# Optical Properties of Electroplated $Bi_2Te_3$ Films

A. Zimmer[1], N. Stein[1], L. Johann[2] and C. Boulanger[1]
[1] Laboratoire d'Electrochimie des Matériaux – UMR CNRS 7555
Université de Metz, 1 Boulevard Arago, F-57078 Metz Cedex 3, France
e-mail : stein@sciences.univ-metz.fr
[2] Laboratoire de Physique des Liquides et des Interfaces,
Université de Metz, 1 Boulevard Arago, F-57078 Metz Cedex 3, France

## Abstract

This work is about the optical characterizations of electroplated $Bi_2Te_3$ films by Spectroscopic Ellipsometry (SE). Telluride bismuth films of about 4 µm thickness were prepared from a galvanostatic electrochemical process. The synthesis method allows to obtain crystallized films with a low roughness (RMS about 10 nm) and with an excess or a default of bismuth by comparison with the $Bi_2Te_3$ stoichiometry (Bi = 40 at.%, Te = 60 at.%).

The scanned spectral range was from the visible to the middle infrared domain (0.4 – 1.3 µm and 1.6 – 38 µm). The dielectric functions were systematically determined for all the samples. Our experimental data appear to be lower than the literature results, which were obtained from single crystals or from epitaxial layers. In the visible domain, no significant differences between the studied films were observed. The optical roughness was determined by SE and agreed with the Atomic Force Microscopy (AFM) results. The optical data recorded in the infrared range allowed to access to the electronic parameters of the films through a dielectric function. Thus a constant value of the energy band gap was found to be about 0.11eV whatever the film composition. Moreover other physical parameters have been calculated by this optical method : the electrical resistivity, the scattering time and indirectly the carrier mobility and the carrier concentration.

## Introduction

Many deposition techniques, such as sputtering, metallorganic chemical vapor deposition, molecular beam epitaxy and electrodeposition have been already used to obtain thin films of bismuth telluride compounds. Electrodeposition may offer a low-cost growth method with a high deposition rate. Several electrochemical processes have been developed leading to different compositions of $Bi_2Te_3$ binary compounds [1,2].

The stoichiometry of these thermoelectric films directly influences their electronic and transport properties. The aim of this study is to evaluate the physical properties of the materials, which are obtained using established electrochemical methods. The used analysis method is the Spectroscopic Ellipsometry in the visible range and in the middle infrared range.

At first, we have directly determined the optical constants of the materials by this original approach. Moreover the layers morphology were estimated through an optical model of the film | ambient medium interface. We can note that SE is a non destructive technique, which allows to monitor the electrodeposition of thin films. Thus the growth of $Bi_2Te_3$ layers can be clearly seen by in situ SE data and by the knowledge of their optical constants [3,4].

Secondly, this technique allowed us to determine the electronic properties of the studied samples through their dielectric functions [5]. In particular the energy band gap can be evaluated by this non-contact method for different compositions of $Bi_2Te_3$. Consequently we performed a comparison of the properties of the electroplated bismuth telluride films with the properties of the bismuth telluride materials obtained by classical methods.

## Experimental setup

The preparation parameters were based from previous work [1] in order to obtain $Bi_{2-x}Te_{3+x}$ films with x varying from –0.2 to +0.2. Electrolytes were prepared with deionized water. To ensure the stability and the solubility of bismuth (III) solutions, the selected solvent was 1 M aqueous $HNO_3$. The $Bi^{III}$ solutions were obtained by dissolution of $Bi(NO_3)_3,5H_2O$ (analytical grade) and the $Te^{IV}$ solutions were prepared from the reaction of nitric acid on elemental tellurium. The $Bi^{III}$ and $Te^{IV}$ electrolyte mixtures were obtained from the above solutions and a $|Bi|/|Te|$ ratio of 1 was employed. A surfactant reagent (Arabic gum, ~0.02 weight%) was added to the electrolyte in order to obtain a surface with a low roughness.

Commercial evaporated gold films (Maxtek inc., P/N 149238-1) were chosen as substrate for the preparation of $Bi_2Te_3$ films. The working electrodes were located vertically in a cell, which was specially designed in our laboratory. An area of 1.37 cm² was exposed for deposition. The cathodic depositions were carried out at room temperature without stirring with a large platinum counter electrode facing the working plate and with a saturated calomel electrode (SCE). 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 polarizations ranging between –0.139 $A/dm^2$ and –0.256 $A/dm^2$ following the required films stoichiometry [1]. The growth time was adjusted in order to obtain film thickness of 4 µm taking the Faraday law into account.

Samples were prepared after electrodeposition by thorough rinsing in three steps (nitric acid solution pH=1, deionized water and methanol) followed by air drying. Then they were characterized by spectroscopic ellipsometry.

Ellipsometry is an optical method for surface analysis, which is based on measuring the change of the polarization state of a light beam during reflection [6]. The complex-reflectivity ratio is defined by $\rho = r_p/r_s = \tan(\psi).\exp(i\Delta)$,

where $r_p$ and $r_s$ are the complex Fresnel coefficients for the reflection beam. The angles $\psi$ and $\Delta$ are the conventional ellipsometric parameters. The ratio $\rho$, as well as $\psi$ and $\Delta$, explicitly depend on the wavelength $\lambda$ and the angle of incidence.

Two different spectroscopic ellipsometers were used, the first one for measurements in extended Visible domain (0.4-1.3μm) and the second one for measurements in Middle Infrared domain (1.6-38μm). The visible range was explored with a fixed polarizer rotating polarizer and fixed analyzer spectroscopic ellipsometer (PRPSE), which was developed at the laboratory [7]. Variable angle Infrared Spectroscopic Ellipsometry (IRSE) measurements were performed on a IR-VASE$^{TM}$ J.A. Wollam system. All the samples were investigated at 3 incidence angles 45°, 55° and 65°.

The morphology was studied using a Scanning Electron Microscope (Hitachi model S 2500LB) and an Atomic Force Microscope (Topometrix Explorer Ecu+TMX1010) in contact mode. The elemental analyses were achieved by X-ray fluorescence spectrometry (XRF) (Bruker S4 Explorer).

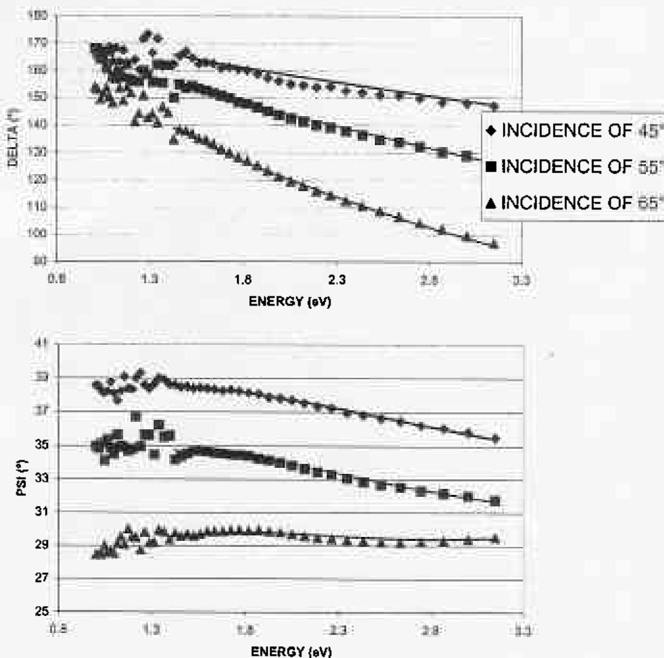


Figure 1 : Experimental (points) and simulated (lines) ellipsometric spectra of an electroplated $Bi_{2.02}Te_{2.98}$ film in the visible range at different angles of incidence.

**Results and discussion**

**1. Visible domain**

Figure 1 shows experimental $\Psi$, $\Delta$ spectra measured on a stoichiometric film ($Bi_{2.02}Te_{2.98}$) from 0.95eV to 3.1eV. We have made a fundamental hypothesis to exploit these data of this work : we have assumed that the films are optically isotropic. Indeed from previous results [1, 8], we have already shown that the electroplated films are polycrystalline and textured. Then, due to the presence of crystallites, no optical overall anistropic feature can be detected.

A first approach is to consider the sample as a substrate. This simplified model allows to directly calculate from the ellipsometric angles the dielectric function $\varepsilon$, called the pseudo dielectric function of the material. The results are shown in the figure 2. The experiments were extended to the other film compositions and no important differences were observed. Our results were compared to the data of Cui *et al.* [9], which were estimated from $Bi_2Te_3$ thin film with a single crystallinity. In addition we have compared our results with the data of bulk single crystal from the paper of Greenaway and Harbeke [10]. The figure 2 clearly shows that our experimental dielectric functions are lower than the literature data in the scanned range.

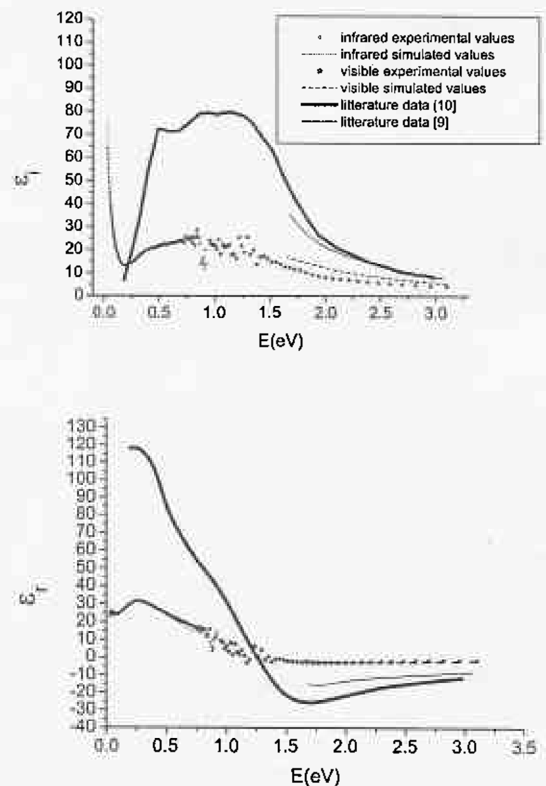


Figure 2 : imaginary and real part of the dielectric function of $Bi_2Te_3$ from the infrared domain up to the visible domain. Our experimental and simulated spectra, obtained from an electroplated $Bi_{2.02}Te_{2.98}$ film, are compared with the literature

In the visible domain, the ellipsometric measurements are strongly dependent on the microroughness of the surface [11]. The electroplated bismuth telluride films exhibit no surface contamination, as contrary as the films obtained from evaporation techniques [9]. However the roughness may be important following the electrochemical experimental parameters. In this work, the irregularities on the surface were reduced by using galvanostatic mode [12] and by adding a surfactant reagent.

A model of the ambient medium-sample interface was introduced to take the roughness into account (figure 3). The bismuth telluride film is topped by a rough layer, which is considered as an effective medium of optical properties intermediate between those of the components, i.e. the ambient medium and the underlying layer. There are several effective medium models that represent a heterogeneous dielectric mixture by a single parameter : the void volume fraction. We have used the Bruggeman effective medium approximation (BEMA), which accurately simulates the microscopic roughness [11].

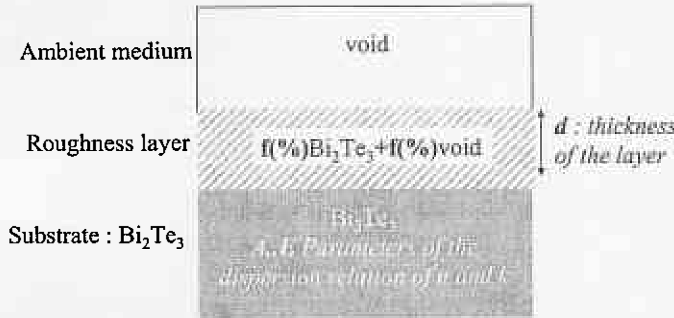


Figure 3 : Optical model of the $Bi_2Te_3$ film used for the exploitation of the optical data in the visible range. The fit parameters are f($Bi_2Te_3$), d , A..E.

The layers used in the modeling were supposed to have a refractive index (n) and an extinction index (k) which has a dispersion relation based on the Sellmeier formula [13] :

$$n^2(\lambda) = \frac{1+A}{1+\frac{B\times 10^4}{\lambda^2}} \; ; \qquad (1)$$

$$k(\lambda) = \frac{C}{n(\lambda)\times D\times 10^{-2}\times\lambda + \frac{E\times 10^{-2}}{\lambda} + \frac{1}{\lambda^3}}$$

where the wavelength λ is in µm and A...E are the fit parameters.

The dielectric function is calculated from the optical index following the relations :

$$\varepsilon_r = n^2 - k^2 \text{ and } \varepsilon_i = 2nk \qquad (2)$$

The fitting procedure was strictly applied to the visible domain (*i.e.* from 1.38 eV to 3.1 eV) since the data between 0.95 eV and 1.38 eV were too noised (figure 1). Consequently the proposed dispersion law is only valid in the Visible domain. In the table 1, the model parameters are presented with the best values calculated by a fitting procedure [13]. We can observe that the optical roughness ($d^{SE}$) is similar to the RMS value obtained from a topographic image by AFM although the scanned area were different, respectively around 1 $mm^2$ for the ellipsometric analyses and 10 $\mu m^2$ for the AFM analyses.

| Parameter | Value |
|---|---|
| A | 27± 4 |
| B | -266± 36 |
| C | 59± 8 |
| D | 0.18± 0,03 |
| E | 118± 18 |
| f(%) | 18± 3 |
| $d^{SE}$ (nm) | 9± 2 |
| rms (nm) | 13.03 |

Table 1. The results of the fitting data set in the visible range of an electroplated $Bi_{2.02}Te_{2.98}$ film. The rms value is obtained from AFM data.

The dielectric functions calculated from the model parameters are shown in the figure 2. Whereas the real part of the dielectric function is very closed to the pseudo constant, the imaginary part is superior to the pseudo constant. So this figure evidences that the surface roughness, even in the range below 10 nm, significantly influences the n and k values. We can observe that the dielectric functions of the electroplated films remain inferior with the literature data. This difference can be explained by the presence in the films of either micro voids or micro crystallites.

### 2. Infrared domain

In the infrared domain, the roughness can be neglected. Thus we have considered the bismuth telluride layers as a substrate. Consequently the imaginary and the real parts of the dielectric function were directly calculated from the ellipsometric angles. In the figure. 2, we can observe on a stoichiometric film ($Bi_{2.02}Te_{2.98}$) that the IR estimated values (from 0.03eV to 0.9eV) are connected to the extended Visible values (from 0.93eV to 3.1eV). The dielectric function values in the whole scanned domain (IR and Visible) can be compared with the data of Greenaway and Harbeke [10], which were obtained from a bismuth telluride single crystal (figure 2). We can note that the global trends of the curves are similar. However the work data display oscillations with lower amplitudes in comparison to the literature data.

An interesting feature of the IR ellipsometric investigation is that the electronic parameters of the studied sample can be estimated through his dielectric function. From the experimental data, we have proposed a dielectric function with two contributions. At the lowest energies, the function is governed by the classical Drude model (equation 3), which describes the free carrier effects on the dielectric response. This contribution may be explained by the fact that bismuth telluride compounds are considered as a narrow band gap semiconductor. The adjustable Drude fit parameters are electrical resistivity (ρ) and scattering time (τ) :

$$\varepsilon Drd(E) = \frac{-\hbar^2}{\varepsilon 0\,\rho(\tau\, E^2 + j\hbar E)} \qquad (3)$$

The second contribution is a Tauc-Lorentz oscillator [14], which describes the single observed interband transition of $\varepsilon_i$ (figure 2).

$$\varepsilon_{TL}(E) = \varepsilon_{1TL}(E) + j\varepsilon_{2TL}(E) \qquad (4)$$

$$\varepsilon_{2TL}(E) = \frac{A(E-E_g)^2}{(E^2-E_0^2)^2+C^2} \cdot \frac{\Theta(E-E_g)}{E} \qquad (5)$$

where A is the amplitude term (dimensionless), $E_0$ is the peak transition energy (eV), C is the broadening term (eV), $E_g$ is the optical band gap (eV) and $\Theta$ is the Heaviside Theta function where $\Theta(x) = 0$ for $x<0$ and $\Theta(x) = 1$ for $x \geq 0$.

The real part of the dielectric function $\varepsilon_r$ is obtained by Kramers-Kronig integration and is solved analytically [14]. The integral form is presented here for the sake of brevity :

$$\varepsilon_{1TL}(E) = \varepsilon_1(\infty) + \frac{2}{\pi} P \int_{E_g}^{\infty} \frac{\xi \varepsilon_2(\xi)}{\xi^2 - E^2} d\xi \qquad (6)$$

where the $P$ stands for the Cauchy principal part of the integral and an additional parameter $\varepsilon_1(\infty)$ has been included.

The fitting calculations were successfully applied to the experimental data of different composition films. For example, the figure 2 unambiguously shows that the calculated dielectric function rightly simulates the results obtained from stoichiometric sample in the scanned range (0.03eV-0.9eV). The best fit parameters are tabulated in Table 2.

| Fitting parameter | Value |
|---|---|
| $E_0$ (eV) | 0.87 ± 0.02 |
| C (eV) | 1.70 ± 0.07 |
| A | 46 ± 2 |
| $\varepsilon_1(\infty)$ | 6.6 ± 0.4 |
| $E_g$ (eV) | 0.112 ± 0.002 |
| ρ (μΩ.m) | 29 ± 6 |
| τ (fs) | 2.25 ± 0.04 |

Table 2. The results of the fitting data set of an electroplated $Bi_{2.02}Te_{2.98}$ film

In the figure 4, we have presented the calculated optical band gap for different compositions of electroplated $Bi_2Te_3$ films. Except for the $Bi_{1.91}Te_{3.09}$ samples, all the values are around 0.11eV, which corresponds to the theoretical findings of Mishra *et al.* for perfect bulk-like crystals [15].

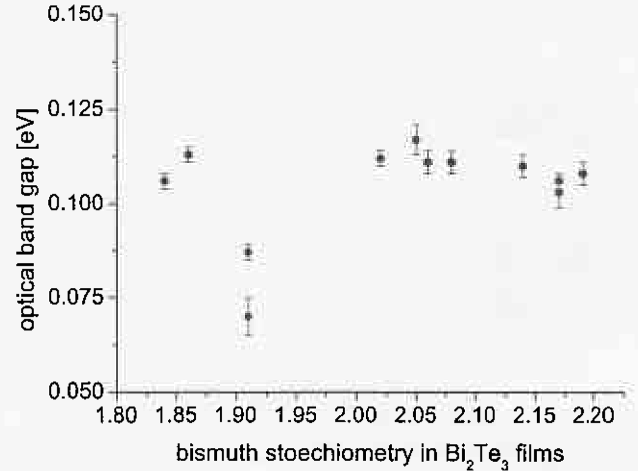


Figure 4. Optical band gap $E_g$ obtained from the ellipsometric data for different compositions of $Bi_2Te_3$.

The electrical resistivity values *versus* the film compositions are shown in figure 5. We can observe a decrease with the bismuth enrichment of the layer. The results, which are comprised between 14 μΩ.m and 27μΩ.m, are similar to $n$-$Bi_2Te_3$ co-evaporated thin films[16]. However our data are quite lower than Goldsmid obtained from pure intrinsic $Bi_2Te_3$ ingots (71.4μΩ.m) [17].

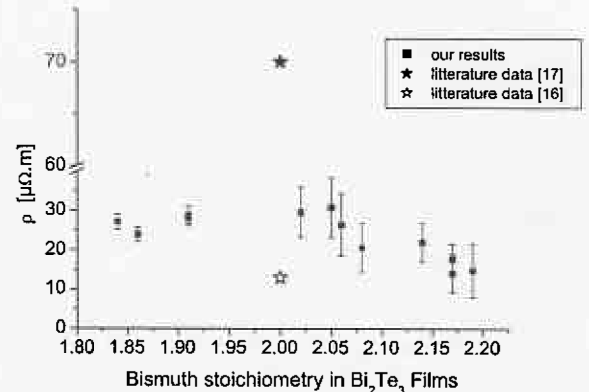


Figure 5. Resistivity ρ obtained from the ellipsometric data for different compositions of $Bi_2Te_3$. Our experimental data are compared with the literature.

From the fitted parameters ρ and τ, we have deduced the carrier concentration N ($cm^{-3}$) and the carrier mobility ρ ($cm^2V^{-1}s^{-1}$) with this following relation :

$$\rho = \frac{m^*}{N q^2 \tau} = \frac{1}{q\mu N} \qquad (7)$$

where m* is the effective mass and q is the electron charge.

To access to N and ρ, it was necessary to propose a value of the carrier effective mass. We have chosen $m^*=0.58m_0$, which corresponds to the effective mass of $n$-type bismuth

telluride compound at 297K [18]. The results show that the carrier concentration heavily increases with the atomic percent of bismuth (figure 6) and that carrier mobility gradually decreases with the atomic percent of bismuth (figure 7). By comparison with the value given by Nolas [18], the experimental carrier mobilities appear to be clearly inferior to the *n*-type $Bi_2Te_3$ reference value of 1200 $cm^2.V^{-1}.s^{-1}$ but they are closed to crystalline films grown using the Hot-Wall Epitaxy (HWE) [19]. This result can be explained by the fact that our films are polycrystalline. Consequently the presence of local defaults and grain boundary may reduce the carrier mobility in comparison with single crystals.

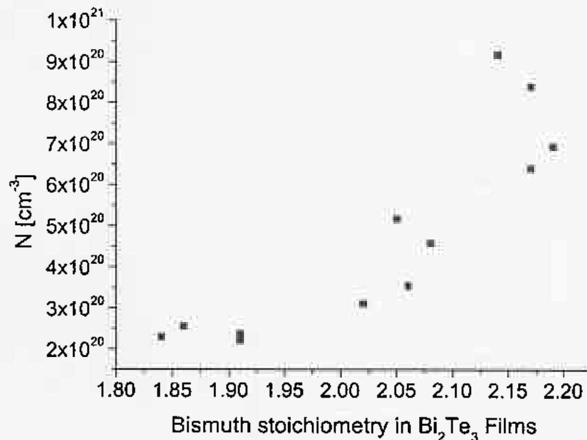


Figure 6. Carrier concentration N calculated from the experimental values of $\tau$ and $\rho$ for different compositions of $Bi_2Te_3$.

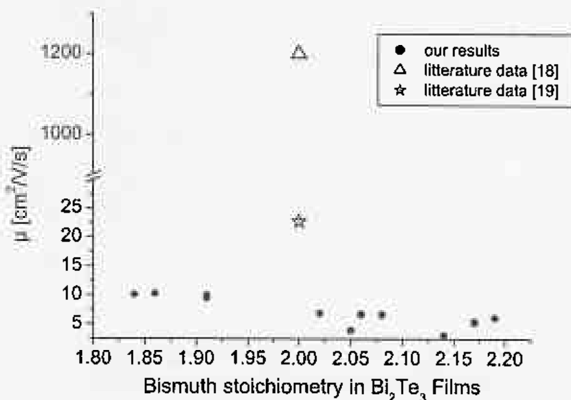


Figure 7. Carrier mobility calculated from the experimental values of $\tau$ and $\rho$ for different compositions of $Bi_2Te_3$. Our experimental data are compared with the literature

## Conclusions

Spectroscopic ellipsometry is a powerful method for characterizing thin films. This work has established the dielectric function of electroplated films from the Infrared to the Visible energy domain. From 1.5eV to 3eV, the optical constants do not seem to depend to the films compositions ($Bi_{2-x}Te_{3+x}$ with x varying from –0.2 to +0.2).

From the IR results, electronics parameters were determined. The electronic parameters are in good agreement with the values of crystalline films obtained with other methods. The energy band gap appears to be constant about 0.11eV, which is consistent with theoretical predictions and experimental measurements. The resistivity, the carrier mobility and the carrier concentration of the studied films are related with the bismuth content.


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