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Electrochemical characterization and electrode kinetics for antimony electrodeposition from its oxychloride solution in the presence of tartaric acid

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ABSTRACT

This work is devoted to investigate the process of the electrochemical deposition of antimony from antimony oxychloride solution in the presence of tartaric acid in aqueous media. The kinetics and the mechanism of the electrodeposition process at the electrode surface are studied and proposed by the aid of cyclic, linear sweep voltammetric and chronoamperometric characterization methods. It is found that, the process is affected by the presence of tartaric acid and some factors during the electro-reduction process. The results also show that, the temperature, the potential sweep rate and the concentration of antimony have a great influence on the achievement of the electrodeposition process. Some important parameters are calculated such as, the activation energy of the electrochemical reaction, the diffusion coefficient and the number of saturated nucleation sites. The electrodeposited film is examined using X-ray diffraction, scanning electron microscopy and Energy Dispersive Spectroscopy.

1. Introduction

Nowadays, due to the rapid development of nanotechnology and microelectronics, the narrow-gap, as well as, $A_2(V)B_3(VI)$ type semiconductors have attracted more considerable attentions for using in solar cells application [1–5]. Hence this will lead to increase and enhancement in the production of photovoltaic cells and solar panels.

Nano-metal and nano metal-chalcogenides coatings or nano-films have unique properties differ from the bulk materials, so it has a significant important utilizes in the electrical engineering and electronics. Among of these important materials is the antimony selenide. Many Scientific literature reported the Sb_2Se_3 obtaining by different methods [6–8]. Obtaining of the semiconductor thin films by electrochemical methods is of interest of many researchers [9–11]. Because by these methods, it is possible to get almost porous or nonporous structured films and films with very small size grains of nano dimension which have application in the sensitized solar cells [12].

One of the most promising representatives of $A_2(V)B_3(VI)$ type semiconductors is the antimony selenide (Sb_2Se_3). Antimony selenide is a semiconductor chalcogenide with high photoelectric properties. Sb_2Se_3 has a band gap of about 1.78 eV, hence it meets the requirements of materials for solar cells. That's give a strong reason for why the process of the production of that type of semiconductor material be on the basis priority area for the electrochemistry work. Crystalline Sb_2Se_3 with adequate photoelectric properties used for the production of solar cells was obtained by thermal evaporation [6].

The method of chemical precipitation of Sb_2Se_3 under nitrogen atmosphere was also used [7]. At other work [8], Sb_2Se_3 was obtained by mixing ethylene glycol with antimony oxide, and sodium seleno sulfate. The precipitation is obtained after 10–12 h at the temperature of 423 K (150 °C). Nano-rods with 10–15 μm length and 200–450 nm width were obtained.

By reading and analysis of literature data, it has been noted that the applied methods for production of Sb_2Se_3 are complicated and the obtaining of these thin films by electrochemical method is more accurate and efficient. Mechanisms, connected with the nucleation, and growth of semiconductor compound of antimony selenide

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(Sb_2Se_3) on indium doped with tin oxides (ITO) were investigated using chronoamperometric method [11].

It is well known that, the electrodeposition of antimony without complexing agent is difficult and usually occurs at relatively high voltages, for that it is always needed to add a complexing agent in order to increase the solubility of Sb(III) and also its stability [13,14]. Aliyev et al. [15,16], studied the process of the electrochemical reduction of antimony by cyclic voltammetric method from an electrolyte containing fluoroboric acid. The obtained results show that the process of electrochemical reduction of antimony in this electrolyte depends on temperature and scan rate and increases proportionally with them. It was also established that the polarization in this process is controlled by diffusion and adsorption character. Furthermore the electrodeposition process of antimony is retarded and slow and a very weak reduction peak combined with hydrogen evolution appeared at −0.4 V.

Our main aim here is how to solve the above mentioned problem to obtain high quality deposits of antimony metal by improvement the electrodeposition process of antimony via studying the mechanism of electrodeposition through applying certain conditions.

2. Experimental part

All chemicals are of grade analytical from Merck and BDH were used without further purification. The process of the electrochemical reduction of antimony ions was carried out as in the following way;

2.1. Preparation of the electrolyte of the deposition bath

At first appreciated amount tartaric acid was dissolved in bidistilled water. Then the solution of tartaric acid was added to an appreciated amount of the antimony oxychloride - SbOCl. Thus the electrolyte with the composition of 0.05 M SbOCl + 0.007 M $C_4H_6O_6$ (tartaric acid) was obtained.

2.2. Electrochemical measurements

Polarization curves were obtained by using IVIUMSTAT Electrochemical Interface potentiostat. The electrochemical three-electrode cell with 100 ml capacity and provided with a slot for nitrogen purging was used. Silver/Silver chloride/Saturated Potassium Chloride electrode was used as reference electrode, while the platinum sheet with 2 cm^2 area was used as an auxiliary electrode. Platinum wire of 2 mm^2 area or Nickel sheet of 0.25 cm^2 area were used as working electrodes. The working electrode was cleaned via ultra-sonication in 1:1 acetone/alcohol mixture and rinsed with deionized water before the experiment. The universal ultra thermostat UTU-4 was used for temperature regulation of the electrolysis process.

2.3. Characterization of the electrodeposits

The crystallinity degree and phase compositions of the electrodeposits were studied via x-ray diffraction (XRD) using TD-3500 diffractometer at room temperature with Ni-filtered Cu Kα radiation (λ = 0.15418 nm), at 35 kv and 25 mA. The morphology and the chemical composition of electrodeposits were studied by using scanning electron microscope (SEM) and energy-dispersive X-ray analysis (EDAX) of mark “Carl Zeiss Sigma”. SEM image of electrodeposited film on Ni substrate was captured using a JEOL T330A SEM from Japan. The prepared sample was captured at fixed temperature of 20 °C at working distance of 10 mm, at power of 20 KeV and at magnification factor of 3000 times from the real sample.

3. Results and discussion

Tartaric acid is chosen as organic additive and gives some acidity to the electrodeposition bath. Hence, it is favored for giving antimony thin films of fine-grained which can be used as decorative protective coatings. The cyclic voltammetric method was used for the investigation of the electrochemical reduction of antimony oxide ions SbO^+ from tartaric acid solution as shown in Fig. 1. A crossover at the reverse scan has been observed at potential around −0.5 V in Fig. 1, which is ascribed to a nucleation process [17]. The electrooxidation process is observed at about 0.1 V which is related to the oxidation of antimony (Sb to Sb(III)).

It is known that, the acidity of the electrodeposition bath of metals has a significant influence on the structure and properties of precipitates. In our investigation, the pH of solutions was varied between 0.8 −2.0 ranges. It is noted that amphoteric precipitates were obtained at pH < 1.

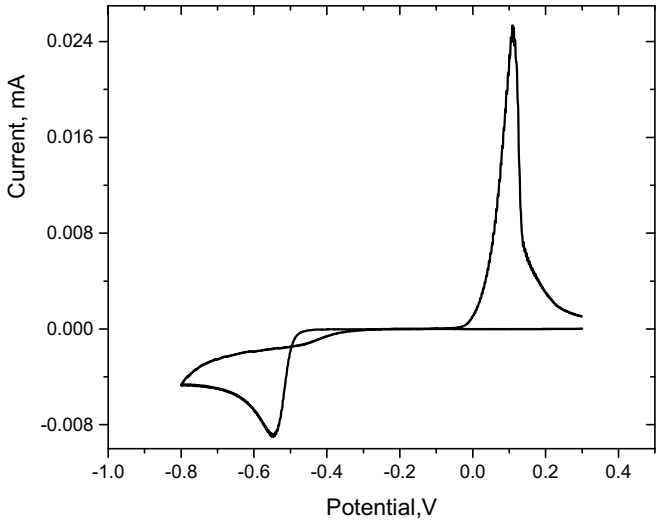

Fig. 1. Cyclic voltammetric behavior of a solution consists of 0.05 M SbOCl+0.007M $C_4H_6O_6$ at scan rate = 0.02 Vs^{-1}, Pt- electrode, T = 295 K (22 °C) and pH = 1.3.

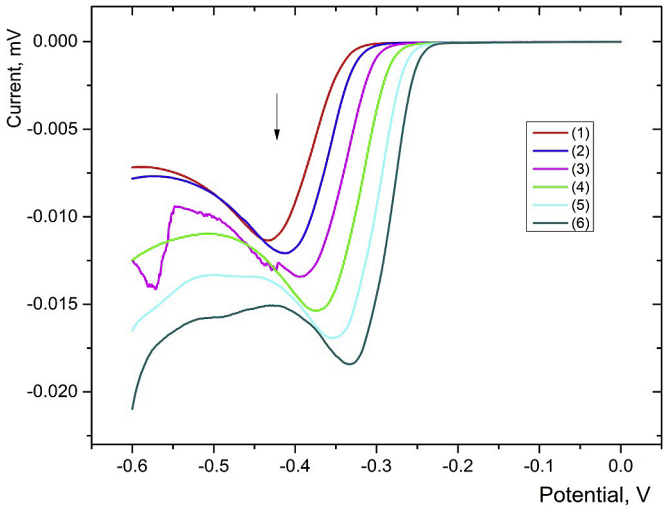

Fig. 2. Effect of temperature on the electroreduction of antimony; 1–308 K (35 °C); 2–318 K (45 °C); 3–328 K (55 °C); 4–338 K (55 °C); 5–348 K (65 °C); 6–358 K (75 °C). Composition of the electrolyte: 0.05 M SbOCl+0.007 M $C_4H_6O_6$, scan rate = −0.02 Vs^{-1}, Pt-electrode, pH = 1.3.