

Some Aspects of Mechanism of Electropolishing of Copper in Phosphoric Acid

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In this study, electrochemical impedance spectroscopy (EIS) and electron spectroscopy for chemical analysis (ESCA) were used to investigate copper electropolishing in phosphoric acid. The experimental results indicate that a bright and smooth surface can be obtained using 85 wt% phosphoric acid at the applied potential, which leads to a limiting current. The surface treated using 30 wt% phosphoric acid was not glossy, and conventional electropolishing models could not adequately explain the results. Based on the results of EIS and ESCA analyses, a dual-layer model was proposed in this study. The two layers consist of a passive precipitate because of anodic polarization and a diffusion layer because of lack of water near the copper surface. Therefore, the dual layers limited the mass transfer rate. In addition, the polymeric characteristic of concentrated phosphoric acid enhanced the formation of dual layers, which significantly limited mass transfer and thus produced a glossy surface. Consequently, concentrated phosphoric acid demonstrates better electropolishing performance than low-concentration phosphoric acid.

Keywords: copper, phosphoric acid, electropolishing, dual-layer model, electrochemical impedance spectroscopy.

1. INTRODUCTION

Electropolishing technology was developed approximately 100 years ago. It can visibly improve metal surfaces and enhance anticorrosion capability. It has been verified that electropolishing has superior finishing performance to the conventional mechanical method. Electropolishing, because of its noncontact characteristic, is being considered as a possible replacement for, or complement to, copper chemical-mechanical polishing used in semiconductor interconnect metallization [1-2]. Thus, electropolishing can be used with fragile low-k dielectric materials [3]. In addition, it is appropriate for

processing through-silicon vias in 3D integration because it allows for efficient removal of overburden copper [4].

Copper electropolishing in concentrated phosphoric acid (H_3PO_4) was first investigated by Jacquet in 1936 [5]. He determined that a plateau appears in the anodic polarization curve of Cu in a concentrated H_3PO_4 solution, which is the crucial part of the process. Wagner indicated that the plateau is related to species transport between the metal surface and bulk solution [6]. Subsequently, several electropolishing models have been proposed to explain the species-transport-controlled process. The acceptor mechanism and anodic film mechanism are two widely discussed electropolishing models [7-13]. An acceptor is a species that combines with copper ions at the anode. Water molecules or some anions can be acceptors. Generally, an anodic film is generated by slat precipitation or surface oxidation.

Concentrated H_3PO_4 solution is an efficient agent for Cu electropolishing; therefore, many researchers have attempted to investigate the mechanism of polarization and brightening in H_3PO_4 solution using electrochemical techniques and *in situ* and *ex situ* surface analytical methods [14-17]. However, these investigations have not reached a consensus. For example, some investigators have claimed that there was no film on the Cu surface during electropolishing, and some have reported that a solid film or a viscous layer was observed when surface analysis was applied.

Electron spectroscopy for chemical analysis (ESCA) was applied to study the mechanism of the electropolished surface and understand the electropolishing phenomenon. The electropolishing performance of copper in a concentrated H_3PO_4 solution was investigated using scanning electron microscope (SEM) and atomic force microscope (AFM). The mass transport effect was determined using electrochemical impedance spectroscopy (EIS). Consequently, a dual-layer model was proposed in this study.

2. EXPERIMENTAL

Commercial copper sheets sized 1 cm \times 1 cm were used as the working electrodes. The surface of the electrode specimen was cleaned in 3 wt% H_2SO_4 solution using ultrasonic oscillation. The specimen was rinsed with deionized water, dried in nitrogen gas, and set in an electrochemical cell for electropolishing. Phosphoric acid solutions with various concentrations were used as the electrolytes.

To measure the change in electrolyte level during electropolishing, the solution near the copper surface was collected using a syringe, and its viscosity, density, pH, and conductivity were analyzed. In the electropolishing system, platinum sized 3 cm \times 5 cm and Ag/AgCl were used as the counter and reference electrodes, respectively. The potentiodynamic analysis was at a 5 mV/s of scan rate, and potentiostatic electropolishing at various potentials versus Ag/AgCl was performed in turn by using a potentiostat (Autolab PGSTAT30, Metrohm Inc.). A 10-mV sinusoidal potential was superimposed over a frequency range of 0.1–100 kHz to measure electrochemical impedance (Autolab FRA2, Metrohm Inc.). In these experiments, the cell was operated at room temperature.

After electropolishing, the copper specimen was removed from the system before power was turned off and was immediately heat dried in N_2 ambient. The composition of the surface film was

analyzed using ESCA (Thermo Fisher Scientific, Theta Probe). The change in depth was observed by etching the sample using argon plasma for 10–20 min. The surfaces of specimens were characterized using SEM; surface roughness was estimated using AFM (Veeco Dimension-3100), and standard specular gloss values were measured using a gloss meter (Zehntner GmbH, ZGM1120) with an angle of incidence of 20°. For each specimen, five measurements of roughness and gloss value were conducted, which were used to calculate the average value and absolute error.

3. RESULTS AND DISCUSSION

Figure 1 presents the SEM images of the copper surface electropolished in various solutions and indicates the corresponding gloss values and surface roughnesses. Surface roughness is a microscopic state of the metal surface, and gloss value is the macroscopic state of the entire sample. Fig. 1(b) demonstrates that by electropolishing in 30 wt% phosphoric acid, surface roughness can improve but the gloss value decreases. The surface improvement obtained from electropolishing in 30 wt% H_3PO_4 cannot be reproduced and is unpredictable. However, the improvement from electropolishing in 75 wt% H_3PO_4 is clear, as presented in Fig. 1(c). The resulting gloss value was to approximately twice that of the original sample. Electropolishing decreased the variance of gloss value from 3.4% to 2.7% and visibly decreased the surface roughness from 67 to 14 nm. These two indices demonstrate that electropolishing in concentrated H_3PO_4 is effective. The electropolishing performance was enhanced when 85 wt% H_3PO_4 was used at 1.0 V, as presented in Fig. 1(d).

In addition to the concentration of H_3PO_4 , the applied potential is a crucial factor. Figure 2 presents polarization curves of copper in 30 wt%, 75 wt%, and 85 wt% H_3PO_4 solutions. The result is consistent with the previous study by Li et al. [18] The anodic curve of copper in H_3PO_4 can be divided into four stages. In stage A, because of anodic dissolution of copper, the current increased as the applied potential increased. In stage B, the current density decreased for potential values from 0.29 to 0.6 V. Appearance of the current peak corresponds to a competition between dissolution and passivation. The passivation effect occurs because of slow diffusion of solvated copper ions generated from surface dissolution and because of the formation of surface film. If electropolishing is conducted at stage A, stochastic dissolution could occur on the entire sample, which may or may not improve the surface quality. With respect to stage C, Fig. 1(e) demonstrates that electropolishing at 0.2 V only slightly improved the surface gloss and roughness, which indicates that electropolishing performance at 0.2 V is much inferior to that at 1.0 V.

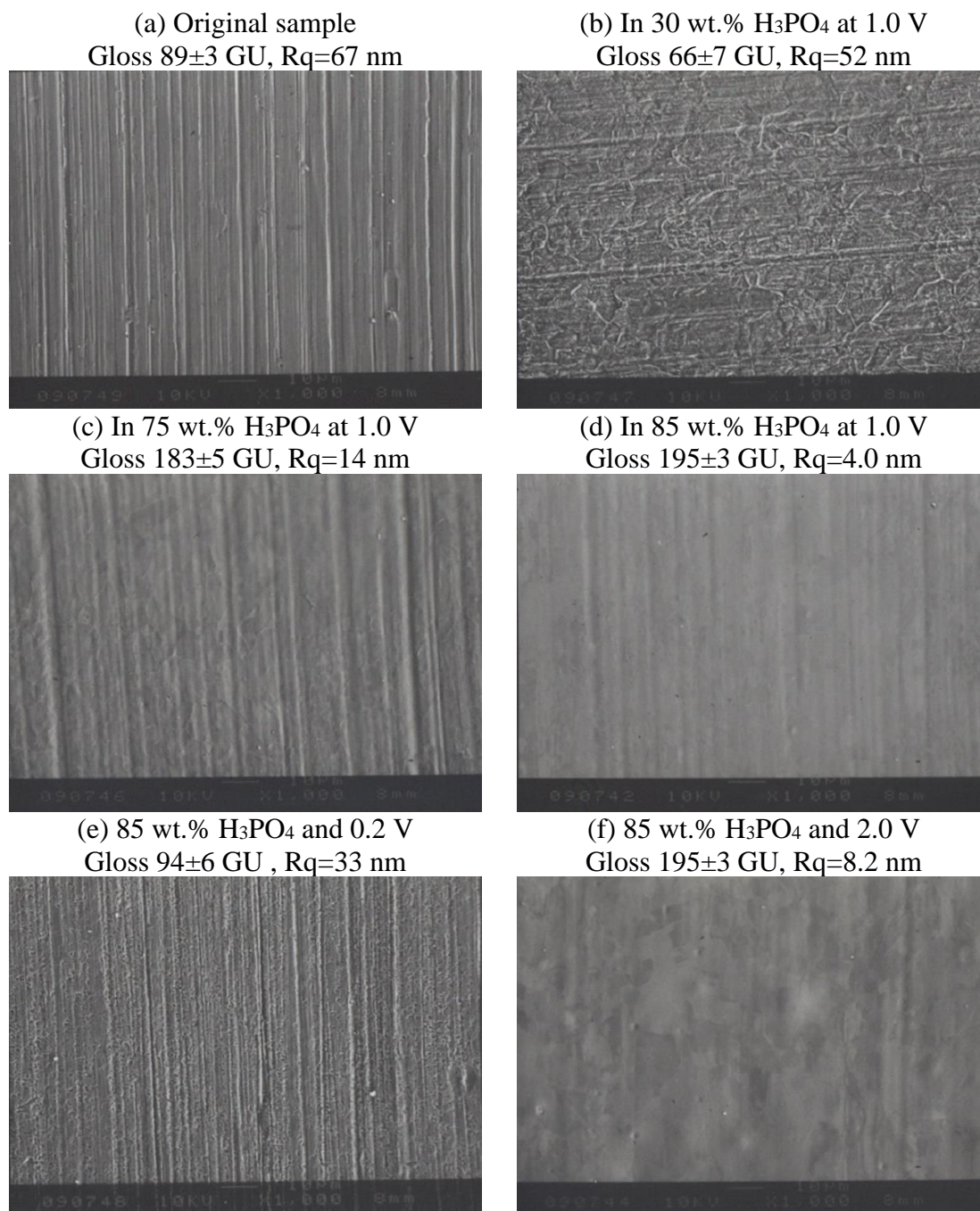


Figure 1. SEM images of (a) the original copper surface and (b)-(f) the electropolished copper in various conditions for 5 min. The gloss values and surface roughness are also displayed.

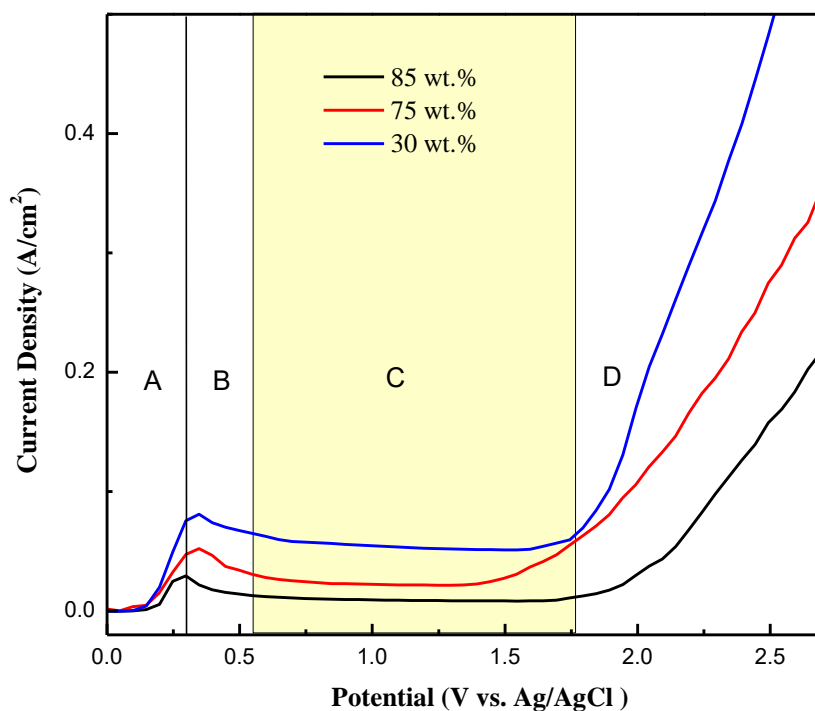


Figure 2. Polarization curves of copper in 30 wt%, 75 wt% and 85 wt% phosphoric acids.

In Fig. 2, when the applied potential approaches the peak value, most dissolved copper ions cannot rapidly detach from the electrode surface, and thus, they accumulate on the surface to inhibit the oxidation reaction of copper, according to the Le Chatelier principle. Beyond the peak, the mass transfer rate, instead of electrochemical action, limited copper dissolution. Therefore, the current density declined to a limited value, which almost remained constant as the applied potential increased. For 85 wt% H_3PO_4 , the current plateau remained approximately constant from 0.6 V to 1.7 V, which is denoted as stage C. In the electropolishing process, the copper surface is brightest and flattest in stage C. Electropolishing in this current plateau is adopted by most researches, and some of them further inhibit the limiting current densities by adding organic aldehydes [19] or organic acids [20].

However, as the potential increased beyond 1.7 V, the current density increased significantly because of oxygen evolution in stage D, as evident in Fig. 2. The oxygen bubbles may agitate the solution, increase the mass transfer rate, and thus enhance metal dissolution. Fig. 1(f) demonstrates that when the copper sample was electropolished at 2.0 V, its surface exhibited acceptable gloss; however, many pits were clearly visible. Surface roughness obtained at 2.0 V was larger than that at 1.0 V, which proves that the surface treated at 2.0 V has pits, even though their gloss values were similar. The similar pitting phenomena can be found during electropolishing stainless steel 304 and simulated by Lee et al [21]. Consequently, to obtain acceptable surface quality, the applied potential of electropolishing depicted in stage C of Fig. 2 is the best choice [1, 2]; however, it remains unexplained how the mass transfer limitation controls the surface change. Some engineers select the applied potential to be within stage D to enhance the production rate and obtain an acceptable bright surface with few pits [2, 22]. Therefore, mass transfer limitation may not be the only factor that ensures a

bright surface. For example, the concentration of phosphoric acid is also a crucial factor that affects flatness and brightness.

A series of EIS experiments were conducted at various potentials to understand the surface change mechanism during electropolishing. Fig. 3 shows the Nyquist plot corresponding to the applied potential in stage A. A dual-loop curve is observed, and thus, an equivalent circuit consisting of two pairs of RC and an individual R in series was considered, where R and C represent resistor and capacitor, respectively. According to the physical view of this system [23], the individual R comes from the solution, one parallel RC consists of charge-transfer resistance (R_{ct}) and double-layer capacitance (C_{dl}), and the other parallel RC consists of film resistance (R_f) and film capacitance (C_f). The R_f and C_f imply that a layer covers the copper surface. The Nyquist plot, however, changes, as shown in Fig. 4, when the applied potential decreases in stage B. The curve obtained at 0.3 V mainly consists of a semicircular loop at high frequency, an unclear loop at middle frequency, and a straight line at low frequency. In a Nyquist plot, a straight line with slope 1 represents an impedance that results from mass transfer of the reactant, which is called Warburg impedance. A comparison of Figs. 3 and 4 indicates that an unexplained film remains on the copper surface, but the mass transfer effect is enhanced as applied potential increases. The fitting between experimental data and equivalent circuits was used to obtain the impedances of the aforementioned components, as listed in Table 1, which indicates that when the applied potential increases from 0.2 to 0.3 V, R_f increases but C_f decreases. It also indicates that the thickness of the unexplained film increases as the applied potential increases, which decreases mass transfer near the surface. If the applied potential is further increased, the decrease in the mass transfer rate is expected to dominate the process of copper removal from the surface.

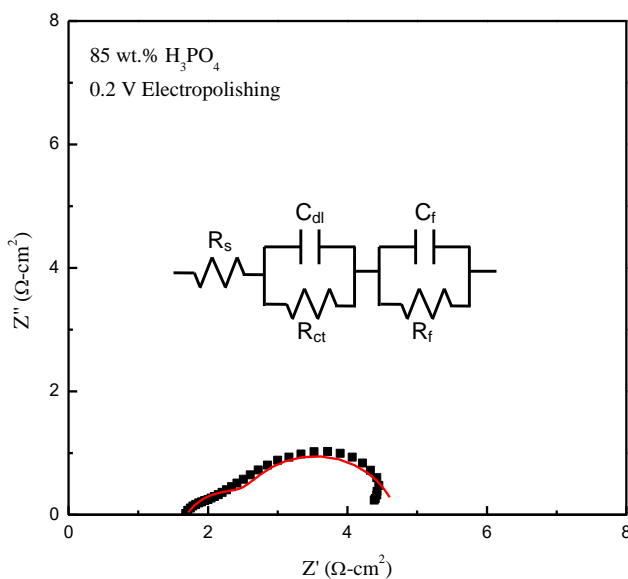


Figure 3. Nyquist plot and the proposed equivalent circuit of copper in 85 wt.% phosphoric acid at 0.2 V (vs. Ag/AgCl). R and C in the equivalent circuit represent resistor and capacitor.

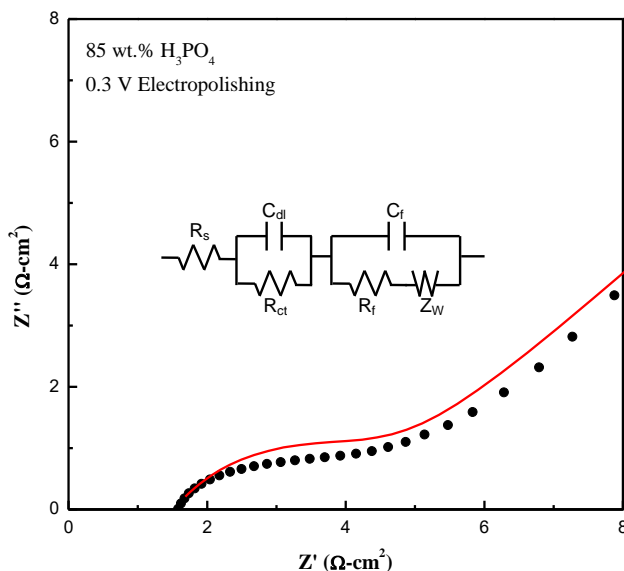


Figure 4. Nyquist plot and the proposed equivalent circuit of copper in 85 wt.% phosphoric acid at 0.3 V (vs. Ag/AgCl). In the equivalent circuit, R, C and Z_w represent resistor, capacitor and Warburg impedance, respectively.

Figure 5 shows the Nyquist plot at various values of applied potential in stage C of Fig. 1. The results are clearly different from those at 0.3 V. The slope of the straight line at low frequency increases as the applied potential increases. The data for electropolishing at 1.5 V exhibit a vertical line, which is characteristic of bounded diffusion in a porous material. Therefore, the change in slope indicates a structural transformation in the unexplained film. A series of fitting processes were used to obtain the impedances in the proposed equivalent circuit, which are listed in Table 1. Table 1 indicates that the R_f resulting from the cases operated in stage C is visibly larger than those in stage A and B, which indicates that thickness and density of the film increase at a higher potential (i.e., higher coverage or lower porosity). Therefore, apparent bounded diffusion occurs at 1.5 V. In addition, corresponding to the change in coverage or porosity, a trend of saturation in R_f can be observed.

Table 1. Simulated values of R_s , R_{ct} , R_f , C_f and C_{dl} in Nyquist plots.

Condition	R_s ($\Omega\text{-cm}^2$)	C_{dl} ($\mu\text{F}/\text{cm}^2$)	R_{ct} ($\Omega\text{-cm}^2$)	C_f ($\mu\text{F}/\text{cm}^2$)	R_f ($\Omega\text{-cm}^2$)
0.2 V	1.67	202	0.84	6650	2.17
0.3 V	1.52	62.5	2.78	2180	21.0
0.8 V	1.65	7.23	8.45	1273	557
1.0 V	1.59	7.53	8.48	1381	763
1.5 V	1.68	10.6	8.99	1408	950
2.0 V	1.72	11.7	2.92	2936	7.41
1.0 V(agitation)	2.59	4.90	5.28	1026	589
2.0 V(agitation)	2.51	3.11	2.77	4335	4.57

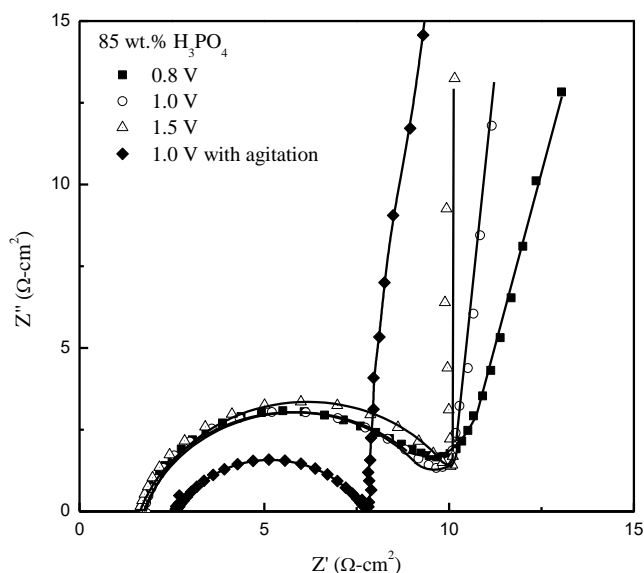


Figure 5. Nyquist plots of copper electropolishing in 85 wt.% phosphoric acid at 0.8V, 1.0 V and 1.5 V (vs. Ag/AgCl). Agitation of solution is applied at 1.0 V.

Regarding the mechanism of electropolishing, two types of models were proposed to describe the effect of mass transfer. In one model, the effect is attributed to the copper precipitate, and in the other, it is attributed to the ligand of the copper ion. When using an H_3PO_4 solution, the reactant of copper precipitate can be phosphate anion, and the ligand of copper ion can be water. The ratio of phosphate anion and water varies with the concentration of the H_3PO_4 solution; therefore, electropolishing performance should also change with concentration. If the copper precipitate forms locally, the dissolution at that location would be retarded. During anodic treatment on a copper surface, dissolved copper ions tend to move radially inward in the recess region and radially outward in the convex region. The copper precipitate is readily generated near the recess region, which inhibits subsequent dissolution, and thus levels the surface. When the concentration of H_3PO_4 is high, there are fewer water molecules, which limits hydration of the copper ion and inhibits dissolution of copper. Especially when the surface dissolution proceeds, water content near the surface decreases significantly. As the difference in water supply between convex and recess regions becomes apparent, the local dissolution rate deviates from the average value and the surface is leveled. The aforementioned two types of mechanisms may occur together during electropolishing in a concentrated H_3PO_4 solution. Therefore, a dual-layer model, as illustrated in Fig. 6, was proposed to explain the experimental results of electropolishing. The dual-layer model includes not only a diffusion layer of water but also a passive layer of precipitate. The synergistic effect of the dual layers may result in a nearly vertical line in a Nyquist plot. The probable form of hydrated copper ion is $\text{Cu}(\text{H}_2\text{O})_6^{2+}$ [7]. Thus, six water molecules are required for each copper ion, which causes a concentration gradient of free water molecules from bulk solution to copper surface. In addition, the H_2PO_4^- anion may also grab copper ions to form a precipitate. In an 85 wt% H_3PO_4 solution, the ratio of water to H_3PO_4 molecule is approximately 1:1, which indicates a strong trend to form a precipitate, particularly in the recess region. After power was turned off, no more copper ions were produced, the diffusion layer disappeared, and the passive layer gradually dissolved. Some researchers, therefore, have claimed that

no film exists to support the precipitate model [24]. If the acceptor model is considered to be suitable to describe electropolishing, then the mass transfer rate of the water molecule will be the most crucial factor.

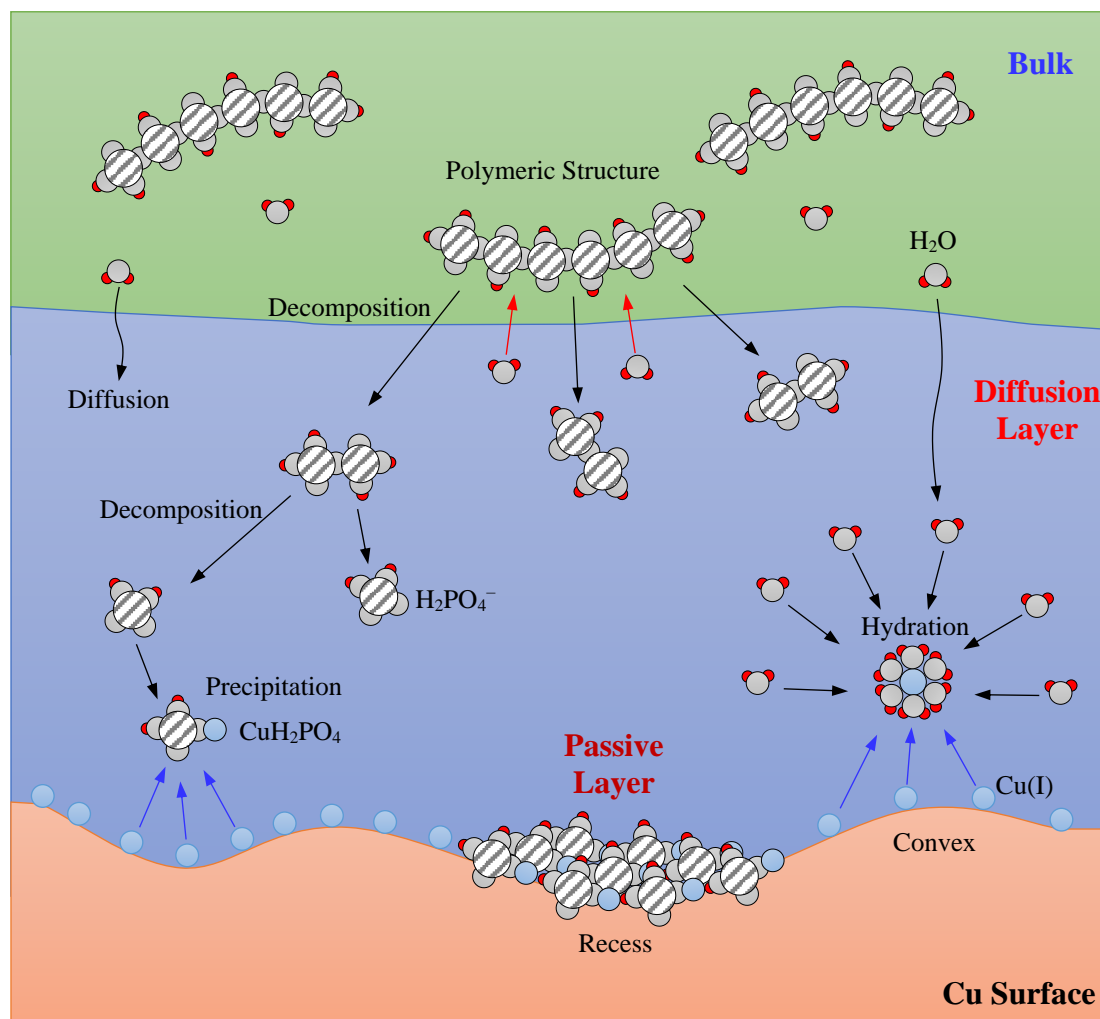


Figure 6. Schematic diagram of the dual-layer model for copper electropolishing in concentrated phosphoric acid.

Figure 5 presents the EIS experimental results with strong agitation. At 1.0 V, the curve shapes with and without agitation are similar and consist of a loop and a straight line. The straight line for the agitated system is, however, not vertical, which indicates that agitation alleviates the bounded diffusion, which is similar to the curve obtained at 0.8 V without agitation. In addition, for the agitated sample, the size of the loop shrinks, which suggests that a thinner film covers the copper surface. This assumption is demonstrated by the corresponding R_f value in Table 1.

In addition to agitation, increasing the applied potential to generate O₂ on the surface can enhance the mass transfer rate. The corresponding EIS results presented in Fig. 7 differ from those in stage C. The Nyquist plot for electropolishing at 2 V exhibits two distinct loops, but the loop at low frequency passes through the axis of abscissa. Generally, this result can be attributed to a decrease in

film coverage or an increase in bubble adsorption. In the case of electropolishing, film coverage and bubble evolution definitely occur at a sufficiently high potential. Data fitting can be used to demonstrate that the magnitude of R_f at 2.0 V is similar to that at 0.2 V, which indicates a balanced competition between passive film covering and peeling. The covering effect is predominantly the result of high applied potential, and the peeling effect is the result of O_2 bubble desorption. Film cover may enhance the protection of the recess region, but O_2 evolution may agitate the solution and increase the mass transfer rate. If the agitation is strengthened by an external force, the peeling effect is enhanced. Fig. 6 presents the Nyquist plot at 2.0 V with agitation by an external force. It is clear that loop sizes at high frequencies are similar for curves obtained with and without agitation; however, at low frequency, loop size with agitation is significantly smaller than that without agitation. Therefore, agitation enhanced O_2 desorption rate and released active sites for the following reaction. The results at extremely high frequencies also indicate that external agitation increases the O_2 content in the solution because R_s increases due to agitation. O_2 distribution on the copper surface is, however, not uniform. Compared with an O_2 -poor site, an O_2 -rich site tends to act as a cathode, which causes pit corrosion. From the experimental results at 2.0 V, it can be concluded that the surface can be brightened (Fig. 1), a passive material can be generated at high potential, and mass transfer can be enhanced by O_2 adsorption (Fig. 7). Neither the film model nor the acceptor model could completely explain the result at 2.0 V, and thus, a dual-layer model was proposed in this study.

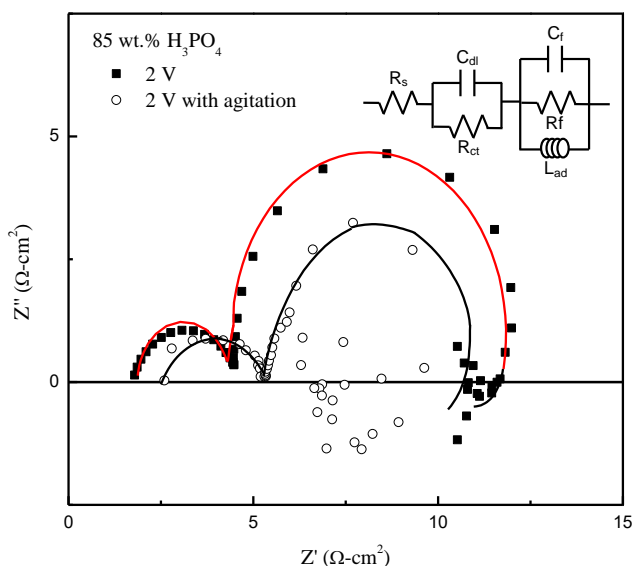


Figure 7. Effect of agitation on Nyquist plot for copper in 85 wt.% phosphoric acid at 2 V (vs. Ag/AgCl) and the proposed equivalent circuit. In the equivalent circuit, R, C and L represent resistor, capacitor and inductor, respectively.

The concentration of the H_3PO_4 solution is also a crucial factor for electropolishing, but the conventional models could not clearly explain its effect. The trace of the solution on the copper surface during electropolishing in 85 wt% H_3PO_4 at 1.0 V was collected and analyzed, and it was determined that the surface solution viscosity was 76% of the bulk and surface solution density was 89% of the bulk. In addition, surface pH was lower than bulk pH, but surface electrical conductivity was higher

than bulk electrical conductivity. The difference between surface solution and bulk solution, however, decreased when the concentration of H_3PO_4 solution decreased. These findings may be attributable to the polymerization of concentrated H_3PO_4 in bulk solution and depolymerization of H_3PO_4 near the copper surface. Formation of a polyphosphate structure releases water into bulk solution, and decomposition of a polyphosphate structure consumes water near the copper surface. Therefore, decomposition not only provides another source of water gradient from surface to bulk but also enhances the generation of phosphate precipitate on the surface. As the concentration of the H_3PO_4 solution decreased, the trend of H_3PO_4 polymerization in bulk solution weakened. Therefore, the mass transfer limitation required for electropolishing is less significant.

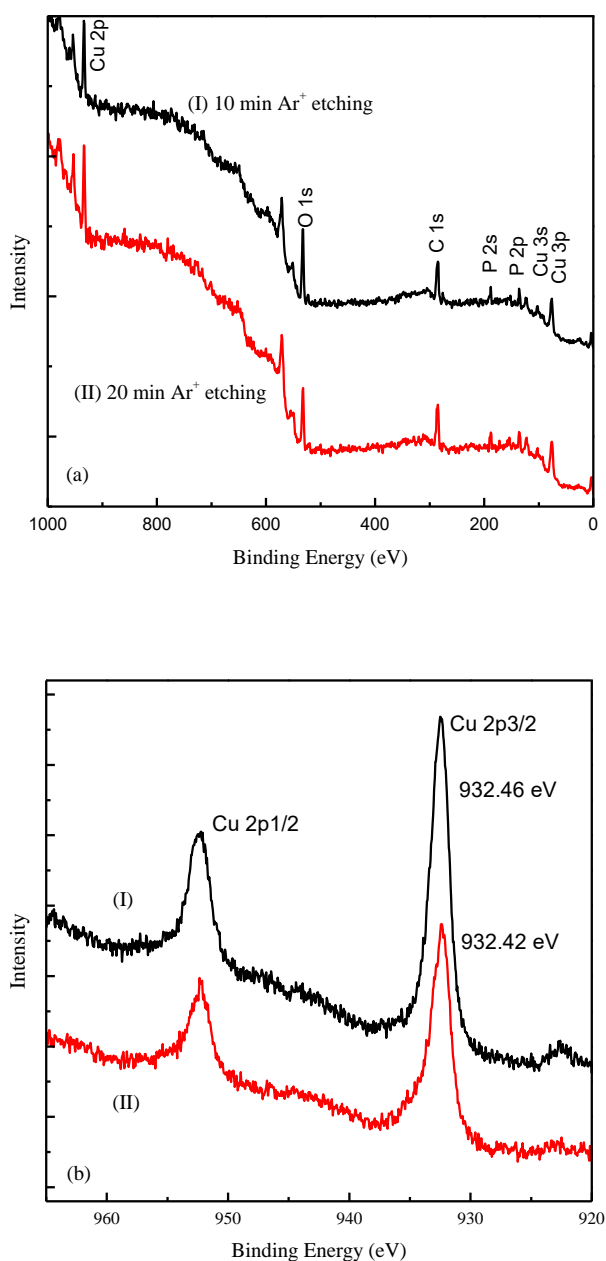


Figure 8. ESCA spectroscopy of the surface film in 85 wt.% phosphoric acid: (a) wide-scan and (b) Cu 2p peak for (I) 10 min Ar^+ etching and for (II) 20 min Ar^+ etching.

To confirm the existence of the passive layer, the electropolished copper was removed from the H_3PO_4 solution before power was turned off and was dried and analyzed using ESCA with Ar^+ sputtering. Fig. 8(a) presents the ESCA spectroscopy images after 10 min and 20 min of sputtering. It is clear that the composition of the surface layer remained almost constant during the 20-min dry etching, which indicates that the layer consisting of Cu, O, and P is, probably, a homogeneous material. The ratio of Cu:O:P is, approximately, 17.0:66.5:17.5. In addition, the Cu 2p peak is clearly visible in Fig. 8(b) by zooming in on the spectroscopy image. The peak is located at 932.4 eV; therefore, it can be inferred that Cu(I)-O bonds appeared in the surface layer. According to the ratios of O/P and Cu/P, the predicted surface layer may be CuH_2PO_4 , but it easily dissolved when rinsed with water. The CuH_2PO_4 layer was generated by the H_2PO_4^- anion by decomposition of polyphosphate and the copper ion under anodic polarization. The possibility of CuH_2PO_4 formation was higher at the recess site than at the convex site, and thus, the dissolution of recess site was inhibited. Contrarily, the decomposition of polyphosphate required water, which led to a thicker diffusion layer and a smaller gradient of water at the recess site than at the convex site. The smaller water gradient further decreased the mass transfer at the recess site. The proposed dual-layer mechanism considers the polymeric characteristic of concentrated H_3PO_4 ; therefore, the poor performance of electropolishing in low-concentration H_3PO_4 solution can be significantly explained.

4. CONCLUSION

This study proposed a dual-layer model to describe copper electropolishing in H_3PO_4 solution. The two layers consist of a passive film covering on a copper surface and a diffusion layer of water molecules. ESCA of electropolished copper proved the existence of the passive film and indicated that its composition should be CuH_2PO_4 . In addition, the EIS of electropolished copper demonstrated the mass transfer effect, which is related to the diffusion layer of water. The polymeric characteristic of concentrated H_3PO_4 solution also influences the electropolishing performance. Decomposition of polyphosphate near the copper surface not only enhances the generation of passive film but also consumes water, which suggests a strong lack of water near the surface. Therefore, a concentrated H_3PO_4 solution may provide better electropolishing performance than low-concentration H_3PO_4 solution.

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