



## Improvement of Bismuth Telluride electrodeposited films by the addition of Sodium Lignosulfonate



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### ABSTRACT

In this work we report the improvement on the electrodeposition of Bi<sub>2</sub>Te<sub>3</sub> films with the *c*-axis parallel to the surface of the substrate. This has been done with the addition of a surfactant agent (sodium lignosulfonate) to the electrochemical bath. A thorough study of the electrodeposition parameters and the material composition, morphology, crystallographic orientation and transport properties was performed. High quality films oriented along the (1 1 0) plane and with a dense morphology were obtained, showing an improved Seebeck coefficient up to 33% bigger than previously reported values. The differences in the morphology due to the presence of the surfactant have been further analyzed studying the shape of films grown from discrete nucleation sites.

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## 1. Introduction

Bismuth telluride (Bi<sub>2</sub>Te<sub>3</sub>) is a quite appealing material that is being studied nowadays for a variety of applications, such as in thermoelectric devices for room temperature operation [1] and as topological insulator [2]. Its fabrication in the form of films via electrodeposition represents a low cost method which is easily scalable to the industry. The mechanism of the electrodeposition of bismuth telluride has been widely investigated [3], but there is still room for improvement to optimize its performance.

As far as thermoelectric applications are concerned, a great effort is being made to study how to increase the efficiency of energy transformation while reducing the wasted heat that is produced in both transport and conversion of this energy into electrical power. A quite appealing use for that wasted heat is transforming it into usable electrical power via thermoelectric conversion. Devices based on the thermoelectric effect take advantage of the high thermoelectric properties of some solid-state materials, which offer the direct conversion of heat into electric energy. On the one hand they are characterized by being robust, silent, and reliable, with low or no maintenance, and long lifetime. On the other hand, they present

a great disadvantage for their use, which is their low conversion efficiency, mainly due to the low efficiency of the thermoelectric materials available. Thermoelectric efficiency is related to the Figure of Merit *ZT*, which is defined as  $ZT = (S^2 \cdot \sigma / \kappa) \cdot T$ , where *S* is the Seebeck coefficient,  $\sigma$  the electrical conductivity,  $\kappa$  the thermal conductivity, and *T* the absolute temperature. Thus, to enhance the thermoelectric efficiency of these materials, it is necessary to find a way of increasing their Seebeck coefficient and/or electrical conductivity, along with reducing their thermal conductivity.

Among the most widely used thermoelectric materials available, bismuth telluride stands out for applications around room temperature. Although the electrochemical deposition of bismuth telluride has been extensively used to prepare thermoelectric devices, mainly due to the suitability of the technique for industrial applications, it presents a main drawback: to the best of our knowledge, the usual value of the Seebeck coefficient achieved in electrodeposited bismuth telluride films without ulterior thermal treatments is around  $-70 \mu\text{V/K}$  [3,4], much lower than the value obtained in bulk material,  $-240 \mu\text{V/K}$  [5]. The reason behind this low value is that electrochemistry fabrication changes the electrical and morphological characteristics of the films when compared with more expensive techniques which provide an epitaxial growth. Given that these techniques are not easily used for actual applications at large scale, the search for a way to increase the Seebeck coefficient in electrochemically grown Bi<sub>2</sub>Te<sub>3</sub> films is mandatory.

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Therefore, research is underway to gain better control over the growth parameters of electrodeposited  $\text{Bi}_2\text{Te}_3$  films in order to improve their quality and obtain properties closer to those of bulk. Taking into account that the thermoelectric performance in bismuth telluride is related to its grain size and the homogeneity in its composition [6], a way of controlling its morphology and the presence of defects could lead to a way of improving the efficiency of electrodeposited bismuth telluride films. Moreover, once films with better quality via electrodeposition have been obtained, the fabrication of nanowire arrays of bismuth telluride using alumina templates to further increase their efficiency for thermoelectric applications by nano-structuring [1] appears as a natural and straightforward step.

In this work we have focused on obtaining dense and highly oriented bismuth telluride films with their *c*-axis parallel to the surface of the substrate. The reason to search this particular orientation is the anisotropy of bismuth telluride, which presents minimum thermal lattice conductivity and maximal electrical conductivity along the direction perpendicular to the *c*-axis [7]. Therefore, the thermoelectric efficiency for out-of-plane configurations, which are the most convenient for film applications, is maximal. Moreover, the use of bismuth telluride as topological insulator requires the fabrication of nanometer thin films with an optimized morphology. Much research is being devoted to obtaining high quality films for this application by techniques which do not involve high vacuum expensive facilities [8].

Our first approach was to modify the growth parameters until the films presented a preferential (1 1 0) orientation. To that end, we employed different applied potentials, substrates and cell configurations. In a next step, to further improve the quality and morphology of the films, we modified the composition of the solution including additives. Different substances have been studied as additives to tailor different aspects of bismuth telluride films, such as ethylene glycol for increasing the thickness of the films [9], paper glue to improve the adhesion and smoothness of their surface [10], etc. In our case, since we want to reduce the morphological defects and produce smoother films, we studied the addition of a surfactant that modifies the interfacial tension between the solution and the working electrode. The surfactant chosen was Sodium Lignosulfonate (SLS), which had been historically used as brightener agent for the electrodeposition of Nickel [11] and Lead, [12], and as anti-coagulant for the electrochemical deposition of Selenium [13]. More recently, this surfactant has been used in the electrochemical fabrication of  $\text{Bi}_{0.5}\text{Sb}_{1.5}\text{Te}_3$  films [14]. In the case of  $\text{Bi}_2\text{Te}_3$  we showed promising results in the European Thermoelectric Meeting 2011 [15], although another work published in 2012 by Naylor et al. showed a poor improvement of the Seebeck coefficient when SLS was added to the electrochemical bath [16]. There, the Seebeck value obtained was  $-15 \mu\text{V/K}$  and a power factor of around  $10^{-4} \text{ W/m}^2\text{K}^2$ .

Lignosulfonates, particularly alkali salts, are stable in solutions with acidic pH such as the one used for bismuth telluride electrodeposition. The effect of this surfactant in selenium-containing baths is to avoid the formation of clusters of particles in liquid suspensions, producing a more homogeneous composition of the films. The present study was carried out varying both the SLS concentration and the applied potential. Finally, in order to assess the thermoelectric performance of these films, their transport properties (Seebeck coefficient and electrical resistivity) have been measured for in-plane and out-of-plane configurations.

## 2. Experimental

Films were fabricated on substrates that consist of a silicon (100) wafer metallized by evaporating 50 Å chromium and 1500 Å gold layers. The wafer was then cut to rectangular pieces of  $10 \times 15 \text{ mm}^2$

approximately. Prior to the electrodeposition, the edges of the substrate were covered with Kapton® tape, which was removed after the  $\text{Bi}_2\text{Te}_3$  layer fabrication. To form the working electrode a metallic wire was connected mechanically to the substrate with the aid of Kapton® tape.

Bismuth telluride films were synthesized by electrodeposition. A conventional three-electrode cell was used, with Ag/AgCl (saturated KCl) as the reference electrode, platinum counter electrode, and the aforementioned silicon substrate coated with chromium and gold as working electrode. The solution used to perform the experiments was a nitric acid bath consisting in  $0.75 \cdot 10^{-2} \text{ M Bi}^{3+}$ ,  $10^{-2} \text{ M HTeO}_2^+$ ,  $1 \text{ M HNO}_3$  in de-ionized water [17]. Cyclic Voltammograms (CVs) were recorded with the aid of an Autolab potentiostat and the NOVA software. In order to make the comparison between different CVs easier, the area of the working electrode was kept the same in all cases, (a circle of 5 mm in diameter). The potential limits for the CVs were chosen as  $-0.8 \text{ V}$  in the negative range to  $1.0 \text{ V}$  in the positive with respect to Ag/AgCl reference electrode with a scanning rate of  $0.01 \text{ V/s}$ . The electrodepositions were carried out at constant potential using the same Autolab potentiostat. The films obtained have a thickness of around  $7 \mu\text{m}$ .

In order to detach the samples from the substrate a novel procedure was developed. Although there have been some processes reported to remove the substrate, such as [18], in our case we had to develop a different process which allowed the ulterior measurement of the properties of the films up to  $105^\circ\text{C}$ . Therefore, we glued the surface of the film to a piece of glass with an epoxy adhesive (Araldite® high temperature, from Ceys®, which stands up to  $120^\circ\text{C}$ ). Once the glue dried, we immersed the samples into liquid nitrogen. In that way, the bismuth telluride film gets detached from the Si/Cr/Au substrate, due to the different thermal expansion coefficients of the gold and the  $\text{Bi}_2\text{Te}_3$  layer. Thus, the films were transferred to a non-conductive substrate for the measurement of the transport properties without any rest of the substrate.

The fabricated bismuth telluride films were morphologically characterized using SEM (Hitachi S-800 and high resolution field emission SEM Philips XL30 S-FEG microscopes). Atomic Force Microscopy (AFM) images were obtained with a Nanotec [19] microscope. Their thicknesses were measured prior to the detachment of the films from the substrate with a Veeco Dektak stylus profiler system. The crystal orientation of the films was studied with XRD Philips X'Pert four circles diffractometer with a  $\text{CuK}\alpha$  X-Ray transmitter. Raman Spectroscopy was carried out with a Jobin Yvon LabRam HR using a Nd:YAG laser of 532 nm wavelength. The quantitative composition of the films was measured with an EDX Jeol JSM6335F microscope and Rutherford Back-Scattering (RBS) measurements, carried out with the standard line of 5 MV tandem accelerator at the CMAM (Centro de Microanálisis de Materiales de Madrid [20]). The RBS analysis was performed in vacuum using a 4 MeV  $\text{He}^+$  beam. A careful quantification of the RBS spectra was achieved using the simulation code RBX [21].

The measurements of the transport properties in-plane were made with a Seebeck coefficient and electrical resistivity measurement equipment model LSR-3 from Linseis once the samples were detached from their substrates (to avoid the influence of the gold layer which forms part of the working electrode) from room temperature (RT) to  $105^\circ\text{C}$ . In the case of the out-of-plane transport measurements (Seebeck coefficient and electrical conductivity determination), the samples were measured before detaching. A house-made two probe-station was used for the measurement of the resistance in the out-of-plane configuration of the films. Finally, the out-of plane Seebeck coefficient was also measured with a house-made setup where a temperature gradient around room temperature was established along the thickness of the sample and recorded with thermocouples at both ends while the voltage produced across the thickness of the film was recorded.

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