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# Growth Mechanism during the Early Stages of electrodeposition of Bismuth telluride films

Alexandre Zimmer[a,b,1,*], Laurent Broch[b], Clotilde Boulanger[a], Nicolas Stein[a]

[a] Institut Jean Lamour, Université de Lorraine, UMR 7198 CNRS, 1 Bd Arago CP 87811, F-57078 Metz Cedex 3, France
[b] LCP-A2MC, Institut Jean Barriol, Université de Lorraine, 1 Bd Arago CP 87811, F-57078 Metz Cedex 3, France

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ABSTRACT

An optical-electrochemical study on the initial stages of bismuth telluride ($Bi_2Te_3$) electrodeposition onto gold substrate is presented in this work. Numerical methods were applied on both electrochemical and optical data to obtain the relevant kinetic parameters from electrocrystallization theoretical equations and ellipsometric models in order to describe this system in the relevant 0-15 seconds range. The in-situ ellipsometry and electrodeposition analysis reveals a three-step mechanism. After an induction time including the double layer charge, the formation of a monolayer of tellurium is highlighted, followed by the adatom surface diffusion. Then, the growth of three-dimensional $Bi_2Te_3$ crystallites is observed according a progressive nucleation and a linear growth rate. Experimental and theoretical details about each technique are given and analyzed.



## 1. Introduction

Nowadays it is a challenging requirement in a great number of devices in the field of energy to achieve a finer control of morphology of thin film components in regard of their respective efficiency maximizing research efforts. In this purpose, in situ characterization techniques are of helpful interest, especially in situ real time visible spectroscopic ellipsometry that is a nondestructive surface-sensitive metrology tool [1]. For solar cells, such control can concern heterostructure devices based on sputtered (Ag,Cu)(In,Ga)$Se_2$ thin films [2], where in situ ellipsometry can monitor the nucleation, coalescence, and grain or bulk growth processes together with an access to an optical composition or particle size fingerprint and will constitute a prospective way for tunable optical properties e.g. band gap engineering.

In the same way, complex electrolyte/electrode interfaces which exist during electrochemical processes in liquid media can also be studied by in situ ellipsometry. Recent examples were given by Prato et al. [3] who distinguished over- and under-potential deposition regimes (OPD and UPD, respectively) of copper electrodeposition on gold substrate or by Ahlers et al. [4] who studied the macroscopic properties of a collagen film on a gold substrate evidencing a change of water content during the potential induced adsorption process. In addition to in situ ellipsometry, simultaneous recording of gravimetric data through the use of a synchronized electrochemical quartz crystal microbalance (EQCM) has been proposed by our group for the purpose of studying the electrodeposition (ECD) of $Bi_2Te_3$ films in aqueous medium [5,6]. Similar approach was used by Rodenhausen et al. for the monitoring of ultra-thin organic layers [7].

$Bi_2Te_3$ and related materials are the best thermoelectric material operating at room temperature [8]. Due to their limited efficiency, efforts are made to enhance their transport properties through nanostructuration [9]. Thus, superlattices could be an attractive way as proven by the results of Venkatasubramanian [10]. Among the methods synthesizing $Bi_2Te_3$ films, ECD appears as an interesting low cost approach with high growth rate [11]. However the electroplating of compact thin films with the targeted composition of binary or ternary compounds remains challenging due to three dimensional and non-epitaxial growth modes. The most promising results were obtained by Zhu et al. [12,13] thanks to the Electrochemical Atomic Layer Epitaxy technique in the UPD regime but exhibiting low growth rate in contrast with the OPD mode.

In that context, we have investigated the first steps of electrocrystallization of bismuth telluride in order to have a better understanding of the OPD growth mechanism. Alternatively to conventional in situ approaches like Scanning Tunneling Microscope, the used methodology was to study jointly the evolution of the optical response, the gravimetric data and the current transient, when operated in the potentiostatic mode with a fixed cathodic potential value applied to the electrode.

* Corresponding author.
*E-mail address:* alex.zimmer@ellipsometrie.fr (A. Zimmer).
[1] Permanent address: ICB UMR 6303 CNRS-Université de Bourgogne Franche-Comté, 9 Av. A. Savary, BP 47870 F-21078 Dijon Cedex, France

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## 2. Experimental

$Bi_2Te_3$ thin films were electroplated using an homemade setup that combines the monitoring of simultaneous electrochemical, gravimetric, and spectroscopic ellipsometric parameters [5,14]. Spectroscopic ellipsometry (SE) measures the changes in the polarization state between incident and reflected light on the samples. The measured values are the $\psi$ and $\Delta$ ellipsometric angles. They are related to the ratio of the Fresnel amplitude reflection coefficients of the sample, $r_p$ and $r_s$, respectively for p-polarized (parallel to the plane of incidence) and s-polarized light (perpendicular to the plane of incidence) by fundamental ellipsometric equation [15]: $r_p/r_s = \tan\psi \exp(i\Delta)$.

For each monitoring we measured the spectroscopic ellipsometric angles through $\tan\Psi(\lambda)$, $\tan\Delta(\lambda)$ in the spectral range 450-700 nm, the current response $I$ at applied voltage $E$, and the frequency $\Delta f$ of an EQCM. For the sake of clarity and readability, the usual terminology $\Psi(\lambda)$, $\Delta(\lambda)$ will be used in the rest of the text. Integrating times were of 70, 30 and 160 ms for ($\Psi$, $\Delta$), ($I$,$E$) and $\Delta f$, respectively. The measurements are performed at angle of incidence of 66.38°. Recently Broch et al. [14] proposed a new upgrade of the initial rotating compensator ellipsometer [5] of particular interest, which provides ellipsometric spectra free from systematic errors yielding a better trueness in extraction of dynamic fitted parameters. More details are given in ref. [14].

The electrolyte concentrations were fixed at $[Bi^{3+}] = [HTeO_2^+] = 10$ mM in 1 M $HNO_3$ medium. All potentials were measured and expressed related to the reference electrode (KCl saturated Ag/AgCl electrode, Bioblock). The syntheses were conducted at fixed applied potential of −25 mV to obtain the required binary stoichiometry [16–20]. The growth times were fixed to 60 s. EQCM sensors, composed of gold films evaporated on glass (5 MHz AT-cut quartz from Maxtek, Inc., Ref. P/N 149238-1) were chosen as working electrodes exposing a S=1.37 $cm^2$ surface area in a ~100 $cm^3$ volume of electrolytic solution. The gravimetric sensors were calibrated, exhibiting a sensitivity of 37.9 Hz/μg, whereas their measured surface roughness was inferior to 10 nm (rms). The counter electrode was made of platinum. The monitoring was made at room temperature. Prior to each electrodeposition the gold surface was electrochemically cleaned in a solution of 0.1 M $HClO_4$ by cycling 50 times between oxygen and hydrogen evolutions at 10 mV/s.

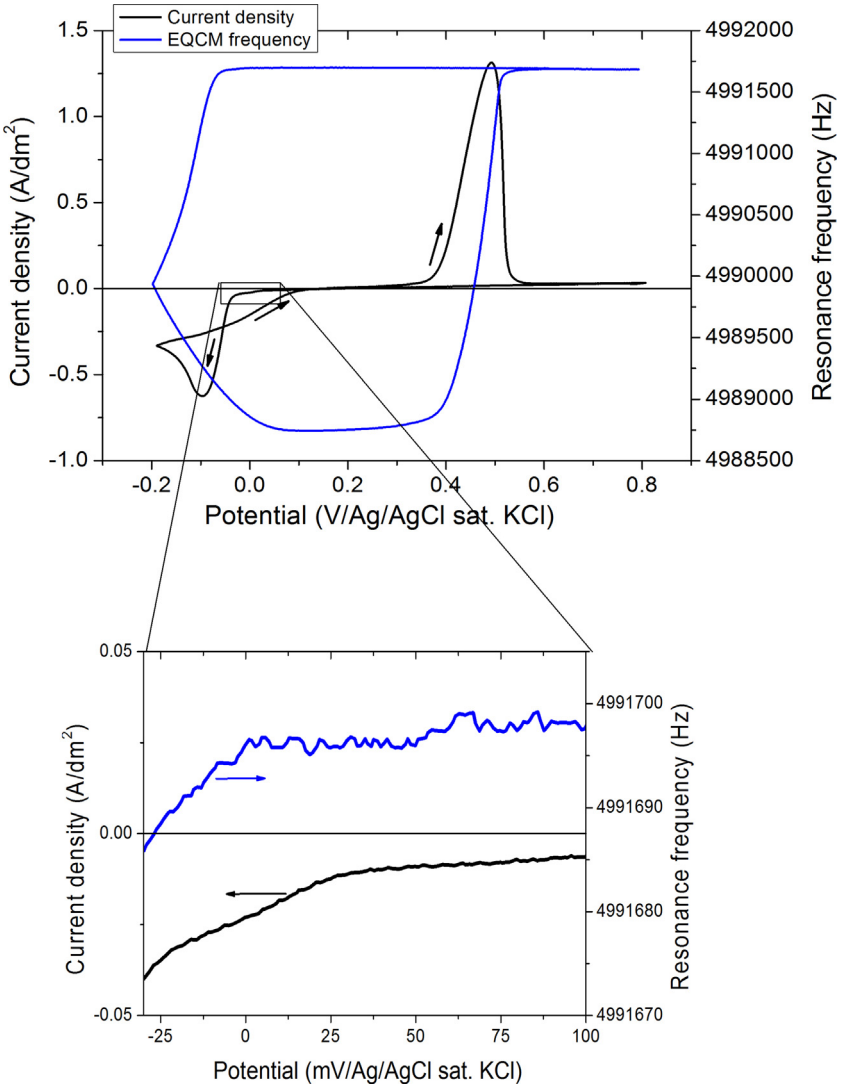


**Fig. 1.** Cyclic voltammogram of the Au EQCM electrode recorded at 100 mV/s in solution containing 10 mM $Bi^{3+}$, 10 mM $HTeO_2^+$ and 1 M $HNO_3$ (Bi/Te=1) with simultaneous EQCM resonance frequency f on the right axes. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)