Available online at www.sciencedirect.com
ScienceDirect
Electrochimica Acta 52 (2007) 3105–3113
ELECTROCHIMICA Acta
www.elsevier.com/locate/electacta

Voltametry and EQCM study of copper oxidation in acidic solution in presence of chloride ions

S. Kologo[a], M. Eyraud[b,*], L. Bonou[a], F. Vacandio[b], Y. Massiani[b]

[a] *Lab. Chimie Physique et Electrochimie, University Ouagadougou 03, BP 7021, Burkina-Faso*
[b] *UMR Madirel, University Provence, Centre de Saint Jérôme, 13397 Marseille Cedex 20, France*

Received 27 July 2006; received in revised form 22 September 2006; accepted 23 September 2006

Abstract

Cyclic voltametry experiments coupled with electrochemical quartz crystal microbalance (EQCM) measurements showed the corrosion mechanism of electrodeposited copper in presence of chloride ions. The oxidation of copper in acidic solution containing high concentration of Cl^- begins with formation of Cu^+ ions. The Cu^+ concentration at the vicinity of the electrode increasing, the small solubility product of CuCl is then exceeded, leading to a CuCl precipitation on the gold covered quartz crystal used as working electrode. For highest anodic potentials, the oxidation of electrodeposited copper or CuCl precipitate phases could occur. A combination with structural techniques like SEM, EDAX, AFM and DRX gives insight into the morphology and the nature of these CuCl precipitates.

Keywords: Copper oxidation; Chloride solution; EQCM; CuCl precipitate

1. Introduction

Electrochemically deposited copper is an important material in the field of nanotechnology, particularly for the microfabrication of integrated circuit interconnects. Its better electrical conduction and high electromigration resistance make it attractive and aroused some ten years ago a new interest in the study of the mechanism of copper electrodeposition in acidic baths [1–3].

Typically, acid copper baths for electrodeposition contain $CuSO_4 + H_2SO_4$ with a small amount of additives, at concentrations up to a few millimoles per litre. In particular, chloride ions are used in most organic additive combinations [4,5]. A diligent selection of the additives makes it possible to fill submicron damascene structures without defects, a phenomenon called super-filling. However, the super-filling also creates excessive non-uniformity in terms of over-plating at sites with high pattern density. Indeed, it has been shown that the deposits have bumps over the small features and dishes over the wide ones. The extra copper must be removed by a planarization process [6,7].

At present, chemical mechanical planarization (CMP) is the primary method used for removing the extra copper and the removal rate is controlled essentially by the mechanical force. But the ability to achieve good polishing rates with CMP may be compromised by the introduction of low-*k* materials that do not have the requisite mechanical properties to endure high mechanical forces and require utilization of alternative low-stress copper removal techniques. Electrochemical dissolution methods, which can be considered as a zero-stress removal, may either be a replacement or a complement to CMP [6]. That is why electrochemical dissolution presents nowadays a technological interest, notably for surface polishing processes at a nanometric scale.

Numerous works have been devoted to copper dissolution particularly for studying the corrosion and the passivation mechanisms in aqueous media [8–13]. Copper is known to be a relatively noble metal and is un-attacked in non-oxidising acid environment. Nevertheless, most acidic solutions contain dissolved oxygen that enables some corrosion to take place [14]. Thus most of the studies made in aqueous solutions conclude on the important role of the cuprous ion Cu^+ in the dissolution mechanism. The results also show the formation of different copper oxides, such as Cu_2O which forms cathodically during electrolysis from acid solutions of copper sulphate. In presence

---

[*] Corresponding author. Tel.: +33 491 63 71 29; fax: +33 491 63 71 11.
E-mail address: meyraud@up.univ-mrs.fr (M. Eyraud).

0013-4686/$ – see front matter © 2006 Elsevier Ltd. All rights reserved.
doi:10.1016/j.electacta.2006.09.052

of chloride ions, some authors revealed the formation of copper chloride species associated with Cu_2O [10,14,15].

Even though copper dissolution has been widely studied, the subject is still of importance and more information is necessary on the species that form during the electrochemical dissolution of copper. Moreover, the use of an electrochemical quartz crystal microbalance (EQCM), which allows to follow the in situ mass change, is a useful tool to study the dissolution of copper. The formation of a CuCl complex has already been discussed for copper electrodeposition from 10 mM $CuSO_4$ + 0.1 M NaCl utilizing the EQCM technique, however this was done in acid medium (0.1 M H_2SO_4) [16,17].

In this paper, our aim was to determine the mechanism of copper dissolution in an acidic copper sulphate bath in presence of chloride ions. We used a combination of the EQCM technique with a potentiodynamic method. In this way the potentiodynamic curves (cyclic voltamograms) are easily compared to the mass evolution curves during the electrochemical process. The information coming from the two techniques allowed us to propose a sequence of chemical and electrochemical steps for copper dissolution in presence of Cl^-.

Scanning electron microscopy (SEM) coupled with energy dispersive X-ray analysis (EDAX), atomic force microscopy (AFM) and X-ray diffraction (XRD) were applied on bulk deposits partially anodised with or without Cl^- to support the electrochemical study.

2. Experimental

A classic three-electrode cell was used for electrochemistry experiments. The saturated calomel electrode (SCE) was used throughout the work, and all potentials are given with respect to this reference. The counter electrode was a platinum grid.

For EQCM measurements, quartz crystals of nominal frequency $f_0 = 5$ MHz, gold plated on both sides (Maxtek, CA), were used as working electrode. In that case, the geometric area of the gold surface in contact with the electrolyte was 1.37 cm^2, the roughness was 4.1 nm as measured by AFM. The EQCM Maxtek PM 710 used was described in a precedent publication [18]. Prior to the measurements the EQCM sensitivity was determined using a chronoamperometry calibration method described by Vatankhah et al. [19].

The experiments were conducted with an aqueous base electrolyte consisting of H_2SO_4 1 M + $CuSO_4{\cdot}5H_2O$ 0.1 M for which chloride ions (as NaCl) were added. The solution without additive was noted Cu_0 and those containing Cl^- were noted Cu_c. The electrolytes were prepared using deionized water (18.2 $M\Omega\,cm^{-1}$) treated by a Millipore system.

Electrochemical experiments consisted in cyclic voltametry ran using a EG&G-PAR model 273 potentiostat–galvanostat coupled with the EQCM. The two instruments were controlled by the same computer running the software EG&G M270. In that way, simultaneous measurements of current evolution and mass variation on the quartz crystal were acquired as a function of the potential applied. Voltamograms and mass evolution curves were recorded according to the Cl^- concentration in solution and the potential scan parameters.

Bulk deposits were obtained under voltametric conditions, from copper solutions with and without chloride ions. In that case, the substrate was a 1.775 cm^2 vitreous carbon sample stuck with silver glue on a conductive sheet isolated from the solution by an araldite coating. The roughness measured by AFM was 5.2 nm close to the gold surface quartz one. Indeed, the surface roughness can impact on the nucleation mechanisms, entrapment of fluid or bubbles, and change in consequence the roughness of the deposit. The substrates were easily released from the support to be analyzed. Morphology and composition of the deposits after a slight electrochemical oxidation were determined by SEM and EDAX on a Cambridge S90B microscope equipped with a tungsten source. The roughness of the deposit was obtained with an AFM autoprobe CP of Park Scientific Instrument in contact mode. Low angle X-ray diffraction patterns (Siemens D-5000 diffractometer with a copper anode), were used to evidence the formation of precipitation products on the surface during oxidation.

3. Results

3.1. Electrochemical experiments

3.1.1. Determination of the EQCM sensitivity coefficient C_f

For the calibration of the EQCM, the chronoamperometry method of Vatankhah et al. [19] is used in a Cu_0 solution. The potential is stepped from an initial value $E_i = +400$ mV, where no copper is deposited on the electrode surface, to a final potential E_f between −300 and −390 mV with an interval of 10 mV. For each final potential, an I versus t curve is recorded during 60 s, and the corresponding Q versus t curve is deduced. Simultaneously, the frequency variation Δf is recorded versus time. Fig. 1a–d shows, respectively, the variations of I, Q, Δf versus time, and Q versus Δf, recorded for a final potential $E_f = -300$ mV. The graphs obtained for other potentials are all similar to these ones. The Q–t, Δf–t and Q–Δf, curves are linear after 20–25 s.

By a combination of the Faraday and the Sauerbrey laws, we can deduce the following equation to calculate the C_f value for each E_f potential

$$C_f = -\left(\frac{M_{Cu}}{zF}\right) \times \left(\frac{\Delta q}{\Delta f}\right),$$

where Δq is the charge measured from the electrochemical response in $C\,cm^{-2}$, Δf the frequency change in Hz, z the number of transferred electron, M_{Cu} the atomic mass of copper (63.5 $g\,mol^{-1}$) and F the Faraday constant. An average value of C_f is deduced from the calculated values. For the Cu_0 solution used, the average value calculated is $C_f = 21.06\ ng\,Hz^{-1}\,cm^{-2}$. This value is slightly different from the theoretical one predicted by the Sauerbrey equation (17.93 $ng\,Hz^{-1}\,cm^{-2}$) and must be taken into account for the treatment of all mass data. The data were represented as the direct mass variation (Δm) versus E or as the rate of mass change ($d\Delta m\,dt^{-1}$) versus E called massograms [20–22]. The massograms obtained are in complete analogy with the corresponding voltamograms because the rate of mass transfer can be recorded directly and compare with the