Evaluation of K₃Fe(CN)₆ on Deposition Behavior and Structure of Electroless Copper Plating

Jianhong LU, Mingyong WANG, Xiaomei DENG, Jianhei YAN, Jimmy YUN, and Shuqiang JIAO

ABSTRACT

Potassium ferricyanide (K₃Fe(CN)₆) as a stabilizer was used for electroless copper plating in EDTA/THPED dual-ligands system. The deposition behavior and surface structure of copper layer were studied systematically. The results indicated that the overall deposition process was divided into three regions designated as induction, transitional and stable regions. It was confirmed that K₃Fe(CN)₆ can delay the fall-off trend of electrode potential, which may be related to the competitive adsorption between Fe(CN)₆³⁻ with large radius and OH⁻ with small radius on the electrode surface. The addition of K₃Fe(CN)₆ led to a decrease of 70% in redox current density, which reduced obviously Cu deposition rate. Meanwhile, the decomposition time of electroless solution sharply increased and the reoxidation of Cu(I) ion was effectively inhibited in the presence of K₃Fe(CN)₆. Metallographic studies of copper layers with and without K₃Fe(CN)₆ stabilizer revealed that surface structures and fine particle distribution were uniform. The resultant product was high-purity without detectable iron impurities. Moreover, the addition of K₃Fe(CN)₆ was favorable to the formation of the preferred orientation on (220) crystal plane, and the grain size decreased from 61.5 nm to 40.4 nm with the addition of 50 mg L⁻¹ K₃Fe(CN)₆.

Keywords : Potassium Ferricyanide, Electroless Copper, Mixed Potential, Preferred Orientation

Electroless copper plating has been applied in the fields of electronics and decoration. The structure-properties of Cu coating and reaction mechanism are widely studied. It is confirmed that additives are crucial to electroless copper plating. Stabilizers play an important role to inhibit the incomplete redox reaction (Reaction (1)) in the electroless copper solution except the normal reduction reaction of copper complex ions.

$$2\text{Cu}^{2+} + \text{HCHO} + 5\text{OH}^- \rightarrow \text{Cu}_2\text{O} + \text{HCOO}^- + 3\text{H}_2\text{O} \quad (1)$$

The resulting cuprous oxide is very harmful due to the production of copper powders by reduction and disproportionation reaction (2)-(4). Copper powder as the catalytic activity center will be extensively studied by mixed potential, linear sweep voltammetry (LSV), Scanning Electron Microscopy (SEM), Energy Dispersive Spectrometer (EDS), and X-ray Diffraction (XRD).

1. Experimental

1.1 Materials and chemical

Potassium ferricyanide (Sinopharm Company), 2,2'-Dipyridyl (Aladdin), Copper(II) sulfate, EDTA, PEG6000, formaldehyde (LingFeng Chemical), THPED (Dow Chemical) and sodium hydroxide (Binghai Chemical) were used. All chemical reagents were analytical grade.

The plating tests were performed on a pure copper foil (150 mm × 100 mm × 0.5 mm) in a 500 ml glass beaker in a thermostatic water bath. The pretreatment steps of the sample: cleaning (ethanol) → rinsing (deionized water) → degreasing (5% NaOH) → rinsing (deionized water) → micro-etching (5% cit-
The mixed potential is a main method to study mechanism of electroless plating. When the mixed potential of the electroless copper plating system,24,26 \( E_{\text{mix}} \) is the thermodynamic factor for the electroless plating. When the mixed potential of the electroless solution is only more negative than the reduction potential of the metal complex ions, the reduction reaction of the metal complex ions happens.8 In other words, the more negative potential of electroless solution is favorable to the deposition reaction of metal ions. Previous studies have confirmed that the reduction rate of metal ions become faster with the negative shift of the mixing potential.22

Figure 1 showed the change of mixed potential \( E_{\text{mix}} \) with and without \( K_3\text{Fe(CN)}_6 \) on pure copper electrode surface at 23 ± 1°C. The trend of \( E_{\text{mix}} \) illustrates that the overall process can be divided into three regions designated the induction region (a), transitional region (b) and stable region (c).27 For the induction region, the potential fell off rapidly in the first 45 seconds, and the fall-off value \( \Delta E \) of \( E_{\text{mix}} \) is about 60%. The fall-off value \( \Delta E \) of \( E_{\text{mix}} \) due to the rapid adsorption of the charged ions (such as CuL+ and \( \text{OH}^- \)) on the copper surface. This phenomenon happened once the copper electrode was immersed into the electroless plating solution. Due to the large size of electropositive ions (CuL+), the diffusion-migration velocity of electronegative ions (\( \text{OH}^- \)), the diffusion-migration velocity of electronegative ions was greater than that of electropositive ions. Therefore, more electronegative ions were adsorbed on the copper overall electrode potential of electroless plating solution, as well as mixed potential.22–26

| Table 1. Solution composition for electroless copper. |
|-------------------------------------------------------|-----------------|
| Chemical   | CuSO\(_4\) mol L\(^{-1}\) | EDTA mol L\(^{-1}\) | THPED mol L\(^{-1}\) | NaOH mol L\(^{-1}\) | Formaldehyde mol L\(^{-1}\) | PEG6000 mg L\(^{-1}\) | 2,2',dipyridyl mg L\(^{-1}\) |
| Conc.      | 0.05 | 0.03 | 0.025 | 0.2 | 0.13 | 30 | 8 |

| Table 2. Fall-off value of mixed potential at different \( K_3\text{Fe(CN)}_6 \) concentration. |
|-------------------------------------------------|-----------------|
| Sample number | Conc. of \( K_3\text{Fe(CN)}_6 \) | Fall-off value \( (\Delta E) \) of \( E_{\text{mix}} \) |
|----------------|-----------------|
| 1              | 0 mg L\(^{-1}\) | 0.11 V |
| 2              | 10 mg L\(^{-1}\) | 0.083 V |
| 3              | 20 mg L\(^{-1}\) | 0.082 V |
| 4              | 30 mg L\(^{-1}\) | 0.061 V |
| 5              | 40 mg L\(^{-1}\) | 0.055 V |
| 6              | 50 mg L\(^{-1}\) | 0.043 V |

Figure 1. Mixed potential-time curves in dual-ligands electroless copper solution with different \( K_3\text{Fe(CN)}_6 \) concentration.
electrode surface, which led to the negative shift of electrode potentials quickly.

With the accumulation of positive and negative ions on the electrode surface, the redox reactions happened. The electropositive ions (CuL$^2^{+}$) and the electronegative ions (OH$^-$) were consumed. While the diffusion-migration velocities of the former were still slower than the latter, the supplement of electronegative ions (OH$^-$) were faster than the electropositive ones. So, the potential continued to shift negatively, $\Delta E$ of this region accounted for about 20% of total $\Delta E$, but shift rate was slower than in the induction region. This process was named as the transitional region. After about 100 seconds, the consumption and supplement rates of positive and negative ions gradually reached equilibrium. At this stage, mixed potential became stable. Notably, three regions existed in a continuum without obvious demarcation.

The fall-off value ($\Delta E$) was defined as the difference of mixed potentials before and after 400 s measurement in Fig. 1. From Table 2, it was found that $\Delta E$ value decreased with the addition of K$_3$Fe(CN)$_6$. The $\Delta E$ value was only 0.043 V due to the addition of 50 mg L$^{-1}$ K$_3$Fe(CN)$_6$, and much lower than that (0.11 V) without K$_3$Fe(CN)$_6$. In aqueous solution, K$_3$Fe(CN)$_6$ would be immediately dissociated to electronegative Fe(CN)$_6^{3-}$ ions, allowing OH$^-$ to be adsorbed competitively onto copper electrode surface. The radius of Fe(CN)$_6^{3-}$ was greater than the OH$^-$ particle radius, causing the decrease of the charge number of electronegative ions in unit area. Therefore, $\Delta E$ value reduced. The higher K$_3$Fe(CN)$_6$ concentration was, the smaller $\Delta E$ value was.

### 2.2 Linear sweep voltammetry (LSV) studies

LSV was used to test the cathode reduction behavior of copper-ligand component with different K$_3$Fe(CN)$_6$ concentration (Fig. 2). Table 3 showed the current density of cathodic reduction with different K$_3$Fe(CN)$_6$ concentration. With the increase in K$_3$Fe(CN)$_6$ concentration, the current density of the reduction peak decreased from 13.6 µA (0 mg L$^{-1}$) to 3.62 µA (50 mg L$^{-1}$) and the decrease ratio was up to 73.4%.

Figure 3 and Table 4 showed LSV curve of the formaldehyde oxidation. It can be seen that the oxidation potential of formaldehyde with different K$_3$Fe(CN)$_6$ concentrations were similar, with an oxidation peak around $-0.47$ V. The current density of oxidation peak decreased due to the addition of K$_3$Fe(CN)$_6$, from 12.08 µA (0 mg L$^{-1}$) to 3.91 µA (50 mg L$^{-1}$) and ratio was 67.6%. The results indicated that K$_3$Fe(CN)$_6$ can decrease the reaction rates of both formaldehyde oxidation and copper (II) reduction. The decrease ratios were similar for both reactions. This may be related to the absorption of K$_3$Fe(CN)$_6$ on the copper electrode surface, which may reduce the effective area for redox reactions.

### 2.3 Influence of K$_3$Fe(CN)$_6$ on deposition rate

Figure 4 showed the copper deposition rate at different K$_3$Fe(CN)$_6$ concentration. The deposition rate decreased from 5.96 µm/h to 2.43 µm/h with the increase of K$_3$Fe(CN)$_6$, concentration from 0 mg L$^{-1}$ to 50 mg L$^{-1}$ and the decrease ratio was about 60%. The result was also consistent with previous studies of mixed potential and linear voltammetry scanning. With the addition of the K$_3$Fe(CN)$_6$, the fall-off trend of the mixed potential became slow, which led to the decrease of the reaction driving force. So, current density of Cu reduction decreased, as measured by the linear sweep voltammetry test. This result explained the reason of reduction of plating rate.

### 2.4 Bath stability

Table 5 showed the decomposition time of electroless solution with different K$_3$Fe(CN)$_6$ concentration. It was found that the decomposition time was 22 mins for the solution without additive. However, the time increased sharply to 65 mins by the addition of 10 ml/L K$_4$Fe(CN)$_6$. The time was up to 158 mins in the presence of 50 ml/L K$_3$Fe(CN)$_6$. The results indicated that K$_3$Fe(CN)$_6$ can effectively inhibit the reoxidation of Cu(I) ion due to the formation of stable Cu(CN)$_2^{2-}$ complex by the reaction between Cu(I) and CN$^-$ ($K = 24$) according to Eq. (6).

$$\text{Cu}^+ + 2\text{CN}^- \rightarrow \text{Cu}^+\text{(CN)}_2^{2-} \quad (6)$$

The decomposition times of electroless copper solution with K$_3$Fe(CN)$_6$ and K$_4$Fe(CN)$_6$ were examined and listed in Table 5. It was seen that the decomposition times of K$_3$Fe(CN)$_6$ were shorter than those of K$_4$Fe(CN)$_6$. It meant that K$_3$Fe(CN)$_6$ was more effective stabilizer for electroless copper solution.
2.5 Influence of K₃Fe(CN)₆ on surface microstructure of Cu layer

Figure 5 displayed SEM images of the copper layers obtained in the solution with different K₃Fe(CN)₆ concentration. The surface of copper layers was uniform. It can be seen that the particle sizes in copper layers obtained with and without additives were similar and the values were about 0.2–0.5 μm. However, steps in the copper particles can be observed for the copper layer obtained in the solution without additives. The element compositions of copper layers were further examined by EDS and the results were shown in Fig. 6. Only characteristic peaks of pure copper existed and iron element was not detected. It indicated that K₃Fe(CN)₆ was not involved in the reduction reaction.

Figure 7(a) presented the XRD patterns of copper layer obtained by electroless deposition with K₃Fe(CN)₆ as stabilizer. Three diffraction peaks displayed at 43.0° ± 0.1°, 50.1° ± 0.1° and 73.9° ± 0.1° correspond to crystal planes of Cu (111), (200) and (220). The results were very close to the powder diffraction standards (PDF card number 040836: 43.297°; 50.433°; 74.140°), which represented a face-centered cubic lattice structure. According to the intensity percents (R) of diffraction peak for each crystal plane in Fig. 7(b) and Table 6, R₁₁₁ and R₂₀₀ decreased, while R₂₂₀ increased from 25.7% (0 mg L⁻¹) to 70.4% (50 mg L⁻¹). The values of η[R₂₂₀/R₁₁₁] and η[R₂₂₀/R₂₀₀] increased from 0.46 and 1.43 to 5.88 and 4.01 with the increase of K₃Fe(CN)₆ concentration from 0 mg L⁻¹ to 50 mg L⁻¹, respectively. These results demonstrated that the preferred orientation was (111) crystal plane for the copper layer obtained in the solution without K₃Fe(CN)₆. However, with the addition of K₃Fe(CN)₆, (111) crystal plane became the preferred orientation.

The average grain size of the electroless copper layer can be calculated by full width at half maxima (FWHM) of crystal plane diffraction peak by Scherrer formula:

\[ D = \frac{K \lambda}{β \cos θ} \]  

(7)

Where \( K \) is Scherrer constant and the value is usually 0.89; \( λ \) is the wavelength of X-ray (0.15418 nm), \( β \) is full width at half maxima (FWHM), \( θ \) is Bragg diffraction Angle. The average grain sizes were

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**Table 5.** Decomposition time (min) of electroless solutions containing K₃Fe(CN)₆ and K₄Fe(CN)₆·3H₂O stabilizer at 65°C.

| Conc. of stabilizer (mg L⁻¹) | 0  | 10 | 20 | 30 | 40 | 50 |
|-----------------------------|----|----|----|----|----|----|
| Decomposition time (K₃Fe(CN)₆) | 22 | 65 | 106 | 127 | 145 | 158 |
| K₄Fe(CN)₆ | 22 | 61 | 101 | 119 | 136 | 150 |

**Figure 5.** SEM micrographs at different K₃Fe(CN)₆ concentration (Sample number as shown in Table 2).
Figure 6. EDS analysis at different K₃Fe(CN)₆ concentration (Sample number as described in Table 2).

Figure 7. (a) XRD patterns of electroless copper layer at different K₃Fe(CN)₆ concentration (b) The value (R) of preferred orientation at different K₃Fe(CN)₆ concentration. $R_{(111)} = I_{(111)}/\Sigma (I_{(111)} + I_{(200)} + I_{(220)})$ and $R_{(220)} = I_{(220)}/\Sigma (I_{(111)} + I_{(200)} + I_{(220)})$. 

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shown in Table 6. It was found that the average grain size of the layer decreased from 61.5 nm (0 mg L⁻¹) to 40.4 nm (50 mg L⁻¹). It suggested that even a small addition of K₃Fe(CN)₆ can refine the crystalline grain of electroless copper.

3. Conclusions

K₃Fe(CN)₆ as an stabilizer for electroless copper plating was proposed and the adjustment action on deposition behavior and surface structure of Cu layer was confirmed. The fall-off trend of the mixed potential was slowed due to the addition of K₃Fe(CN)₆, which was related to the competitive adsorption between Fe(CN)₆³⁻ and OH⁻ on the copper electrode surface. The current densities of Cu reduction and formaldehyde oxidation decreased approximately 70% with competitive adsorption of K₃Fe(CN)₆. The deposition rate of Cu layer also reduced from 5.96 µm/h to 2.43 µm/h with the increase of K₃Fe(CN)₆ concentration from 0 mg L⁻¹ to 50 mg L⁻¹ and the decrease ratio was about 60%. The addition of K₃Fe(CN)₆ could effectively inhibit the reoxidation of Cu(I) ion and increase sharply the decomposition time of electroless solution. Copper layers prepared by EDTA/THPED dual-ligands system exhibited uniform particle distribution and possesses high-purity. Moreover, the addition of K₃Fe(CN)₆ was favorable to the formation of the preferred orientation on (220) crystal plane and also led to grain refinement with the decrease of grain size from 61.5 nm to 40.4 nm. This work supported continue research and applications of K₃Fe(CN)₆ as a stabilizer for electroless copper plating.

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Table 6. The intensity ratio of the XRD characteristic peaks at different K₃Fe(CN)₆ concentration.

| Conc. K₃Fe(CN)₆ | Crystallite size | R₁₁₁% | R₂₀₀% | R₂₂₀% | ηR₂₂₀/R₁₁₁ | ηR₂₂₀/R₂₀₀ |
|----------------|-----------------|-------|-------|-------|-------------|-------------|
| 0 mg L⁻¹       | 61.5 nm         | 56.4  | 17.9  | 25.7  | 0.46        | 1.43        |
| 10 mg L⁻¹      | 57.0 nm         | 24.5  | 28.6  | 46.9  | 1.91        | 1.64        |
| 20 mg L⁻¹      | 51.9 nm         | 17.5  | 27.4  | 55.1  | 3.15        | 2.01        |
| 30 mg L⁻¹      | 48.7 nm         | 15.3  | 25.4  | 59.3  | 3.86        | 2.33        |
| 40 mg L⁻¹      | 45.2 nm         | 15.1  | 19.0  | 65.9  | 4.35        | 3.46        |
| 50 mg L⁻¹      | 40.4 nm         | 12.0  | 17.6  | 70.4  | 5.88        | 4.01        |

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