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ScienceDirect
Electrochimica Acta 52 (2007) 3053–3060
ELECTROCHIMICA Acta
www.elsevier.com/locate/electacta

Pulsed electrodeposition of bismuth telluride films: Influence of pulse parameters over nucleation and morphology

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Received 6 July 2006; received in revised form 5 September 2006; accepted 21 September 2006
Available online 27 October 2006

Abstract

Pulsed electrodeposition methods were applied to the preparation of bismuth telluride films. Over the potential ranges from −170 mV to −600 mV, the formation of Bi_2Te_3 nuclei proceeded through a three-dimensional instantaneous nucleation mode. The nuclei densities for several values of potential were ranged between $\sim 10^6$ nuclei cm^{-2} and $\sim 10^8$ nuclei cm^{-2}. For a pulsed galvanostatic electroplating, the best covering percentage and a stoichiometry close to the desired Bi_2Te_3 were obtained with the parameters t_{on}, t_{off} and J_c, respectively, equal to 10 ms, 1000 ms and -100 mA cm^{-2}.

Keywords: Bismuth telluride; Electrodeposition; Pulse plating; Nucleation; Morphology

1. Introduction

Continuous advances in electronics and micro-nanotechnologies require the use of sensors, energy generators, local coolers and temperature stabilizers with a significantly reduced size, a light weight and a long life duration. The thermoelectric technology converting heat to electricity or using electricity to pump heat from cold to hot is a good alternative to make such devices. This technology can be easily miniaturized contrary to compressors or batteries due to the absence of moving parts. Moreover, it is an ecological technology without fluids noxious to the environment, such as chlorofluorocarbons (CFCs) or hydrochlorocarbons (HCFCs) refrigerants. In addition, a thermoelectric generator can cool and heat faster than conventional refrigeration. The semiconductor Bi_2Te_3 is the parent compound of a family of technologically important semiconductors as they are the best room-temperature bulk thermoelectric properties materials found to date [1,2]. These semiconductors are generally prepared by high temperature solidification methods from the elements in bulk form [3]. But the process is not suited for the industrial manufacturing of thermoelectric micro-systems in response to the current trend towards miniaturization. The use of thin film thermoelectric devices better meets the miniaturization challenge. Thin films can be obtained using chemical (MOCVD [4,5]) and physical vapour deposition [6]. But these deposition techniques have a high production cost. Electrodeposition has interesting characteristics for large area, low cost and generally low temperature and soft processing of materials. Several electrochemical processes have been developed leading to different compositions of Bi_2Te_3 binary compounds [7–12]. Nevertheless, the transport properties and in particular the Hall mobility of the electroplating films are lower than in single crystal [13]. This can be due to the microstructure affecting the films. Defaults and cracks, grain boundaries in the films cause a strong decrease of these physical properties.

In order to optimize the material morphology and then the electrical properties, pulsed electrodeposition can be used. This technique is an advanced form of electrodeposition, which offers better control over deposit properties by controlling the interfacial supply and electrochemical reaction. A high number of variables, such as pulse waveform, cathodic/anodic pulses, on/off pulse time or duty cycle, applied and mean current density, etc., offers effective ways to control macroscopic properties, such as better adhesion, crack free hard deposits, fine grained films with a higher uniformity and a lower porosity [14–17].

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0013-4686/$ – see front matter © 2006 Elsevier Ltd. All rights reserved.
doi:10.1016/j.electacta.2006.09.042

The aim of this study was to contribute to a better understanding of bismuth telluride deposition by pulse technique. Firstly, the nucleation mode was investigated by potential step experiments. Our experimental results were compared with the corresponding theoretical models. This work investigated the dependence of pulse parameters on growth, morphology, stoichiometry and coverage of the films in order to define the optimum conditions for pulsed electrodeposition of Bi_2Te_3.

2. Experimental

2.1. Deposition conditions

Pulsed electrodeposition refers to deposition where a current density or a potential is rapidly alternated between two values. In the simplest case, it consists in a series of pulses of equal amplitude, duration and polarity. Each pulse consists of an "On" time t_{on} during which a cathodic current density I_c or potential E_c is applied and an "Off" time t_{off} during which zero current density or potential which corresponds to a zero current density is applied (Fig. 1).

Stainless steel plates were chosen as substrate for the voltammetric study and for the pulsed deposition experiments. Plates were mechanically polished with silicon paper followed by diamond paste (1 μm size). The electrodes were then cleaned with distilled water followed by rinsing with ethanol. The working electrodes were located vertically in a glass cell, whose electrolyte volume was 0.1 dm^3. A 1.24 cm^2 area was exposed for deposition, which was carried out at room temperature without stirring. The electrochemical potentials of the working electrode were measured and expressed by reference to a saturated calomel electrode (SCE) and the counter electrode was a platinum disc (1 cm^2). The experiments were carried out using Autolab PGSTAT 100 potentiostat with GPES software. The electrolyte baths were prepared with Millipore^{TM} water (10 MΩ cm) and analytical reagents. To ensure the stability and the solubility of bismuth(III) and tellurium(IV), the selected solvent was nitric acid (1 M), according to previous work done using continuous method [7,12]. The solutions were obtained by dissolution of Te^0 and $Bi(NO_3)_3{\cdot}5H_2O$. According to Michel et al. [12], the cation ratio ([Bi]/[Te]) was fixed at 1 and the tellurite concentration was fixed at 2×10^{-2} M for all mixtures.

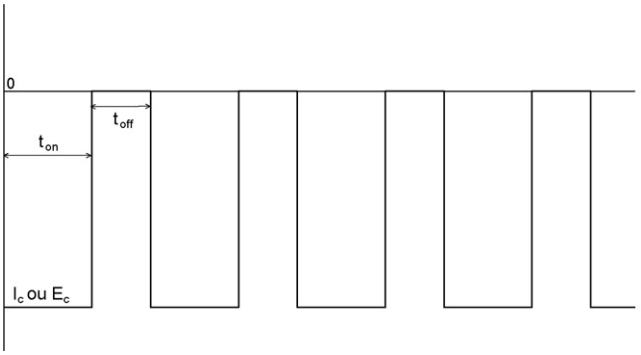

Fig. 1. Theoretical diagram of the pulse plating electrodeposition process.

2.2. Deposition characterizations

Samples were prepared after electrodeposition by thorough rinsing in three steps (nitric acid solution pH 1, Millipore^{TM} water and ethanol) followed by drying in air. The morphology, the covering percentage and the grain size were determined using a scanning electron microscope (SEM; PHILIPS XL30). This equipment included an EDS detector, which was used to determine the composition. X-ray diffraction data were obtained with an Inel diffractometer (XRG 2500 CPS 120, Co Kα or Cu Kα radiation).

3. Results and discussion

3.1. Voltammetry

The present study was carried out with a stationary electrode in order to be in the same conditions as the synthesis. Fig. 2 shows the cathodic curve obtained with the electrolyte used for all experiments. The range of the potential exploration was conducted from the open current potential down to the proton reduction potential (−500 mV).

This voltammogram shows two reduction waves. The first wave is centred at −50 mV and the second at −100 mV. A plateau is observed at potentials between −150 mV and −400 mV. The curve also shows that a reduction wall occurs at ca. −400 mV. These results are in good agreement with previous results, which were carried out with a rotating electrode [7,12]. Michel et al. [12] have determined the stoichiometry of the film for each potential. These authors have shown that the deposits synthesized at −50 mV are rich in tellurium and that the electrodeposits obtained at −100 mV correspond to Bi_2Te_3. The deposits obtained under −400 mV have a powdery aspect due to the proton reduction. The plateau is due to the diffusion of Bi^{III} and Te^{IV} and corresponds to the deposition of Bi_2Te_3. According to these results, synthesis parameters in pulsed electroplating have to be controlled in order to avoid the application of a potential lower than −400 mV which corresponds to the proton reduction.

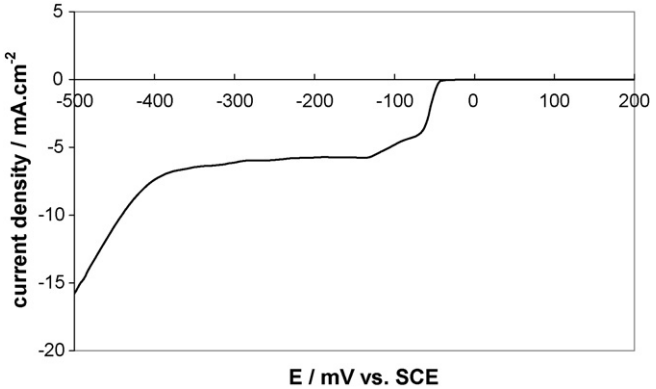

Fig. 2. Voltammogram in 1 M HNO_3, $[Te^{IV}] = 2 \times 10^{-2}$ M, [Bi]/[Te] = 1, working electrode: stainless steel, surface area = 1.24 cm^2, counter electrode: platinum disc, scan rate = 60 mV min^{-1}.