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Kinetic Study of Electroless Copper with Glycine as Complexing Agent

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In this work, the effect of Cu^{2+}, Ni^{2+}, glycine, sodium hypophosphite, pH value and temperature on the deposition velocity was studied by weight method. In addition, the deposition rate equation was calculated in the system using glycine as the complexing agent and sodium hypophosphite as the reducing agent.

Key Words: Electroless copper plating, Sodium hypophosphite, Glycine, Rate equation.

INTRODUCTION

Electroless copper plating technique is widely used in electronics for deposition of metallic copper layers on semiconductors or dielectrics (silicon wafers, resins, *etc.*)[1,2]. In electroless copper plating solutions all use formaldehyde as reducing agents. However, formaldehyde has been forbidden to be used in some country, because hazardous gases may release during electroless deposition process with pH > 11. Sodium hypophosphite as reducing agents is especially attractive because of its low pH, low cost and relative safety. Several papers have studied the electroless copper solutions using hypophosphite as reducing agent[3-5]. Norkus *et al.*[6] have used saccharose as the ligand, which can reacted with Cu^{2+} to form stable complex in the alkaline system. Moreover, the complex system composed of Cu^{2+} and citrate is drawing scholars' attention as well[4,5].

Aim of this study is to apply the electroless copper plating using hypophosphite as reducing agent and glycine as complexing agents. The effects of several important factors in the system of glycine electroless copper plating on the deposition rate are studied and the rate equation is also calculated.

EXPERIMENTAL

All the chemical reagents used in this experiment are analytically pure and the purity of the copper sheet is 99.9 %. Before electroless plating, the copper sheet was polished with 600# abrasive paper, electrolytic degreased, washed with distilled water and finally activated using ionic palladium chloride. In this experiment, the solution was composed of $CuSO_4$ 7.5 g/L, $NiSO_4$ 1 g/L, NH_2CH_2COOH 10 g/L, $NaH_2PO_2·H_2O$ 30 g/L, NaOH 6.5 g/L and $K_4Fe(CN)_6·3H_2O$ 30 mg/L. In addition, the electroless copper deposition was carried out at 60 °C and took 20 min. The electroless deposition rate was calculated by weight method.

RESULTS AND DISCUSSION

Figs. 1 and 2 show the scanning electron microscope (SEM) image and the energy dispersive X-ray spectroscopy (EDX) results of the electroless copper plating sample, respectively. It can be seen that the obtained copper film is crystallined and the atomic contents of Cu, Ni, P elements are 97.8, 2.1 and 0.09 %, respectively.

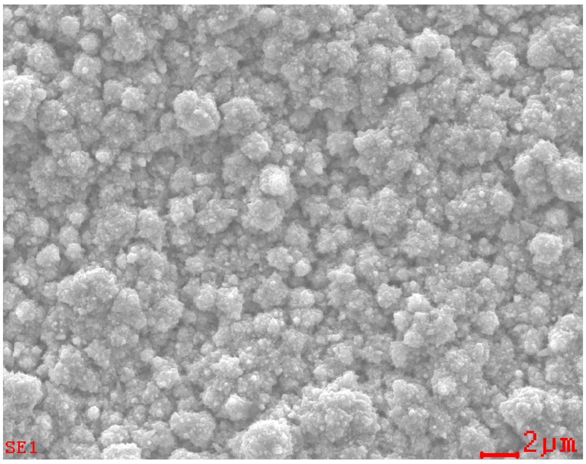


Fig. 1. SEM image of the electroless copper plating sample

The deposition rate (r) of electroless copper plating at different temperatures was calculated by weight method, as

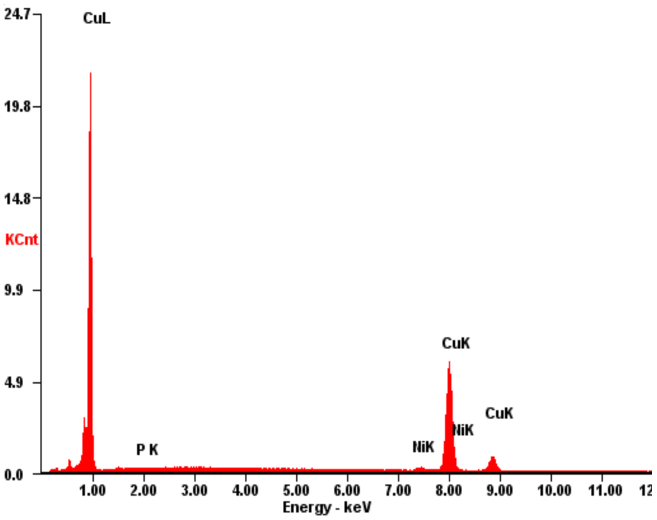


Fig. 2. EDX of the electroless copper plating sample

shown in Table-1. On plotting a graph with the logarithm of r as ordinate and the reciprocal of temperature (T) as abscissas, log r T^{-1} relational graph and then a straight line was obtained using the linear regression analysis (Fig. 3).

TABLE-1
DEPOSITION RATE (r) OF ELECTROLESS COPPER PLATING AT DIFFERENT TEMPERATURES

T (K)	r (g/m² min)	1/T × 1000	log r
323	2.2665	3.0960	0.3559
333	4.2320	3.0030	0.6265
343	6.9998	2.9155	0.8451
353	9.9159	2.8329	0.9963
363	10.3671	2.7548	1.0157

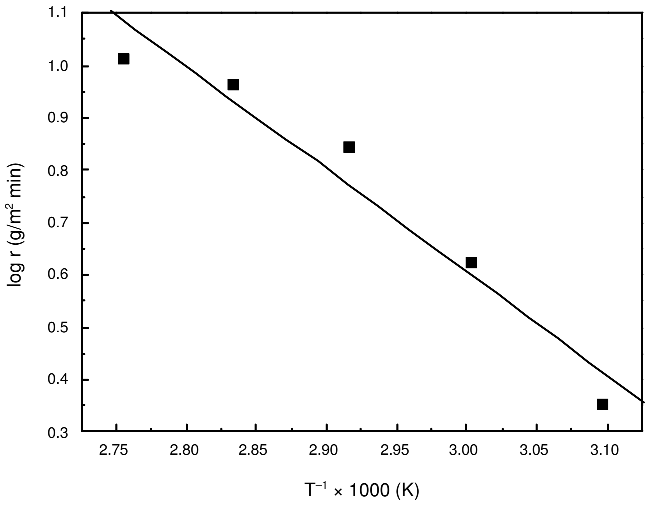


Fig. 3. Logarithmic relation curve of deposition rate as a function of temperatures

The activation energy for the reaction can be calculated through the formula below.

$$E_a = -2.303R\left(\frac{\partial \lg r}{\partial (T^{-1})}\right)_u \qquad (1)$$

It can be obtained from Fig. 3 that the slope of this line is -1.96256 and the linear correlation coefficient is -0.97257. According to the above formula, the apparent activation energy E_a for the reaction of the electroless copper plating is 37.58 kJ mol^{-1}. And this result is lower than that of the electroless copper plating used methanal as the reducing agent (E_a = 46-50 kJ mol^{-1}), but is higher than that of using citric acid as the complexing agent and sodium hypophosphite as the reducing agent (E_a = 8.04 kJ mol^{-1}), which is close to the activation energy used glyoxylic acid as the reducing agent (E_a = 37 kJ mol^{-1}).

The deposition rate of electroless copper plating is affected by many factors, such as Cu^{2+}, Ni^{2+}, $H_2PO_2^-$, glycine, pH and temperature, *etc*. And the relation between the deposition rate and every factor can be expressed through the equation below.

$$r = k_0\,[Cu^{2+}]^{\alpha}\,[Ni^{2+}]^{\beta}[H_2PO_2^-]\gamma[OH^-]^{\delta}[NH_2CH_2COOH]^{\xi}\ \exp(-E_a/RT)$$

Here α, β, γ, δ, ξ are all constants. Take the logarithm for both sides of the above equation and then we can obtain the following results.

Here p, q, r, s, t mean that other variables remain unchanged except the variable in each equation. If one factor among the factors affecting the deposition rate was changed while the other factors remained the same, the logarithmic relation curve between this factor and the deposition rate is a straight line and the slopes of the straight lines are the values of the kinetic parameters α, β, γ, δ, ξ.

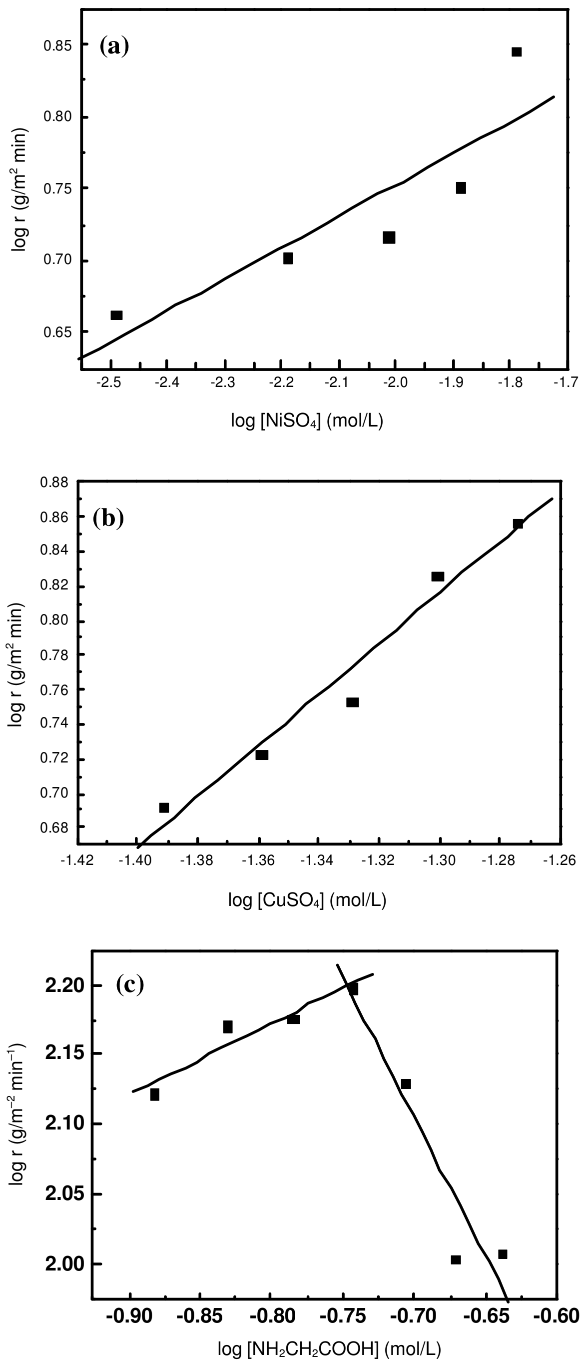
In this experiment, the deposition rate varied with the concentration of $CuSO_4$, $NiSO_4$, NH_2CH_2COOH, NaH_2PO_2 and OH^- are determined in the case of other components and technological conditions remaining the same (Fig. 4). It can be obtained from this experiment that the slopes of the five straight line. So the corresponding kinetic parameters are $\alpha = 1.480$, $\beta = 0.219$, $\gamma = 0.509$ (log $[NH_2CH_2COOH] < -0.75$), $\delta = -2.01$ (log $[NH_2CH_2COOH] > -0.75$), $\delta = 0.808$, $\xi = -0.140$, respectively. Then substitute these values into the rate equation:

$$r = k_0[Cu^{2+}]^{1.480}[Ni^{2+}]^{0.219}[H_2PO_2^-]^{0.509}[OH^-]^{0.808}[NH_2CH_2COOH]^{-0.140}\ \exp(-37.58/RT)$$

It can be seen from the equation that the concentration of $CuSO_4$ has the biggest influence on the deposition rate, followed by pH and NaH_2PO_2. In practice, we also find that a little variation of the pH value can result in the noticeable change of the deposition rate. The influence of $CuSO_4$ in this system is bigger than that in the system of citric acid (the reaction order is 0.121).

Conclusion

In the process of electroless copper plating, we chose glycine as the complexing agent and sodium hypophosphite as the reducing agent, then obtained a copper coated in which the contents of Cu, Ni and P were 97.8, 2.1 and 0.09 %, respectively. The effect of $CuSO_4$, $NiSO_4$, NH_2CH_2COOH, NaH_2PO_2 and OH^- on the electroless deposition rate was studied. In addition, the deposition rate equation of electroless copper plating was calculated and its apparent activation energy E_a was 37.58 kJ mol^{-1}. According to the obtained rate equation, the reaction orders for $CuSO_4$, OH^- and NaH_2PO_2 were 1.480, 0.808 and 0.314, respectively.



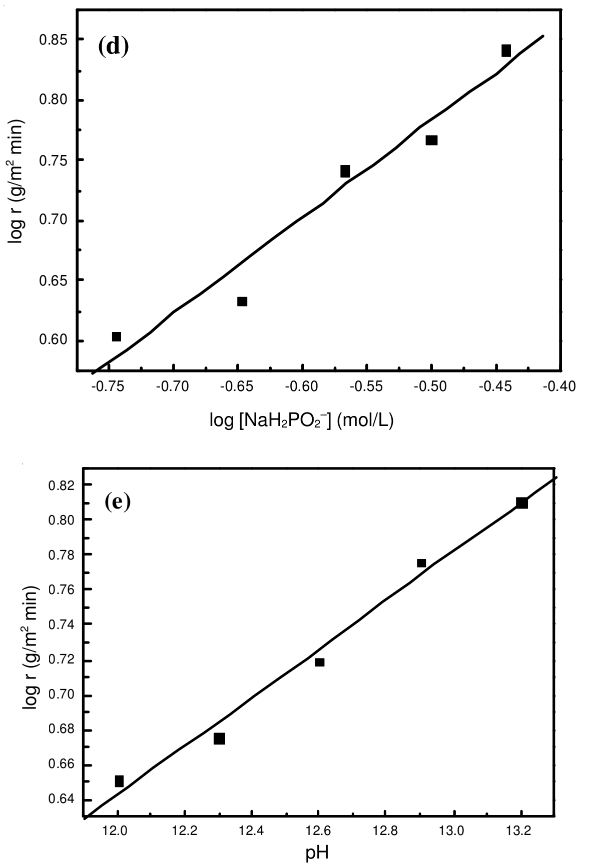


Fig. 4. Logarithmic relation curve for deposition rate as a function of the concentration of $CuSO_4$ (a), $NiSO_4$ (b), NH_2CH_2OOH (c), NaH_2PO_2 (d) and OH^- (e)

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