

Chapter 17

Electroless Plating Of Silver

N. Koura

It is frequently required to coat insulators such as glass and ceramics with metals. Many methods are available for coating, e.g., baking, chemical vapor deposition, ion-sputtering, and chemical plating. The chemical plating method is very effective because the apparatus is simple, it can be done on a complex substrate, and it is suitable for mass production. This method can be classified into two categories: (1) the galvanic exchange deposition method, where the potential difference between metals is utilized; and (2) the electroless plating method, where reducing agents are used. In this chapter, only electroless plating will be reviewed.

The silvering reaction is a well-known example of the electroless plating of silver. This reaction was devised by Drayton (1) in 1830 and developed by Liebig (2). This method is normally used to make mirrors. On the other hand, electroless plating methods, which are utilized in the printed circuit industry, have come into the limelight with the development of the electronics industry. The electroless silver plating method (including the silvering reaction) is important because any substance, i.e., both metals and insulators, can be coated with silver by using this technique. Here the fundamental research and applications of this method will be reviewed.

PLATING PROCESS AND THE REACTION MECHANISM

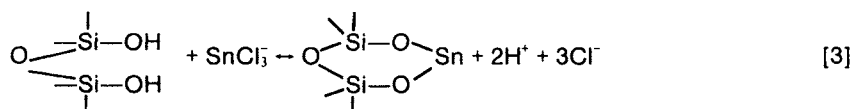
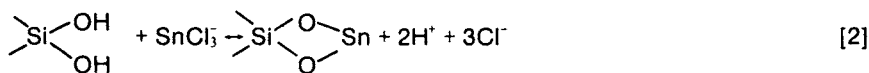
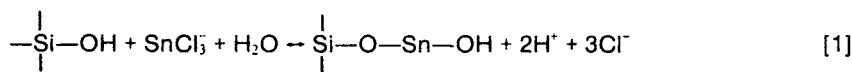
The substrate pretreatment for electroless silver plating affects early stages of the plating itself, and it plays an important role in the success of the plating process.

The reactions that occur in the pretreatment and the plating processes are separately summarized.

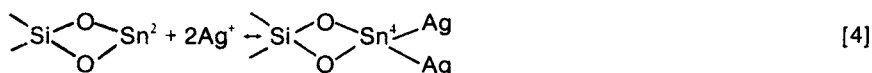
Pretreatment Process

The treatment for glass will be described first because electroless silver plating is usually carried out on glass. The plating is done soon after the pretreatment (3). In the pretreatment process, the glass is degreased with acetone and alcohol,

immersed in a SnCl_2 solution for 1 to 2 minutes, then rinsed in warm water. A SnCl_2 solution has been used as the pretreatment bath for a long time (4) and is thought to have two effects (1). Fine silver particles, which have a positive charge in the solution, adhere easily to the glass because the SnO_2 generated in the solution from the hydrolysis of Sn^{2+} adsorbs on the surface of the glass, and the negative charge on the surface increases. Ag^+ is reduced by Sn^{2+} and is then adsorbed on the surface. Recently, the mechanism was discovered (5). The behavior of Sn on glass was analyzed with X-ray photoelectron spectroscopy by Pederson (6) as follows:



First, the exchange reaction of the Sn^{2+} ion occurs on the surface of the glass according to Eqs. 1-3. Then silver deposits onto the glass in the early stages of the plating reaction, as shown in Eq. 4:



In this manner, the deposition of silver onto the pretreated glass surface is induced early in the reaction. Then the plating reaction progresses according to the theory stated in the next section. Geelen (7) also proposed a similar mechanism by using the model as shown in Fig. 17.1.

Plating Reaction

It is well known that the silvering bath is highly unstable. The bath decomposes as soon as the silvering reaction starts, and becomes muddy. Therefore it was believed that the silvering occurs through the adhesion of silver particles with positive charges generated in the solution (8). With this in mind, attempts were made to improve the silvering bath by stabilizing the fine silver particles in the solution with a protective colloid (9). Gelatin, arabic gum, organic acids, inorganic salts of zinc and lead, and copper sulfate were used as protective colloid reagents.

There are many reports (10,11) on the reaction mechanism of electroless plating. One study states that the plating reaction progresses with a combination of a cathodic reduction of a cation, i.e., $\text{M}^{n+} + ne \rightarrow \text{M}$, and an anodic oxidation of

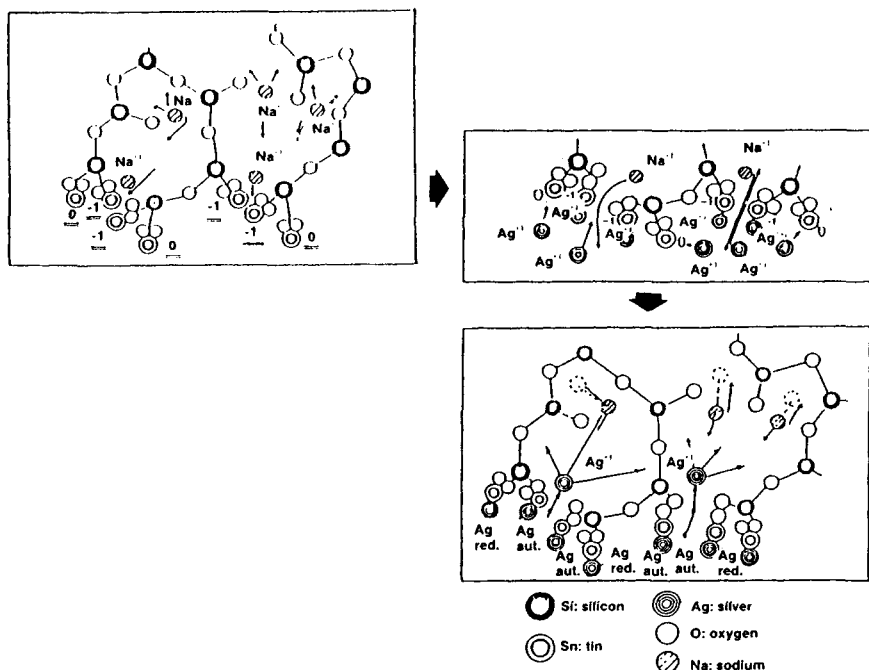


Fig. 17.1—Model of the early stages of silver plating reaction on a glass substrate (7).

the reducing agent, i.e., $\text{R} \rightarrow \text{O} + n\text{e}$. In this case, it is thought that a metal ion is cathodically reduced to metal on the surface, which is activated by a catalyst.

The above theory of electroless plating is applicable to silver plating because silver is a metal on which an autocatalytic reaction occurs (12) as shown in Table 17.1. The concept of potential-pH diagram is very important in this theory. The potential-pH diagrams for $\text{Ag}-\text{NH}_3-\text{H}_2\text{O}$ and $\text{Ag}-\text{CN}-\text{H}_2\text{O}$ systems and various reducing agents are shown in Figs. 17.2, 17.3, 17.4 and Table 17.2 (11,13). As the potential of silver is very noble, as can be seen in Fig. 17.2, many reducing agents can be used in electroless silver plating. There are 14 kinds of commercially available reducing agents: formalin; dextrose; Rochelle salts; Rochelle salts + silver nitrate; glyoxal; hydrazine sulfate; a boiled mixture solution of Rochelle salts and crystallized sugar; sugar inverted by nitric acid (14); KBH_4 or DMAB; aldonic acid and aldonic lactone (2,15); cobalt ion (16); sodium sulfide (17); triethanol amine (18); and $\text{CH}_2\text{OH}(\text{CHOH})_n\text{CH}_2\text{OH}$ ($n = 1-6$) (19).

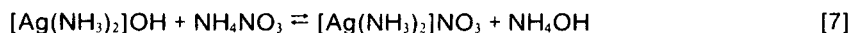
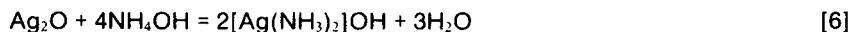
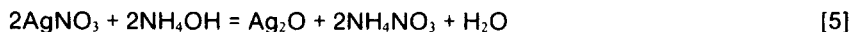
Several examples of the reaction with representative reducing agents are described below. Ag_2O precipitation in the bath must be avoided because the electroless silver plating is generally carried out in a basic solution. A

Table 17.1
Metals Plated Autocatalytically (12)

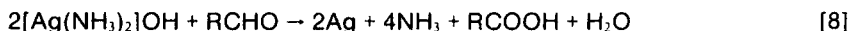
Period	Group					
	VB	VI B	VIII			IB
3	V	Cr	Fe	Co	Ni	Cu
4			Ru	Rh	Pd	Ag
5			(Os)	(Ir)	Pt	Au

() = no report.

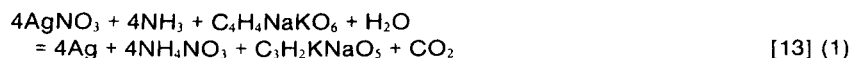
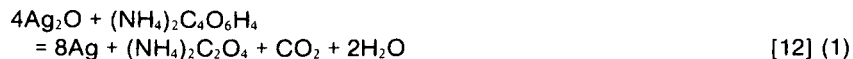
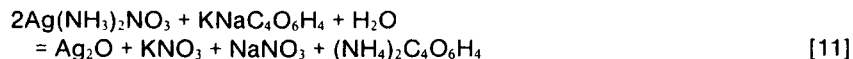
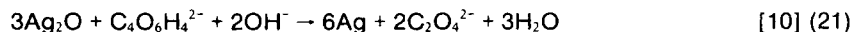
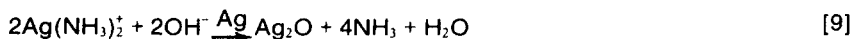
complexing agent such as ammonia is added to the solution. The complex formation reactions are thought to be as follows (14):

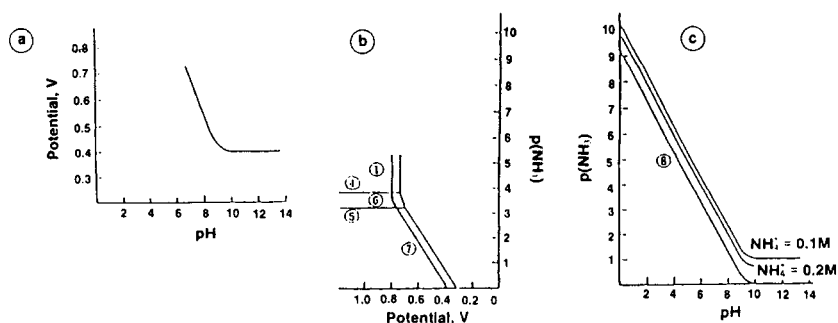


The silver plating is carried out by the reaction of the ammonia complex with aldehyde, as in Eq. 8 (14). The electromotive force is 0.971V at pH 10.0 (20).



There are many studies on the reaction with Rochelle salt as the reducing agent. They are as follows:

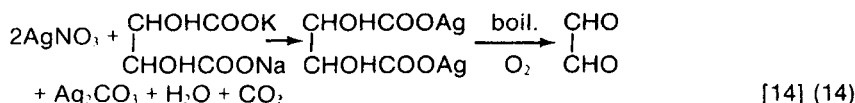




ΔG° , kcal/mol	Dissociation constant
Ag s 0	$\text{NH}_4^+ \rightarrow \text{H}^+ + \text{NH}_3, K = 10^{-9.3}$
Ag^+ aq -18.43	$\text{Ag}(\text{NH}_3)_2^+, K_1 = 10^{-3.83}$
Ag_2O s -2.58	$K_2 = 10^{-1.23}$
NH_3 aq -6.3	
NH_4^+ aq -19.0	

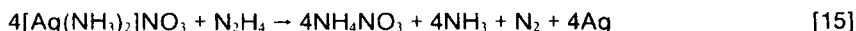
- $\text{Ag}^+ + e \rightarrow \text{Ag}, E = 0.8 + 0.06 \log [\text{Ag}^+]$
- $\text{Ag}_2\text{O} + 2\text{H}^+ \rightarrow 2\text{Ag}^+ + \text{H}_2\text{O}, \text{pH} = 6.32 - \log [\text{Ag}^+]$
- $\text{Ag}_2\text{O} + 2\text{H}^+ + 2e \rightarrow 2\text{Ag} + \text{H}_2\text{O}, E = 1.17 - 0.06 \text{pH}$
- $\text{Ag}^+ + \text{NH}_3 \rightarrow \text{Ag}(\text{NH}_3)^+, \text{p}[\text{NH}_3] = 3.83 + \log [\text{Ag}^+] - \log [\text{Ag}(\text{NH}_3)^+]$
- $\text{Ag}(\text{NH}_3)^+ + \text{NH}_3 \rightarrow \text{Ag}(\text{NH}_3)_2^+, \text{p}[\text{NH}_3] = 3.23 + \log [\text{Ag}(\text{NH}_3)^+] - \log [\text{Ag}(\text{NH}_3)_2^+]$
- $\text{Ag}(\text{NH}_3)_2^+ + e \rightarrow \text{Ag} + \text{NH}_3, E = E^\circ + 0.06 \text{p}[\text{NH}_3] + 0.06 \log [\text{Ag}(\text{NH}_3)_2^+]$
- $\text{Ag}(\text{NH}_3)_2^+ + e \rightarrow \text{Ag} + 2\text{NH}_3, E = E^\circ + 0.12 \text{p}[\text{NH}_3] + 0.06 \log [\text{Ag}(\text{NH}_3)_2^+]$
- Relationship between pH and $\text{p}[\text{NH}_3], \text{p}[\text{NH}_3] = 9.3 - \text{pH} + \log [10^{(9.3 - \text{pH})} + 1] - \log A$

Fig. 17.2—Potential-pH diagram of Ag-NH₃-H₂O system (13).

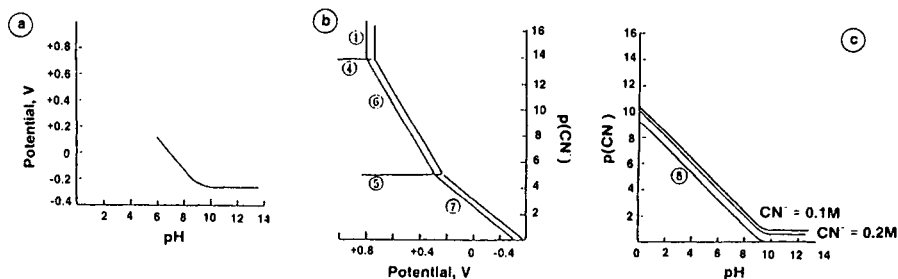


In Eq. 14, glyoxal (CHO-CHO) generated in the bath acts as a reducing agent. Silver carbonate is filtered off.

The following plating reactions are reported for hydrazine (22) and hydrazineborane (23):



The plating rates for various reducing agents are shown in Figs. 17.5-17.7 (20,24,25). The rate for borohydride is somewhat faster than that for other



ΔG° , kcal/mol	Dissociation constant
Ag s 0	HCN, $K = 10^{-9.4}$
Ag ⁺ aq 18.43	Ag(CN) ₂ ⁻ , $K = 3.8 \times 10^{-19}$
Ag ₂ O s 2.58	
CN ⁻ aq 39.6	
AgCN s 39.2	
Ag(CN) ₂ ⁻ aq 72.05	

1. $\text{Ag}^+ + e \rightarrow \text{Ag}$, $E = 0.8 + 0.06 \log [\text{Ag}^+]$
2. $\text{Ag}_2\text{O} + 2\text{H}^+ \rightarrow 2\text{Ag}^+ + \text{H}_2\text{O}$, $\text{pH} = 6.32 - \log [\text{Ag}^+]$
3. $\text{Ag}_2\text{O} + 2\text{H}^+ + 2e \rightarrow 2\text{Ag} + \text{H}_2\text{O}$, $E = 1.17 - 0.06 \text{pH}$
4. $\text{Ag}^+ + \text{CN}^- \rightarrow \text{AgCN}$, $\text{p}[\text{CN}^-] = 13.8 + \log [\text{Ag}^+]$
5. $\text{AgCN} + \text{CN}^- \rightarrow \text{Ag}(\text{CN})_2^-$, $\text{p}[\text{CN}^-] = 5.0 - \log [\text{Ag}(\text{CN})_2^-]$
6. $\text{AgCN} + e \rightarrow \text{Ag} + \text{CN}^-$, $E = -0.017 + 0.06 \text{p}[\text{CN}^-]$
7. $\text{Ag}(\text{CN})_2^- + e \rightarrow \text{Ag} + 2\text{CN}^-$, $E = -0.31 + 0.12 \text{p}[\text{CN}^-] + 0.06 \log [\text{Ag}(\text{CN})_2^-]$
8. $\text{H}^+ + \text{CN}^- \rightarrow \text{HCN}$, $\text{p}[\text{CN}^-] = 9.4 - \text{pH} + \log \{10^{(6.4 - \text{pH} - 9.4)} + 1\} - \log A$

Fig. 17.3—Potential-pH diagram of Ag-CN-H₂O system (13).

reagents. Moreover, hydrazine is often used in the spray method for mirror production, as the deposition rate is fast (24).

The activation energies of the silver plating reaction for the glucose method (26) and the Rochelle salt method are 27.1 kcal/mol and 22.0 kcal/mol, respectively. Activation energies of electroless nickel plating for the alkane succinic acid bath and the KBH₄ bath are 16.9 kcal/mol and 9.9 kcal/mol, respectively. These values indicate that the deposition rate for the electroless silver plating is strongly influenced by temperature.

The polarization curves for the electroless silver plating bath that uses these reducing agents are shown in Figs. 17.8-17.11 (21,29,30). A polarization curve for the solution containing both silver and formalin cannot be determined, because the solution is unstable (31).

The effect of pretreatment and the mechanism of electroless silver plating can be studied from the partial anodic and cathodic polarization curves (32). Both the partial cathodic polarization curve for a solution without Rochelle salt as the reducing agent and the partial anodic curve for a solution without silver nitrate are shown in Fig. 17.12. The 3,5-diiodotyrosine added bath (DIT bath), which is

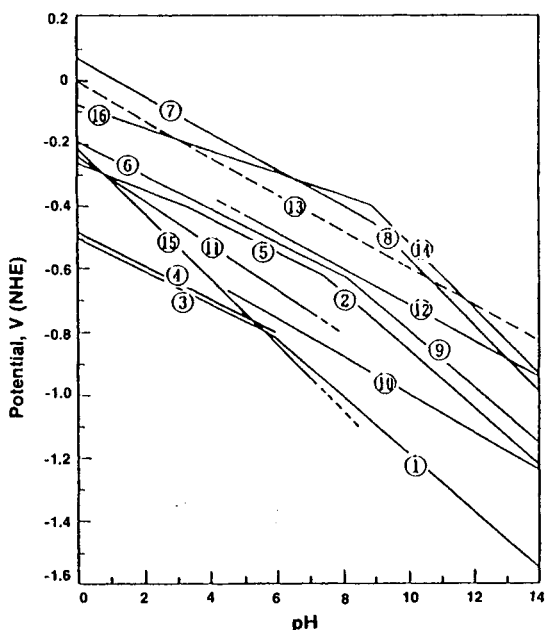


Fig. 17.4—Potential-pH diagram of various reducing agents (11). (For Explanation of the numbers (1) to (16), see Table 17.2)

the long-life bath described later, is used. The result for the electrode pretreated with a SnCl_2 solution is shown with a solid line and that for the non-treated one is shown with a dotted line. The difference between the partial cathodic polarization curves in Fig. 17.12 is minimal. On the other hand, the difference between the partial anodic polarization curves of the treated and the untreated electrodes is clearly seen. In the case of the treated electrode, an anodic current appears also in the range of 100-600 mV vs. SCE. At the same time, the rest potential of the untreated electrode becomes 25 mV vs. SCE, and that of the treated one becomes -81 mV vs. SCE. The difference in the rest potential is attributed to the adsorption of Sn^{2+} ions on the electrode. Namely, it is thought that the anodic current due to oxidation of the Sn^{2+} ion flows at potentials of 100-600 mV vs. SCE. When the anodic and cathodic polarization curves for the treated electrode are combined, a point of intersection appears at 0.02 mA/cm^2 of current density. When this value of 0.02 mA/cm^2 is converted to a plating rate, the value is equivalent to $0.04 \text{ mg/cm}^2/30 \text{ min}$. This converted value is close to the plating rate that is determined from the deposition quantity in Fig. 17.13. In the case of the untreated electrode, the current density at the intersection is

Table 17.2
Equilibrium Potential of Various Reductants (11)

No.*	Electrode reaction	Equilibrium potential (E)
1	$\text{H}_2\text{PO}_3^- + 3\text{OH}^- = \text{HPO}_3^{2-} + 2\text{H}_2\text{O} + 2\text{e}$	-0.31 @ 0.09 pH
2	$\text{HPO}_3^{2-} + 3\text{OH}^- = \text{PO}_3^{3-} + 2\text{H}_2\text{O} + 2\text{e}$	0.14 @ 0.09 pH
3	$\text{H}_2\text{PO}_3^- + \text{H}_2\text{O} = \text{H}_2\text{PO}_3^- + 2\text{H}^+ + 2\text{e}$	-0.504 @ 0.06 pH
4	$\text{H}_2\text{PO}_3^- + \text{H}_2\text{O} = \text{H}_3\text{PO}_3 + 2\text{H}^+ + 2\text{e}$	0.499 @ 0.06 pH
5	$\text{H}_3\text{PO}_3 + \text{H}_2\text{O} = \text{H}_3\text{PO}_3 + 2\text{H}^+ + 2\text{e}$	-0.276 @ 0.06 pH
6	$\text{HCOOH} = \text{CO}_2 + 2\text{H}^+ + 2\text{e}$	-0.199 @ 0.06 pH
7	$\text{HCHO} + \text{H}_2\text{O} = \text{HCOOH} + 2\text{H}^+ + 2\text{e}$	0.056 @ 0.06 pH
8	$2\text{HCHO} + 4\text{OH}^- = 2\text{HCOO}^- + \text{H}_2 + 2\text{H}_2\text{O} + 2\text{e}$	0.32 @ 0.12 pH
9	$\text{HCOO}^- + 3\text{OH}^- = \text{CO}_3^{2-} + 2\text{H}_2\text{O} + 2\text{e}$	0.25 @ 0.09 pH
10	$\text{BH}_4^- + 8\text{OH}^- = \text{BO}_2^- + 6\text{H}_2\text{O} + 8\text{e}$	-0.45 @ 0.06 pH
11	$\text{N}_2\text{H}_4 = \text{N}_2 + 4\text{H}^+ + 4\text{e}$	-0.23 @ 0.075 pH
12	$\text{CN}^- + 2\text{OH}^- = \text{CNO}^- + \text{H}_2\text{O} + 2\text{e}$	-0.13 @ 0.06 pH
13	$\text{H}_2 = 2\text{H}^+ + 2\text{e}$	0.000 @ 0.06 pH
14	$\text{S}_2\text{O}_4^{2-} + 4\text{OH}^- = 2\text{SO}_3^{2-} + 2\text{H}_2\text{O} + 2\text{e}$	0.56 @ 0.12 pH
15	$\text{S}_2\text{O}_8^{2-} + 2\text{H}_2\text{O} = 2\text{SO}_4^{2-} + 4\text{H}^+ + 2\text{e}$	-0.22 @ 0.12 pH
16	$\text{HS}_2\text{O}_4^- + 2\text{H}_2\text{O} = 2\text{HSO}_3^- + \text{H}^+ + 2\text{e}$	-0.056 @ 0.03 pH

*Numbers correspond to those in Fig. 17.4.

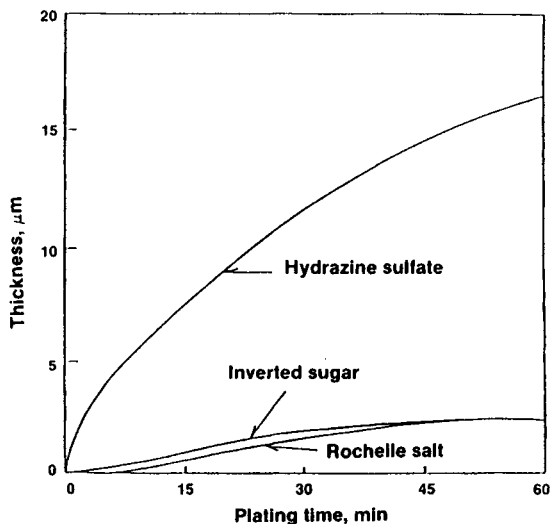


Fig. 17.5—Plating rates for solutions using hydrazine sulfate, inverted sugar or Rochelle salt as reducing agents.

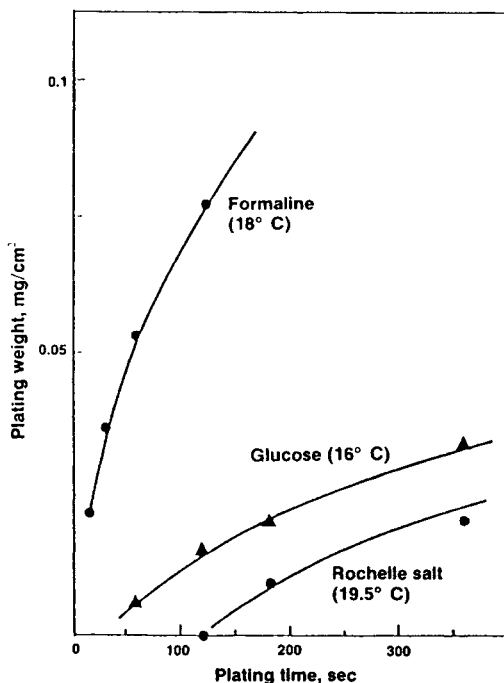


Fig. 17.6—Plating rates for solutions using formaline, glucose or Rochelle salt as reducing agents.

extremely small. Therefore, in the case of the DIT bath, it is thought that the electroless silver plating reaction proceeds only on the substrate surface treated with the SnCl_2 solution and does not occur on the untreated surface.

Reaction in Non-Aqueous Solution

The silvering reaction in a non-aqueous solution is also reported (33). Figure 17.14 represents the reaction mechanism. A silver soap, which forms the micelle, is stable in the solution. Since the soap adheres to the substrate surface, the silvering reaction progresses.

Stability of the Plating Bath

It is very important to stabilize the bath even for the electroless plating of Cu and Ni. As stated above, the electroless silver plating bath is very unstable and short-lived. Therefore, if the bath were made more stable, it would become more useful. Many attempts have been made to improve the bath stability. It has been determined that a small amount of 3-iodotyrosine or 3,5-diiodotyrosine added to the bath works well as a stabilizer (34).

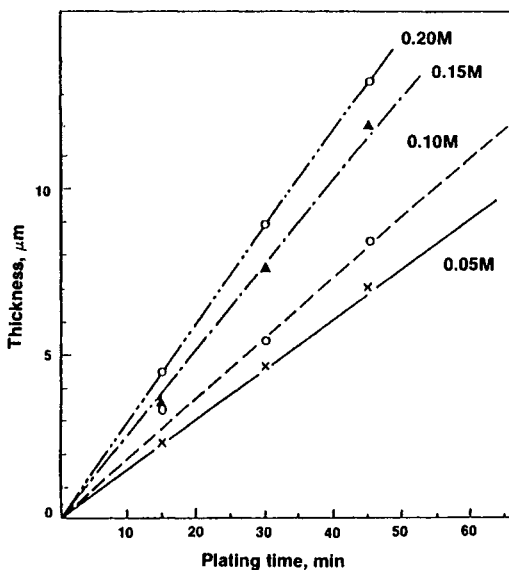


Fig. 17.7—Plating rates for bath containing various concentrations of KBH_4 (25). Bath composition = 0.05M NaAg(CN)_2 , 0.10M NaCN , 0.40M NaOH , temperature $75 \pm 2^\circ \text{C}$.

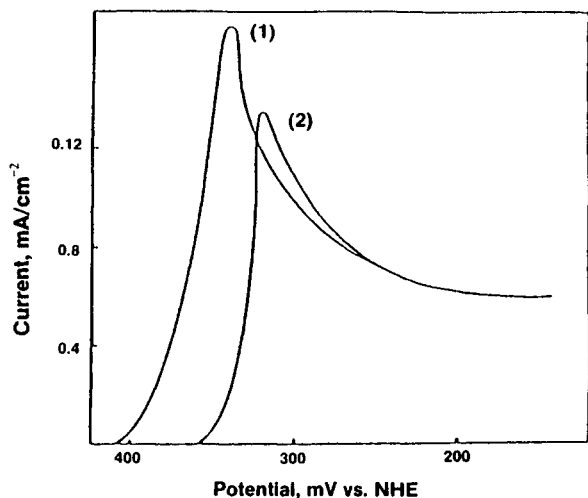


Fig. 17.8—Cathodic polarization curves for Ag-NH_4 -tartaric acid solution (21). Curve 1 = 0.02M AgNO_3 , 0.15M NH_4 , 0.1M NaOH ; Curve 2 = 0.02M AgNO_3 , 0.15M NH_4 , 0.1M NaOH + tartaric acid. Sweep rate = 0.2 V/min .

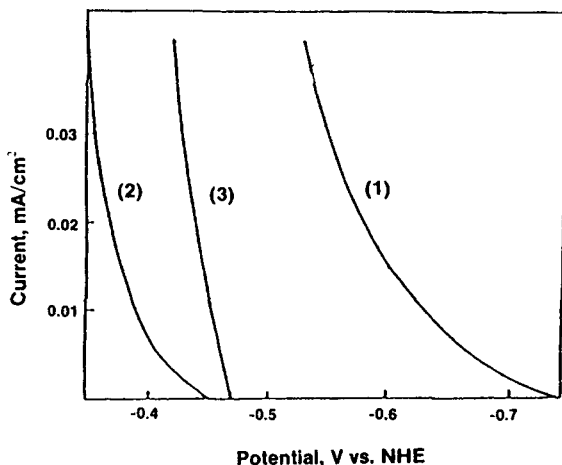


Fig. 17.9—Partial anodic polarization curves for N_2H_4 solution with various CN^- concentrations (29). Bath composition = 6M N_2H_4 + 1.5M NaOH at 40° C. Curve 1 = 0mM NaCN; Curve 2 = 5 mM NaCN; Curve 3 = 40 mM NaCN.

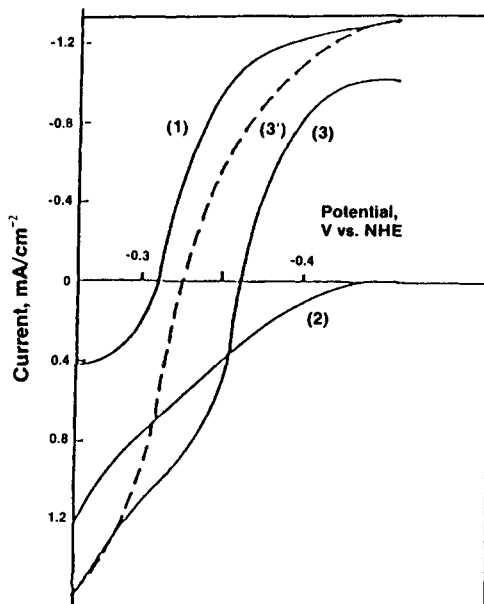


Fig. 17.10—Polarization curves for $\text{Ag-CN-N}_2\text{H}_4$ solutions (29). (1): partial cathodic polarization curve for solution containing 0.03M AgNO_3 , 0.1M NaCN, and 1.0M NaOH; (2): partial anodic polarization curve for solution containing 6M N_2H_4 , 0.04M NaCN, and 1.0M NaOH; (3): total curve (experimental) for solution containing 0.03M AgNO_3 , 0.01M NaCN, 6M N_2H_4 , and 1.0M NaOH; (3'): total curve (calculated).

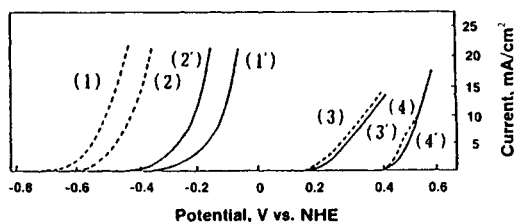


Fig. 17.11—Partial anodic polarization curves for various reductants (30): formaline (1, 1'); BH_3^- ion (2, 2'); ascorbic acid (3, 3'); Fe^{2+} ion (4, 4'). Dotted line = activated electrode; solid line = inactive electrode.

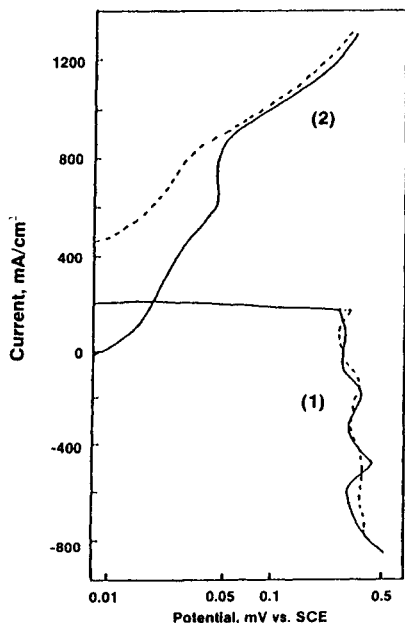


Fig. 17.12—Partial polarization curves for various electrodes: (1) partial cathodic polarization curve of electroless silver plating solution without Rochelle salt— AgNO_3 (8.8×10^{-3} M), ethylenediamine (5.4×10^{-2} M), DIT (4×10^{-5} M), 35°C , pH 10.0; (2) partial anodic polarization curve for electroless silver plating solution without silver nitrate—ethylenediamine (5.4×10^{-2} M), Rochelle salt (3.5×10^{-2} M), DIT (4×10^{-5} M), 35°C , pH 10.0. Solid line = Pt electrode sensitized with SnCl_4 ; solution; dotted line = Pt electrode, not sensitized.

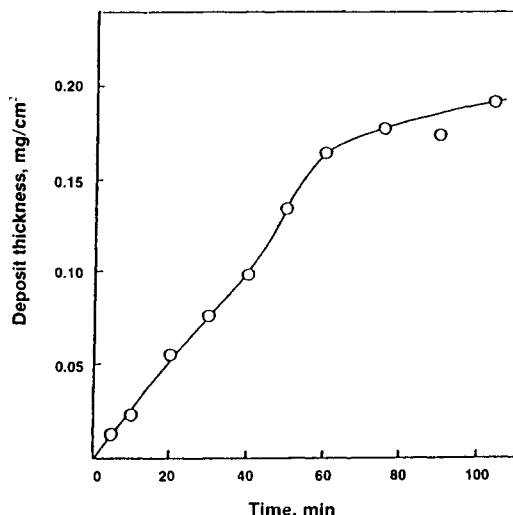


Fig. 17.13—Relationship between amount of silver deposit and plating time. Bath composition: AgNO_3 (8.8×10^{-1} M), ethylenediamine (5.4×10^{-2} M), Rochelle salt (3.4×10^{-2} M), DIT (4×10^{-3} M), pH 10.0, 35°C .

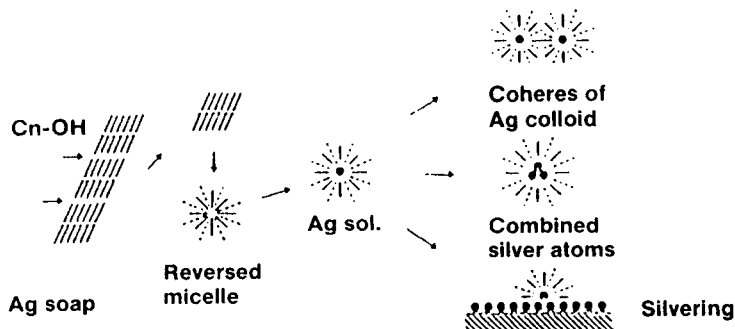


Fig. 17.14—Silvering reaction mechanism from nonaqueous solution (32).

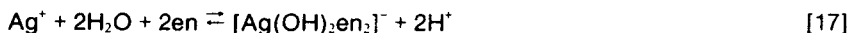
The bath conditions are as follows:

Silver nitrate 3×10^{-3} M
 Rochelle salt 3.5×10^{-2} M
 pH 10.0-10.5

Ethylenediamine 1.8×10^{-2} M
 3,5-diiodotyrosine 4×10^{-5} M
 Temperature $35-40^\circ\text{C}$

It was found that the plating rate and the bath stability were greatly affected by the pH of the bath, therefore the factors affecting the bath pH were studied (34). The bath pH was found to change with the addition of silver nitrate. The change

was remarkable at pH values <10.5 . The complex formation between silver ion and ethylenediamine (en) is believed to be as follows:



The equilibrium consideration of this reaction shows that the bath pH must change with concentrations of Ag^+ and ethylenediamine. On the other hand, even with the stable bath (DIT bath), the plating reaction almost stopped after 24 hours and the pH of the bath dropped. It was thought that the pH change strongly affected the life of the bath, because a slight drop in the bath pH reduced the plating rate significantly, as seen in Fig. 17.15. When a bath of small temporal change was used (Table 17.3), the same plating quantity was obtained even after 24 hours. The life of this bath increased to one week by adjusting the bath pH occasionally.

The life of the DIT bath was also studied from partial polarization curves (32). As seen in Fig. 17.16, the DIT controls the cathodic reaction. This effect may contribute to the bath stability. Moreover, the temporal changes of rest potential and bath pH were measured for the DIT bath (Fig. 17.17a), for the bath without Rochelle salt (Fig. 17.17b), and for the bath without silver nitrate (Fig. 17.17c). Those pH values remained unchanged. In the case of Fig. 17.17b, the rest potential moved to a noble potential and the color of the solution gradually changed from colorless to yellow. The color change suggested that the fine

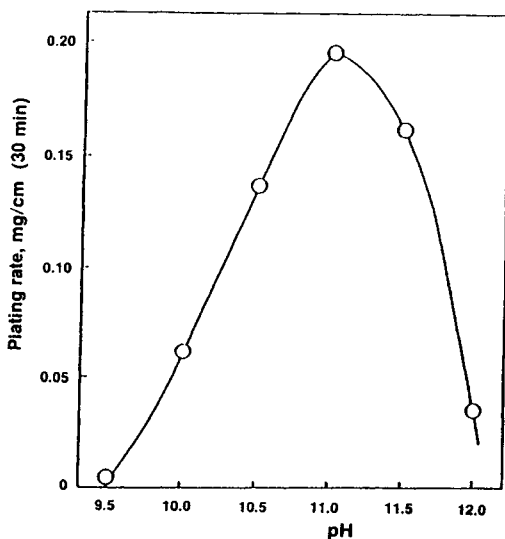


Fig. 17.15—Electroless plating rate of silver as a function of bath pH: AgNO_3 (2.9×10^{-1} M), ethylenediamine (1.8×10^{-2} M), Rochelle salt (3.5×10^{-2} M), 3,5-diiodotyrosine (4×10^{-3} M), 35°C .

Table 17.3
Deposit Thickness as a Function
Of Bath pH and Plating Time

Bath*	pH	Deposit thickness, mg/cm ²	Silver content, %
Initial	9.97	0.115	
After 24 hr	9.95	0.092	96.0

Bath composition: AgNO₃ (8.8×10^{-3} M); Ethylenediamine (5.4×10^{-2} M); Rochelle salt (3.5×10^{-2} M); 3,5-diiodotyrosine (4×10^{-3} M); temperature 35° C.

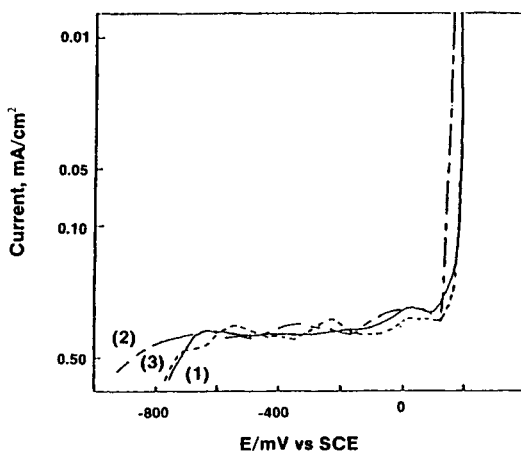


Fig. 17.16—Effects of various additives on the partial cathodic polarization curve for the Pt electrode in electroless silver plating solution without Rochelle salt. Bath composition: AgNO₃ (8.8×10^{-3} M), ethylenediamine (5.4×10^{-2} M), pH 10.0, 35° C. (1) No additive; (2) DIT (4×10^{-3} M); (3) KI (4×10^{-3} M).

silver particles were growing in the bath (35). Based upon the theory of Vaskelis (36) concerning the electrode potential and the particle size in an electrolyte, it was also believed that the potential becomes noble when the particle size increases. The temporal changes for the non-additive bath (Fig. 17.17b), the KI-added bath, and the DIT bath (Fig. 17.17a) were 2.1, 1.9, and 1.1 mV per 24 hours, respectively. From these facts, it can be stated that DIT restricts the reaction at the electrode surface by controlling the partial cathodic reaction, and stabilizes the bath by controlling the growth of fine silver particles in the solution.

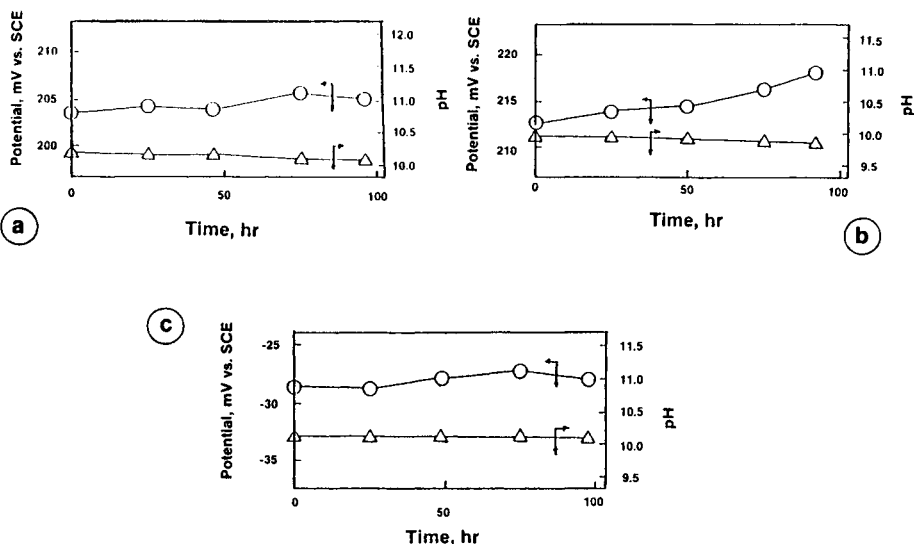


Fig. 17.17—Change of rest potential and bath pH with plating time. Bath composition: (a) AgNO_3 ($8.8 \times 10^{-1} \text{ M}$), ethylenediamine ($5.4 \times 10^{-2} \text{ M}$), DIT ($4 \times 10^{-5} \text{ M}$); (b) AgNO_3 ($8.8 \times 10^{-1} \text{ M}$), ethylenediamine ($5.4 \times 10^{-2} \text{ M}$), Rochelle salt ($3.5 \times 10^{-2} \text{ M}$), DIT ($4 \times 10^{-5} \text{ M}$); (c) ethylenediamine ($5.4 \times 10^{-2} \text{ M}$), Rochelle salt ($3.5 \times 10^{-2} \text{ M}$), DIT ($4 \times 10^{-5} \text{ M}$).

Other stabilizers reported include: metal ions (Cu^{2+} , Ni^{2+} , Co^{2+} , Zn^{2+}) (37); Na-2,3-mercaptopropane sulfonate (NaBH_4 , N_2H_4 , CN^- system bath) (38); cystine, cysteine, dimethyldithio carbamate, NaSCN (N_2H_4 , NH_3 bath) (39); RCONHR' (e.g., dodecylammonium acetate), $[\text{AgNO}_3]$, $(\text{NH}_4)_2\text{Fe}(\text{SO}_4)_2$, $\text{Fe}(\text{NO}_3)_3$, citric acid system bath] (40), and CaO (41).

PLATED FILM

There are many reports about the characteristics and the protective nature of the plated film that is obtained by the silvering method.

Dense plating is obtained by using glucose and formalin as the reducing agent. The X-ray diffraction pattern for the chemical plating method (the silvering method) is similar to those of a metal silver plate and a silver film obtained by the vapor deposition method as shown in Fig. 17.18 (42) and Table 17.4 (20). The diffraction pattern changes slightly with different reductants (Fig. 17.19). Etching and sensitizing during pretreatment are important in order to obtain good adherent plating (43).

The thickness of the coated silver film was measured by quantitative analysis with KSCN (44), the β -ray method (45), and the iodine-ring method (46). The plated silver film was usually protected by a polymer film such as lacquer. Multiple platings of Cu or Ni improve durability (14).

PRACTICE OF ELECTROLESS SILVER PLATING

Bath Composition

The immersion and the spray methods are known as the commercialized electroless silver plating technique. As it is impossible to review all reports with respect to the bath composition for the immersion method, some typical examples are presented in this chapter. (A and B denote a silver ion solution and a reducing agent solution, respectively.)

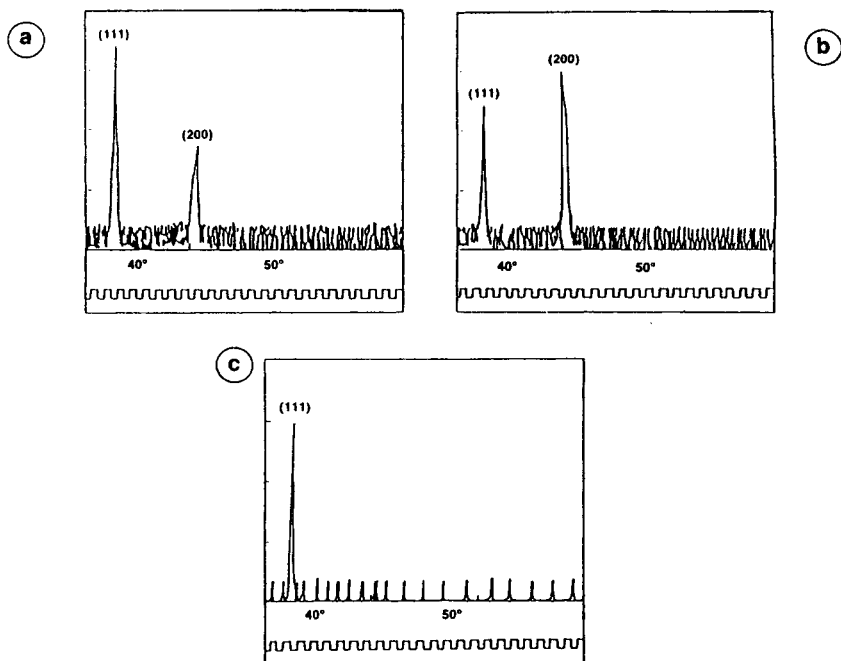


Fig. 17.18—X-ray diffraction patterns of various silver films (42). (a) Ag film obtained by chemical plating (thickness—1000 angstroms); (b) Metal Ag film (thickness—1 mm); (c) Ag film obtained by vapor deposition method (thickness—1000 angstroms).

Table 17.4
X-ray Diffraction Patterns
Of Various Silver Films

Plane orientation	Intensity		
	Metal Ag film	Chemical plating	Vapor deposition
(111)	100	100	100
(200)	40	41	13.5
(220)	25	23	—

Glucose method (47)

Although the operation is complex, a good plating is obtained.

A: Silver nitrate 3.5 g, ammonia solution proper quantity, water 60 mL, sodium hydroxide solution 2.5 g/100 mL.

B: Glucose 45 g, tartaric acid 4 g, water 1 L, alcohol 100 mL.

Rochelle salt method (48)

Because handling Rochelle salt is easy, this method is widely used.

A: Silver nitrate 454 g, ammonia solution 355 mL, water 5.45 L.

B: Rochelle salt: 1590 g, Epsom salt 114 g, water 3.64 L.

Distilled water of 3.61 L is added to the mixture of A (256 mL) and B (256 mL) solutions.

Formaldehyde method (1)

The deposition rate is fast, but a cloudy film is obtained or peeling occurs.

A: Silver nitrate 20 g, ammonia solution proper quantity, water 1 L.

B: Formaldehyde 40 mL, water 200 mL.

A and B are mixed at the ratio of 5:1.

Hydrazine method (48)

This is used for the spray method.

A: Silver nitrate 114 g, ammonia solution 227 mL.

B: Hydrazine sulfate 42.5 g, ammonia solution 45.5 mL.

A and B are diluted to 4.55 L and mixed in a ratio of 1:1.

Organic borane method (49)

The plating rate is very fast.

A: Na[Ag(CN)₂] 1.83 g/L, NaCN 1.0 g/L, NaOH 0.75 g/L.

B: DMAB (dimethylamine borane) 2.0 g/L.

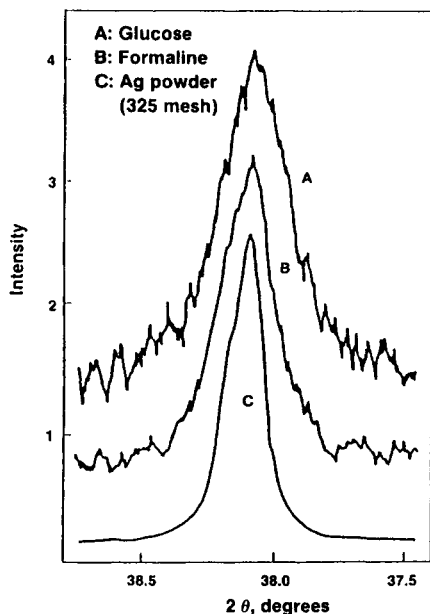


Fig. 17.19—X-ray diffraction patterns of the silvering films obtained by using (a) glucose, (b) formaline, and (c) Ag powder (325 mesh) as reductants (20).

Aldonic acid and lactone methods (15)

The deposition rate is fast. The yield of silver is very high.

A: $\text{Ag}(\text{NH}_3)_2^+$ 5×10^{-3} M, NaOH 4.0×10^{-3} M.

B: δ -gluconolactone $0.5\text{--}2.0 \times 10^{-3}$ M.

In the silvering method, the silver ion solution and the reducing agent solution are prepared separately, then combined just before plating. In order to prepare the silver ion solution with ammonia as a complexing agent, a black-brown precipitate is produced upon addition of ammonia solution to a silver nitrate solution; then the ammonia solution is added until this precipitate almost dissolves. This solution is dark brown and clear. Reducing agents are prepared by the specific methods.

In the spray method, various guns have been devised (50). For example, the gun may have two tubes. The silver ion solution and the reducing agent are sprayed separately, and mixed on the substrate.

Other distinctive baths are as follows: long life bath (34); good adherence (51) or high speed (52); for semiconductors (53); mixture of silver and copper ions (54); for substrate pretreated by hydrazine or dextrine (55); for plating on Si (56);

Table 17.5
Effects of Chemical and Mechanical^a
Etching on Adhesion Strength
Of Electroless Copper Plating^b

Chemical etchant	Adhesion strength^c, g/4 mm²
None	499.4 (613.2) ^{d,e}
HCl (20 wt. %), 100° C, 15 min	501.8 (467.9)
NaOH (10 wt. %), 100° C, 15 min	498.3 (750.0)
NaOH (10 wt. %) + NaCl (10 wt. %) 100° C, 15 min	780.2 (933.0)

^aMechanical etching (Al₂O₃ powder treatment): alumina powder (0.5 wt. %); ultrasonic agitation for 15 min.

^bUndercoated with Ag (0.05 μm) by electroless plating.

^cL-type tensile strength.

^d() = with mechanical etching.

^eWhen Ag was not undercoated, the value was 206.0.

with cyanides of the platinum group (57); electrolyzed Rochelle salt solution (58).

The displacement plating method is usually used in order to electroless-plate Ag on metals (59). For example, the bath composition for Ag plating on a Cu alloy consists of silver nitrate (7.5 g/L), sodium thiosulfate (105 g/L) and ammonia (75.0 g/L). There are many other reports (60).

Applications

There are applications for electroless silver plating in many fields. They are broadly divided into two categories:

1. Optics and decoration.
2. Electrical conductivity or for undercoating prior to other plating.

A good example of the first category is a mirror. There are many reports about this process (61). The second application makes the best use of the characteristics of electroless silver plating, including silvering, which is used for all insulators because the plated layer has electrical conductivity. For example, the plating is used as an undercoating (62) for electroless gold plating, for Ag plating on ceramics, for Sn-Pb alloy plating (63), and electrolytic plating (64).

When electroless plated silver was used as the undercoating on 96 percent Al₂O₃ ceramics, an improvement in the adhesion of copper plating on the ceramics was obtained (32). SEM photographs confirmed that electroless silver

plating was useful in obtaining smooth and uniform electroless copper plating. Furthermore, the adhesion was greatly increased by etching the ceramics by both mechanical and chemical techniques, as shown in Table 17.5.

In other cases, silver plating on ceramics is used for SEM measurement of the surface (65). The plating is also used for quantitative analysis of trace arsenic (66), for determination of the pore diameter of a membrane (67), and for recovery of mercury.

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