanoparticles form on the Au (1 1 1) surface from well-separated crystal nuclei rather than from a saturated chemisorbed monolayer. As the time for electrodeposition increases to 3 and 5 min, the diameter, height, and density of these structures increase, as indicated in Fig. 6b and c. As shown in Fig. 7a–c, these nanostructures grow in time and form a nanostructured thin film of Bi₂Te₃. All these time-dependent AFM and STM images clearly show that the electrodeposition of Bi₂Te₃ in acidic medium follows 3D nucleation and growth kinetics with a progressive growth mode.

In the presence of EDTA, evenly distributed nano-seeds of approximately the same size are observed on the surface of the Au (1 1 1) electrode after 3 min of electrodeposition at −600 mV in basic solutions (pH: 9.0). Most of the nanoparticles have a uniform width and thickness in the ranges of ∼20 nm and ∼0.3–0.4 nm, respectively (Fig. 8a). As the time for deposition increases to 6 min, the diameter of nanoparticles increases and new ones form at the surface but the height of these nanoparticles stays constant as ∼0.3–0.4 nm (Fig. 8b). The subsequent growth is governed by the lateral growth. Finally one can observe complete growth of the
first layer, which seems to be about fully closed at 5–6 min. STM images and the cross-sectional profiles in Fig. 8a and b obviously indicate 2D nucleation and that the growth mode is operative for the initial stages of electrodeposition of Bi$_2$Te$_3$ in these conditions. Fig. 9a shows that the growth direction changes from lateral to vertical after the first layer is almost complete. These vertically aligned wire-like nanostructures are 20 ± 5 nm in diameter and 15 ± 5 nm in height. It could be considered as a transition from 2D growth to 1D growth mode finally resulting in the formation of horizontally aligned nanowires of Bi$_2$Te$_3$ with a diameter of 25 ± 5 nm and a length of 400 ± 150 nm as shown in Fig. 9b. The subsequent AFM image (Fig. 9c) obtained after 55 min of electrodeposition shows that the growth mode changes from 1D to 2D and the nanowires are converted into a belt-like structure with a width of approximately 200 nm.

The XRD diffractograms of Bi$_2$Te$_3$ electrodeposited at different times and in different conditions (Figs. 10 and 11) correspond to a rhombohedral phase with hexagonal crystal structure (JCPDS-ICDD card 15-0863) and consist of diffraction peaks at 27.7°, 41.1°, 44.6°, 50.3°, 57.1°, and 67.0° (2θ scale) arising from (0 1 5), (1 1 0), (0 0 1 5), (2 0 5), (0 2 1 0), and (1 2 5) reflection, respectively, and a peak at 38.2° arising from the (1 1 1) reflections of Au (JCPDS-ICDD card 04-0784), which belongs to a single crystalline substrate used in this study. XRD patterns obtained after 15 and 35 min of electrodeposition in acidic medium (pH: 1.5) show that the peak at 27.7° (0 1 5) is the dominant peak and its intensity increases with increasing deposition time. While the intensity of the other peaks stays almost constant, the intensity of Au (1 1 1) reflection decreases. All these XRD results indicate that nanostructures are randomly oriented at the early stages of electrodeposition but they transform in a preferential orientation of the nano-structured films along the (0 1 5) as the electrodeposition time increases in acidic conditions. Fig. 11 shows the XRD patterns obtained for the electrodeposition in basic conditions in the presence of EDTA as a complexing agent for Bi. XRD patterns in both cases are almost the same but the dominant peak is the reflection from (1 1 0) at 41.1°, indicating that the growth of Bi$_2$Te$_3$ nanostructures is preferentially oriented along the (1 1 0) and morphologies are 1D wire-like in shape [9]. There are several factors that affect the orientation of Bi$_2$Te$_3$ nanostructures during the electrochemical deposition, but in the present study two factors (pH and EDTA additive) are different in both deposition conditions. Thus, the different orientations could have resulted from pH and/or EDTA. In order to test the pH effect, we carried out the electrochemical deposition in acidic and basic solutions without adding EDTA, and we saw the same nanofilm structured Bi$_2$Te$_3$ morphology having preferential orientation along the (0 1 5) as obtained in acidic condition. In addition to this test, we also carried out the electrochemical deposition in acidic medium in the presence of EDTA. However, we observed the same orientation in this case as well. Nanowire structured Bi$_2$Te$_3$ deposits preferentially oriented along (1 1 0) were obtained only in the basic solutions containing EDTA additives. These results suggest that the presence of EDTA during the electrochemical deposition has a great influence on the growth of Bi$_2$Te$_3$ structures. However, some researchers have reported that the EDTA can bind to the specific crystal faces and promote crystal growth along the

<table>
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<th>Table 1</th>
<th>Dependency of band gap on the deposition time, the thickness and the number of coulombs passed.</th>
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<td>Acidic medium (pH: 1.5)</td>
<td>Basic medium (pH: 9.0)</td>
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<td>Deposition time (min)</td>
<td>Charge (mC/cm$^2$)</td>
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other directions due to increasing interparticle repulsions [35–38]. Most researchers, including ourselves, think that the preferred orientations of Bi$_2$Te$_3$ along (0 1 5) planes in the presence of EDTA are due to controlled nucleation processes associated with the low deposition rate. The EDTA will coordinate strongly with Bi$^{3+}$ by a formation constant of 22.8 yielding a log conditional stability constant of 9.4 (pH: 1.5) and of 21.5 (pH: 9.0) [31]. Since the Bi$_2$EDTA$^{-}$ complex has a high stability constant in basic conditions, which will result in a decrease in the concentration of free Bi$^{3+}$ in the solution, the electrodeposition rate of Bi$^{3+}$ will be relatively small. This conclusion was further supported by the potential controlled coulometric measurements. As shown in Table 1, the deposition rate in basic conditions (with EDTA) is almost three times smaller than that in acidic conditions at the beginning of electrodeposition. Thus, we are not able to obtain measurable absorption by RA-FTIR at deposition times less than 10 min. When the solubility of Bi is fairly low in the solution, the Bi atom will prefer to incorporate itself into existing nuclei with less energy instead of forming new nuclei. Therefore, preferential growth proceeding on the kinetically favorable planes similar to preferred orientations in crystal growth has been observed in the presence of EDTA by us [22–25] and others [35–38].

3.4. Optical characterization

The optical properties of electrodeposited Bi$_2$Te$_3$ nanostructures were determined by RA-FTIR measurements. Figs. 12 and 13 are the absorption spectrums of Bi$_2$Te$_3$ obtained in the range 7000–1000 cm$^{-1}$ at pH: 1.5 and pH: 9.0 (with EDTA), respectively. The absorption onsets measured for deposits at 5–35 min in acidic solution and 10–55 min in basic solution are 4050–1350 and 5640–1350 cm$^{-1}$, respectively. The room temperature absorption measurements of Bi$_2$Te$_3$ for both nanofilms and nanowires show very strong blue shifts of the fundamental absorption edge with decreasing deposition time, which result from quantum confinement in the nanostructures. The band-gaps of Bi$_2$Te$_3$ nanostructures were determined by linear extrapolation to the X-axis ($h\nu$) from the straight part of the curve. The plots of $(h\nu)^2$ vs. $h\nu$ should be straight lines and intercepts on the energy axis would give the band-gap of the film [39]. The band-gap values for Bi$_2$Te$_3$ nanostructures electrodeposited at various times in acidic and basic (with EDTA) solutions are shown in Table 1, in which the band-gaps for both Bi$_2$Te$_3$ nanofilms and nanowires decrease with deposition times and finally reach the value for the band gap energy of bulk Bi$_2$Te$_3$ [40]. In order to find out the thickness-band-gap dependency of Bi$_2$Te$_3$ nanostructures, we carried out coulometric measurements during the electrodeposition for both acidic and basic conditions [25,26]. The charge consumed during the electrodeposition for different times was determined using Faraday’s law and the anodic processes shown below in acidic and basic solutions. Then the thicknesses of the nanostructures were calculated by assuming that smooth and nonporous films of Bi$_2$Te$_3$ formed at the Au (1 1 1) surfaces.

$$2\text{Bi}^{3+} + 3\text{HTeO}_2^{2+} + 9\text{H}^+ + 18\text{e}^- \leftrightarrow \text{Bi}_2\text{Te}_3 + 6\text{H}_2\text{O} \quad (7)$$

$$2\text{BiEDTA}^- + 3\text{TeO}_3^{2-} + 11\text{H}_2\text{O} + 18\text{e}^- \leftrightarrow \text{Bi}_2\text{Te}_3 + 2\text{HEDTA}^{3-} + 20\text{OH}^- \quad (8)$$

The band-gap dependency of Bi$_2$Te$_3$ nanostructure as a function of the deposition time, the number of coulombs passed during the electrodeposition, and the film thickness are summarized in Table 1. The experimental band-gap values for all nanostructures increase as the deposition time, consumed charge, and the thickness (or diameter) of deposits increase because of the quantum-size effect. It is interesting to note that the observed band-gap values of nanowires and nanofilms differ from each other for the same amounts of deposits having thicknesses lower than 40 nm. However, both deposits have the same band-gap value for thicknesses higher than 40 nm (Fig. 14). In other words, the blue shift in the band-gap for wire-like nanostructures is more pronounced than that for film-like nanostructures. Fig. 14 suggests that the quantum confinement is weakened in the film-like deposits relative to wire-like deposits at dimensions lower than 40 nm due to Bi$_2$Te$_3$.
nanowires with small diameters behaving as 2D quantum confined systems, while the nanostructures with diameters greater than 40 nm behave as 1D quantum confined systems. As we discussed for the AFM images obtained after 40 min of electrodeposition, this is expected due to the shape and size of Bi$_2$Te$_3$ nanowires, which change into a belt-like structure and may be considered a nanofilm. Recently, Buhro et al. reported that the effective band-gap energy in colloidal GaAs [41] and InAs [42] nanostructures increases as its size decreases in one or more dimensions. Similar observations have been experimentally reported for SnO$_2$ quantum dots and wires [43]. Our experimental results clearly demonstrate that the band-gap of the materials is not only related to the thickness (or diameter) of nanostructures but is also related to the shape of the nanostructures.

3.5. Compositional characterization

The elemental compositions (Bi/Te) of electrodeposited Bi$_2$Te$_3$ were determined by EDS. A representative EDS spectrum is presented in Fig. 15, since we observed that the EDS spectra of Bi$_2$Te$_3$ deposits obtained in acidic and basic conditions are identical. Fig. 15 demonstrates the presence of Bi and Te with no detection of any impurities above the detection limit with the exception of the Au substrate. Quantitative analysis of the spectrum reveals that the atomic ratio of Bi to Te is 2:3 with compositional homogeneity.

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**Fig. 9.** AFM images and cross-sectional profiles of Bi$_2$Te$_3$ nanostructures electrodeposited in pH: 9.0 at $-600$ mV: (a) 10; (b) 30; and (c) 55 min.

**Fig. 10.** The XRD patterns of the Bi$_2$Te$_3$ nanofilms electrodeposited onto single crystal Au (1 1 1) in pH: 1.5 at the different deposition times: (a) 15 and (b) 35 min.

**Fig. 11.** The XRD patterns of the Bi$_2$Te$_3$ nanowires electrodeposited onto single crystal Au (1 1 1) in pH: 9.0 at the different deposition times: (a) 30 and (b) 55 min.
Fig. 12. RA-FTIR spectra of Bi$_2$Te$_3$ nanostructures deposited in acidic medium at different deposition times.

Fig. 13. RA-FTIR spectra of Bi$_2$Te$_3$ nanostructures deposited in basic medium at different deposition times.

Fig. 14. Band gap dependency of Bi$_2$Te$_3$ nanostructures as a function of the thickness.

Fig. 15. A typical EDS spectrum of Bi$_2$Te$_3$ nanostructures grown on the single Au substrate.

4. Conclusions

In summary, highly crystalline and preferentially oriented nanofilms, nanowires, and nanobelts of Bi$_2$Te$_3$ were successfully synthesized by electrochemical co-deposition based on UPD at room temperature in acidic and basic medium. We observed that EDTA as a complexing agent has a great influence on the growth kinetics of Bi$_2$Te$_3$ nanostructures. We found that the quantum confinement is weakened in the film-like nanostructures relative to wire-like nanostructures. Moreover, EDS results indicate that Bi$_2$Te$_3$ nanostructures obtained by this simple and one-pot electrodeposition method have the right stoichiometry and are in pure phase.

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