

Investigation of nucleation and growth mechanism during electrochemical deposition of nickel on fluorine doped tin oxide substrate



Ali Mashreghi*, Hajar Zare

Department of Materials Science and Engineering, Shiraz University of Technology, Shiraz, 71555-313, Iran

ARTICLE INFO

Article history:

Received 17 January 2016

Received in revised form

9 March 2016

Accepted 10 March 2016

Available online 11 March 2016

Keywords:

Electrochemical deposition

Chronoamperometry

Nickel

Fluorine doped tin oxide

ABSTRACT

Electrochemical deposition is an alternative method for metallization of semiconductors due to its low cost, simplicity and scalability. Knowing the mechanism of nucleation and growth during electrochemical deposition of metal films on semiconductor substrates is required for obtaining metallization with superior performance. In the present work, the mechanism of nucleation and growth during electrochemical deposition of Ni on fluorine doped tin oxide (FTO) substrate was investigated using a physical model which was proposed by Scharifker-Hills in 1983. Voltammetric and chronoamperometric measurements were performed using three electrodes electrochemical cell. Scan rate dependence of anodic and cathodic peaks of voltammograms showed that the nucleation and growth are controlled by diffusion of Ni^{2+} ions to growing centers. Moreover, the measured current transient curves were compared to those calculated from Scharifker-Hills model for both instantaneous and progressive nucleation mechanisms. It was found that instantaneous nucleation mechanism governs the nucleation and growth of Ni on FTO substrate during electrochemical deposition.

© 2016 Elsevier B.V. All rights reserved.

1. Introduction

Metallization of semiconductors is one of the important technological processes which is employed in different industries, such as microelectronic, optoelectronic, magneto-optic and photovoltaic industries. Metallization is usually employed for the fabrication of grid network of photovoltaic modules, Schottky barriers, diffusion barriers, ohmic contacts, interconnections and multilayer read/write heads. Metallization of semiconductors is usually carried out by physical vapor deposition techniques, such as molecular beam epitaxy and sputtering [1,2]. However, electrochemical deposition technique has received considerable attention as an alternative approach for deposition of metallic films on semiconductor surfaces, due to its lower cost, more scalability and more simplicity [3,4]. Electrochemical deposition of metals on semiconductor surfaces differs significantly from that of metals on metallic surfaces. Due to the weak interaction energy between adsorbed metal atoms and semiconductor surface, electrochemical deposition of metal

films on semiconductor surfaces requires high overpotential and it follows a three dimensional (3D) island formation mechanism, also known as Volmer-Weber mechanism [5,6]. According to this mechanism, 3D nucleation takes place at possible active sites of substrate surface and then all nuclei grow three-dimensionally until they collide with each other to form a continuous metallic film [7]. Thus, for the formation of metallic film with superior characteristics it is required to understand the mechanism of nucleation and subsequent growth of nuclei at early stage of electrochemical deposition.

In 3D island film formation, the nucleation and the subsequent diffusion controlled growth can take place by two different mechanisms; instantaneous nucleation and progressive nucleation [5]. Instantaneous nucleation takes place when the rate of nucleation is faster than subsequent growth rate of nuclei. In this case, all nuclei are formed within very short time at early stage of electrochemical deposition. In progressive nucleation, the nucleation rate is comparable to the subsequent growth rate and the nucleation process will continue while priori formed nuclei are growing. A most successful physical model for the description of 3D nucleation with subsequent diffusion controlled growth is that proposed by Scharifker and Hills [8]. Current transient technique, also known as

* Corresponding author.

E-mail addresses: mashreghi@sutech.ac.ir, alimashreghi@yahoo.com (A. Mashreghi).

chronoamperometry, is a well-known electrochemical technique for determining the mechanism of nucleation and growth. In this technique, variation of current versus time is recorded under a constant applied working electrode potential. Then, mechanism of 3D nucleation and growth and some other information can be determined from the shape of the measured current transient curve, using a suitable physical model proposed by Scharifker and Hills. Using this method, the mechanism of nucleation and growth, under diffusion controlled mode, has been studied for the electrochemical deposition of different metals on different semiconductor substrates [5,6,9–14].

Metallized current collecting grid network is an essential part of 1st, 2nd and 3rd generation solar cells [15–17]. Dye sensitized solar cell (DSSC), as a third generation solar cell, is usually fabricated on fluorine-doped tin oxide (FTO) coated glass and thus, their current collecting grid network is metallized on the FTO surface, which is an n-type transparent semiconductor [18–21]. Requirements of DSSC metal grid network are its corrosion resistance against I^-/I_3^- redox couple of electrolyte and its low dark current density to electrolyte. Recent investigations have shown that Ni is the most appropriate choice for current collecting metal grid of DSSC [19,21]. Several techniques have been employed for deposition of Ni on FTO surface, such as physical vapor deposition and electrochemical deposition [19,21–24]. Again, lower cost, more scalability and more simplicity are the advantages of electrochemical deposition of Ni on FTO. However, discontinuity and low adherence of coating are two important issues in electrochemical deposition of metals on semiconductors and investigations to address these issues are very scarce. In this respect, knowing and studying the mechanism of nucleation and subsequent growth at early stage of electrochemical deposition of Ni on FTO surface can be useful for subsequent investigations on improving continuity and adherence of Ni coating on FTO. However, to the knowledge of the authors, the mechanism of nucleation and subsequent growth at early stage of electrochemical deposition of Ni on FTO surface has not been studied yet.

In the present work, the mechanism of nucleation and growth at early stage of Ni electrodeposition on FTO surface was studied by cyclic voltammetry and chronoamperometry methods. The measured current transient curves were interpreted using the physical model of Scharifker and Hill.

2. Experimental

FTO coated glass (solaronix) with 15 Ω /square sheet resistance was used as substrate. Before electrochemical deposition, FTO surface was ultrasonically cleaned in acetone, isopropanol and ethanol, respectively. The Watt's bath was used for electrochemical deposition. The composition of bath was; 256 g/L $NiSO_4 \cdot 6H_2O$ (Kimia-mavad Co., 99.0%), 32 g/L $NiCl_2 \cdot 6H_2O$ (Kimia-mavad Co., 99.0%) and 40 g/L H_3BO_3 (Kimia-mavad Co., 99.0%) dissolved in deionized water. At this composition pH of bath was 3.9. Electrochemical deposition was performed at 45 $^\circ C$. The effective area of FTO during electrochemical deposition was 0.5 cm^2 .

Electrochemical measurements were performed using three electrodes electrochemical cell. Reference electrode, working electrode and counter electrode were Ag/AgCl, FTO and Ni, respectively. Potentiostat/galvanostat (Ivium, Verten) was used for voltammetric and chronoamperometric measurements. The voltammetric measurement was performed at three scan rates; 5, 30 and 150 mV/s. Current transient curve was measured by chronoamperometric technique. This measurement was carried out by stepping the potential from -0.300 V vs Ag/AgCl (as initialization step) to different potentials; -0.750 , -0.780 , -0.800 , -0.825 , -0.850 , -0.880 and -1.000 V vs Ag/AgCl. The original curves were reported, without any smoothness. To exactly determine the maximum point of

current transient curve, a polynomial curve was fitted to it around the peak. In addition, scanning electron microscopy (SEM) and x-ray diffraction (XRD) methods were used for morphological analysis and phase identification, respectively.

3. Results and discussion

Fig. 1 shows the voltammograms measured at different scan rates; 5, 30 and 150 mV/s. The equilibrium reduction potential of Ni^{2+}/Ni system was determined from crossing of reverse branch of voltammograms with potential axis, (where the current density is zero) and it was equal to -0.4 V vs Ag/AgCl. According to this figure, the electrochemical deposition of Ni on FTO requires high overpotential about 0.4 V, which implies the high energy barrier against nucleation. High overpotential required in electrochemical deposition of metals on semiconductor substrates has been reported in literature [5,10,11,22,24]. In anodic part of voltammograms, the anodic peak is clearly observed, however in cathodic part, the cathodic peak is not observed and the absolute value of cathodic current density increases continuously with increasing overpotential. The absence of cathodic peak in voltammograms, corresponding to electrochemical deposition of Ni on other semiconductor substrates, was reported in previous works [14,22–25]. One reason of this observation might be the side reduction of H^+ ions at high negative potentials [5,14]. Anodic peak of Fig. 1 shows a shoulder which can be related to dissolution of hydrogen and of previously deposited Ni. Also, the main anodic peak is associated to oxidation of Ni [11].

Furthermore, by increasing the scan rate, the anodic peak maximum increases and its peak position shifts to more positive potentials. Also, the cathodic current density increases and its peak position shifts to more negative potentials with increasing the scan rate. This dependence of cathodic peak on the scan rate can be deduced from the slope of forward cathodic branch and the potential at which the falling portion of cathodic curve begins, although the cathodic peak can not be observed. These observations are characteristics of diffusion-limited electrochemical deposition process [6,11,14,26]. It predicts that the nucleation and subsequent growth of Ni on FTO, during electrochemical deposition, are controlled by diffusion of Ni^{2+} ions to the growing centers, which is prerequisite for the applicability of Scharifker-Hills model [8].

Chronoamperometry was used to obtain the current transient

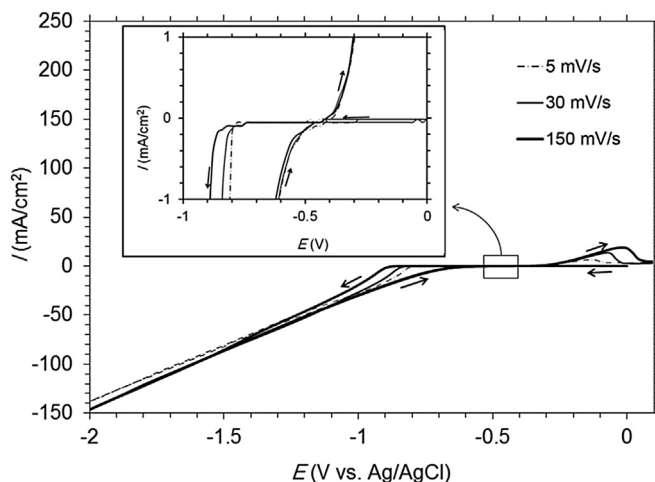


Fig. 1. Voltammograms for electrochemical deposition of Ni on FTO at different scan rates; 5, 30 and 150 mV/s.

Download English Version:

<https://daneshyari.com/en/article/1785381>

Download Persian Version:

<https://daneshyari.com/article/1785381>

[Daneshyari.com](https://daneshyari.com)