Behavior of 2, 9-Dimethyl-1, 10-phenanthroline Additive in Electroless Copper Plating

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無電解銅めっきにおける2, 9-ジメチル-1, 10-フェナントロリン添加剤の挙動

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Key Words : Electroless Copper Plating, Phenanthroline, Copper Deposition, Colorimetry, Additive

Introduction

Electroless copper plating is also referred to as chemical copper plating. As its name implies a copper complex is chemically or autocatalytically reduced to copper on a catalytic surface. In general, a copper deposit obtained in this plating has poor physical properties compared with one obtained in copper electroplating. For the improvement of properties of electroless copper, some additives have been proposed^{1), 2)}. Among them, 2,9-dimethyl-1,10-phenanthroline (2,9-dmph), which is a Cu(I) chelating ligand and often used for a reagent for the spectrophotometric analysis³⁾ of copper is known to give rise to a ductile copper deposit¹⁾. Since little is known about the working mechanism of 2,9-dmph in this plating, studies on it have been done. Our previous publication⁴⁾ could give considerable insight into its working mechanism. Whether 2,9-dmph was reproduced in the bath, however, was a matter for argument. As for the behavior of 2,9-dmph, it is intriguing to note that its effects such as giving the deposit good ductility last long, although it is added in a small amount in the bath. From this fact, it can be assumed that there is the possibility of reproduction of 2,9-dmph in the bath. Such being the case, a further study has been made for confirming this view.

Experimental

Bath.-The bath composition was 0.030mol/L $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$, 0.036mol/L EDTA, 0.068mol/L

HCHO , and 50mg/L 2,9-dmph as an additive. The bath was adjusted to pH12.0 prior to plating. The temperature of the bath was maintained at 70°C in the process of plating.

Colorimetry.-Collecting 5mL of the bath in a test tube, a copper wire 0.6mm in diameter and 0.8m in length was soaked in the bath and plated for a given period of time. After the wire was withdrawn from the bath, 7mL isoamyl alcohol preheated at 70°C was added to the bath to extract the colored 2,9-dmph-Cu(I) complex formed in the bath by use of a separatory funnel. The extract was made up to 10mL with ethyl alcohol. For the colorimetric determination of the Cu(I) complex, the absorption spectra of the extract were measured with a Shimadzu Sp20 spectrophotometer by use of isoamyl alcohol as the reference solution.

A calibration curve was obtained by reference to Gahler's work³⁾. The curve obeyed Beer's law in the range of Cu concentration of 0.005 to 0.05 mg/10mL.

Results and Discussion

Cu(I) complex of 2,9-dmph.- Fig.1 shows the comparison of the absorption curves of extracts obtained in the bath before and after electroless plating. Curve a shows the absorption spectra of extract obtained in the bath after 3min of plating. The wavelength of maximum absorption at 450

Fig. 1 Absorption curves of 2,9-dmph-Cu(I) complex extracted from the bath described in Experimental.
a : after plating for 3min, b : before plating.

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nm⁴⁾ is almost identical with the 454nm reported by McCurdy, Jr. and Smith⁵⁾ for the cuprous complex of 2,9-dmphp. This accounts for the forming of 2,9-dmphp-Cu(I) complex in the bath as a result of electroless plating. Absorbance at 450nm and a calibration curve prepared in advance allow us to estimate the amount of the Cu(I) complex formed in the bath. In contrast, since absorption curve b obtained from the extract of the bath before plating did not exhibit any measurable effect on the intensity of absorption spectra, little of the Cu(I) complex was found to be formed. From these data and previous paper⁴⁾, it is elucidated that 2,9-dmphp is adsorbed on the copper wire to be plated and that reaction between the adsorbed 2,9-dmphp and the copper wire occurs to form the 2,9-dmphp-Cu(I) complex and that the resulting Cu(I) complex dissolves satisfactorily in the bath, rendering the color of the bath greenish.

Behavior of 2,9-dmphp additive.—From the determination of the Cu(I) complex, the ratio of 2,9-dmphp forming the Cu(I) complex to a total amount of 2,9-dmphp added in the bath was observed as a function of plating time. The data obtained are shown in Fig. 2. The ratio increased gradually with plating time and a plateau was reached in 10–15min. This plateau indicates a steady state where approximately 30 % of 2,9-dmphp added in the bath formed the Cu(I) complex. Paying attention to developments of the 2,9-dmphp-Cu(I) complex thus formed in the bath is interesting. After the copper wire was plated for 3min and then taken out of the bath, the bath was allowed to stand for given periods of time. The ratio of 2,9-dmphp forming the Cu(I) complex to a total amount of 2,9-dmphp as a function of standing time is shown in Fig. 3. The ratio decreased gradually with standing time and after 7min of standing, the Cu(I) complex present in the bath almost disappeared. In the course of standing, the bath had a color varying from green to blue to the naked eye too. This means that the Cu(I) complex can be no longer formed in the bath in the absence of the wire to be plated and that reaction between the Cu(I) complex formed so far and free EDTA present in the bath occurs, yielding blue CuY^{2-} and colorless 2,9-dmphp. From these results and previous paper⁴⁾ as well, one can conclude that the working of 2,9-dmphp is the following steps of 1) adsorption of 2,9-dmphp on the copper electrode to be plated, 2) formation of the 2,9-dmphp-Cu(I) complex on the copper electrode, 3) transference of the Cu(I) complex in the solution, and 4) reproduction of 2,9-dmphp in the bath. With the reproduction step included, it is easily understood that the working of 2,9-dmphp

Fig. 2 Effect of plating time on Cu(I) complex formed in the bath described in Experimental.

Fig. 3 Effect of standing time on Cu(I) complex amount in the bath after 3min of plating.
bath: described in Experimental

is constantly repeated during the course of plating. This is responsible for prevention of depletion of 2,9-dmphp in the bath and for its continuing effectiveness of yielding ductile copper.

Conclusion

- (1) The additive 2,9-dmphp was reproduced constantly in the plating bath and this was responsible for the continuing effect of yielding ductile deposits.
- (2) The amount of the 2,9-dmphp-Cu(I) complex formed in the bath increased with plating time; at a steady state about 30 % of 2,9-dmphp present in the bath formed the Cu(I) complex.
- (3) Little of the 2,9-dmphp-Cu(I) complex was formed before plating.

(Received February 14, 1994 ; Accepted March 28, 1994)

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