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In situ analysis of bismuth telluride electrodeposition using combined spectroscopic ellipsometry and electrochemical quartz crystal microbalance

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Abstract

Electrodeposition of bismuth telluride (Bi_2Te_3) in an acidic medium with Arabic gum by galvanostatic polarization has been investigated. Simultaneous in situ spectroscopic ellipsometry and gravimetric measurements have been performed to study the morphological evolution of the compound. A progressive covering stage was demonstrated and revealed that a 40 nm thick film has already acquired morphological and optical behavior similar to that of thicker films. The optical thickness and electrochemical quartz crystal microbalance (EQCM) mass are coherent with a density of 7.06. Combined gravimetric and coulometric data confirm the formation of Bi_2Te_3 by determining the ratio *m*/*z*.

Keywords: Bismuth telluride; Electrodeposition; EQCM; In situ spectroscopic ellipsometry; Growth process

1. Introduction

The control of the morphological aspect of electroplated thin films is important today in a great number of applications. In the thermoelectric (TE) field, such control can be attained with heterostructure devices based on bismuth telluride polycrystalline films [1]. Ellipsometry provides a powerful tool for in situ characterisation of film growth and film structure [2–5]. More recently, our group proposed a new system in which an electrochemical quartz crystal microbalance (EQCM) is used: it allows recording additional gravimetric data [6]. In this way, the complex electrolyte|electrode interfaces which exist during electrochemical and chemical processes in liquid media can be studied. This work focuses on the bismuth telluride electrodeposition system.

The Bi_2Te_3 alloy is a V_2–VI_3 semiconductor material with a narrow band gap which is generally used for cooling and power generation applications. Peltier coolers are made with Bi_2Te_3-based compounds, the best materials to date for room temperature operation [7]. It has become well established that electrochemical deposition is a particularly attractive route for processing thin film semiconductor materials [8]. It offers the advantages of a low synthesis temperature, low cost, high throughput, large area deposition and high growth rates. Moreover, the synthesis experiments can be made under laboratory atmosphere, as opposed to physical growth techniques. Electrodeposition has been successfully applied to the production of bismuth telluride by different authors [9–14]. Optical properties of electroplated Bi_2Te_3 films were studied previously showing isotropic features [15] and establishing their dielectric functions in the visible and infrared range [16]. In this paper, we study the electrocrystallization of bismuth telluride by monitoring mass and optical responses of the surface electrode. These investigations are complemented by scanning electron microscopy (SEM).

2. Experimental

2.1. Electrochemical conditions

The electrolyte was prepared using 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} and

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Te^{IV} solutions were obtained by dissolution of $Bi(NO_3)_3{\cdot}5H_2O$ and TeO_2 (analytical grade), respectively. The electrolyte concentrations were fixed at [Bi] = [Te] = 10 mM [12]. The surface roughness was reduced by using a galvanostatic mode and by adding a surfactant reagent (Arabic gum, ∼0.02 wt.%) to the electrolyte [17]. Thus, all the electrodeposited bismuth telluride layers exhibit mirror-like surfaces [3].

The electrodeposition experiments were carried out with a PGP 24-1 Radiometer potentiostat-galvanostat using a large platinum counter electrode facing the working plate. Evaporated gold films on glass (Maxtek Inc. P/N 149273-1) were chosen as the conductive substrate for the preparation of Bi_2Te_3 films and microbalance sensor. The working electrodes were vertical and an area of 1.37 cm^2 was exposed for deposition. The electrochemical cell had an electrolyte volume of about 0.1 dm^3. The solutions were de-aerated by bubbling argon through the solution both before and during the deposition.The depositions were conducted at a galvanostatic polarization of −0.2 A/dm^2 to obtain the required film composition [12]. During the electrodeposition, the potential of the working electrode versus the reference electrode (saturated calomel electrode or sce) was monitored. As studied previously [12], the value of this potential is strongly linked to the film composition.

2.2. Optical and electrochemical instrumentation

An electrochemical cell was specially designed to monitor the optical and gravimetric responses of the working electrode during the electrochemical sequence. The angle of incidence was fixed at 66° (Fig. 1).

Spectroscopic ellipsometry (SE) is an optical method for surface analysis, which is based on measuring the change of the polarization state of a light beam during reflection [18]. The complex-reflectivity ratio is defined by $\rho = r_p/r_s = \tan\Psi\, e^{j\Delta}$, where r_p and r_s are the complex-amplitude reflection coefficients. The angles Ψ and Δ are the conventional ellipsometric parameters. The ratio ρ, as well as Ψ and Δ, explicitly depend on the wavelength λ and the angle of incidence. The ellipsometer, based on a rotating Horiba Jobin-Yvon S.A.S compensator and using a 75 W xenon lamp, allows the acquisition over the entire visible range every 40 ms with a charge coupled device detector. The mass uptake was recorded during film electrodeposition experiments with the help of a home built electrochemical quartz crystal microbalance setup. The principle of EQCM measurements is based on the Sauerbrey equation [19] in which a mass uptake (Δm) on the quartz gives rise to a linear shift of the measured frequency (Δf) according to the characteristic constant of the quartz crystal (K). The fundamental resonance frequency of the AT-cut quartz was 5 MHz and the sensitivity of the experimental setup was evaluated to be K = 37.9 Hz/μg when the integrating time is fixed at 160 ms. The electrolysis current i and working electrode potential E were recorded every 100 ms. A data acquisition method was developed in order to synchronize SE, EQCM and electrochemical measurements. The instrumental system for in situ ellipsometry and EQCM measurements has been described in detail elsewhere [6].

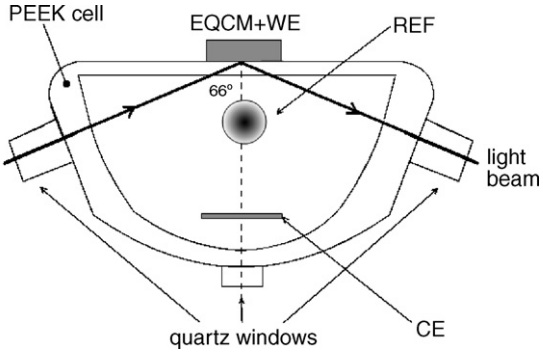

Fig. 1. The electrochemical cell used for the experiments with three electrodes: the working electrode (WE) with a combined microbalance quartz sensor (EQCM, Au surface), the reference electrode (REF, sce) and the counter electrode (CE) in Pt. A visible light beam enters and leaves the Poly Ethylen Ethyl Ketone (PEEK) cell through quartz windows.

3. Results

3.1. Qualitative description of growth monitoring parameters

All parameters were kept constant over a period of 30 s before the ECD process. The potential E corresponded to the mixed potential (+350 mV/sce; see Fig. 2a) and no current density j was applied (Fig. 2a). The frequency variation Δf was null yielding no attached surface mass Δm on the gold substrate (Fig. 2b). The values of Ψ and Δ corresponded to a gold surface (Fig. 2c and d).

The ECD process began when j = −0.2 A/dm^2 was applied (Fig. 2a): E dropped and then progressively reached a plateau of −50 mV/sce at 20 s. This stable value corresponds to a thermodynamic polarization state leading to Bi_2Te_3 compound formation [12]. Δf decreased immediately after application of the cathodic current yielding a mass uptake following the Sauerbrey theory. Consequently, the initial drop of the cathodic potential cannot be attributed only to a double layer charging since EQCM data simultaneously show a mass uptake. The variation was strongly linear after a period of ∼20 s (Fig. 2b). Concerning the ellipsometric angles Ψ and Δ, a first strong variation was observed up to 30 s. Subsequently, the optical parameters vary slowly and continuously whatever the wavelength in the range 400–800 nm (Fig. 2c and d).

3.2. Gravimetric study

An analytical approach was based on the following considerations. The evolutions of the quantity of electricity Q and the frequency Δf during deposition stages allow accessing the so-called m/z ratio, where m is the molar mass of the electrodeposited compound X in the overall reaction: $X \rightarrow X^{Z+} + ze^-$ and, where z is the number of electrons involved in the process. Combined coulometry/EQCM experiments yield direct access to this ratio. Indeed the two parameters, Q and Δf, can be connected via the Faraday law (assuming 100% current efficiency) and the