Electrochimica Acta 54 (2009) 1529–1536

Contents lists available at ScienceDirect

Electrochimica Acta

journal homepage: www.elsevier.com/locate/electacta

Influence of organic additives on the initial stages of copper electrodeposition on polycrystalline platinum

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ARTICLE INFO

Article history:
Received 25 March 2008
Received in revised form
16 September 2008
Accepted 17 September 2008
Available online 5 October 2008

Keywords:
Copper electrodeposition
Thiourea
Saccharin
Electrochemical quartz crystal microbalance
X-ray photoelectron spectroscopy

ABSTRACT

Effects of two additives, thiourea and saccharin, on copper electrodeposition from acid sulphate solutions were investigated by different electrochemical methods (cyclic voltammetry, chronoamperometry, and electrochemical quartz crystal microbalance) as well as by different observation techniques (scanning electron microscopy and atomic force microscopy). The morphology of copper coating obtained with thiourea leads to a smooth and bright deposit whereas it is only slightly modified by saccharin. The electrochemical reactions of copper electrodeposition were modified by the formation of complexes between thiourea and copper. However, in presence of saccharin, the kinetics and morphology of copper coating remain unchanged. From X-ray photoelectron spectroscopy analysis, thiourea was found to react with copper or copper ions by strong bond formation between the sulphur atoms of thiourea molecule and copper. This is the evidence of the adsorption of thiourea on the coating. Moreover, the thiourea action starts in the initial stages, allowing a homogeneous nuclei size and a large nuclei density. Finally, the nucleation mechanism of electrodeposition appears to be modified according to the additives used.

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1. Introduction

Integrated circuit size becomes increasingly small in the electronic industry, with the consequence that the copper electrodeposition process has been used extensively to replace aluminium as metal for connectors. Copper can be deposited by many techniques, chemical vapor deposition, physical vapor deposition, electroless deposition and electrochemical deposition. This last technique offers many advantages: it is the least expensive, it has the highest deposition rate, the lowest toxicity and is readily adoptable [1–3]. The main electrolytes used for copper electrodeposition are acidic and contain copper sulfate as a metal source [1,4–8], but apparently electrical properties as well as resistance to corrosion have to be warranted. This can be achieved by small amounts of organic additives, such as DPS [9], PEG [9–12], SPS [10,11], IT-85 [13,14],thiourea [13,15–24], to the copper electrolytes. Thiourea is one of the most common organic additives, particularly in copper sulphate electrodeposition, and is known to improve the required qualities like conductivity [9,18], brightness [13,15,22], smoothness. Some studies are even dedicated to evaluating its use for integrated circuits [16,18,23]. It influences the morphology of copper coatings by decreasing the grain size, ensuring smoother and brighter films [15,17,19–22,24,25]. This effect is the consequence of the action of this additive on the electrochemical reactions. Thiourea forms complexes with copper ions (Cu(II) or Cu(I)). The oxidised form of thiourea (formamidine disulphide (FDS)) also yields complexes with cuprous ions [15,17,20,24,26–29]. Saccharin is another organic additive frequently used, in particular for cobalt or nickel electrodeposition, and contains sulphur and nitrogen. It acts as a levelling agent and brightener and has been reported to have an effect on the decrease of internal stress [30–33].

This paper presents the investigation of effects of two additives (thiourea and saccharin) on the electrodeposition of copper and in particular the influence of these additives on the initial stages of copper electrodeposition. While many authors have shown the influence of additives on the copper morphology [13,16,21,23,24,34,35] or on the electrochemical reactions, by the formation of different complexes which block the active sites [17,24,26–29,36], some of them have investigated the first stages of copper electrodeposition in presence of additives by chronoamperometry [19,21,37,38] to determine the nucleation mechanism. Most of these studies have used glassy carbon as substrate electrode, sometimes gold, but more rarely platinum. In the few such studies reported in the literature, one deals with underpotential deposition on single crystal platinum [39], and the other one is a chronoamperometric study on polycrystalline platinum [38]. The nucleation

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doi:10.1016/j.electacta.2008.09.052

mechanism appears to be modified even for small changes in the nature of the substrate, copper and thiourea concentrations and applied potential.

The aim of this work is to give evidence of the influence of thiourea and saccharin in the initial stages of copper electrodeposition by combining different analysis techniques for a given set of operating conditions i.e applied potential as well as copper and organic additive concentrations, in a range which makes possible the different nucleation mechanisms. The chosen substrate is a polycrystalline platinum electrode, which presents advantage to be a metal without the risk of copper diffusion.

Thus, an electrochemical study using polarisation curves, chronoamperometry and electrochemical quartz crystal microbalance (EQCM) has been developed. The microscopic morphology has been evaluated using scanning electron microscopy (SEM) and atomic force microscopy in air (AFM ex-situ). The AFM images are taken at very short intervals to observe the nucleation mechanism. The composition of the coating and in particular the evidence of the adsorption of additives on the coating is based on X-ray photoelectron spectroscopy (XPS). This quantifies the effect of both additives.

2. Experimental

2.1. Reagents

The aqueous solution used for copper electrodeposition contains the following reagents: copper sulfate (5×10^{-3} M), sulphuric acid to adjust the pH to 1, and sodium sulfate (1 M) as background electrolyte. Saccharin (Sac) and thiourea (Tu) were added to yield a concentration of 5×10^{-4} M. All solutions were prepared from high quality MilliQ water (18 MΩ cm).

2.2. Electrochemical details

All electrochemical measurements were taken using an EQCM-equipped CHI-440 potentiostat (CH Instruments). The electrochemical measurements were carried out in a conventional three-electrode cell. A saturated mercurous sulfate electrode (MSE, 650 mV vs. standard hydrogen electrode, SHE) was used as reference electrode, and a Pt wire was used as counter electrode. The working electrode is an 8 MHz AT-cut quartz crystal coated with 100 nm Pt film on both sides. Platinum adhesion to the crystal was enhanced by a 10 nm Ti sublayer (CHI 123). According to Sauerbrey's equation, quartz crystal frequency change (Δf) is proportional to the mass change (Δm) that occurs on the crystal, expressed as $\Delta f = -2f_0^2 \Delta m/[A\sqrt{(\rho\mu)}]$, where A is the area of platinum disk coated on the crystal (0.205 cm^2), ρ the density of the crystal (2.684 g cm^{-3}) and μ the shear modulus of quartz (2.947×10^{11} g cm^{-1} s^{-2}). The surface of platinum is oxidised after each experiment and dipped in an acid solution. Electrochemical quartz crystal microbalance (EQCM), polarisation and chronoamperometric curves were recorded simultaneously.

2.3. Characterisation

Scanning electron microscopy (SEM) and atomic force microscope (AFM) images were obtained from copper coatings deposited on a polycrystalline platinum disk substrate. Platinum substrates were polished to a mirror finish (1 μm diamond powder), and rinsed 7 min with ethanol in an ultrasonic cleaner prior to each experiment to ensure a reproducible surface. The copper coatings were deposited by polarisation at a potential of −650 mV/MSE over various periods of time in a three-electrode cell. For the SEM analysis, the coatings were deposited for 30 min, but only for 0.5 s for the AFM ones. SEM experiments were performed with a JEOL JSM 5600 model. AFM analysies were conducted using a PSIA XE-150 AFM in non-contact mode (320 kHz). Measurements were performed in air (ex situ) using a high resonance frequency silicon probe (51 N m^{-1}).

The X-ray photoelectron spectroscopy (XPS) spectra were recorded at a 35° take-off angle relative to the surface with a Surface Science Instruments spectrometer (SSX-100) using monochromatised X-ray Al Kα radiation (1486.6 eV). The analysed core-level lines were calibrated against the C 1s binding energy set at 284.6 eV. The pressure in the analysis chamber was maintained at approximately 4×10^{-9} Torr. The signals were deconvoluted using mixed Gaussian-Lorentzian curves where the Gaussian character was set at 80%.

3. Results and discussion

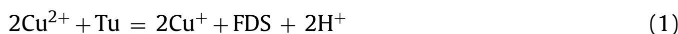
3.1. Electrochemical studies

3.1.1. Polarisation curves

Linear potential scans were performed between the open circuit potential down to −900 mV/MSE, at a scan rate of 10 mV s^{-1} using a platinum substrate in an acidic 5×10^{-3} M $CuSO_4$ solution (pH 1) with additives. Fig. 1 shows the typical polarisation curves and the associated mass change recorded simultaneously during copper electrodeposition from solution with and without additives.

In the additive free solution, the only species able to undergo an electrochemical reduction are cupric ions, while in the case of solution with additives, saccharin, for example, can also be reduced to different compounds. The main products are *o*-toluene sulphonamide and benzamide [40–42].

In presence of thiourea, both cupric ions and thiourea species are concerned. Several authors have revealed that thiourea is known to form stable complexes with both cupric and cuprous ions in acidic solution [21,26–29]. Thiourea (Tu) can also be oxidised in the presence of cupric ions to produce cuprous ions and formamidine disulphide (FDS):



$$2Cu^{2+} + Tu = 2Cu^{+} + FDS + 2H^{+} \quad (1)$$

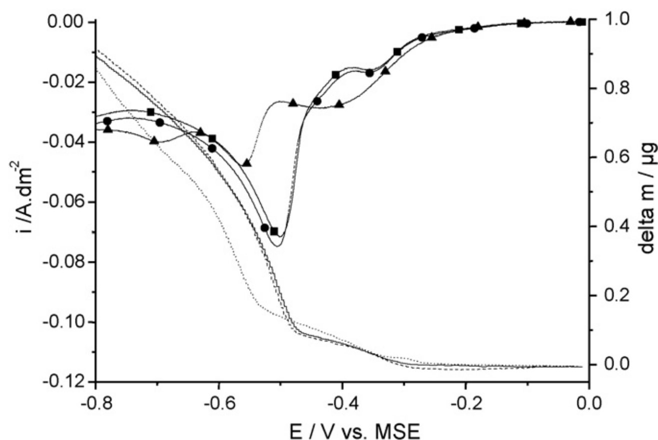


Fig. 1. linear potential scan obtained on platinum substrate immersed in 1 M Na_2SO_4, pH1 with 5×10^{-3} M $CuSO_4$ (■-), containing 5×10^{-4} M saccharin (●), containing 5×10^{-4} M thiourea (▲), and mass change recorded simultaneously: with 5×10^{-3} M $CuSO_4$ (—), containing 5×10^{-4} M saccharin (- - -), containing 5×10^{-4} M thiourea (···). Scan rate: 10 mV s^{-1}.

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