Trench Wiring Process Applying Electroless Nickel Plating for Fine and High-Aspect-Ratio Pattern

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As increasing demand for advanced electronic devices, finer pitch and higher integration of wirings are required. The trend tends to increase the electrical resistance of wirings. In order to suppress the resistance, it is necessary not only to reduce wiring length, but also to increase the aspect ratio of the finer wiring to ensure its cross-sectional area. We investigated embedded Cu wiring formation process, called as “trench process,” and newly developed a photosensitive material and its seeding process. The photosensitive material showed the capability to form resist pattern (line/space=1 μm/1 μm and aspect ratio=5.0) and Cu wiring (line/space=1.2 μm/1.2 μm and aspect ratio≥3.0) with electroless nickel plating. The material is suitable for trench process.

Keywords: Photosensitive material, Electroless nickel plating, Trench wiring formation process

1. Introduction
Currently, novel electronic devices, such as personal digital assistant, automotive electric devices and IoT devices are progressing. Especially in highly integrated packaging, Cu wiring and blind via are progressing for downsizing and multilayer substrate [1]. Semi-additive process (SAP) is the major Cu wiring formation technology in packaging substrate manufacturing [2,3]. However, the fabrication of Cu wiring less than 5 μm has some problems of the low adhesion strength between insulation layer and Cu wiring due to its small contact, and the collapse of Cu wiring at the etching process of seed layer. Increase in the electric resistance of fine Cu wiring is also an issue [4,5]. To suppress the resistance, it is necessary not only to reduce the wiring length, but also to increase the aspect ratio to ensure its cross-sectional area.

To overcome the issues with Cu wiring formation below 5 μm, embedded Cu wiring formation process, called “trench process,” was reported [6-9]. One of advantages of the process is no collapse of fine wiring since the wiring is supported by insulation material in three directions. In the reported trench process, trench patterns are formed by laser drilling of non-photosensitive insulation layer using UV-YAG or excimer laser [10,11]. Seed layer is deposited on the surface of trench patterns and the patterns are filled up with electroplated Cu. However, laser drilling has difficulties in controlling the shape of patterns. In the previous report, we developed a photosensitive material as insulation layer and found that it was suitable to trench process with good controllability of pattern shape by photolithography. We also reported that the aspect ratio of Cu wiring by the trench process was 3.3 (line/space = 3 μm/3 μm) [7]. Figure 1 shows trench wiring formation process with the photosensitive material.

In this report, we describe the developed process of Cu wiring below 3 μm with higher aspect ratio. At first, we tried to develop a new photosensitive material that enables finer and higher-aspect-ratio pattern based on the previous photosensitive material. Then we studied the process of making thin and uniform seed layer. We studied liquid-type, negative-tone resist which comprises phenolic resin as base resin, epoxy monomer as photosensitive cross-linker (CL), photo acid generator (PAG), and thermal CL [12-17]. We investigated the molecular
weight of phenolic-resin to improve lithographic properties. Then, we examined electroless nickel (Ni) plating [18,19] and sputtering as seed layer [20]. Finally, we evaluated bias-HAST resistance with Ni-capped structure of Cu wiring with the photosensitive material.

Fig. 1. Process flow of trench wiring formation.

2. Experimental

2.1. Resist solution preparation

Phenol resin, epoxy monomer, PAG and thermal CL were formulated in 1-Methoxy-2-propyl acetate (PMA) as solvent. The viscosity was adjusted for coating process by changing the amount of solvent.

2.2. Lithographic evaluation

Resist solution was spun onto bare Si wafer for lithographic evaluation. Its process flow is shown in Table 1.

Table 1. Process flow of lithographic evaluation.

| Process       | Equipment       | Conditions          |
|---------------|-----------------|---------------------|
| Coating       | Spinner         | Spin speed adjusted |
| Prebake       | Hot plate       | 120 °C/3 min        |
| Exposure      | 1-line stepper  | NA=0.24             |
|               |                 | 100-1000 mJ/cm²     |
| Post exposure | Hot plate       | 85 °C/4 min         |
| bake          |                 |                     |
| Development   | Spray developer | 72 s at 23 °C       |
|               |                 | 2.38 wt% TMAH       |
| Post Cure     | N₂ Oven         | Ramp-up: RT → 180 °C, |
|               |                 | 3 °C/min            |
|               |                 | Hold:180 °C/60 min  |

2.3. Dissolution rate

Dissolution rate (DR) was calculated from development time and thickness loss of photosensitive material film during development as below [21]:

\[
V_x = \left( \frac{T_{PB} - T_{Dev}}{t_{Dev}} \right) / t_{Dev}. \quad (1)
\]

\( V_1 \): Dissolution rate of exposed area
\( V_2 \): Dissolution rate of unexposed area
\( T_{PB} \): Film thickness before development
\( T_{Dev} \): Film thickness after development
\( t_{Dev} \): Development time.

2.4. Seeding process

Seeding layer was formed on cured photosensitive material layer. Sputtering of Ti/Cu and electroless plating of Ni were examined for seed layer followed by embedding Cu. Thickness of Ti and Cu was 50 and 250 nm respectively for sputtering process. Thickness of Ni was 150 nm for electroless plating. Table 2 shows the details of electroless Ni plating process. The plating reagents were provided by Meltex Inc. The adhesion between seed layer and photosensitive material layer was evaluated by 90° peel strength test. A 10 µm electro-plated Cu samples were used after seeding.

Table 2. Process flow of electroless nickel plating process.

| Process      | Reagent/Equipment       | Conditions          |
|--------------|-------------------------|---------------------|
| UV reforming | UV Lamp : 25W x6, Wave length 185,254 nm | 0-600 s |
| Degreasing   | Ethanol 80 % aq.        | 30 s/RT             |
| Rinsing      | Pure water              | 2 min/RT            |
| Conditioning | Melpate Conditioner (trial product) | 5 min/RT |
| Rinsing      | Pure water              | 2 min/RT            |
| Activating   | Melpate Activator (trial product) | 5 min/RT |
| Rinsing      | Pure water              | 2 min/RT            |
| Post-Activating | Melpate PA (trial product) | 5 min/RT |
| Rinsing      | Pure water              | 2 min/RT            |
| Ni plating   | Melpate NI (trial product) | 2 min/70 °C |
| Rinsing      | Pure water              | 2 min/RT            |
| Annealing    | N₂ Oven                 | 1 h /180 °C         |

2.5. Embedded Cu wiring formation process

The wiring was formed on the seed layer by electrolytic Cu plating, and excess plated copper
was removed and planarized by CMP process. Then, the top of Cu wiring was capped by electroless Ni plating. The barrier effect of the nickel layer on electromigration was evaluated by bias HAST (b-HAST). The cross-section of the wiring after b-HAST was observed by SEM-EDX.

3. Results and discussion

3.1. The effect of phenolic resin on dissolution rate contrast

The effect of molecular weight ($M_w$) on dissolution rate contrast was evaluated. Sample A contained phenolic resin with higher molecular weight ($M_w = 14000$, alkaline-solution dissolution rate (ADR) = 0.02 [μm/s]) and sample B contained one with lower molecular weight ($M_w = 3500$, ADR = 0.40 [μm/s]). In this study, DR represents dissolution rate of resist film and ADR represents the dissolution rate of resin film. Figure 2 shows DR of each sample. $V_2$ of sample B was 2.8 times higher than that of sample A. Dissolution rate contrast was improved with lower molecular weight.

The photolithographic properties of sample A and B were evaluated. Sample A showed resolution of 1.5/1.5 μm (line/space) and aspect ratio of 2.6 with thickness at 5 μm. On the other hand, the sample B showed resolution of 1.0/1.0 μm (line/space), aspect ratio of 5.0 and via size ($φ$) of 2 μm with thickness of 5 μm (Figs. 3(a) and 3(b)). Lithographic properties were also improved with lower molecular weight.

Since there was possibility that lowering molecular weight of main resin could cause decrease in physical properties, the amount of CL for sample B was increased for sample A. Sample B showed excellent photolithographic properties and heat resistance (Table 3).

3.2. Seed layer forming process

Sputtering of Ti/Cu and electroless plating of Ni were examined on trench pattern of sample B. Cross-section of pattern sputtered with Ti/Cu was shown in Fig. 4. Ti of 50 nm and Cu of 250 nm in thickness were formed on the upper surface of the photosensitive layer but Ti/Cu didn’t deposit on lower sidewall of trench pattern. With longer sputtering to deposit Ti/Cu on the lower part, the upper part of trench opening was clogged with the metal, and the trench couldn’t be embedded with plated Cu. Sputtering of Ti/Cu wasn’t effective for seeding for high-aspect-ratio pattern.

On the other hand, electroless plating could form conformal Ni layer on the surface of trench pattern and was suitable for seeding process (Fig. 5).

Fig. 2. Dissolution rate of sample A and B.

| Item                        | Unit | Sample A | Sample B |
|-----------------------------|------|----------|----------|
| Resolution (5 μm thick)     | Line/space | 1.5/1.5 | 1/1      |
| Via                         | μm   | 4        | 2        |
| Young modulus               | Gpa  | 2.6      | 2.7      |
| Tg (TMA)                    | °C   | 196      | 192      |
| CTE                         | $α_1$ | 52       | 62       |
| Weight loss temp. (5 wt%)   | °C   | 283      | 286      |
One of the requirements for seed layer is enough adhesion strength between seed layer and photosensitive material layer. To improve adhesion strength between sample B and Ni, we examined UV pretreatment process before electroless Ni plating. We evaluated peel strength in several UV pretreatment conditions with Melplate Conditioner (Table 4). Peel strength was improved surface condition with longer UV irradiation in the presence of Melplate Conditioner (Fig. 6).

Table 4. UV pretreatment conditions with Melplate Conditioner.

| Test No. | 1 | 2 | 3 | 4 | 5 | 6 |
|----------|---|---|---|---|---|---|
| Melplate Conditioner | None | Done | Done | Done | Done | Done |
| UV irradiation [s] | 0 | 0 | 150 | 240 | 500 | 700 |

3.3. Trench wiring formation and barrier effect

We demonstrated Cu-embedded wiring structure by trench process with sample B and electroless Ni plating (Fig. 7). The top part of Cu wiring was capped with 150 nm-thick Ni as overlayer. The width of Cu embedded wiring was 1.2 μm with aspect ratio of 3. The condition of bias-HAST was 3.3 V/200 h with 130 °C/85%RH. Figures 8(a) and 8(b) show cross-section of the wiring and element mapping after b-HAST. There was no Cu migration during the test. We found Ni seed layer and Ni capping was effective as barrier layer for fine and high-aspect-ratio Cu wiring.

![Fig. 5. Cross-section image after Ni electroless plating.](image1)

![Fig. 6. Peel strength with UV pretreatment.](image2)

![Fig. 7. Cross-section image of trench pattern by SEM.](image3)

![Fig. 8. EDX mapping images after b-HAST. (a)Ni, (b)Cu.](image4)

4. Conclusion

We developed new photosensitive material and applied it to trench process. We found the following results:

1. Low molecular weight of phenolic resin effectively enhanced dissolution rate contrast.
2. The new photosensitive material showed fine and high-aspect-ratio pattern (line/space = 1.0/1.0 μm, aspect ratio = 5.0 and via size = 2 μm φ with thickness of 5 μm).
3. Electroless Ni plating was preferable for seeding process of high-aspect pattern to sputtering.
4. Peel strength between Ni seed layer and photosensitive material was increased with UV pretreatment in the presence of Melplate Conditioner.
5. Ni seed layer and Ni capping were effective as barrier layer for fine and high-aspect-ratio Cu wiring.
6. Cu embedded wiring (width = 1.2 μm, aspect ratio = 3) could be formed by trench process with new photosensitive material and electroless Ni plating.

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479