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XPS and AES studies of the composition of the viscous liquid film in the electropolishing of copper*

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Phosphorus was detected with XPS and AES on the electropolished copper obtained in different hydroxyethylidene-diphosphonic acid (HEDP) concentrations, at different pH values and in various solutions (H_3PO_4, HEDP, and HEDP + H_3PO_4). The results show that no phosphorus appears on the copper surface, so that the viscous liquid film formed can be easily removed by washing. The viscous liquid film obtained from H_3PO_4 + HEDP solution possesses very good film-forming characteristics. The composition of the viscous film can be established from the constant composition region of the depth profile curve and may be considered to be a polynuclear coordination polymeric compound with a structural unit of approximately $[Cu_4(PO_4)\ (HEDP)]_n$.

1. Introduction

Since Jacquet first proposed a phosphoric acid electropolishing solution in 1935, this acid had been used by several investigators for the electropolishing of copper and other metals [1, 2]. No completely satisfactory electropolishing solution for copper has been found up to the present, although chromic acid, sulphuric acid, sodium tripolyphosphate and potassium cyanide have been used as the electropolishing agents for copper separately or together with H_3PO_4 [3, 4]. The high phosphoric acid concentration and slow electropolishing rate are disadvantages of the phosphoric acid solution.

Recently we found that 1-hydroxyethylidene-1.1-diphosphonic acid (HEDP) was an excellent electropolishing sequestering agent for copper and electroplating complexing agent for various metals [5–7]. The high electropolishing rate, low concentration of sequestering agent, wide operating voltage range and no pollution were the features of the HEDP electropolishing solution.

Although the electropolishing of metals has been known for many years, its mechanism remains obscure. The original ideas of Jacquet [8], Edwards and Wagner were based mainly on the establishment of a diffusional field at the metal–solution interface, composed of either a salt of the metal or a metal ion acceptor diffusing to the metal surface. Ismail *et al.* [9] proposed a mass transfer anodic film model for surface brightening in phosphoric acid. According to this model, surface brightness is obtained when the mass transfer rate for the dissolution products is exceeded, causing oxide formation at the anode. Hoar *et al.* [10] proposed that surface brightening is caused by the formation of a compact viscous liquid film or solid film on the metal surface. The composition of the viscous liquid film is very complex – some authors have proposed that a supersaturated solution of phosphate [11], a hydroxy complex salt of copper [12], and an acid copper phosphate [13] are possible components of the viscous liquid film in the Cu/H_3PO_4 system.

In this paper XPS and AES (Auger line) techniques were used to determine the composition and structure of the solidified viscous liquid film obtained from HEDP and HEDP + H_3PO_4 electrolytes.

2. Experimental method

The bath compositions and operating conditions were as shown in Table 1. The specimen was made of 99.99% Cu plate, the area of which was $5 \times 2\,cm^2$. Before electropolishing the specimens were polished with MgO powder, chemically degreased and washed in deionized water. Then the specimens were dipped in 10% H_2SO_4 and rinsed with deionized water.

After electropolishing for 2 min in HEDP + H_3PO_4 solution, the specimen was taken out very slowly with the current still flowing, and the viscous film on the surface of the specimen was dried immediately by air blast. It was then rinsed in deionized water and again dried by air blast. The solidified viscous film was a transparent glassy solid film.

A Perkin-Elmer PHI 550 ESCA/SAM electron spectrometer with Mg Kα X-ray anode was used for measurements [14, 15]. The surface compositions and species of the electropolished copper were determined by XPS and $L_3M_{4.5}M_{4.5}$ Auger line [16, 17]. The pass energy was 100 eV for XPS full spectrum measurement and 50 eV for high resolution XPS spectrum measurement. Ar^+ sputtering was used for determination of the depth profile of specimen.

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Table 1. Compositions and conditions of various electropolishing baths

HEDP solution	*HEDP + H_3PO_4 solution*	*H_3PO_4 solution*
HEDP 200 $g l^{-1}$	HEDP 200 $g l^{-1}$ H_3PO_4 40 $g l^{-1}$	H_3PO_4 800 $g l^{-1}$
pH6–8	pH6–8	
T = 60–80° C	T = 60–80° C	T = 40° C
voltage = 2–4 V	voltage = 2–4 V	voltage = 2–5 V
t = 2–4 min	t = 2–4 min	t = 8–12 min

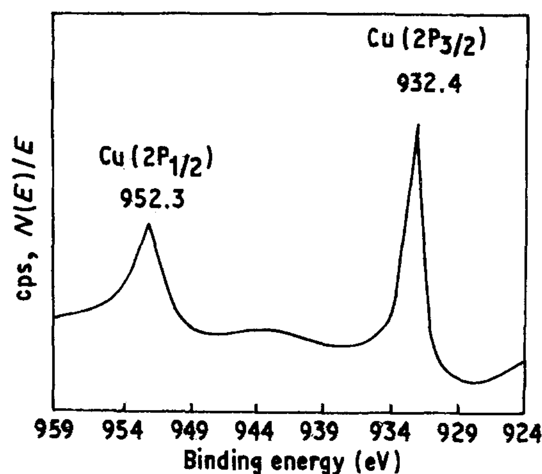

Fig. 1. Cu(2p) high resolution XPS spectrum of clean Cu standard.

3. Results and discussion

3.1. *The peak values of Cu(2p) and CuL_3VV in pure copper and copper oxide*

After removing the XPS peaks of carbon and oxygen on copper surface with Ar^+ sputtering, peak values of CuL_3VV spectrum and Cu(2p) high resolution XPS spectrum of clean copper standard, toasted red copper, Cu_2O and CuO were determined. The results were as shown in Figs 1 and 2 and are listed in Table 2.

3.2. *Peak values of CuL_3VV and Cu(2p) of electropolished specimens under different bath voltages*

Copper specimens were electropolished under different bath voltages. The surface composition elements and values of CuL_3VV and Cu(2p) of the copper were determined and the results are listed in Table 3.

From Tables 2 and 3, it may be seen that Cu_2O was formed on electropolished copper exposed to air [20] and on blank copper exposed to air.

3.3. *Thickness of oxidation layer*

The thickness of the oxidation layer on the copper surface can be expressed as the period of time necessary from the beginning of sputtering to the appearance of a standard copper peak value. Results show

Table 2. Peak Values of Cu(2p) and CuL_3VV of specimens (eV)

Specimen	*CuL_3VV*		*Cu($2p_{3/2}$)*	
	Measured	*Reference*	*Measured*	*Reference*
Cu standard (after sputtering)	335.0	335.0 [17] 334.6 [18]	932.4	932.2 [19]
Cu standard (before sputtering)	336.2	336.2 [18]	932.4	932.4 [18]
Cu_2O	336.4	336.2 [18]	932.4	932.2 [18]
Cu (toasted	336.0	336.2 [18]	932.3	932.2 [19]
CuO	335.5	335.3 [18]	933.6	933.5 [19]

Table 3. Peak values of CuL_3VV and Cu(2p) of the electropolished specimen under different bath voltages

Specimens	*Bath voltage (V)*	*Elements of surface*	*CuL_3VV (eV)*	*Cu($2p_{3/2}$) (eV)*	*Cu($2p_{1/2}$) (eV)*
1	1.5	C, O, S, Cl, N, Cu	336.4	932.7	952.5
2	2.3	C, O, S, Cl, N, Cu	337.0	932.7	952.7
3	2.7	C, O, S, Cl, N, Cu	336.8	932.6	952.7
4	3.5	C, O, S, Cl, N, Cu	336.5	932.5	952.5
5	4.5	C, O, S, Cl, N, Cu	337.0	932.7	952.6
Cu_2O	–	–	336.4	932.4	–
CuO	–	–	335.5	933.6	–
Cu (toasted)	–	–	337.0	932.3	952.3
Cu (no sputtering)	–	–	337.0	932.5	952.5

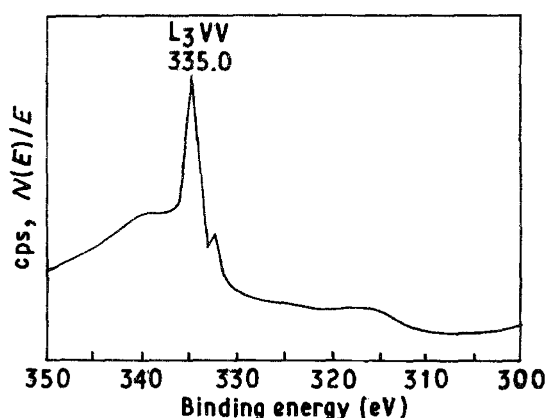

Fig. 2. CuL_3VV high resolution AES spectrum of clean Cu standard.

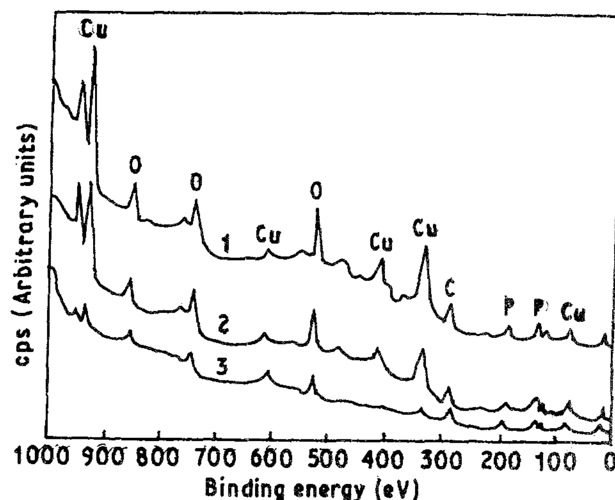

Fig. 3. The XPS spectra of solidified viscous liquid film before and after sputtering. 1, sputtering for 30 min; 2, sputtering for 5 min; 3, no sputtering.

that the necessary period of the time for metallic copper under different bath voltages is about the same (30–60 s) as that of blank copper. This indicates that Cu_2O is formed on the electropolished copper surface after exposure to air. Thus it may be deduced that surface layer of the electropolished copper was still metallic copper, i.e. bath voltage only affects the surface state of the copper, but does not affect the chemical composition of the surface (see Table 4).

From Table 4 it can be seen that oxygen evolved at the anode under 3.5–4.5 V bath voltage does not affect the period of the appearance of standard copper peak value. This result shows that the copper surface for electropolishing for 4 min was not oxidized by evolved oxygen.

3.4. *Detection of phosphorus on electropolished copper surfaces*

Detection of phosphorus on the electropolished clean copper surface obtained from three different electropolishing baths (HEDP, H_3PO_4 and HEDP + H_3PO_4) was carried out by high resolution XPS.

Results showed that no phosphorus appears on electropolished copper surface obtained from different HEDP concentrations, different bath pH values and different kinds of electropolishing sequestering agent solutions. This means that the viscous liquid film formed in the electropolished process is very soluble and can be easily removed by washing with water.

Table 4. Period of the time from the beginning of sputtering to the appearance of standard copper peak value

Specimen	*Bath voltage (V)*	*Period of the time to reach standard copper peak values (s)*
1	1.5	30–60
2	2.3	30–60
3	2.7	30–60
4	3.5	30–60
5	4.5	30–60
Blank copper	–	30–60
Toasted copper	–	1020

3.5. *Depth profile of viscous liquid film with XPS*

The XPS spectra of solidified viscous liquid film before and after sputtering for 5, 10, 15, 20, 30, 40, 50 and 60 min under 2 kV accelerating voltage, $4 \mu A\ cm^{-2}$ ion beam density and $8 \times 8\ mm^2$ scan area were determined. The results were shown in Fig. 3. It can be seen that the viscous liquid film is a homogeneous phase film and is only composed of the elements Cu, O, P and C.

3.6. *Composition and structure of the viscous liquid film*

The viscous liquid film obtained from H_3PO_4 + HEDP electropolishing solution possesses very good film-forming characteristics and electrical conductivity. The solidified viscous liquid film, in appearance, is the same as that from H_3PO_4 electropolishing solution. All are hard transparent glassy solid films.

The composition of the viscous liquid film at different depths was determined by the XPS technique after sputtering the copper surface by Ar^+ beam for different times. The relative atomic content (percents, AC %) of the elements Cu, O, P and C were calculated by computer. Figure 4 shows the variation of the composition of viscous liquid film with sputtering time. The composition of the viscous liquid film established from the constant composition region of the depth profile curves (see Fig. 4) are:

C, 34.8%; P, 13.4%; O, 36.3%; Cu, 15.5%
O/Cu = 2.34; Cu/P = 1.15 (mole ratio)

These values are close to that of the polynuclear coordination compound $[Cu_4(PO_4)\ (HEDP)]$. Thus the viscous liquid film may be considered to be a polynuclear coordination polymeric compound with structural unit of approximately $[Cu_4(PO_4)\ (HEDP)]_n$. The structure unit is shown in Fig. 5.

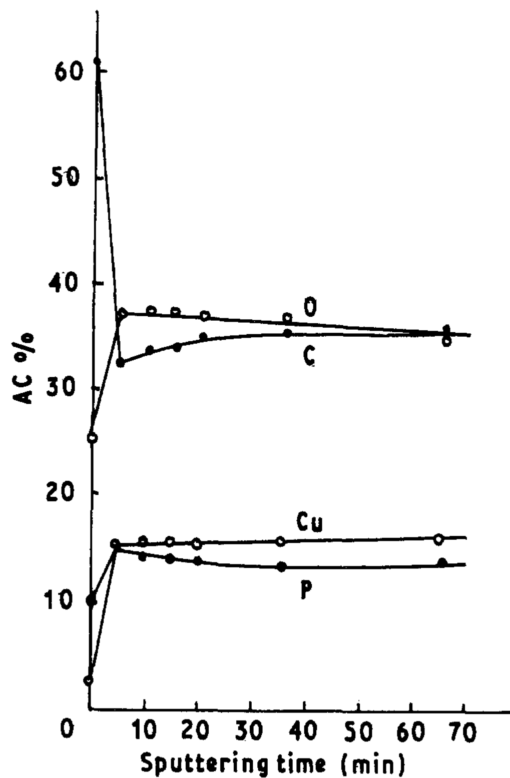

Fig. 4. Variation of composition of viscous liquid film with sputtering time.

4. Conclusion

From the above results, it is concluded that:

1. The brightening of copper in electropolishing is accomplished through the viscous liquid film mechanism.

2. The viscous liquid film is very soluble and can be easily removed by washing with water. No phosphorus was found on electropolished copper surfaces.

3. No solid film was found on the electropolished copper surface. The thin Cu_2O layer on the electropolished copper surface is the oxidation product of copper in air.

4. The composition of the viscous liquid film established from the constant composition region of the depth profile curves is close to $[Cu_4(PO_4)\ (HEDO)]_n$; a coordination polymeric compound.

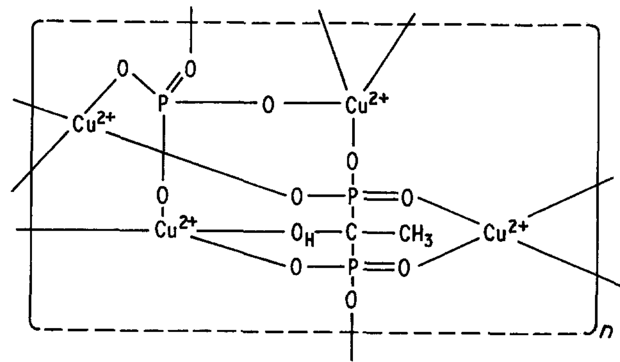

Fig. 5. Structural unit of coordination polymeric compound $[Cu_4(PO_4)(HEDP)]_n$.

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