

Early stages of cobalt electrodeposition on FTO and n-type Si substrates in sulfate medium

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ABSTRACT

The mechanism of cobalt electrocrystallization on fluorine-doped tin oxide (FTO)-coated conducting glass substrate has been studied and compared with results obtained on n-type Si electrodes. The initial stages of metal deposition from a solution of 0.25 M CoSO₄, 1 M Na₂SO₄ and 0.5 M H₃BO₃ (pH 3.5) were investigated using cyclic voltammetry, and chronoamperometry measurements. Important kinetics parameters were estimated from the analysis of current transients on the basis of the Scharifker–Hills model for electrochemical nucleation and diffusion-controlled growth. From the analysis of the experimental current transients, it was found that the process of cobalt deposition involves a three-dimensional (3D) electrochemical nucleation and diffusion-controlled growth. A strong dependence of the number density of active sites N_0 with applied potential was observed on both FTO and n-type Si electrodes.

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1. Introduction

The electrochemical formation of thin metallic film formed on foreign substrates (metals and semiconductors) has received considerable attention from both fundamental and applied viewpoints [1–3]. Generally, these materials are elaborated by physical vapor deposition techniques such as sputtering or molecular beam epitaxy. Electrochemical deposition is an attractive method for the elaboration of thin films. In general, for the electrochemical growth process, the growth mechanism of the deposition of metals onto semiconductors substrates takes place at 3D island growth (Volmer–Weber) mechanism due to the weak interaction energy [4]. A crucial step in nucleation and growth processes is the initial formation of growth centers whose number, nature and distribution on the substrate surface may strongly influence the final characteristics of electrodeposits [5].

The current transient technique, also known as chronoamperometry, is a technique which is commonly used to determine the nucleation mechanism. A potential step is applied from an initial potential at which the nucleation rate is negligible, to a fixed overpotential [4]. The formation of stable nuclei and their growth can be observed by monitoring the current and information on the rate of nucleation, the density of nuclei and the mechanism of growth can be obtained from the shape of the resulting current–time transient plots [4]. Chronoamperometry has been used to study the nucleation mechanisms of Co metal on different

substrates and different experimental conditions [6–12]. Correia et al. [6] and Gómez et al. [7] studied the electrodeposition of Co from chloride solutions on carbon and gold substrates respectively. By using chronoamperometric experiments, they showed a progressive nucleation followed by 3D growth limited by diffusion. During the early stage of deposition, it was established that the electrodeposition of Co depends generally on pHs solution [8,9]. Effectively, at pH 9.5 a transition from 2D instantaneous to 3D progressive nucleation mechanism was observed. At pH 4.5 the nucleation mechanism is 3D progressive. In sulfate solution, pH 6, the Co deposition consistent with the progressive nucleation model followed by three-dimensional diffusion-limited growth [10]. However, in mixed chloride sulfate solution a transition from progressive to instantaneous nucleation mechanism was established for Co deposition on Pt and Au(1 1 1) substrates at pH 4.2 [11,12]. However, to our knowledge the study of influence of the semiconductor substrate type on the nucleation and growth process of cobalt under similar conditions (Co²⁺ concentration, pH) has not been undertaken. Consequently, the aim of the present work is to study the influences of FTO-conducting glass and silicon n-type electrode on the initial stages of cobalt electrodeposition from aqueous cobalt sulfate solution.

2. Experimental

The Co films were electrodeposited from an aqueous solution containing 0.25 M CoSO₄·7H₂O, 1 M Na₂SO₄ and 0.5 M H₃BO₃ (pH 3.5). Boric acid was added to the bath in order to control the pH of the solution and improve the quality of the deposit. The deposition process was performed at 25 °C in three-electrode cell with a platinum wire counter electrode and a saturated calomel reference electrode (SCE, +0.241 V vs SHE). Polycrystalline F-tin oxide (FTO) conducting (10–15 Ωcm) glass substrates of 3 cm² area and n-type Si wafers of 2 cm² areas are assembled as the working

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electrodes. Before electrodeposition, the FTO substrate with an exposed area of $1\text{ cm} \times 2\text{ cm}$ was first degreased in acetone and ethanol by ultrasonication for 15 min, and lastly well rinsed with distilled water. In addition, $1\text{ cm} \times 1\text{ cm}$ n-type Si wafer pieces were cut and used as substrates. The latter were cleaned in a 5% HF solution and then immediately transferred to the electrodeposition cell.

The electrochemical depositions were performed using a VoltaLab 40 potentiostat/galvanostat controlled by a PC. The electrodeposition mechanisms were studied by cyclic voltammetry (CV) at a scan rate of 20 mV s^{-1} . The nucleation behavior of the Co films was analyzed with the theoretical growth model.

3. Results and discussion

The electrochemical nucleation and growth processes involved in the initial stages of cobalt electrodeposition on FTO and n-type Si substrates were investigated by cyclic voltammetry and potentiostatic transient measurements. The cyclic voltammograms in Fig. 1a and b show the electrochemical behavior during Co electrodeposition onto FTO and n-type Si(100) surfaces in the sulfate solution. The CV curves recorded between 0.6 and -1.5 V vs SCE are related to deposition and dissolution of metals. The sharp increase of the cathodic current observed at potential more negative than -1.15 and -0.92 V for Co deposited on FTO-coated glass and n-Si(100) surfaces electrodes, respectively, indicates an increase of the density nuclei and the crystal growth. The cobalt reduction current peak is observed at -1.36 and -1.27 V into FTO and n-Si(100) surfaces, respectively, followed by a significant increase in the cathodic current for all curves, which can be associated with proton reduction. Furthermore, from Fig. 1a one can observe an intense anodic peak with a shoulder during the cobalt dissolution. This shoulder, reported in literature [13–18], could be related to the dissolution of hydrogen and to that of cobalt deposited previously during the direct potential scan [14]. Moreover, from Fig. 1b, the only one anodic peak is associated to oxidation of Co. Although the general profile of these two voltammograms (Fig. 1) has the same behavior for both substrates, some important issues can be pointed out: (i) the overpotential of the cobalt deposition onto n-Si(100) is smaller than the one in FTO-coated glass substrate and (ii) the dissolution current peak related to the rich hydrogen phase is more evident in the Co electrodeposition onto FTO.

In order to determine the type of control limiting the Co deposition process, a plot of peak current (i) vs the square root of scan rate

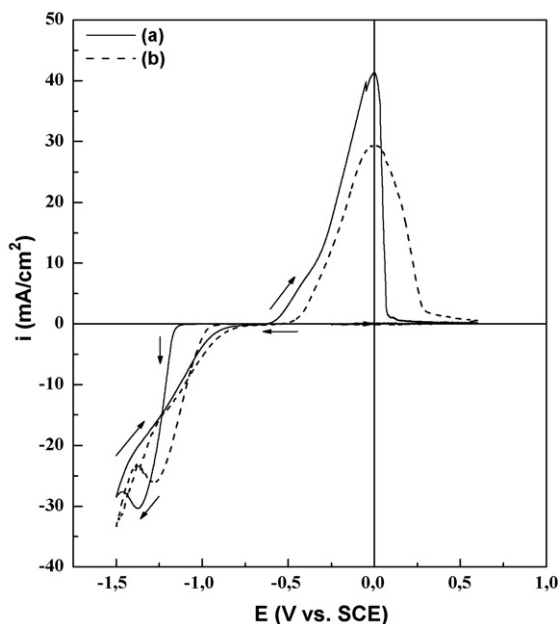


Fig. 1. Cyclic voltammograms of Co on (a) FTO and (b) n-type Si electrodes from aqueous solution of $0.25\text{ M CoSO}_4 + 1\text{ M Na}_2\text{SO}_4 + 0.5\text{ M H}_3\text{BO}_3$. Scan potential rate of 20 mV s^{-1} .

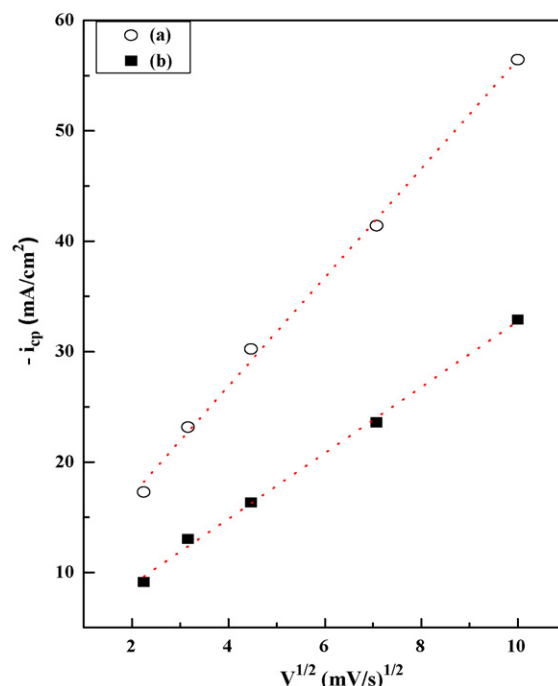


Fig. 2. Plot of peak deposition current (i_{pc}) vs square root of scan rate ($v^{1/2}$), for cobalt deposition onto (a) FTO and (b) n-type Si, respectively, at the same conditions as in Fig. 1. Experimental data (square and circle). Line corresponds to the linear adjustment.

for the deposition process is shown in Fig. 2. A linear relationship was found for both cases, and then the nucleation process can be defined as a diffusion-limited process.

Chronoamperometry is an important diagnostic electrochemical technique as it provides the current transients, used by Scharifker and Hills [19] to describe the nucleation process: instantaneous and progressive. The first nucleation type corresponds to a slow growth of nuclei on a less number of active sites, all activated at the same time. The second one corresponds to fast growth of nuclei on many active sites, all activated during the course of electroreduction [20]. Hence, the size distribution for instantaneous nucleation is expected to be much narrower than for progressive nucleation. It is well known that the analysis of current time transient is an important tool for studying the kinetics of electrocrystallization [4].

Using information gained from the cyclic voltammetric experiments, different potentials were applied to the clean FTO and n-Si surfaces. In order to examine the nucleation of Co at the electrode surface, the current was recorded as a function of time. Fig. 3 shows a family of current–time transients for the deposition of cobalt at potentials in the range of -1.10 to -1.30 V vs SCE onto FTO-coated conducting and n-type Si surfaces, respectively. These transients are typical of those for a metal deposition process involving 3D nucleation and diffusion-controlled growth [19]. At very short time, a sharp decrease in the current is observed and in the succeeding part of the transient, the current increased with time and passed through a maximum value, i_{max} , at the time t_{max} . The decreasing part of the transients obeys the Cottrell equation. For a less negative potential, the current gradually decreased with time without reaching a maximum. The decrease in current in the initial stages of the transients is related to double layer charging. Then the current rises to a steady-state value for a given potential, which is determined by diffusion.

In this case no overlapping of growing nuclei is considered, i.e., only isolated nuclei are present on the surface. From the Scharifker

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