Optical and thermoelectric characterizations of electroplated n-Bi$_2$(Te$_{0.9}$Se$_{0.1}$)$_3$

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Abstract

Bismuth selenotelluride (Bi$_2$(Te$_{0.9}$Se$_{0.1}$)$_3$) films were electrodeposited at constant current density from acidic aqueous solutions with Arabic gum in order to produce thin films for miniaturized thermoelectric devices. X-ray fluorescence spectroscopy determined film compositions. X-ray diffraction pattern shows that the films as deposited are polycrystalline, isostructural to Bi$_2$Te$_3$ and covered by crystallites. Mueller-matrix analysis reveals that the electroplated layers are optically like an isotropic medium. Their pseudo-dielectric functions were determined using mid-infrared spectroscopic ellipsometry. Tauc–Lorentz combined with Drude dispersion relations were successfully used. The energy band gap $E_g$ was found to be about 0.15 eV. Moreover, the fundamental absorption edge was described by an indirect optical band-to-band transition. From Seebeck coefficient measurement, films exhibit n-type charge carrier and the value of thermoelectric power is about $-40 \mu$V/K.

Keywords: A. Chalcogenides; A. Semiconductors; D. Transport properties

1. Introduction

V–VI binary compounds such as Bi$_2$Te$_3$, Sb$_2$Te$_3$, and Bi$_2$Se$_3$ are narrow band gap semiconductors and are well known as materials for thermoelectric (TE) devices [1]. A selection criterium of these TE materials is given by the dimensionless figure of merit $ZT = (S^2/\rho\kappa)T$ where $S$ is the Seebeck coefficient as TE power, $\rho$ the electrical resistivity, $\kappa$ the thermal conductivity, and $T$ the absolute temperature. Non-stoichiometric compound (Bi$_{1.8}$Te$_3.2$), considered as n-type semiconductor, presents a ZT value of 0.66 at 300 K and an improvement to 0.9 is observed for n-Bi$_2$(Te$_{0.9}$Se$_{0.1}$)$_3$ [1]. Thus these compounds are considered to be the best materials for use in TE refrigeration at room temperature (RT).

It has become well established that electrochemical deposition (ED) is a particularly attractive route for processing thin film semiconductor materials [2,3]. It offers the advantages of low synthesis temperature, low cost, large area deposition, high growth rates and high throughput. Moreover, the synthesis experiments can be made in laboratory atmosphere as compared to standard physical and chemical vapor deposition techniques. Electrodeposition has been successfully applied to the production of bismuth telluride binaries [4–9] and Se-ternary [10]. Concerning Bi$_2$(Te$_{0.9}$Se$_{0.1}$)$_3$ compounds, there are only reported values on optical and transport properties of bulk samples [11]. From results by Champness et al. [12], it appears that lattice thermal conductivity is minimum ($\kappa \sim 1 \text{W/m/K}$) for this composition at 300 K. The Seebeck coefficient is high ($-208 \mu$V/K) and electrical resistivity is about 10$\Omega$m [1]. Recent data of carrier concentration give values about 0.9$\times$10$^{19}$ cm$^{-3}$ [13,14]. Concerning the optical properties of the alloy system Bi$_2$Te$_3$–Bi$_2$Se$_3$, the absorption edge of a number of ingot samples of different compositions was first measured by Austin and Sheard [15] then by Greenaway and Harbeke [16]: they found a maximum energy bandgap $E_g$ of $\sim 0.3$ eV close to the
composition Bi$_2$Te$_2$Se and a bandgap of $\sim0.2$ eV for Bi$_2$(Te$_{0.9}$Se$_{0.1}$)$_3$ at RT. TE properties of Bi$_2$Te$_3$--Se$_x$ films are studied for the different compositions ($x = 0.12, 0.45$ and $0.9$) with and without annealing [17]. Concerning the electroplated films of bismuth selenotelluride system, literature data give only details about the ED process, the morphology and the crystallographic structure [10,18,19]. Thus this paper is devoted to investigate their optical and TE properties. For this purpose, the complex dielectric function $\varepsilon$ in the mid-infrared range was determined by infrared spectroscopic ellipsometry (IRSE).

Ellipsometry is an optical powerful method for surface analysis based on the measurement of the change of the polarization state of a light beam during reflection [20]. This method allows the access to the dielectric function (DF) with analytical formula for bulk materials or with an appropriate fitting procedure for thin films. Then electronic properties can be calculated through their DFs in the IR domain [21]. IRSE represents an original way to access the electrical resistivity without electrical contact. Moreover the energy band gap can be characterized by this approach. Since the crystallographic structure of Bi$_2$(Te$_{0.9}$Se$_{0.1}$)$_3$ is rhombohedral with the space group $D_{3d}^5$ (class $R \bar{3} m$), the optical properties of polycrystalline electroplated thin films may be anisotropic. Prior to IRSE experiments, analysis by Mueller matrix ellipsometry (MME) checked any optical anisotropic feature. The TE behaviors of the samples were investigated by the measurement of the Seebeck coefficient $S$ at RT, the sign of $S$ giving the type of conduction.

2. Experimental

2.1. Electrodeposition parameters

Electrolyte was prepared in solution with deionized water. To ensure the stability and the solubility of bismuth (III) solutions, the selected solvent was 1 M aqueous HNO$_3$. The Bi(III), Te(IV) and Se(IV) solutions were obtained by dissolution of Bi(NO$_3$)$_3$·5H$_2$O, TeO$_2$ and Na$_2$SeO$_3$ (analytical grade), respectively. The electrolyte concentrations were fixed as follows: $10^{-2}$ M for bismuth, $0.6 \times 10^{-2}$ M for tellurium and $0.65 \times 10^{-3}$ M for selenium [22]. The roughness on the surface was reduced by using galvanostatic mode and by adding a surfactant reagent (Arabic gum, $\sim0.02$ wt%) to the electrolyte at RT [23].

Evaporated gold films on glass (Maxtek, Inc.) were chosen as substrate for the preparation of Bi$_2$(Te$_{0.9}$Se$_{0.1}$)$_3$ films. The working electrodes were located vertically and an area of $1.37\text{cm}^2$ was exposed for deposition. The cathodic depositions were carried out without stirring using a large platinum counter electrode facing the working plate and a saturated calomel electrode. The electrochemical cell had an electrolyte volume of about 0.1 dm$^3$.

Electrochemical sequences were carried out using a computer driven Autolab potentiostat. The depositions were conducted at galvanostatic polarization of $-0.11$ A/dm$^2$ to obtain the required film composition [22]. The growth time was adjusted in order to obtain film thicknesses of 5$\mu$m, which were estimated from the Faraday law. In the calculations, we have assumed that the films were compact without porosity.

2.2. Characterizations

The elemental analyses were achieved by X-ray fluorescence spectrometry (XRF, Bruker S4 Explorer). X-ray diffraction (XRD) was obtained with a curve detector (Inel, Co K$_\alpha$ radiation).

2.3. Ellipsometry

MME measurements were performed using a Mueller-matrix ellipsometer MM-16 (Jobin-Yvon Horiba S.A.S.) in the range 470–830 nm at 69.5° of incidence. IRSE measurements were performed on a rotating-compensator, Fourier-transform based infrared spectroscopic ellipsometer IR-VASE (J.A. Wollam Co., Inc.). The ellipsometric spectra were determined by using the variable angle spectroscopic ellipsometry technique at three incidence angles ($45°, 55°$ and $65°$).

2.4. Seebeck coefficient

The Seebeck coefficient was calculated from the variation of the electromotive force with temperature gradient ($\Delta V/\Delta T$). Two thermocouples (K-type) were directly attached at two opposite points to the outer sample surface allowing measuring temperature gradient by in-plane method at RT. The applied $\Delta T$ was about 1.5 K. The electromotive force was measured by a couple of copper probes, on the same locations of the thermocouples.

3. Results and discussion

3.1. Surface characterizations

The SFX analysis confirms the expected film composition: Bi$_{2.06}$Te$_{2.71}$Se$_{0.29}$. The XRD pattern (Fig. 1) revealed a single phase with a good crystallinity. The compound is isostructural to Bi$_2$Te$_3$, this feature was already observed for potentiostatic conditions in previous work [10]. The ratio of the peak intensities is different with the reference data, implying a {11.0} preferential orientation [19]. The size of the crystallites is calculated by using the simplified Scherrer formula (Eq. (1)), which gives an estimation of the mean particle diameter $D$ in powder diffraction patterns:

$$D = \frac{\lambda}{HWHM \times \cos(2\theta)},$$

where $HWHM$ is the measured angular half width at half maximum, $\lambda$ the wavelength, 2$\theta$ the Bragg angle. Following the (110) peak intensity, the grain size is about 39 nm.
3.2. Mueller-matrix analysis

Treatment of anisotropic media can be done within the Mueller-matrix (MM) and Stokes-vector approach [20,21,24]. In terms of the p- and s-polarized coordinate system of the electromagnetic plane wave, the four real-valued Stokes parameters having dimensions of intensities are expressed as $S_0 = I_p + I_s$, $S_1 = I_p - I_s$, $S_2 = I_\text{45} - I_{-45}$, and $S_3 = I_\sigma + I_\pi$ where $I_p$, $I_s$, $I_{45}$, $I_{-45}$, $I_\sigma$ and $I_\pi$ denote the intensities for the p-, s-, +45°, -45°, right-, and left-handed circularly polarized light components, respectively. Arranging these elements into a column vector, the MM then describes the changes of each quantity upon interaction of the electromagnetic plane wave with any optical system (sample, mirrors, rotators, and any combinations thereof):

$$
\begin{bmatrix}
S_0 \\
S_1 \\
S_2 \\
S_3
\end{bmatrix} =
\begin{bmatrix}
m_{11} & m_{12} & m_{13} & m_{14} \\
m_{21} & m_{22} & m_{23} & m_{24} \\
m_{31} & m_{32} & m_{33} & m_{34} \\
m_{41} & m_{42} & m_{43} & m_{44}
\end{bmatrix}
\begin{bmatrix}
S_0 \\
S_1 \\
S_2 \\
S_3
\end{bmatrix}, \quad (2)
$$

In the case of a non-depolarizing isotropic substrate the matrix is expressed as

$$
\begin{bmatrix}
1 & -Ic' & 0 & 0 \\
-Ic' & 1 & 0 & 0 \\
0 & 0 & Ic & Is \\
0 & 0 & -Is & Ic
\end{bmatrix}, \quad (3)
$$

where $Ic' = \cos 2\Psi$, $Is = \sin 2\Psi \sin \Delta$ and $Ic = \sin 2\Psi \cos \Delta$. $\Psi$ and $\Delta$ are the standard ellipsometric angles [20]. Fig. 2 shows the experimental MM for a representative sample. The eight off-diagonal blocks $m_{ij}$-elements ($ij = 13, 14, 23, 24, 31, 32, 41$ and $42$) are almost null versus the wavelength, whereas $m_{11}$ and $m_{22}$ are close to one.

Consequently, Bi$_2$(Te$_{0.9}$Se$_{0.1}$)$_3$ polycrystalline electroplated thin films appear optically isotropic. This result has to be related to the crystallographic texture of these films. Indeed they exhibit a preferential orientation, where c-axis is parallel to the surface with a freedom degree around the sample normal. The random c-axis orientation of anisotropic crystallites implies that polycrystalline electroplated thin films are optically like an isotropic medium. A similar behavior was observed for electroplated n-Bi$_{1.8}$Te$_{3.2}$ film [25,26].

3.3. Infrared ellipsometric study

3.3.1. Experimental spectra

Figs. 3a and b show experimental ellipsometric spectra corresponding to a representative sample from 0.03 to 0.80 eV. In order to determine the optical constants from the ellipsometric data, a model for the film structure was necessary. The samples were considered as semi-infinite substrate of isotropic optical medium allowing to calculate the so-called pseudo-dielectric function $\varepsilon = \varepsilon_0 + j\varepsilon_2$ directly from $\Psi$, $\Delta$ spectra: [20]

$$
\varepsilon = \varepsilon_0 \sin^2(\phi) \left[ 1 + \tan^2(\phi) \left( \frac{1 - \rho}{1 + \rho} \right)^2 \right] = (n + jk)^2, \quad (4)
$$

where $\rho = \tan \psi \phi^4$, $\phi$ is the angle of incidence, $\varepsilon_0$ is the ambient medium DF, $n$ is the refractive index and $k$ the extinction coefficient.

3.3.2. Physical description of the dielectric function

The analytical calculated DF displays the same shape of n-Bi$_{1.8}$Te$_3$ compounds [25] (Fig. 4). As a consequence, the previously model used for binary films can be applied to describe the DF of Bi$_2$Te$_{2.7}$Se$_{0.3}$:

$$
\varepsilon(E) = \varepsilon_{Drd}(E) + \varepsilon_{TL}(E), \quad (5)
$$

where $\varepsilon_{Drd}$ is the Drude contribution and $\varepsilon_{TL}$ is the Tauc–Lorentz contribution at energy $E$. At low energies, the function is governed by classical Drude model (Eq. (4)), which describes the free carrier effects on the dielectric response [27]:

$$
\varepsilon_{Drd}(E) = \frac{-h^2}{\varepsilon_0 \rho(\tau E^2 + jhE)}, \quad (6)
$$

with two adjustable fit parameters: the electrical resistivity ($\rho$) and the energy-independent scattering time ($\tau$).

For higher energies, a Tauc–Lorentz (TL) dispersion relation adjusted to the semi-conducting behavior was chosen. The imaginary part of the complex DF is given by [28]:

$$
\varepsilon_{TL}(E) = \frac{\theta(E - E_0)^2}{(E^2 - E_0^2) + C^2} \frac{\phi(E - E_0)}{E}. \quad (7a)
$$

The real part of the DF is obtained by performing Kramers–Kronig integration of $\varepsilon_2(E)$ [28]:

$$
\varepsilon_{1TL}(E) = \varepsilon_{1}(\infty) + \frac{2}{\pi} \int_{E_\nu}^{\infty} \frac{\xi \varepsilon_2(\xi)}{\xi^2 - E^2} d\xi. \quad (7b)
$$
The TL part includes five fitting parameters: $E_0$ is the peak transition energy (eV), $C$ is the broadening term (eV), $A$ is the amplitude term (dimensionless), $E_g$ is the optical band gap (eV) and $\varepsilon_1 (\infty)$ the high-frequency dielectric constant (dimensionless). $\Theta$ is the Heaviside theta function where $\Theta(x) = 0$ for $x < 0$ and $\Theta(x) = 1$ for $x \geq 0$. $P$ stands for the Cauchy principal part of the integral.

### 3.3.3. Fitting results

Using the dispersion relationship with Drude and Tauc–Lorentz contributions, experimental IRSE data were fitted. The best-fit theoretical curves are shown in Figs. 3a and b (lines) along with the experimental spectra. A correct agreement between experimental and calculated spectra is observed. This analysis was realized on four identical samples and the average best-fit parameters are compared with n-Bi$_{1.8}$Te$_{3.2}$ electroplated films in Table 1. The resistivity is found to be higher, whereas the relaxation time is equivalent to binary compound (3.3 fs). This parameter $\tau$ is inferior to related bulk value (40 fs [29]), this can be linked to polycrystalline state. As expected from bulk results [15,16], the bandgap (0.15 eV) of the electroplated selenotelluride is higher than that of electroplated n-Bi$_{1.8}$Te$_{3.2}$ (0.11 eV [25]) but our data are lower than the literature data.

### 3.3.4. Tauc plots

For each value of the absorption index $k$ at a given photon wavelength $\lambda$, the absorption coefficient $\alpha$ was calculated from the relation:

$$\alpha = 4\pi k / \lambda.$$  

(8)

The low constant energy part of the response was extrapolated and subtracted from the total absorption coefficient to obtain the interband absorption coefficient $g_i$. The absorption coefficient is proportional to $(E - E_g)^n$ where $n = 1/2$ for allowed direct transitions and $n = 2$ for...
allowed indirect transitions [30]. Fig. 5 represents a typical result of the spectral dependence of \((\alpha_i E)^2 = f(E)\) and \((\alpha_i E)^{1/2} = f(E)\). The experimental \((\alpha_i E)^{1/2}\) term linearly depends on \(E\) stronger than the \((\alpha_i E)^2\) one. Moreover, extrapolating the straight part of these functions towards lower energies yields the value of the corresponding energy bandgap. This graphical determination shows that the indirect bandgap (0.22 eV) is closer to the average TL value (0.15 eV) than the direct one (0.6 eV). From these observations, the interband transition is probably of indirect type.

3.4. Transport properties

As theoretically expected for this composition [1], all films show n-type conduction since the measured Seebeck coefficients exhibit negative values. The TE performances are disappointing with low values of \(S\) of about 40 \(\mu V/K\). This result is agreement neither with the bulk values of Bi\(_2\)(Te\(_{0.9}\)Se\(_{0.1}\))\(_3\) (−208 \(\mu V/K\), [1]) nor with n-Bi\(_{1.8}\)Te\(_{3.2}\) electroplated films (−167 \(\mu V/K\) [25]). Considering the thermal conductivity of Champness et al., the figure of merit of the films was estimated from the present experimental values of \(\rho\) and \(S\) at 300 K. Whatever the samples, ZT is below 0.01, corresponding to not optimal TE properties and annealing treatment of the samples.
should be considered. Indeed Snyder et al. [31] claimed that an annealing of 2 h at 523 K (7.2% H\textsubscript{2} in air) will significantly enhance the value of n-Bi\textsubscript{2}Te\textsubscript{3} polycrystalline electrodeposited thin films Seebeck coefficient. Recently, Yamashita and Odahara [32] studied the influence of annealing on the distribution of ZT in n-Bi\textsubscript{2}Te\textsubscript{2.82}Se\textsubscript{0.18} ingot and they observed that ZT increases up to 0.92 after annealing of 2 h at 673 K in vacuum.

4. Conclusion

We investigated the electrodeposition of Bi\textsubscript{2}(Te\textsubscript{0.9}Se\textsubscript{0.1})\textsubscript{3} thin films on gold substrates. We found that this process generates well-crystallized polycrystalline layers with mirror-like surface, which permits optical reflection measurements by IRSE. We fitted the pseudo-dielectric function by a combined Drude/Tauc–Lorentz oscillator model. So the indirect bandgap of 0.15 eV and the resistivity of 50 m\Omega m were determined without any contact. Concerning the TE properties, the determination of the Seebeck coefficient shows n-type conduction with relative low value (−40 m\textmu V/K). Annealing treatment is necessary to further improve global TE properties.

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