



## Preparation and characterization of copper thin film obtained by metal plasma immersion ion implantation and deposition



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### ABSTRACT

Copper thin film was obtained by metal plasma ion immersion implantation and deposition (MePIIID). The film structure was characterized by grazing incidence X-ray diffraction whereas its thickness and surface topography were evaluated by field emission scanning electron microscopy and atomic force microscopy, respectively. Rutherford backscattering spectroscopy and X-ray photoelectron spectroscopy were used to evaluate the film chemical states. Electrochemical quartz crystal microbalance (EQCM) analysis coupled to potentiodynamic polarization was employed to investigate the dissolution behavior of the MePIIID deposited layer. The copper film presented a crystalline character and its surface chemical state was mainly comprised of Cu<sub>2</sub>O. EQCM measurements provided good basis for estimating the thickness reduction and anodic dissolution rate of the as-deposited layer, proving to be a valuable tool for developing and evaluating copper-based MePIIID films for electronic applications.

### 1. Introduction

Copper and its alloys find widespread industrial applications due to their outstanding electrical and thermal conductivities [1,2]. Currently, there is a renewed interest in the corrosion behavior of these materials [3]. Such attention derives from their susceptibility to corrosion in chloride-contaminated environments which is a main issue in the electronic, pipeline and automotive industries [4–6]. Structural failure can take place due to deterioration of material's performance by chloride attack. The economic losses associated with copper corrosion are reported to be voluminous, stimulating the development of protective coatings and corrosion inhibitors [7–9]. Copper coatings can be applied in the microelectronic industry to provide a good combination of corrosion resistance and conductivity performance to electrical contacts [10,11]. However, in spite of its relative chemical stability, copper thin film corrosion is a concern in microelectronic applications.

The high sensitivity of electrochemical quartz crystal microbalance (EQCM) to mass changes has been favorably exploited to investigate deposition and dissolution of metallic thin films [12,13]. In EQCM, the mass change is obtained based on the Sauerbrey equation (Eq. (1)), where  $\Delta f$  is the frequency change,  $\Delta m$  is the mass change,  $f_0$  is the resonant frequency,  $\rho_q$  is the quartz density,  $\mu_q$  is the shear modulus of quartz and  $A$  is the electrode area exposed to the electrolyte [14].

$$\frac{\Delta f}{\Delta m} = \frac{-2\pi f_0^2}{A\sqrt{\mu_q \rho_q}} \quad (1)$$

Recently, Ralston et al. [15] employed a combination of EQCM and conventional polarization tests to study the dissolution process of magnesium in NaCl solution. EQCM proved to be reliable to monitor the online mass change either at open circuit or polarized conditions. While several authors have employed the EQCM technique to investigate the efficiency of corrosion inhibitors for copper and its alloys [16–19], the dissolution process of copper films for microelectronic applications is hardly ever reported in the literature.

Thin films obtained by the ion beam technique metal plasma immersion ion implantation and deposition (MePIIID) can have their surface chemistry easily controlled at the nanometer scale [20]. The corrosion resistance of the coated substrate can be advantageously affected by the good adhesion between the topcoat and the underlying substrate, giving rise to a robust surface treatment [21]. The use of MePIIID to produce copper films for electronic applications is hardly reported in the literature.

In this work, we investigated the dissolution process of MePIIID-deposited copper films by EQCM and potentiodynamic polarization tests. The film structure, morphology and chemical composition were studied by grazing incidence X-ray diffraction (GIXD), field emission-

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scanning electron microscopy (FE-SEM), atomic force microscopy (AFM), Rutherford backscattering spectroscopy (RBS) and X-ray photoelectron spectroscopy (XPS).

## 2. Experimental

### 2.1. Sample preparation

Copper films were deposited by MePIIID. The apparatus consists mainly of a plasma gun, a plasma filter and the sample holder. All components are mounted inside a stainless steel vacuum chamber. Plasma of the cathode material is obtained within the gun by a discharge between the cathode and the anode. A ceramic cylinder was applied to isolate the cathode (copper rod) from the anode. The plasma filter guides the generated copper plasma to the substrate and eliminates macroparticles. Details of the apparatus have been described in previous works [22–24]. The films were deposited using Si wafers and glassy carbon as substrates. Before deposition, the substrates were ultrasonically cleaned with acetone and isopropanol for 5 min. Next, the cleaned substrates were heated at 230 °C for 20 min. The deposition chamber pressure was approximately  $7 \times 10^{-4}$  Pa. High purity Cu (99.99%) was employed as cathode for obtaining the metal plasma. Plasma deposition was carried out in repetitive pulsed process. Parameters used for copper deposition were 180 A for the arc current, 5 ms of pulse duration at one pulse per second (1 Hz of frequency). The total number of pulses was 5400.

### 2.2. EQCM analysis

EQCM tests were carried out with AT-cut, gold-coated quartz crystals with nominal resonant frequency of 6 MHz (Autolab-Eco Chemie). Copper coating was deposited on the gold-coated quartz crystals following the same procedure described in Section 2.1. After deposition, the copper-coated crystals were rinsed in deionized water prior to EQCM analysis. After mounting the working electrodes in the EQCM cell, it was filled with 3.5 wt% NaCl solution. Electrochemical tests were conducted with a M101 Autolab potentiostat/galvanostat. Conventional three-electrode cell setup was employed with Ag/AgCl electrode as reference, a platinum wire as the auxiliary electrode and the copper-coated quartz crystals as the working electrodes. In order to ensure a steady state condition, samples were subjected to an initial monitoring of the open circuit potential. Next, potentiodynamic polarization curves were obtained at a scanning rate of  $1 \text{ mV s}^{-1}$  in the potential range from  $-250 \text{ mV}_{\text{Ag/AgCl}}$  versus the open circuit potential up to  $+1.0 \text{ V}_{\text{Ag/AgCl}}$ . The mass change of the working electrode was continuously recorded during the test. The tests were conducted in triplicate.

### 2.3. Film characterization

The atomic structure of MePIIID-deposited copper films on silicon (Si) substrates was characterized by GIXD and the crystalline phases were indexed using the JCPDS catalog. The analysis was performed using a Bruker D8 Discover theta-theta diffractometer provided with a Cu X-ray tube working at 40 kV and 40 mA, with wavelength of 0.1541 nm. A parallel beam optics configuration was used for the grazing incidence measurements with a Göbel mirror and a  $0.2^\circ$  divergence vertical Soller slit in the incident beam and a  $0.1^\circ$  divergence parallel plate horizontal slit coupled to a  $0.2^\circ$  vertical Soller slit in the scattered beam side. The incidence angle of the X-ray beam was fixed at  $0.6^\circ$  and the angular range was scanned from  $10^\circ$  to  $60^\circ$ , with a step size of  $0.1^\circ$  and 30 s/step.

Atomic composition of deposited copper films was assessed by RBS. Measurements were performed using  $\text{He}^+$  ion beam, with energy of 2.2 MeV, scattered at  $120^\circ$  and  $170^\circ$  (with respect to beam direction) and incident angle of  $7^\circ$ . RBS spectra were fitted using SIMNRA code.

The chemical surface state of the copper film was assessed by XPS analysis. The spectra were acquired using a ThermoFisher Scientific K-alpha<sup>+</sup> spectrometer, operating with Al-K $\alpha$  radiation source (1486.6 eV) at ultra-high vacuum at  $10^{-9}$  mbar. The shift of the binding energies was calibrated with respect to C 1s hydrocarbon contamination signal at 284.8 eV. Survey spectrum and high resolution spectra for Cu2p and O1s were recorded. Background subtraction was performed using the Smart™ algorithm.

Scanning electron microscopy was performed using a FE-SEM instrument, JMS-6701-F, JEOL, in secondary electron imaging (SEI) mode operating at 10 kV to determine the thickness of the copper film deposited on the Si substrate.

Morphological characterization of the copper layer surface has been carried out by AFM using a Nanoscope IIIA, Bruker, operating in tapping mode with scanning area of  $1.0 \times 1.0 \mu\text{m}$ .

## 3. Results and discussion

### 3.1. Coating characterization

GIXD analyses were carried out to assess the structure of the MePIIID-deposited copper film. As it can be observed from Fig. 1, the metallic copper arrangement was indexed as a single phase, according to the JCPDS catalog (04–0836). The peak identified as Si was indexed as the silicon phase (JCPDS 05-0565 catalog) related to the silicon wafer substrate.

Using Eq. (2) (Scherrer equation) [25,26], where  $D_{(hkl)}$  is the particle size perpendicular to the diffracting lattice plane,  $k$  is a constant shape factor of 0.9,  $\theta$  is the diffraction angle,  $\lambda$  is X-ray wavelength (0.1541 nm) and  $\beta$  is the full width at half maximum (FWHM), we calculated the copper average crystallite size. The peaks related to crystalline copper, (111) and (200) planes, are located at  $43.43^\circ$  and  $50.53^\circ$  ( $2\theta$ ), respectively. Based on their FWHM,  $0.72^\circ$  for (111) and  $0.96^\circ$  for (200), the crystallite sizes for the (111) and (200) planes were determined as 11.9 nm and 9.1 nm, respectively.

$$D_{(hkl)} = \frac{k \cdot \lambda}{\beta \cdot \cos \theta} \quad (2)$$

The high intensity peak observed at (111) can be associated to a face-centered cubic system of the metallic copper phase [27]. The lattice parameters were calculated according with the Bragg's Law [27] using the free software *CellCalc*. They were estimated considering a

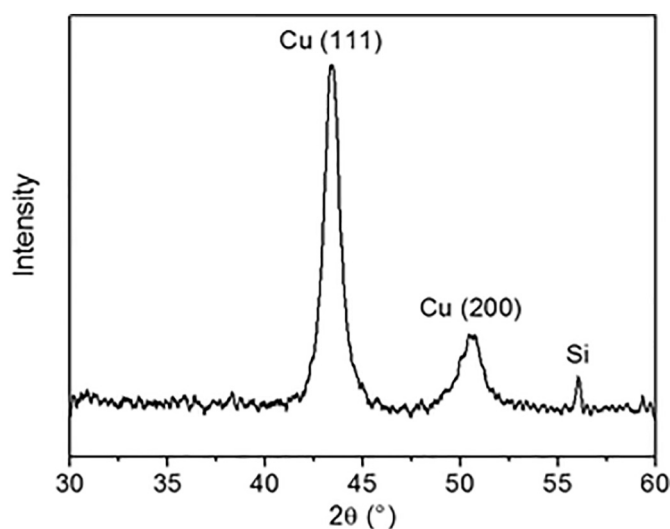


Fig. 1. GIXD pattern of the copper film obtained. The peaks were indexed as metallic copper phase according to the JCPDS catalog (04–0836). The additional peak identified as Si is related to the silicon wafer substrate (JCPDS 05-0565).

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