



A voltammetric study of the underpotential deposition of cobalt and antimony on gold



Yuan Chen^{a,b,c}, Lishi Wang^{a,b}, Annie Pradel^c, Michel Ribes^c, Marie-Christine Record^{a,b,*}

^a Aix-Marseille Univ., IM2NP, 13397 Marseille Cedex 20, France

^b CNRS, IM2NP, 13397 Marseille Cedex 20, France

^c Institut Charles Gerhardt Montpellier, UMR CNRS 5253, ChV, CC1503, Université Montpellier II, Place Eugène Bataillon, 34095 Montpellier Cedex 5, France

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ABSTRACT

This study reports on preliminary experiments which are required to define the experimental conditions for depositing CoSb₃ thin films by the electrochemical atomic layer epitaxy (EC-ALE) method. The underpotential deposition (UPD) of cobalt and antimony on polycrystalline gold substrates has been investigated by means of cyclic voltammetry, anodic potentiodynamic scanning and coulometry. The UPD of Sb on Co-covered Au and of Co on Sb-covered Au have also been studied and compared to those obtained on bare Au substrate.

The UPD potential values for both Co and Sb are reported in this paper, and owing to the flexibility of the EC-ALE equipment, new insights on the Co UPD on gold substrate are presented. This study shows that the subsequent alternate deposition of Co and Sb monolayers is feasible and thus that the EC-ALE method can be used to elaborate CoSb₃ thin films.

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1. Introduction

Skutterudite compounds form a new class of potential candidates for thermoelectric applications at high temperatures [1,2]. The general chemical formula of binary skutterudites is MX₃, where M is a transition metal (Co, Rh or Ir), and X a pnictogen (As, P or Sb). Some of them, such as CoSb₃, show good electrical properties. However, the thermal conductivity of these binary skutterudites is too high (~10 W/mK at 300 K) to get high ZT values [3]. Different approaches have been considered to reduce the thermal conductivity of these compounds and thus increase their thermoelectric efficiency. All of them deal with increasing phonon scattering. This phenomenon can be enhanced by either filling the voids present in the skutterudite crystal structures with foreign elements, or forming solid solutions of skutterudites, or preparing nanostructured materials [4]. While the first two approaches were deeply investigated [5–9], only a few papers are reported on the last one [10,11]. By investigating CoSb₃ thin films, Ito et al. [12] found that their thermal conductivity decrement is proportional to the reciprocal of the film thickness. A minimum thermal conductivity of about 1.1 W/mK was obtained in a ~325 nm-thick CoSb₃ film at room temperature. Thin films are usually

prepared by physical vapor deposition methods although electrochemical deposition may provide an alternative process to these classical methods. Indeed, by contrast to other methods, electrochemical deposition is a low cost, room temperature production technique, which works without vacuum atmosphere and allows one to cover substrates with complex shapes. Some studies have been already reported on electrochemical deposition of CoSb₃ [13–18]. In these works, CoSb₃ thin films or nanowires were obtained by codeposition of cobalt and antimony in electroplating baths containing both SbO⁺ and Co²⁺.

Electrochemical atomic layer deposition (EC-ALE), which was put forward by Gregory and Stickney [19], is a method for preparing thin-film compound semiconductors. This method is based on the alternate underpotential deposition (UPD) of atomic layers of the elements to make up a compound, combining advantageously the technique of electrochemical deposition and that of atomic layer epitaxy. Underpotential deposition is a surface-limited electrochemical phenomenon, which makes the deposition generally limited to an atomic layer. In every cycle one monolayer of the compound is obtained, and the thickness of the deposit will only depend on the number of cycles [20]. Each cycle consists in a series of individual steps, and each step can be optimized independently, resulting in well-controlled deposits. Up to now, EC-ALE method has been applied extensively to obtain thin films of IIB-VIA [21–27], IVA-VIA [28,29], VA-VIA [30–33] and IIIA-VA [34,35] compound semiconductors. A few IIIA-VIA [36], IB-VIA [37] and

* Corresponding author. Tel.: +33 681570880.

E-mail address: m-c.record@univ-amu.fr (M.-C. Record).

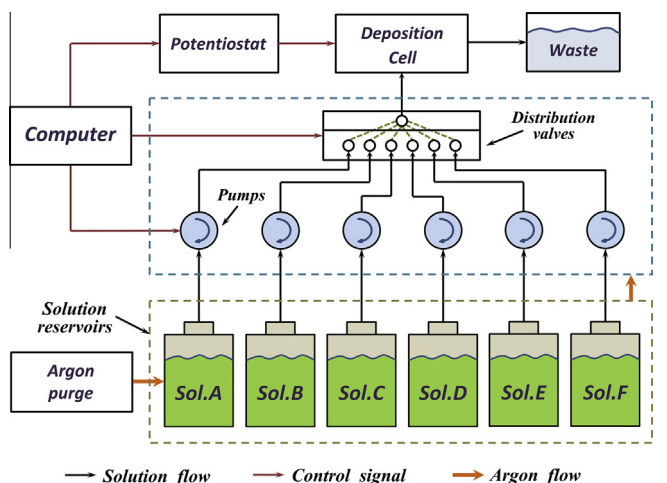


Fig. 1. Schematic drawing of automated electrochemical thin-layer deposition equipment.

VIIIB-VIA [38] compounds and several superlattices [39–45] have also been obtained by EC-ALE.

The present paper reports on the results of preliminary experiments which are required to define the experimental conditions for depositing CoSb_3 thin films by the EC-ALE method. The electrochemical behaviors of antimony and cobalt on polycrystalline gold substrate have been investigated by means of cyclic voltammetry, anodic potentiodynamic scanning and coulometry. The UPD of Sb on Co-covered Au and of Co on Sb-covered Au have also been studied and compared to those obtained on bare Au substrate.

2. Experimental

The EC-ALE equipment used in the present work was built in our group. It is constituted of a series of solution reservoirs, computer-controlled peristaltic pumps (Cole-Parmer, Inc., USA), solenoid distribution valves (NResearch, Inc., USA), a potentiostat (Solartron Analytical, Modulab, equipped with the model Pstat 1 MS/s, AMETEK, Inc., USA) and an electrochemical flow cell (see Fig. 1). The electrochemical flow cell is close to those described by the Stickney [40,46,47] and Zhu–Yang [48] work groups.

A platinum sheet (Sigma–Aldrich, Inc., USA) is used as counter electrode; the working electrode is made of gold substrates (PHASIS, Inc., Switzerland) which consist of quartz slides, coated with 200 nm thick gold films (99.99% pure). Under the Au film, a thin layer of Ti (10 nm) is deposited to improve adhesion of gold onto quartz. All electrochemical potential values are measured with respect to the potential of an Ag/AgCl (3 M NaCl) electrode (AMETEK, Inc., USA) as a reference.

The gold substrates are prepared as follows: they are first annealed at 350 °C for 18 h at 10^{-6} Torr in sealed glass tubes and then soaked in hot nitric acid for 5 min. Before each experiment, cyclic voltammetry (repeated 25 times) of the Au substrate in 0.1 M H_2SO_4 solution is performed with potential scan from -0.30 V to 1.65 V.

Solutions are prepared using ACS reagent grade chemicals (Sigma–Aldrich, Inc., USA) and deionized water (Milli-Q 18.2 M Ω ·cm, Merck KGaA, Darmstadt, Germany). Four different solutions are used in this study. The antimony solution consists in 0.03 mM Sb_2O_3 , pH 5.0 (adjusted with H_2SO_4), buffered with 0.05 M CH_3COONa , and 0.1 M Na_2SO_4 used as supporting electrolyte. The cobalt solution is made of 0.01 M CoCl_2 and 1 M NH_4Cl , at pH 9.5 (adjusted with NaOH). Under these conditions, the main chemical species of the Co(II) ion is the $[\text{Co}(\text{NH}_3)_5(\text{H}_2\text{O})]^{2+}$ complex

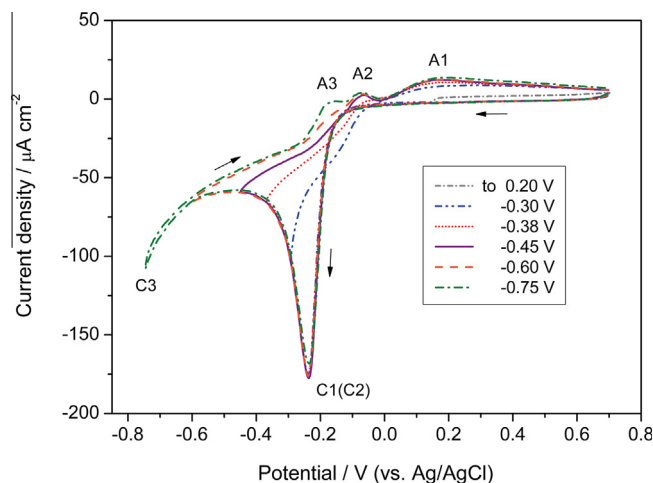


Fig. 2. Cyclic voltammogram of the Au electrode in a 0.03 mM Sb_2O_3 solution (pH 5.0). The curves with different patterns correspond to the cycles with different scanning limits. The scanning rate is 20 mV/s.

[49]. Two rinsing solutions are used, one labeled A containing 0.1 M Na_2SO_4 with pH 5.0, buffered with 0.05 M CH_3COONa , and the other labeled B containing 1 M NH_4Cl , at pH 9.5.

All the solutions are degassed by blowing high purity Ar gas through the solution for 30 min. All experiments are performed at room temperature with solutions maintained under Ar atmosphere.

3. Results and discussion

3.1. Electrochemical behavior of Sb on Au

Fig. 2 shows the cyclic voltammetry (CV) curves of the Au electrode in Sb(III) solution, successively scanned from 0.7 V to various potential limits (see curve legend in Fig. 2). Two reductive features are observed. A large peak marked as C1(C2) is observed at -0.24 V, which corresponds to the UPD of Sb. In fact according to the description reported by Yan et al. [50], this peak results from the overlapping of two different Sb UPD peaks. By considering that three electrons are transferred during oxidation and reduction of Sb, the coverage of the gold substrate is estimated to be 0.81 monolayer (ML). This result indicates that C1(C2) peak indeed corresponds to a surface-limited deposition.

The second reductive peak C3 corresponds to the bulk deposition of Sb.

Three oxidative peaks are evidenced on this figure. A3 corresponds to the stripping of bulk Sb. The peak A2 at -0.07 V and the broad peak A1 both correspond to the oxidative stripping of the UPD Sb.

The CV curves of Au electrode in Sb(III) solution obtained in this work are very similar to those reported by Wade et al. [40] and Yang et al. [51].

3.2. Co electrochemical behavior on Au

Fig. 3 shows the cyclic voltammogram obtained for the $\text{Au}/10^{-2}$ M $\text{CoCl}_2 + 1$ M NH_4Cl (pH 9.5) system. The potential is scanned from 0.52 V to various negative limiting potential values (see curve legend in Fig. 3). Two reductive peaks C1 and C2 appear at 0.09 V and -0.10 V, respectively. The corresponding anodic peaks are A1 and A2, respectively. According to Mendoza-Huizar et al. [52] who reported a cyclic voltammogram similar in shape to ours, C1 and C2 correspond to the UPD of Co(II) onto the gold

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