# In situ *Measurement of the Mixed Potential Of Electroless Copper Deposition*

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**The mixed potential of the electroless deposition has been used as a diagnostic criterion for the feasibility of such depositions. *In situ* measurement method of the mixed potential of electroless copper deposition was studied in this experiment. Using a specially designed working electrode, the mixed potential can be continuously monitored as the deposition reaction proceeds, and the instantaneous rate of deposition can be estimated from this mixed potential.**

**The instantaneous rate of copper deposition decreased as the mixed potential decreased from -0.83V to -0.66V within 15 min, when the palladium catalytic surface was covered by the copper deposit. The experimental result showed that the variation of the mixed potential with time of deposition is dominated by the catalytic activity of the substrate surface. This measurement method should prove useful for facilitating development of electroless copper deposition.**

## Introduction

Electroless deposition is accomplished by the continuous reduction of metal ions by some reducing agents at the catalytic substrate.[1] Typically, the constituents of an electroless plating solution include a source of metal ions, a reducing agent, a complexing agent and a stabilizer or inhibitor.

The chemical and physical properties of the deposit depend on the formulation and operating conditions of the plating solution. For example, the electroless deposits may exhibit special hardness, wear resistance, solderability, conductivity, precious metal diffusion barrier properties, corrosion resistance and electromagnetic interference shielding (EMI).[1,2,3] These various chemical and physical characteristics of electroless deposits make them useful in engineering and electronic applications. One of the most important applications of electroless copper in electronics is plating through holes (PTH) and plating of blind microvias in the fabrication of printed circuit boards .[4,5,6,7]

The instantaneous rate of electroless deposition estimated by the polarization resistance method has been reported.[8,9] A mechanism of electroless deposition has been proposed based on kinetic measurements.[10,11,12,13] The relative catalytic activity of metals for the anodic oxidation of various reducing agents has been determined from the oxidation potential.[14,15]

The theory of electroless deposition is based on the mixed potential theory as a combination of two different simultaneous electrochemical reactions.[16,17,18,19,20] According to the mixed potential theory, the rate of a Faradaic process is independent of the other Faradaic processes occurring at the electrode and depends only on the electrode potential.[21,22] Therefore, the polarization curves for independent anodic and cathodic processes may be added to predict the overall potential (called mixed potential) and rate when more than one reaction occurs simultaneously at an electrode. Therefore, the mixed potential of electroless deposition has been used as a diagnostic criterion for the feasibility of the deposition.

**Table 1**
**Mixed Potentials Obtained By the Potential Scan Method**

| Scan Direction | Scan Rate 0.2 mV/sec | 2.0 mV/sec | 20.0 mV/sec |
|---|---|---|---|
| Anodic | -0.675 V | -0.678 V | -0.685 V |
| Cathodic | -0.685 V | -0.677 V | -0.675 V |

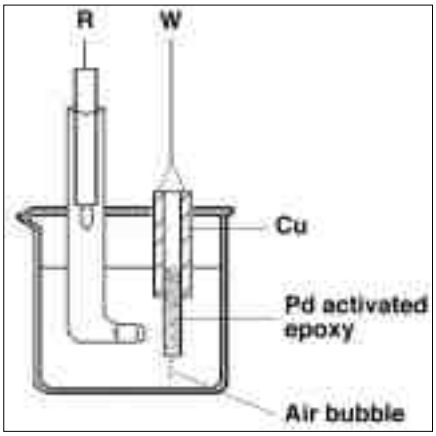


*Fig. 1—Schematic diagram of the cell used for the* in situ *measurement of mixed potential.*

When the mixed potential of the deposition is more negative than a certain optimum value, the deposition rate is faster and the plating solution is less stable. While the mixed potential is less negative than the optimum value, the deposition rate is slower.[23,24,25]

The polarization curves for copper deposition and the oxidation of the reducing agent have been obtained by the steady-state galvanostatic step method and by the potential scan technique. However, the mixed potential obtained by the former method is not valid if the catalytic activity of the electrode surface changes with potential over the range of interest,[1] and the mixed potential obtained by the latter method is dependent on the scan rate. Thus, an *in situ* method for measuring the mixed potential of electroless copper deposition was investigated and compared with the mixed potentials obtained by the steady-state galvanostatic step and potential scan methods.

## Experimental Procedure

The major constituents of the complete electroless copper plating solution were 0.05M $CuSO_4.5H_2O$, 0.10M EDTA and 0.22M formaldehyde. For study of the independent anodic and cathodic processes, the anolyte was 0.22M formaldehyde, and the catholyte was 0.05M $CuSO_4.5H_2O$ plus 0.10M EDTA. The pH of the solutions was adjusted with sodium hydroxide to 12.3 at 25°C. During measurement the aerated solution temperature was kept at 55°C. The flow rate of air was kept at 1000 mL/min.

The polarization curve and mixed potential were determined with an EG&G model 273A galvanostat/potentiostat interfaced with a personal computer. A saturated calomel

**Table 2**
***In Situ* Mixed Potential**

| Deposition Time, min | 0 | 1 | 2 | 5 | 10 | 15 | 60 |
|---|---|---|---|---|---|---|---|
| Mixed Potential, V | -0.830 | -0.720 | -0.685 | -0.670 | -0.664 | -0.660 | -0.660 |

(SCE) electrode was used as a reference electrode. Except for the *in situ* measurement, the working electrode was a copper disk electrode with a surface area of 1 $cm^2$.

The working electrode for the *in situ* measurement of the mixed potential was prepared by etching the lower third of a 1x10 $cm^2$ strip of double-sided copper/epoxy laminate with a copper etching solution to remove the copper (Fig. 1). The laminate was then treated with the usual pretreatment processes for electroless copper deposition on epoxy (Fig. 2).[26] After the accelerator step, the lower half of the laminate was immersed in the 250 mL electroless copper plating solution to deposit copper. Simultaneously, it was connected to a potentiostat as a working electrode to measure the deposition potential (mixed potential) *in situ* (Fig. 1). The variation of the *in situ* mixed potential with time was recorded as the electroless copper deposition proceeded for one hour.

The polarization curves for copper deposition and formaldehyde oxidation were obtained by the galvanostatic step method in the range of $10^{-1}$ to $10^{-6}$ A/$cm^2$ at the copper electrode in the 250 mL electroless copper solution as well as in the 250 mL catholyte or anolyte separately for 40 min. The mixed potential was obtained from a potential scan at the copper electrode in the 250 mL electroless copper plating solution with scan rates of 0.2 mV/sec, 2 mV/sec or 20 mV/sec anodically (-1.00V to -0.2V vs. SCE) or cathodically (-0.2V to -1.0V vs. SCE).

## Results & Discussion

### *Galvanostatic Step Studies*

**Complete Copper Plating Solution.** The polarization curves for copper deposition and formaldehyde oxidation in the complete electroless copper plating solution obtained by the steady-state galvanostatic step method at the copper electrode are shown in Fig. 3. Since the slopes of the polarization curves are the Tafel slopes, the intersection of these two polarization curves would be the mixed potential ($E_{mix}$) and the deposition current (log $I_{dep}$). It appears that the mixed potential was approximately -0.65 V. However, there was no unequivocal way to obtain an accurate Tafel slope. Consequently, the deposition current derived from the interception of the Tafel slopes was also inaccurate. Nevertheless, it still may provide a valuable estimate of the Tafel slopes.

At the mixed potential, the current density of the formaldehyde oxidation measured in the anolyte was considerably lower than that for the copper deposition reaction measured in the catholyte. Therefore, the rate-determining process of the electroless copper deposition was the formaldehyde oxidation reaction. That is, the rate of copper deposition cathodic partial reaction was totally dependent on the kinetics of the anodic partial reaction.

The Tafel slope for the formaldehyde oxidation was greater than 180 mV/decade. The steep anodic Tafel slope indicates that the complex anodic catalytic oxidation reaction of formaldehyde at the copper electrode is activation-controlled in the overall electroless copper reaction. Therefore, the anodic polarization curve should be influenced mainly by the catalytic activity of the copper electrode surface, which in turn is affected by the surface potential.

The Tafel slope for the copper deposition was less than -50 mV/decade. The shallow cathodic Tafel slope indicates that the cathodic partial reaction is diffusion-controlled in the complete electroless copper reaction. Hence, the cathodic polarization curve should be influenced by the rate of air agitation. In the present study, the rate of air bubbling was set at 1000 mL/min which is the same rate at which the mixed potential was measured *in situ*.

**Anolyte & Catholyte Solutions.** The polarization curves for the formaldehyde oxidation in the anolyte and copper deposition in the catholyte measured by the steady-state galvanostatic step method at the copper electrode are shown in Fig. 4.

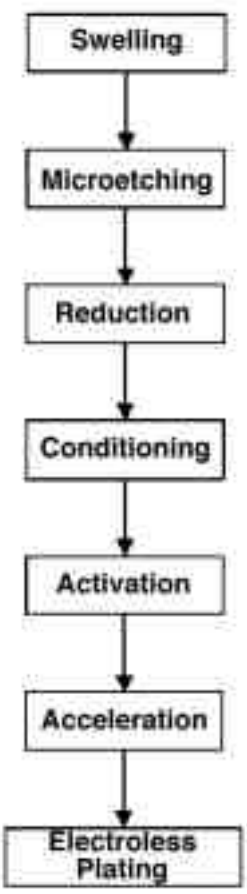


*Fig. 2—Process sequence for metallization.*

For each anodic galvanostatic step, the potential became more positive with time in the anolyte. A steady-state potential was reached and recorded after approximately 20 min for each step. The Tafel slope of the formaldehyde oxidation was calculated to be 65 mV/decade, which is considerably smaller than the value estimated from the anodic partial process for the overall electroless copper reaction described earlier (>180mV/decade). The difference between the reaction in the anolyte and in the complete electroless plating solution may be attributed to the presence of copper ions and cathodic partial reaction in the full plating solution.

For each cathodic galvanostatic step, the potential became more negative with time in the catholyte. A steady-state potential was reached and recorded after 20 min for each step. The Tafel slope of copper deposition was calculated to be -190 mV/decade, which is larger than the value estimated from the cathodic partial process of the total electroless copper reaction described earlier (<-50 mV/decade). The difference between the catholyte reaction and that in the electroless plating solution may be attributed to the presence of the formaldehyde and the anodic partial reaction in the plating solution.

At the intersection of the anodic and cathodic polarization curves, the mixed potential and the copper deposition rate were estimated to be -0.63 V and $1.2 \times 10^{-3}$ A/$cm^2$ respectively. However, the actual electroless copper deposition process involves electrons being released from the anodic partial reaction and consumed by the cathodic partial reaction. Thus, the overall rate of electroless deposition is governed by the slower of the two partial reactions, which is the formaldehyde oxidation reaction described earlier. Therefore, the actual

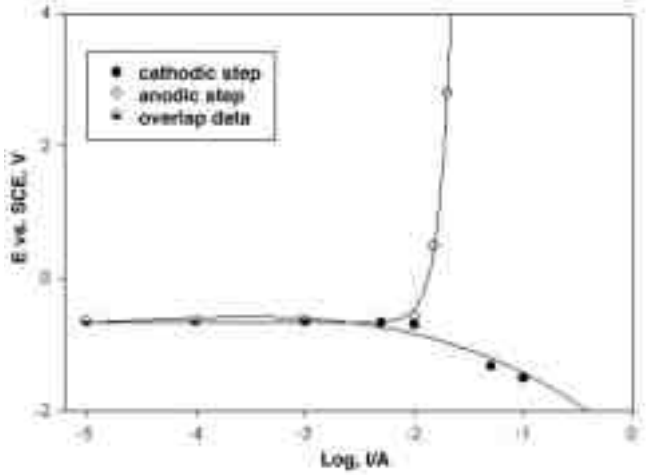


*Fig. 3—Polarization curves obtained from the complete electroless plating solution.*

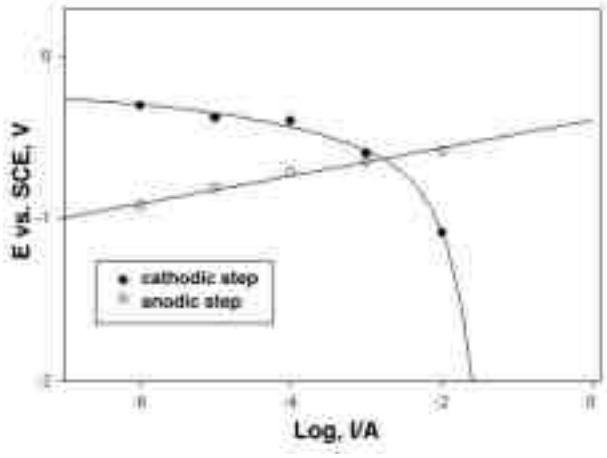


*Fig. 4—Polarization curves obtained from the catholyte and anolyte.*

overall current of the electroless copper deposition reaction should be lower than that obtained from the individual polarization curves. Therefore, the true value of the mixed potential should be more negative and the true deposition rate should be lower than those obtained from the two individual partial electrode processes.

## *Potential Scan Studies*

The logarithmic current-voltage curve obtained by potential scan in the complete electroless copper plating solution would be the Tafel plot. The zero current potential was the mixed potential of the electroless copper deposition. The current of any given potential on the Tafel plot could be calculated from the Butler-Volmer equation which consists of two terms.[27] For the mixed potential with a large cathodic overvoltage, only the cathodic reaction term (copper reduction reaction) is significant, and the anodic reaction term (formaldehyde oxidation reaction) is relatively small. Conversely, for the mixed potential with a large anodic overvoltage, only the anodic reaction term is significant. In the vicinity of the mixed potential, both the cathodic and anodic overvoltages are small in relation to the mixed potential of the electroless copper deposition. Therefore, both terms of the Butler-Volmer equation need to be considered. Besides rate constants of oxidation and reduction, the concentrations of the electroactive species at the electrode surface are relevant to the overall current. Therefore, the mixed potential and the deposition rate obtained from the potential scan method should be influenced by the scan rate.

Theoretically, the extrapolation of the linear portions of the anodic and cathodic Tafel plots to the zero overvoltage (mixed potential) should give an intercept which would be the exchange current corresponding to the copper deposition rate (log $I_{dep}$). However, as was previously described, there was no unequivocal way to get an accurate value for the Tafel slope. Only estimated values of the Tafel slope and deposition current could be obtained. The estimated anodic Tafel slope was approximately 180 mV/decade and the cathodic Tafel slope was approximately -50 mV/decade. The mixed potentials for the various scan rates are shown in Table 1.

The redox reaction of copper ion at copper electrode is a simple reversible reaction. Further, the reduction of copper occurs at the beginning of the anodic scan. At the electrode surface the copper ion concentration decreases to the diffusion steady state value rapidly. As one scans toward the more positive potential, the rate of copper ion consumption at the electrode surface decreases and the rate of formaldehyde oxidation increases. At the mixed potential, the rate of copper ion reduction and the rate of formaldehyde oxidation are equal. Because of the interplay of consumption and diffusion of the surface-active ions, the mixed potential varied with the scan rate. With a high scan rate (20mV/sec), with the fast depletion and slow rate of diffusion of copper ion to the electrode, the concentration of copper ion at the electrode surface was lower at the same potential, resulting a more negative mixed potential (-0.685 V). With a lower scan rate (20 mV/sec → 2 mV/sec → 0.2 mV/sec), the steady-state concentration of copper ion at the electrode surface resulted in a more positive mixed potential (-0.685V → -0.678V → -0.675V, respectively). However, the variation was limited and within experimental error (-0.68 ± 0.01V).

The reaction of formaldehyde at the copper electrode is a slow irreversible catalytic oxidation reaction. Further, the oxidation of formaldehyde occurred at the beginning of cathodic scan. As one scans toward a more negative value, the rate of formaldehyde consumption at the electrode surface decreases and the rate of copper ion reduction increases. Therefore, with a low scan rate (0.2 mV/sec), a steady-state copper ion concentration was established and a more negative mixed potential was obtained (-0.685 V). If the scan rate was increased (0.2 mV/sec → 2 mV/sec → 20 mV/sec), a more positive mixed potential was obtained (-0.685V → -0.677V → -0.675V, respectively), because of nature of the simple reduction of copper ion and the comparatively slow rate of copper ion diffusion. The variation of the mixed potential was within experimental error (-0.68 ± 0.01V).

## *In situ* Measurement

The mixed potential obtained from the *in situ* measurement is shown in Table 2. The mixed potential varied with the electroless copper deposition time. At the beginning of deposition, the deposition reactions took place on the palladium-activated epoxy substrate and the mixed potential was -0.83V vs. SCE. As the copper deposition proceeded, the palladium catalytic surface was gradually covered by the electroless copper deposit, and the mixed potential decreased. After 15 min of deposition, the substrate was completely covered by the copper deposit. Once the deposition reactions occurred on the electroless copper deposit, the mixed potential was -0.66 ± 0.01V. From then on, the mixed potential was fixed at -0.66 ± 0.01 V, up to 60 min of deposition.

The rate-determining process of the electroless copper

deposition was the formaldehyde oxidation. Hence the rate of deposition was lower if the mixed potential was more positive. In the present study, as the mixed potential decreased from -0.83 V vs. SCE to -0.66 V vs. SCE, the instantaneous rate of copper deposition decreased.

The true mixed potential of the electroless deposition is influenced by many factors, such as the catalytic activity of the substrate surface, temperature, pH, and the composition and concentration of the plating solution. In this study, the temperature of the plating solution was fixed at 55°C. As the deposition proceeded, all other factors changed with time. According to the results of the present study (Table 2), the mixed potential was dominated by the catalytic activity of the substrate surface, and it decreased from -0.83V to -0.66V within 15 min as the copper deposit covered the palladium catalytic surface. Because the load (the ratio of substrate surface area to the volume of the plating solution) was low here, the concentration of each component in the plating solution did not change significantly; therefore, the mixed potential remained at -0.66 ± 0.01V up to 60 min of deposition.

## Conclusions

The polarization curves of copper deposition and formaldehyde oxidation have been obtained by the steady-state galvanostatic step method and the potential scan technique to determine the mixed potential of electroless copper deposition. The mixed potential obtained from the galvanostatic step method was -0.63V vs. SCE, and the mixed potential obtained from the potential scan technique was -0.68 ± 0.01V vs. SCE. However, the true mixed potential of electroless deposition varied with the time of electroless copper deposition. At the beginning of the deposition, the mixed potential was –0.83V vs. SCE, measured on the palladium-activated surface of epoxy. The mixed potential and the instantaneous rate of copper deposition decreased as the copper deposit gradually covered the palladium catalytic surface. The mixed potential was –0.66V vs. SCE when it was measured on the copper deposit. These results show that the variation of the mixed potential was dominated by the catalytic activity of the substrate surface. This measurement method should prove useful in facilitating the future development of electroless copper deposition processes.

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