Selective Cu Patterning on Polyimide Using UV Surface Treatment and Electroless Plating

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Needs for an inexpensive and simple technology for fabricating fine copper (Cu) patterns on a polyimide (PI) film have been increasing. In this study, vacuum-UV induced surfactant masking (VISM) process was proposed as a tool for simplifying selective electroless Cu plating. The electroless Cu plating process using VISM is capable of Cu patterning on solvent-soluble siloxane-modified polyimide (PI) without photoresist patterning steps unlike conventional electroless Cu plating process. The relation between the wettability of SBC-PI film surface and the UV/Ozone treatment time was investigated to establish VISM process condition. The feasibility of the proposed process was verified by demonstrating the fabrication of Cu/PI patterns with widths ranging from 5 \( \mu \)m to 50 \( \mu \)m and measuring an electric property of some patterns.

\textbf{Keyword:} Selective electroless copper plating, UV/Ozone treatment, Polyimide, Surfactant

1. Introduction

Copper plating onto PI films is a well-used process in the fabrication of the interconnections in microelectronic devices such as flexible printed circuit board (FPCB) and ultra large-scale integration (ULSI) [1-3]. Recently, demands for the fabrication technologies of fine Cu patterns on a PI film have increased due to the increase in demand for miniaturization and performance enhancement of electronic devices [4,5]. The Cu/PI patterns have been generally fabricated by photolithography and metal-etching technologies such as a subtractive, additive and semi-additive process [6,7]. However, these conventional Cu/PI patterning techniques have some drawbacks (e.g., low cost-efficiency and the numerous lithography steps) [8,9]. Recently, selective Cu metallization processes without going through photoresist patterning process have been considered as an alternative to conventional metallization technologies owing to its high cost-efficiency and process improvement [10-13]. Those approaches using electroless plating technology have been attempted to be utilized in various selective metallization processes such as ink jet printing, laser patterning techniques and micro-contact printing [14,15].

In most studies related to the selective Cu deposition on PI, UV/Ozone treatments are mainly used to enhance the adhesion between Cu and PI. However, in our previous study [13], it was observed that Cu deposition might occur even at an untreated surface region when solvent-soluble siloxane PI was used as the substrate.

In order to overcome problem above, in this paper, vacuum-UV induced surfactant
masking (VISM) process was proposed, by taking attention to the followings: most surfactants are composited of organics and the those can be removed by UV/Ozone treatment [16-18]. After performing adhesion promotion treatment, the entire surface area of PI substrate was coated with surfactant layer. In the subsequent VISM process, the selective areas of surfactant layer were removed by UV/Ozone treatment using Cr/quartz mask. For VISM process, a low-pressure mercury lamp (LP Hg lamp) that emits UV lights with different wavelengths of 184.9 nm and 253.7 nm was used. Such low-pressure lamps are widely utilized for surface cleaning (e.g., glass cleaning process in liquid crystal display (LCD) fabrication) [19,20]. After palladium (Pd) absorption process, Cu patterns with widths ranging from 5 to 50 \( \mu \)m were formed on residual surfactant layers by electroless plating. Finally, the electric resistance of the fabricated Cu interconnections with 300 nm thicknesses was evaluated.

2. Experimental method

Process flow of electroless Cu plating using VISM is shown in Fig. 1. First, the PI films with 24 \( \mu \)m thickness were fabricated on 4 inch Si wafer by spin-coating, prebaking, exposure, and curing process (Fig. 1(a)). Negative photosensitive solvent-soluble siloxane-modified PI (Q-RP-X1149, PI R&D Co., Ltd) varnish was used as a PI substrate material. This PI is made up of two main blocks including imidized polyimide and methyl hydrogen siloxane block, and has hydrophobic and smooth surface owing to methyl group of methyl hydrogen siloxane block. The PI surface was coated with a surfactant layer during the cleaning and conditioning process (Fig. 1(b)). Prior to this, adhesion promotion by UV/Ozone treatment was performed. In the next step, the selective area of the surfactant layer on PI substrate was removed by UV/Ozone treatment using Cr/quartz mask (Fig. 1(c)). UV/Ozone treatments on PI surfaces were conducted by using an UV irradiation system (PL2003N-19, Sen Engineering Co., Ltd). This system has a low-pressure mercury lamp (LP Hg lamp), which emits two types of UV light with wavelengths of about 184.9 nm and 253.7 nm at an atmospheric condition. In the next step, Pd was absorbed on the unremoved surfactant layers as a reducer with Cu ions in plating bath by immersing in the pre-dipping, catalyzing and accelerating solutions (Fig. 1(d)). Finally, Cu was deposited on the partially absorbed Pd layer in the electroless plating bath of 24 °C with pH 12.5 for 15 min, as shown in Table 1.

![Fig. 1. Schematic drawing of process flow of electroless Cu plating using VISM: (a) Formation of PI layer on Si by spin coating, prebake, exposure and curing processes, (b) cleaning and conditioning, (c) VISM process, (d) catalyzing and accelerating for Pd absorption, and (e) electroless Cu plating](image)
UV light power densities used in UV/Ozone treatment were measured at the 10 cm distances from LP Hg lamp by UV power meter controller (C9536, Hamamatsu Photonics Co., Ltd) and UV sensors (H9535-185 and H9535-254, Hamamatsu Photonics Co., Ltd). Additionally, the ozone level in UV irradiation system was measured using an ozone sensor (A-21ZX, KWJ Engineering Inc.). Effect of UV/Ozone treatment conditions on the wettability of a PI surface in the presence of surfactant was evaluated by measuring contact angle of water droplet on PI surface using a potable contact angle meter (PCA-1, Kyowa Co., Ltd). Additionally, electrical property of fabricated Cu interconnections was evaluated by four probe method using semiconductor parameter analyzer (Agilent 4155c, Agilent technologies, Inc.).

Table 1 Bath composition and operating conditions of electroless Cu plating

| Composition | Concentration |
|-------------|---------------|
| CUST - A    | 100 mL/L      |
| Cu(NO_3)_2·H_2O | 10-15 %      |
| HCHO        | 5-10 %        |
| CUST - B    | 100 mL/L      |
| (HOCHCOO)_2KNa·4H_2O | 15-25 %     |
| NaOH        | 6-10 %        |
| NaCN        | 0.01 - 0.02 % |
| CUST - C    | 10 mL/L       |
| (HOCHCOO)_2KNa·4H_2O | 0.5 - 1.5 %  |
| NaOH        | 0.02 - 0.06 % |
| HCHO        | 1-3 %         |
| Bath temperature | 24 ± 2 °C     |
| Bath pH     | 17 %          |
| Agitation   | Mechanical stirring |

3. Results and Discussion

After forming surfactant layer on the PI surfaces, the contact angle was measured under the different conditions of UV/Ozone treatment time (t_t). In the UV/Ozone treatment experiments, Cr/quartz glass with 1 mm thickness was used as a mask. The measured UV light power for the wavelengths of 184.9 nm and 253.7 nm was 3 mW/cm² and 20 mW/cm², respectively. Additionally, the measured value of the ozone level in UV irradiation system was approximately 15 ppm.

Fig. 2. Relationship between contact angles and UV/Ozone treatment time (t_t). It can be divided into two different stages of the (a) removal of surfactant layer and (b) the surface modification of PI.

The change in contact angle for SBC-PI film surface was investigated as a function of UV/ozone treatment time (t_t) as shown in Fig. 2. When t_t < 20 min, the contact angle increased as a result of the progressive removal of surfactant layer with the increase of t_t. (Fig. 2(a)). Around t_t = 20 min, the contact angle reached to peak value (that is almost near value for an untreated SBC-PI) because the surfactant layer was completely removed. On the other hand, when t_t > 20 min, the contact angle decreased with increasing treatment time due to the surface modification effect (Fig. 2(b)). From results above, it was found that the proper UV/Ozone treatment time was 20 min.

Series of electroless Cu plating experiments were performed for 15 min. The bath temperature was 24°C and pH was adjusted to 12.5. After the electroless Cu plating, 300 nm-thick Cu was deposited as known from cross-sectional SEM image of Cu/polyimide in Fig. 3.

Figure 4 shows the microscope images of fabricated Cu/PI patterns. It could be observed that 300 nm-thick line-and-space patterns with widths ranging from 5 μm to 50 μm are well fabricated without defects. For the evaluation of electric property of fabricated Cu/PI interconnection, 50 μm-wide Cu interconnections with different
lengths (1.2 mm, 3.6 mm, 6.0 mm, 8.4 mm and 10.8 mm) were used.

The electric resistance of the fabricated Cu interconnections with 300 nm thicknesses was measured, as shown in Fig. 5. The resistance increased linearly with the increase of the interconnection length. The resistivity of the fabricated Cu interconnections was calculated to $2.00 \times 10^{-8} \ \Omega \cdot m$. From this result, it was verified that the process proposed in this study enables us to fabricate Cu interconnections having the similar resistivity with pure Cu ($1.68 \times 10^{-8} \ \Omega \cdot m$). At the moment, the technique studied here is potentially applicable to the fabrication process of Cu/PI interconnections.

**Fig. 3** Cross-section SEM image of Cu/PI

**Fig. 4** The optical images of the fabricated Cu patterns on solvent-soluble siloxane- modified PI: Line and space patterns with the line widths of (a) 50 µm, (b) 10 µm, and (c) 5 µm. (d) 50 µm-wide Cu interconnections with the different lengths of (1) 1.2 mm, (2) 3.6 mm, (3) 6.0 mm, (4) 8.4 mm, and (5) 10.8 mm

**Fig. 5** Electric resistance of 50 µm-wide Cu interconnections with lengths of (1) 1.2 mm, (2) 3.6 mm, (3) 6.0 mm, (4) 8.4 mm and (5) 10.8 mm

### 4. Conclusion

In this work, vacuum-UV induced surfactant masking (VISM) process was suggested and it was successfully applied to a selective electroless Cu plating process. The VISM process condition was established by investigating the relation between the wettability of the solvent-soluble siloxane-modified PI surface and the UV/Ozone treatment time. As a result, Cu patterns with widths ranging from 5 to 50 µm could be fabricated with good fidelity on the solvent-soluble siloxane-modified PI surface.

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