Electrodeposited copper on indium tin oxide. Reaction and nucleation mechanisms

Ahmed Zouaoui

Laboratoire : Croissance et Caractérisation de Nouveaux Semiconducteurs (LCCNS),
Faculté de Technologie, Université Ferhat Abbas Sétif 1, 19000 Sétif, Algeria.

Abstract :

In this paper, we report on an analysis carried out by using cyclic voltammetric (CV) and chronoamperometric (CA) techniques on the reaction and nucleation mechanisms of electrodeposited copper on indium-doped tin oxide (ITO)-coated glass substrates from sulfate solutions. The present investigation has been performed in an acid solution at pH 5. The Scharifker and Hills model were used to analyze current transients. At relatively low overpotentials, the copper deposition can be described by a model involving instantaneous nucleation on active sites and diffusion-controlled 3D growth. The values of diffusion coefficient D for Cu^{2+} ions are estimated. Atomic force microscopy (AFM) has been used to check on the samples' surface morphology.

Key words: Copper, Electrodeposition, Voltammetry, Chronoamperometry, AFM.

1. Introduction

Electrochemical deposition of copper onto metallic substrates plays an important role in the electronic industry. Copper deposition is widely used for applications in ultra-large-scale interconnection technology where the production of conductive films on different substrates is performed [1]. The control of the electrodeposited copper film properties is one of the most important aspects to solve. The addition of organic compounds to electrolytic baths is widely used to control the plating process as well as the quality and properties of the copper deposits [2]. Copper electro-crystallization and morphology deposition mechanisms on foreign metal substrates are being extensively studied using various techniques [3].

Copper nucleation mechanisms have been investigated on substrates such as vitreous carbon [4], sputtered TiN [5] and copper [6], from solutions containing sulfates [7], pyrophosphate [6] and fluoroborate [5]. Instantaneous copper nucleation mechanisms have been reported to be responsible in each of these studies, despite the fact that from the analysis of the electrode images of the fluoroborate solutions [5] indicates progressive nucleation mechanisms. Furthermore, it has been observed [7] that the type of nucleation mechanism is highly dependent on the pH solution and the supporting electrolyte presence.

Despite the technological importance of metal/semiconductor contacts for the production of Schottky junctions, copper electrodeposition on semiconductor surfaces has been less explored. The change in the nature and electrical properties of the substrates would modify the characteristics of the deposition process and, as a consequence, the properties of the deposit itself [8]. In this paper we present results on the kinetics of copper electrodeposition on indium-doped tin oxide (ITO)-coated glass electrodes from acid solutions.

*Corresponding author: Address: Faculté de Technologie, Université Ferhat Abbas Sétif 1, 19000 Algérie. E-mail : a_zouaoui_dz@yahoo.fr

2. Experimental

Copper thin films have been electrodeposited from a sulfate solution containing $CuSO_4$, $5H_2O$ and Na_2SO_4. The deposition process has been carried out at ambient temperature in a three electrodes cell with a platinum wire counter electrode and a saturated calomel reference electrode (SCE, + 0.241V vs. SHE). Indium-doped tin oxide (ITO)-coated glass substrates with an exposed area of $0.5x1.0$ cm^2 have been used as the working electrode. Prior to the electrodeposition, ITO substrates were first degreased in acetone and ethanol for 15 mins, and then rinsed in ultrasonic distilled water bath. The electrochemical depositions were performed using a standard potentiostat PGZ-301 Voltalab coupled with a microcomputer equipped with a software voltamaster 4 program. The solutions were thoroughly deoxygenated by purging the cell with ultrapure nitrogen flow. Cyclic voltammetry was employed to obtain the electrochemical potentials for the deposition and dissolution of the metal. The nucleation behavior of copper thin films was analyzed on the basis of growth theoretical modelling.

3. Results and discussion

3.1 Cyclic voltammetry

Figure.1. shows the cyclic voltammogram of the electrochemical behavior of Cu during electrodeposition onto the ITO surface substrate in the sulfate solution. The CV curves were recorded between 0.6 and −0.6 (V vs. SCE) at a scan rate of 0.05 V/s in relation to the deposition and dissolution of copper. The sharp increase in the cathodic current that can be observed at the negative potential −0.1V is an indication of an increase in the nuclei density and to crystal growth. The copper reduction current peak is observed at −0.27V. In the reverse scan, the intense anodic peak due to the dissolution of copper is observed at around a potential of 0.11V with the appearance of a shoulder during the copper dissolution.
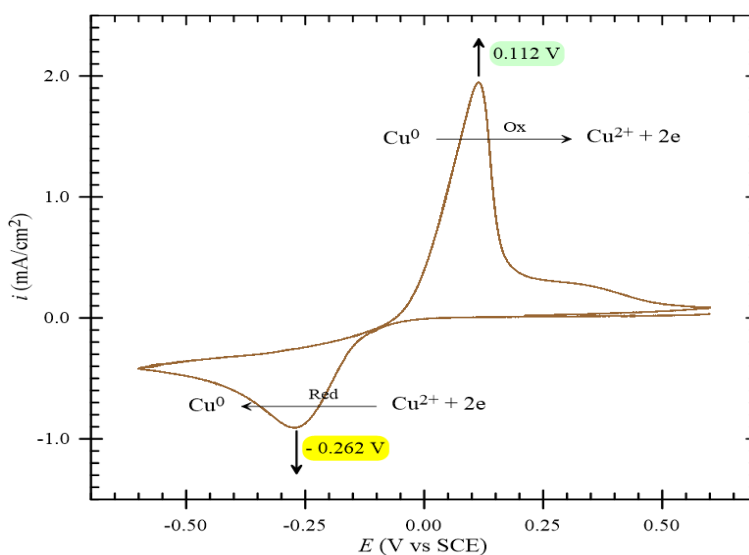

Figure 1: The cyclic voltammogram of Cu on ITO-coated glass substrate from an aqueous solution of 0.008 M $CuSO_4$ + 0.5M Na_2SO_4 with the scan potential rate of 50 mV/s.

Furthermore, in the CV curves, it is worth noting the presence of crossovers of the cathodic and anodic branches, typical of the formation of a new phase, involving a nucleation that is followed by a diffusion-limited growth process [9]. Fig.1 indicates also that copper can be deposited at a potential that is lower than −0.15 V during the negative potential sweep and that an underpotential copper deposition does not occur. The absence of underpotential copper deposition indicates a weak deposit-substrate interaction, i.e. the early stages of the electrodeposition of Cu on the ITO electrode, corresponding to a Volmer–Weber growth mechanism.

3.2 Effect of the scanning rate

The effect of the scanning rate on the cyclic voltammetry at a pH of 5 is shown in figure 2. The voltammograms, starting all from + 0.6 V, were scanned towards the negative direction at rates ranging from 5 to 100 mV/s. From figure 2, the cyclic voltammograms are characterized by the cathodic and anodic peaks.
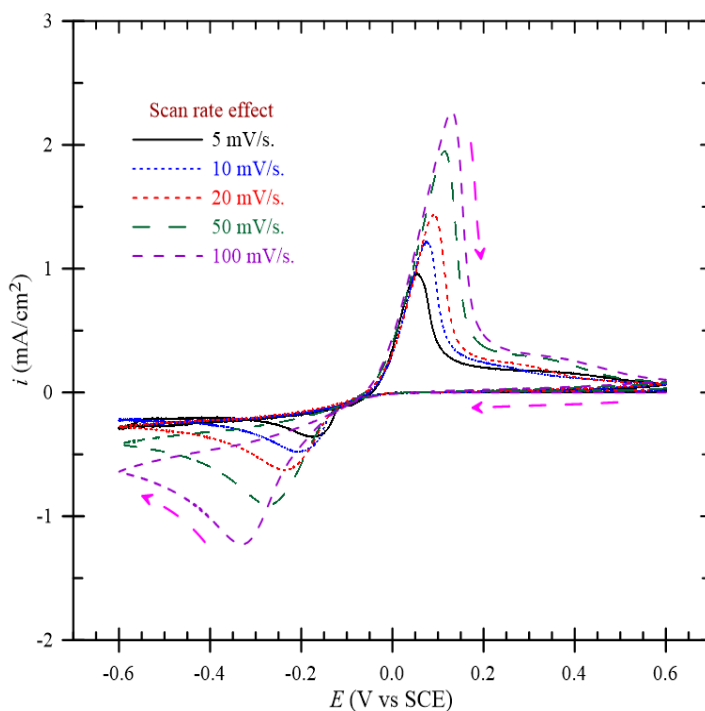

Figure 2 : Cyclic voltammetry of Cu^{2+} (0.008 M) in pH 5 at scan rates ranging from 5 to 100 mV/s.

In order to determine the type of control limiting the Copper deposition process, a plot of peak current (i) versus the square root of scan rate (υ) for the deposition process is shown in figure 3.
A linear relationship was found, and then the nucleation process can be defined as diffusion limited process.
Formation of new phases generally occurs through nucleation and growth mechanisms and the corresponding current transients can provide valuable information about the kinetics of electrodeposition.
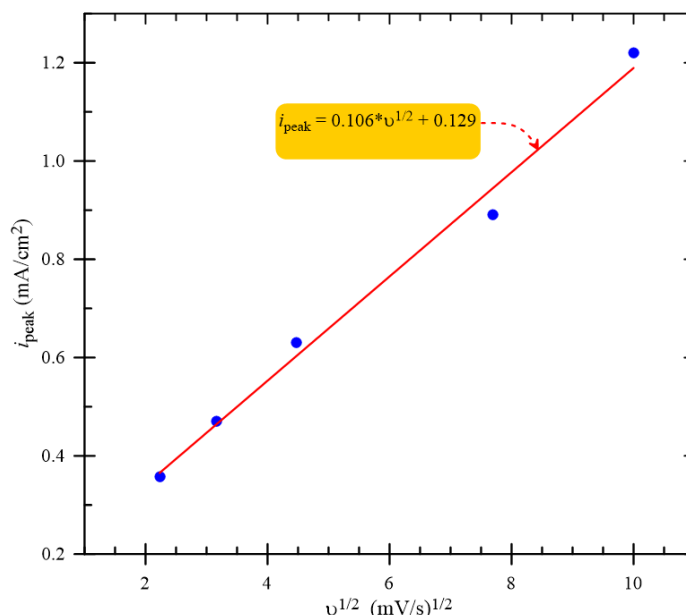
Figure 3 : Plot of the peak deposition current (i_{peak}) against the square root of the scan rate ($\upsilon^{1/2}$), for copper deposition onto ITO-coated glass substrates.

3.2 Chronoamperometry

Chronoamperometry (CA) was used to study the nucleation of copper mechanisms. In order to ensure the mass-transfer limitation, deposition potentials were selected from the corresponding CV's on the more negative side of cathodic peak. In the absence of a nucleation process, the electrochemical equivalent of the potential step is represented by a current transient that persists until the steady-state mass-transport controlled reaction is reached, as described by the Cottrell equation [10]:

where i is the current density, n the number of electrons involved, F the Faraday constant, D the diffusion coefficient, C_0 the concentration of species in the bulk, and t the time. For homogeneous reactions, current transient initially forms an abrupt signal and then promptly decays to the steady-state current. For heterogeneous reactions, nuclei formed on the surface contribute to the overall surface area by defining discrete diffusion zones that control the supply of reactants from the bulk of the solution. The resulting current transient deviates from the theoretical, described by Eq. (1), producing a peak instead of a sharp signal. When the individual diffusion zones eventually overlap, encompassing the entire electrode surface area, the reaction comes to a steady state as described by the Cottrell equation.

3.2.1 Chronoamperometry and nucleation modeling

In order to determine the kinetics of nucleation and growth during the early stages of copper deposition the potential step method was employed. The nucleation process was analyzed by selecting an initial potential (-0.15 V) where no deposition of copper is detected, and a final

potential value (E_f), located in the potential region of the cathodic current peak (-0.325 V < E_f < -0.225 V).

Figure 4 shows the current density-time transients (i-t) for copper deposition on ITO surfaces from 0.008 M CuSO4 obtained at different potentials. The i-t transients exhibit the expected behavior with an initial increase in current density due to the nucleation process and a maximum value, i_{max}, reached at t_{max} time. The maximum in current is followed by a decreasing part of the transient, according to a diffusional control. For long times, all the current transients follow a diffusional control as described by the Cottrell equation (1).
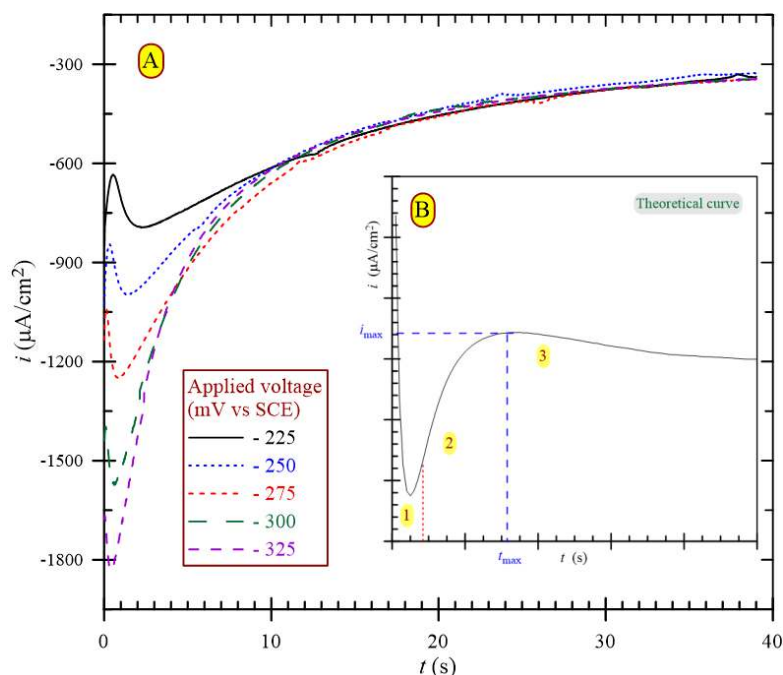

Figure 4 : Transient current after the application of several potentials A: a) -225, b) -250, c) -275, d) -300, e) -325 mV/SCE on ITO electrode ; B : theoretical model

3.4 Morphology of the deposits

AFM surface topography gives further support to theses results of nucleation mechanism. Figure 5 shows typical ex situ 3D AFM image of ITO (**A**) uncovered and ITO/Cu (**B**)substrate, the Copper films electrodeposited at -0.3 V for 200 s.

The films have uniform, compact and granular structure. Also, the figures reveal that the Cu cover all the surface of ITO. From the AFM measurements the root mean square (RMS) surface roughness was calculated for Cu/ITO substrate. The RMS parameter is equal to 362 nm. This shows that when deposits are enriched in copper, the growth of RMS is observed.
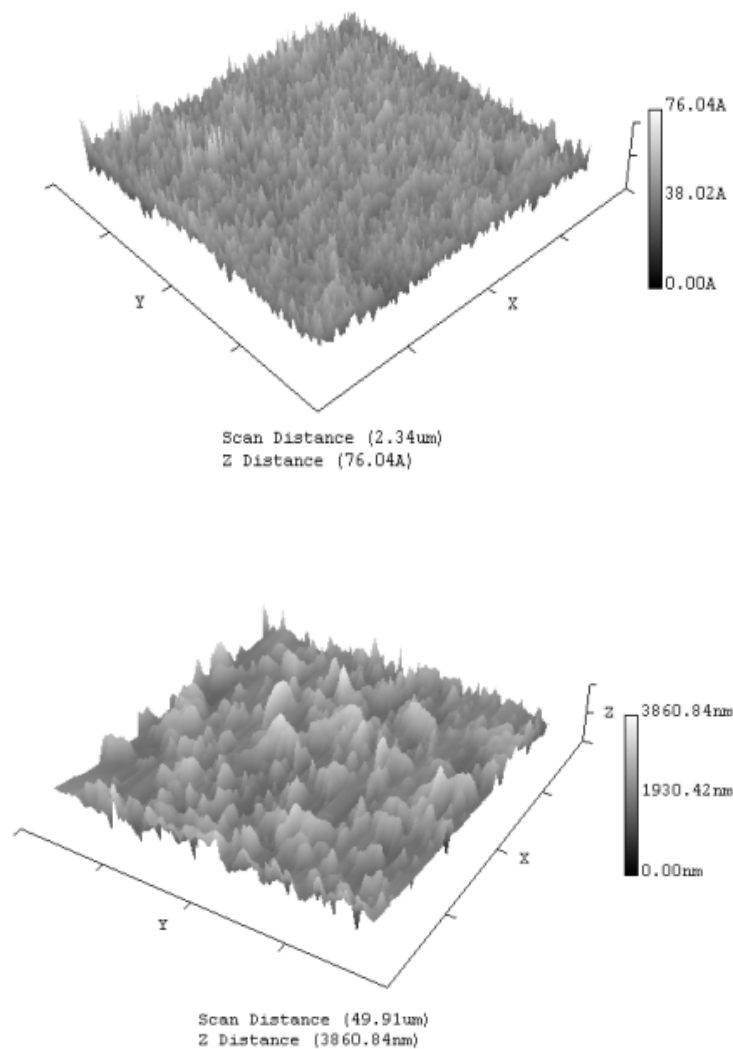
Figure 5 : 3D AFM images of the surface topography of (a) ITO, (b) ITO/Cu electrochemically prepared.

4. Conclusion

This study confirms the possibility of obtaining metal deposits of copper on a semiconductor substrate in an electrolyte solution of sulfate pH5.The electrochemical methods show that the copper electrodeposition reaction is diffusion controlled electrochemical species. Also, it has been demonstrated by application of a theoretical model of nucleation-growth (3D) diffusion limited, the deposited layers follow a model of instantaneous nucleation. Morphological characterization conducted by AFM indicates an islet morphology (3D) extended over the entire surface with a homogeneous distribution of grains.

References

[1] D. Landolt, J. Electrochem. Soc. 149 (2002) S9–S20.

[2] D. Grujicic, B. Pesic, Electrochim. Acta 50 (2005) 4426–4443.

[3] A.L. Portela, M. Lopez Teijelo, G.I. Lacconi, Electrochim. Acta 51 (2006) 3261– 3268.

[4] A.I. Danilov, E.B. Molodokina, A.A. Baitov, I.V. Pobelov, Yu.M.Polukarov, Russ. J. Electrochem.38 (7) (2002) 836.

[5] G. Oskam, P.M. Vereecken, P.C. Searson, J. Electrochem. Soc. 146(4) (1999) 1436.

[6] A. Radisic, J.G. Long, P.M. Hoffmann, P.C. Searson, J. Electrochem.Soc. 148 (1) (2001) C41

[7] D. Grujicic, B. Pesic, Electrochim. Acta 47 (2002) 2901–2912.

[8] J. Sasano, R. Murota, Y. Yamauchi, T. Sakka, Y.H. Ogata, J. Electroanal. Chem.559 (2003) 125–130.

[9] R. Sonnenfeld, J. Schneier, P.K. Hansma, R.E. White, J.O'M. Bockris, in: B.E. Conway (Ed.),Modern Aspects of Electrochemistry, vol. 21, Plenium, New York,1990.

[10] Southampton Electrochemistry Group, in: T.J. Kemp (Ed.), Instrumental Methods. In Electrochemistry, Ellis Horwood Ltd., Chichester, UK, 1985.