Technical Paper:

Electroless Nickel Plating Technique for Depositing a Nano-Scale Layer

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This paper discusses an electroless nickel plating technique. EDTA and potassium sodium tartrate are selected as chelating agents, and both are suitable for producing deposition layers of nanometer scale. The technique is applied to a copper roller mold, the deposition rate is measured at various operation temperatures, and layer thickness is measured by a surface contour meter. The quality of the deposition layer is characterized by SEM, and micrographs show that sharp angles can be reproduced by the deposition layer.

Keywords: electroless plating, roller mold, EDTA, potassium sodium tartrate

1. Introduction

At present, a large amount of roller material is made of copper. **Fig. 1** illustrates the typical fabrication process. A pattern is processed on thick copper material to form the roller mold, but a problem soon arises: the copper roller mold oxidizes extremely easily. Moreover, the environment in which the process is carried out usually has organic solvents, water vapor, high temperatures, etc., which exacerbate the problem. The oxidization layer may increase the roughness of the micro-structural surface and destroy the optical nature of the film, so the service life of the roller mold is typically 5–15 days. As a result, the copper roller mold becomes an expensive, consumable tool. For this reason, the development of an appropriate surface treatment technology that could lengthen the service life of copper roller molds is widely hoped for. Various studies have proposed ways to reduce the oxidization speed of copper, increasing the service life of copper roller molds [1–5]. This paper describes a low temperature, electroless nickel plating technique that achieves a low deposition rate and produces a good-quality deposition layer. The equipment for electroless nickel plating can be seen in **Figs. 2** – **4**, and the process of making optical film is shown in **Fig. 5**.

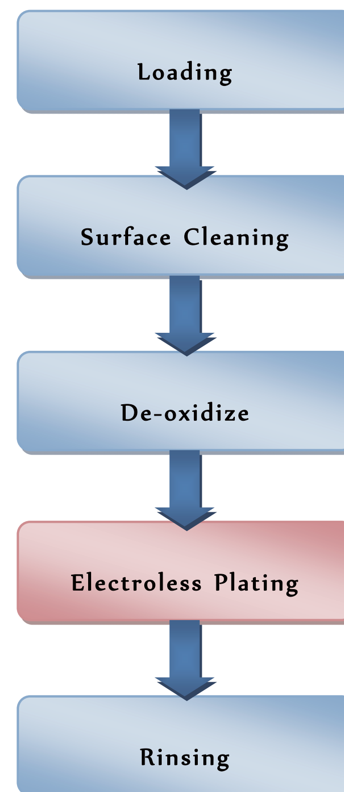

Fig. 1. Typical fabrication process in the making of copper roller molds.

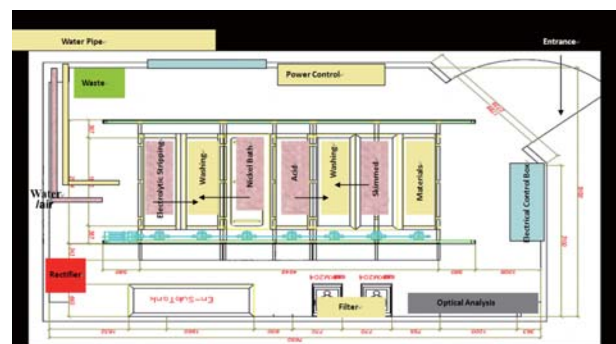

Fig. 2. Electroless nickel plating lab.

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Fig. 3. Electroless nickel plating equipment.

Fig. 4. Exhaust pipe and wastewater processing station.

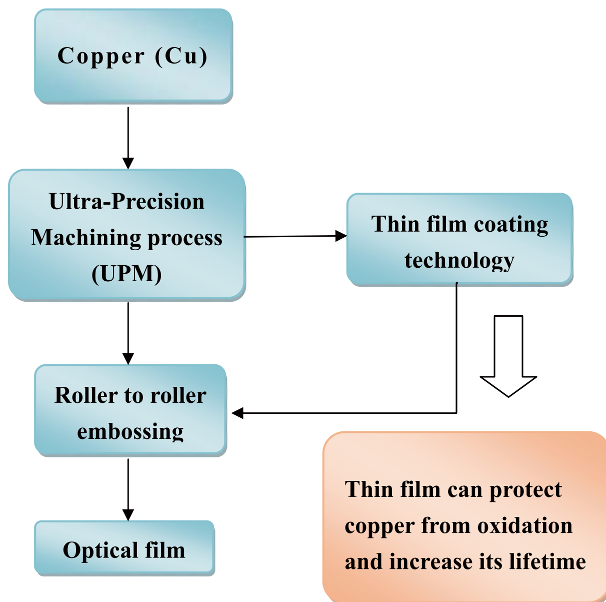

Fig. 5. Process of making optical film with the addition of thin film coating technology.

2. Design Purpose

In order to control the reaction rate so that the nickel is deposited on the copper roller mold uniformly, the following parameters must be considered:

1. The operation temperature of the plating bath should be 40°C±1°C. Since the reaction rate is sensitive to the temperature in electroless nickel plating, the operation temperature must be controlled carefully. This project utilizes two-stage temperature control and an indirect water heating method to control the reaction temperature of the electroless nickel plating.

   In the indirect water heating method, the electroless nickel plating solution is heated evenly in the bath without coming into direct contact with the heater. The two-stage temperature control can prevent the damage and failure of the temperature controller due to the acidic gas and high temperature. It can also prevent the evaporation of the electroless nickel plating solution.

2. The concentration of nickel ions in the solution should be controlled and monitored carefully, as the concentration of nickel ion can also influence the deposition rate of electroless nickel plating. When the concentration of nickel ions is high, the reaction rate increases. What is more, if the concentration is too high, the nickel will decompose. On the other hand, if the concentration of nickel ions is too low, the reaction will not occur. This project utilizes UV-visible lamp spectroscopy to measure and maintain the concentration of nickel ions in the range of 6.00 ± 0.01 g/L.

3. The pH value in the plating solution should be controlled. A low pH value slows the reaction rate, and a change in the pH value changes the proportion of the nickel alloy. Therefore, a pH meter is used to maintain a pH value of 4.50 ± 0.01 in order to ensure the reaction rate of the electroless nickel plating and the proportion of alloy.

Since the alkaline electroless nickel plating solution is prepared at low temperature, the metal ion and initiating agent will produce precipitate. A chelating agent has to be added to prevent the precipitation. This project employs two different chelating agents, EDTA and potassium sodium tartrate, to carry out the electroless nickel plating experiment in an alkaline solution. The composition and function of the electroless nickel plating solution are shown below:

1. Metal ions are the sources of the plating metals.
2. The reducing agent reduces the metal ions to metal.
3. The catalyst brings the catalysis property to the substrate surface.
4. The complex agent can prevent the precipitation of the hydroxide, regulate the deposition rate, prevent the decomposition of the plating solution, and stabilize the plating solution.
5. The stabilizer can adsorb impurities while preventing the decomposition of the plating solution and lengthening its life.
6. The buffer controls the pH value, keeping it within the operation range.
7. The wetting agent produces a good surface reaction.
8. The brightener gives the plating layer a good gloss.

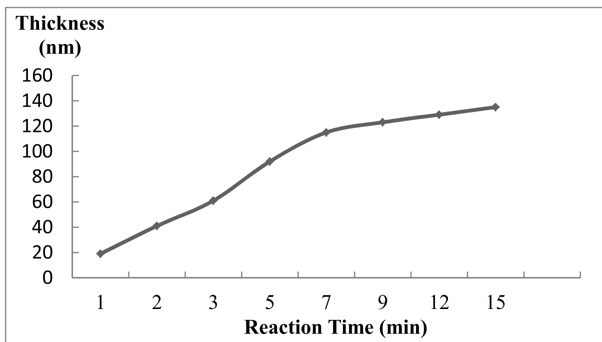

Fig. 6. Relation between deposition thickness and reaction time when using EDTA at 40°C.

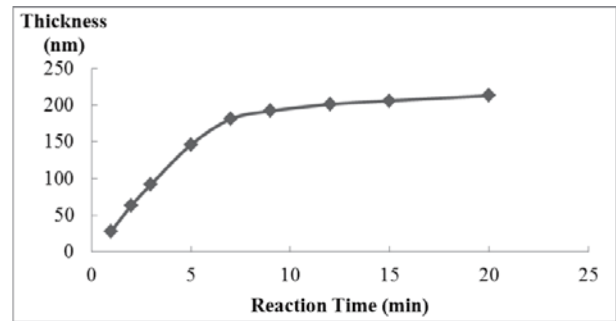

Fig. 7. Relation between deposition thickness and reaction time using potassium sodium tartrate at 40°C.

The main requirements for the electroless nickel plating bath are shown below:

1. The redox potential of the reducing agent should be able to reduce the metal ion to deposit the metal.
2. The plating solution should be stable; it begins to react and deposit the metal layer rapidly only when it starts to contact the catalytic surface of the plating object.
3. The pH value and temperature should be controlled and monitored accurately.
4. The deposited metal must be able to carry out self-catalytic plating so that the plating layer forms continuously and reaches the required thickness.
5. So that the plating bath may last and continue operation for a long time, the product of the plating bath should not hinder its function.

3. Results and Discussion

EDTA has double chelating bonds, so it was used as the chelating agent in electroless plating solution. The solution was comparatively stable, and the reaction rate was relatively slow. It is suitable for conducting electroless nickel plating with EDTA to produce a deposition layer ≤ 200 nm. When the reaction temperature is 40°C, the deposition rate is about 14 nm/min for the first 9 minutes; its thickness is 129 nm. When the reaction time reached 20 min, the deposition thickness was about 161 nm, and the reaction ceased. The experimental results are shown in **Fig. 6**.

Potassium sodium tartrate has a single chelating bond, its reaction rate is relatively fast, and it is suitable for conducting electroless nickel plating to produce a deposition layer ≤ 300 nm. It can also be used in 3D IC crystal seed layers. When the reaction temperature was 40°C, the deposition rate was about 25 nm/min for the first 7 minutes; its thickness was 180 nm. When the reaction time reached 20 min, the deposition thickness was about 215 nm, and the reaction was stopped. The experimental results are shown in **Fig. 7**. **Fig. 8** is an SEM micrograph showing sharp angles were reproduced by nickel plating; thus, optical characteristics are expected to be unchanged.

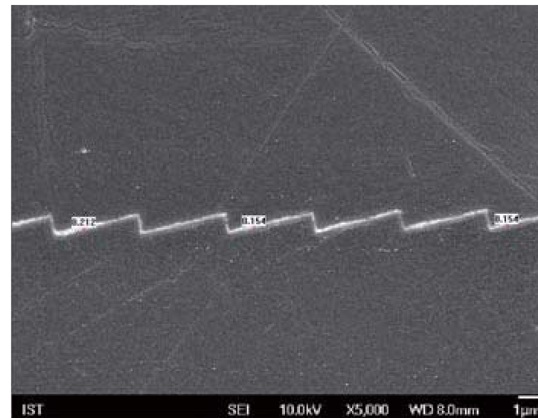

Fig. 8. SEM micrograph showing sharp angles reproduced by deposition layer with thickness 180 ± 30 nm.

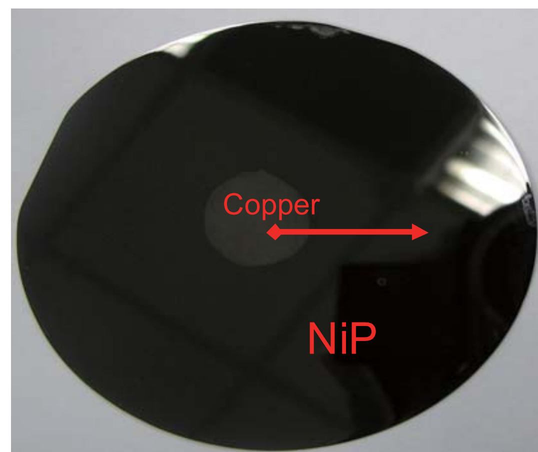

Fig. 9. 4" silicon wafer with sputtered copper and deposited NiP.

The deposition thickness was measured using a 4" silicon wafer. The wafer was sputtered with a thin layer of copper before the electroless nickel plating experiments. Thickness was measured by the surface contour meter. The deposited sample is shown in **Fig. 9**.

Table 1. Deposition rate at 40°C.

Time (hr)	0.50	1.00	1.50	2.00
Thickness (μm)	0.05	0.06	0.07	0.08
Rate (μm/min)	0.0017	0.0010	0.0008	0.0007

Table 2. Deposition rate at 50°C.

Time (hr)	0.50	1.00	1.50	2.00
Thickness (μm)	5.63	8.26	8.68	9.22
Rate (μm/min)	0.19	0.14	0.10	0.08

Table 3. Deposition rate at 70°C.

Time (hr)	0.50	1.00	1.50	2.00
Thickness (μm)	7.54	12.93	17.11	20.00
Rate (μm/min)	0.257	0.22	0.19	0.17

Tables 1 – 3 show the converted deposition rates measured at 40, 50, and 70°C, respectively. The results show that the deposition rate decreased as the reaction proceeded. This was because the tank used in this experiment held only 500 cc, and the nickel ion was not replenished. The slowdown in the deposition rate was therefore expected. The use of a 400 L tank and the replenishment of nickel ion can remedy the change in the deposition rate.

The quality of electroless nickel plating was further characterized using a 3” copper sheet with rhombus micro-structure (width: 25 μm, height: 10 μm). The sheet was placed in the roller frame, and the plating experiment was conducted at 50°C. **Fig. 10** shows SEM micrographs comparing the microstructures with and without plating; the deposition thickness is 0.475 ± 0.29 μm. The appearance of the roller mold is shown in **Fig. 11**. As **Fig. 11** shows, the texture of the copper roller is not visible when the plating thickness is 1.0 μm; however, the texture of copper roller is visible when the plating thickness is 0.5 μm, indicating that the plating film reproduces the original structure accurately.

4. Conclusion

The copper roller mold can be protected from oxidation by using an appropriate surface treatment technology. The electroless nickel plating technique demonstrates a potential solution. The technique is conducted in alkaline solution and at low temperature. Both EDTA and potassium sodium tartrate are suitable as chelating agents. The deposition rate is relatively slow so that the original microstructure can be produced and at a uniform layer thickness. Future work will involve the characterization of the optical properties of Ni-deposited roller molds.

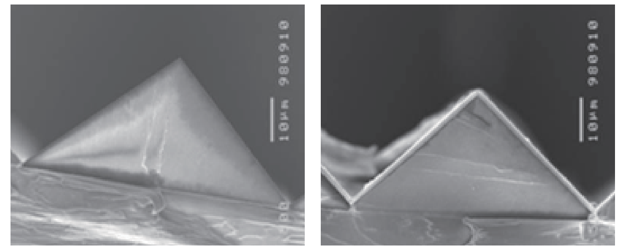

Fig. 10. SEM micrograph showing: (left) before plating; (right) after plating.

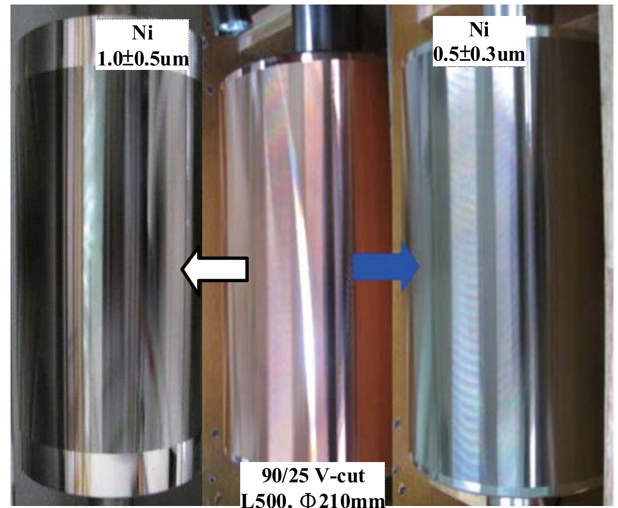

Fig. 11. 1.0 and 0.5 μm plating film with rhombus micro-structure (width: 25 μm, height: 10 μm).

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