

Short Communication

An in-situ Study of Copper Electropolishing in Phosphoric Acid Solution

Deyu Li¹, Ning Li^{1*}, Guofeng Xia¹, Zhen Zheng¹, Jialin Wang¹, Ning Xiao¹, Wenjie Zhai², Gang Wu³

¹ School of Chemical Engineering and Technology, Harbin Institute of Technology, Harbin 150001, P.R.China

² School of Mechatronics Engineering, Harbin Institute of Technology, Harbin 150001, P.R.China

³ Materials Physics and Applications Division, Los Alamos National Laboratory, Los Alamos, NM 87545 USA

*E-mail: lininghit@263.net

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In this work, the interface film in the Cu/H₃PO₄ interface was in-situ studied by tracking the time and potential evolution of the system impedance (R_s) at high-frequency. The fluctuation of R_s upon the applied potentials was confirmed by the R_s -potential plot. A copper oxide film was found formed on the copper surface during the electropolishing process by analyzing the Mott-Schottky curve. Moreover, the copper oxides film exhibited a transition of n -type semiconductor to a p -type one.

Keywords: copper, electrochemical analysis, electrolytic polishing, ECMP, planarization, surface chemistry

1. INTRODUCTION

Cu/H₃PO₄ system was commonly used in Cu electropolishing, such as Cu electrochemical mechanical planarization (ECMP) [1, 2], and Cu chemical mechanical planarization (CMP). During the electropolishing process, the interface layer on Cu played an important role and had attracted much attention [3, 4]. Up to now, two possible mechanisms about the interface layer, the salt film and the acceptor mechanism, had been proposed[5]. The salt film mechanism assumed that there would be a solid porous passivation film at the interface, which further inhibited the metal dissolution to the bulk solution and led to smoothing during electropolishing[6]. The acceptor mechanism suggested that Cu ions complexed by water or other anions could form a viscous liquid boundary layer, hindering the dissolution by the mass transfer limitation and promoting planarization[7].

As an effective tool to characterize the interface phenomenon, electrochemical impedance spectroscopy (EIS) technique had been widely used to investigate the electropolishing process [8-12]. By tracking the magnitude of the system impedance (R_s) of the time and the applied potentials at high-frequency, Kim B S found that the evolution of R_s was closely related to the formation of a resistive film, presumably either a porous salt or viscous liquid, formed over the copper surface[13]. The changes in R_s could be interpreted as the formation of a porous salt or viscous liquid film above the electrode surface.

In this work, we studied the interface film on Cu by analyzing the evolution of R_s , and found the impedance was fluctuated with the applied potential. Moreover, the Mott-Schottky curve revealed that there also existed a copper oxide semiconductor layer on the surface of Cu except the salt film or the viscous liquid layer.

2. EXPERIMENTAL

In this study, the working electrode was a copper wire (99.99%) coated with the polyurethane resin. The wire diameter was 0.4 mm. To generate fresh metal surface for each test, a new disposable surgery blade was used to cut the wire at each time. 85% phosphoric acid aqueous solution was used as the electrolyte. An Hg/HgSO₄ electrode and a Pt foil were used as the reference electrode and the counter electrode, respectively. The CHI 660B workstation was used to carry out all the electrochemical experiments. A potentiodynamic (PD) scan was performed with a 1mV/s scan rate. The profiles of R_s vs the time and vs the potential were recorded at a frequency of 50 kHz. In this way, the evolution of R_s could be monitored with respect to time, providing an insight into the formation of the film above the bare Cu surface. In all cases, a 5 mV ac potential was imposed over the applied potentials. To evaluate the electropolishing effect at different applied potential, 10×10mm copper (99.99%) sheets were used with a rolling strip (about 30 μm wide and 2 μm deep) and were electropolished for 15 minutes. Optical profilometry images and roughness were obtained by a WGL optical profilometer (Shanghai Precision & Scientific Instrument Co. LTD). Grubbs criterion was adopted to verify the rationality of the roughness data. All potentials mentioned in this paper were relative to that of Hg/HgSO₄ reference electrode.

3. RESULTS AND DISCUSSION

Figure 1 is a typical current-voltage plot for the Cu/H₃PO₄ system. This curve is always divided into four regions. In region I, namely active region, the Cu active dissolution leads to the current peak at open-circuit potential (OCP, -0.37 V) to -0.2V and the interface layer begins to form. There is a transition zone in region II at the potential of -0.2V to -0.1V.during which the surface layer begins to inhibit the metal dissolution and results in the current descending. The plate at -0.1 to 1.1V is called the region III or passivation region, where the Cu dissolution rate equals to that of Cu ion diffusion a mass-transfer-limited current plate caused by any porous salt or viscous liquid film presents and the Cu

electropolishing happens[14]. Beyond 1.1V, the oxygen evolution arouses a sharp increment of the current, namely called region IV.

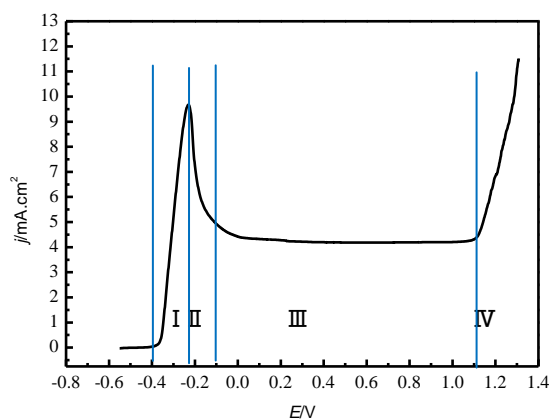


Figure 1. Voltammetric behavior of the Cu/H₃PO₄ interface measured at 1mV/s sweep rate

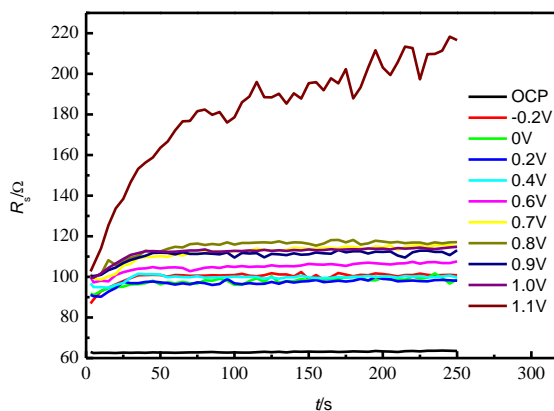


Figure 2. R_s vs time plot of the Cu/H₃PO₄ interface at an ac frequency of 50 kHz at different applied potentials

Fig. 2 shows the evolution of R_s upon time on the Cu/H₃PO₄ interface at different applied potentials. For each potential test, the Cu wire is newly cut by a new deposable surgery blade to offer fresh surface. Although it can't be assured that the section surfaces at each cut are same, just as Fig. 2 shown, all the values of R_s samely gradually increase during the initial 50 s and then reach a steady plateau. It agree well with Kim B S's claim that the total trend of R_s value does not vary with changed section surfaces at each cut. Actually, R_s is the total resistance consisted by the electrolyte resistance (R_e), the contact resistance between the electrodes and the potentiostat (R_m), and the resistance of surface film (any porous salt or viscous liquid film) on the electrode (R_f) [13, 15]. For a given system, R_m and R_e can be treated as two constants during all experiments. So any change of the value of R_s can be interpreted as the change of the surface film on the Cu electrode. Then, the increment in R_s during

the initial 50 s indicates that the surface film does gradually forms. The fluctuation of R_s value upon the applied potentials also reveals the change of the surface layer.

But different to Kim B S's work, it's also known from Fig. 2 that the magnitude of the steady plateau do not increase upon the increasing applied potentials and arrives at the maximum value at 0.8V. Moreover, the plot of R_s vs potential at a 1mV/s sweep rate shown in Fig.3 further confirms the fluctuation of R_s upon the changed potential. Clearly, the R_s evolution tendency agrees well with that shown in Fig.2 and arrives at a maximum value at 0.728 V.

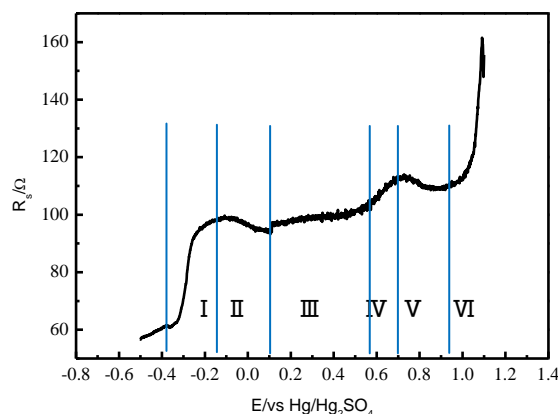


Figure 3. R_s vs E plot of the Cu/ H_3PO_4 interface at an ac frequency of 50 kHz at 1mV/s sweep rate

As discussed above, the evolution of R_s is closely related to the variation of the surface film on Cu. So it can be seen that the surface layer changes with the varied potential. To interpret the evolution of the surface layer, the R_s vs E curve in Fig.3 is divided into six regions and discussed in detail.

In region I (OCP ~ -0.15 V), the increased value of R_s indicates that the surface film (any porous salt or viscous liquid film) become thicker. During region II (-0.15 V~ 0.10 V), by the inhibition of the surface layer, the copper dissolution can not make up the copper ion diffusion to the bulk. Then the thickness of the surface layer decreases and leads to the decline of R_s . In region III (0.10 V~ 0.60 V), because the copper dissolution rate equals to that of copper ion diffusion, the thickness of the surface film on Cu keeps constant, which should theoretically lead to a unchanged R_s . But the slowly increasing R_s declares that new resistant layer should emerge in the interface zone. This film has been proved to be consisting of copper oxides Cu_2O and CuO [16-18]. In region IV (0.60 V~ 0.7 V), R_s increases faster and reaches a maximum at 0.72 V, implying the copper oxide film is thicken. In region V (0.72 V~ 0.95 V), the decreased R_s may be ascribe to the change from the new copper oxide layer[19]. In region VI, the released oxygen adheres on the copper surface and results in a sharp rising R_s .

The Mott-Schottky curve shown in Fig.4 clearly reveals the existence of the copper oxide film. The corresponding positive oblique line over -0.25 V to 0.6 V proves there is a n -type semiconductor layer formed on the Cu/ H_3PO_4 interface. It is consistent with Pointu B's claims that a film of copper oxide Cu_2O begins to form above -0.15V [16]. Noteworthily, the Mott-Schottky curve declines at 0.6 V and shows a turning point, which implying a of n -type semiconductor to a p -type one. This transition further demonstrates the presence of the copper oxide layer. The emerged copper oxide layer obviously

will increase the total system resistance and should be counted into R_s , That is $R_s = R_e + R_m + R_f + R_o$. Because R_e and R_m do not vary for a given system, so any change of R_s , should come from the change of R_f and R_o .

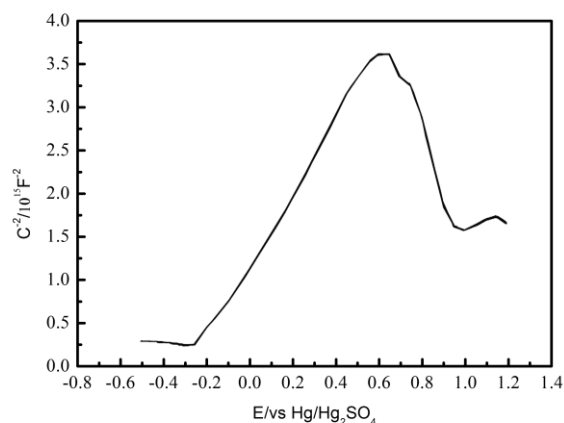


Figure 4. Mott-Schottky curve of Cu/H₃PO₄ interface at an ac frequency of 50 kHz

Fig.5 shows the roughness (Ra) of copper sheet electropolished for 15 minutes under different potential. All value data of Ra are assessed by the Grubbs criterion to assure the rationality. It can be readily seen that roughness of the Cu electrode is significantly decreased after the electropolishing treatment. The minimum Ra is obtained at 0.2 V where the copper oxide film forms. Upon the increasing potential, a turning point at 0.6 V appears and coincides with the transition point in Fig.4. Therefore, it can be sure that the copper oxide film also be involved into the electropolishing process.

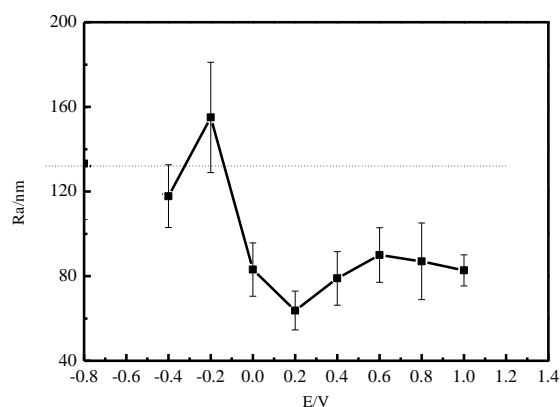


Figure 5. The roughness of copper sheet after electropolishing in 85wt% H₃PO₄ for 15min under applied potential

4. CONCLUSIONS

In this study, we studied the interface film on Cu with the EIS technique, and found that the magnitude of R_s fluctuated with the increasing applied potentials. Moreover, a transition of n -type

semiconductor copper oxide to *p*-type oxide happened at 0.6 V. The copper oxide layer had seemed to be involved into the electropolishing treatment.

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