



## Additive-Free Superfilling in Damascene Cu Electrodeposition Using Microcontact Printing

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To avoid complications brought about by employing organic additives, microcontact printing using a flat stamp was used in forming trench-selective Cu superfilling on damascene structure. Self-assembled monolayers of 1-decanethiol transferred on top surface of the trench could withstand the H<sub>2</sub>SO<sub>4</sub> electrolyte and were used as a barrier for current transfer below a certain potential that was not yet dominated by the tunneling current. Subsequent electrodeposition on the printing area was successfully inhibited. The resulting filling profile was a defect-free superfilling with bumps on top. This is comparable to the three-additive system consisting of accelerator and two-component suppressor.

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For the past several years, fabrication of fast and reliable metal interconnections for high-performance devices has been associated with the defect-free Cu electrodeposition in damascene structure using organic additives. Numerous researches on the function of additives have suggested how some models are represented by diffusion/adsorption,<sup>1,2</sup> competitive adsorption,<sup>3-7</sup> and chemical reaction between thiol/disulfide and copper ions.<sup>8</sup> Nevertheless, the reaction mechanism is intricate and still not understood. Organics in the electrolyte can also affect the properties of deposited Cu film, such as resistivity, crystallographic orientation, grain growth, etc.<sup>8,9</sup> Here, microcontact printing ( $\mu$  CP) is applied to superfilling in place of additives.  $\mu$  CP is a fast and low-cost pattern transfer technique that uses nm thick self-assembled monolayers (SAMs) of alkanethiol,<sup>10-13</sup> silane,<sup>14</sup> alkylphosphoric acids,<sup>15</sup> and so forth. SAMs transferred on a flat metal surface by  $\mu$  CP with a molded Poly(dimethylsiloxane) (PDMS) stamp serve as a barrier/mask for selective wet etching.<sup>10,11,14</sup>  $\mu$  CP is also applied to selective deposition<sup>11,16</sup> using chemical vapor deposition and catalytic particle transfer. Nonetheless, the metal patterning by SAM formation and the subsequent wet etching method can hardly be applied to the deep submicrometer interconnection technology due to the isotropic etching feature and poor resolution of wet etching. Selective deposition requiring a metal layer for SAM formation on the entire surface is also unsuitable for device interconnection where metal lines should be electrically isolated from each other. In this study,  $\mu$  CP was applied to trench-selective electrodeposition using preliminary patterned damascene structures and flat PDMS stamp. SAMs were used as a barrier for current transfer on top surface of the trench and corresponding filling profiles were also investigated.

### Experimental

Figure 1 illustrates the schematic procedure of  $\mu$  CP and the subsequent selective damascene Cu electrodeposition. PDMS was mixed with 10% (volume) curing agent and then poured on a non-patterned Si wafer which had an AFM-measured surface roughness of 0.2 nm. After curing it at 65°C for 1 h, the PDMS stamp was peeled off from the Si substrate. A 5 mM 1-decanethiol ink solution was made by dissolving 1-decanethiol in ethanol. The ink solution was applied to the flat PDMS stamp. The stamp was then dried in a gentle stream of N<sub>2</sub><sup>11</sup> and readied for contact. The substrate where the ink solution would be transferred was a trench type patterned (single damascene, line width of 500 nm, aspect ratio of 2.5) Si wafer with a structure of PVD Cu (70 nm, seed layer)/CVD TiN (10 nm, diffusion barrier)/PVD Ti (15 nm, glue layer)/Si.  $\mu$  CP was performed on the Cu seed layer by applying a constant pressure of

10.35 N/cm<sup>2</sup> on the PDMS stamp for 5 s. To investigate the effects of the contact time on the deposit shape evolution, 30 s of contact time was also applied to the gap filling. From the XRD analysis shown in the Fig. 2, the PVD-deposited Cu seed layer was found to have a strong (111) orientation. The bonding of alkanethiol on (111) surface of the Cu involved the sulfur p-orbitals and the orbitals of the first methyl group,<sup>17</sup> and is known to be independent of the chain length.<sup>17</sup> Subsequent Cu electrodeposition was performed on the SAMs-transferred Cu seed layer in the additive-free base electrolyte composed of 1 M H<sub>2</sub>SO<sub>4</sub>, 0.25 M CuSO<sub>4</sub>·5H<sub>2</sub>O, and DI water with stirring. The three-electrode system made up of Cu wafer cathode, Cu bar anode, and saturated calomel reference electrode (SCE) was used. For comparison, Cu electrodeposition on the SAMs-free Cu seed layer was also done using the three-additive system for superfilling. The corresponding electrolyte was made up of the base electrolyte and 50  $\mu$  M bis(3-sulfopropyl)disulfide (SPS, (Na<sup>+</sup>O<sub>3</sub>S(CH<sub>2</sub>)<sub>3</sub>S<sup>-</sup>)<sub>2</sub>), 88  $\mu$  M poly(ethylene glycol) (PEG, Mw 3400), and 1 mM NaCl.<sup>3,18</sup>

### Results and Discussion

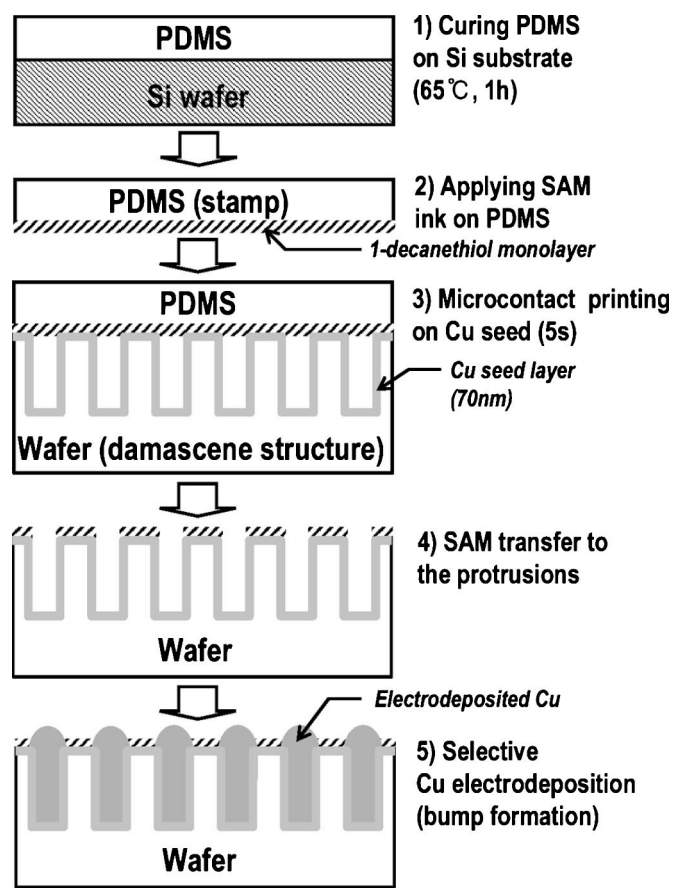
To determine the potential to be applied for electrodeposition, linear sweep voltammetry was performed within the range of 0 to -550 mV with a scan rate of 20 mV/s. The result is presented in Fig. 3. A Cu rotating disc electrode with a rotation speed of 300 rpm was used as a working electrode. The I-V curve shifted to a more negative direction for the microcontact printed Cu seed due to the blockage of the current transfer by the SAMs on the Cu surface. At below -140 mV, the current through the microcontact printed Cu seed was almost 0, while it increased steadily in the case of bare Cu. Figures 4a and b exhibit the difference in deposition thickness according to the existence of SAMs on the Cu seed layer. Electrodeposition was performed at -140 mV for 200 s. Unlike the 700 nm thick deposits on the bare Cu seed layer (Fig. 4a), almost no deposition occurred on the microcontact-printed Cu seed layer (Fig. 4b). Surface-restricted carbon and sulfur contents of specimen (b) from the AES analysis (Fig. 4c) supported this observation. It also indicated that SAMs of 1-decanethiol could stand against sulfuric acid electrolyte and successfully played a role as a barrier against electron transfer.

Figure 5 shows the comparison between  $\mu$  CP and organic additives for superfilling on damascene structure. A typical bottom-up filling profile was observed for the gap filling using the three-additive system (Fig. 5a), of which the mechanism could be explained by curvature enhanced accelerator coverage (CEAC).<sup>4,7</sup> A somewhat different profile was found in the gap filling using  $\mu$  CP (Fig. 5b), however. The top of the trench (protrusions) covered with the transferred SAMs had no deposits. Hilllocklike deposits on the fourth and fifth protrusions implied that there were partially non-contact areas on the Cu seed layer due to the elasticity of the PDMS stamp. Lateral spreading and diffusion of alkanethiol from the stamp

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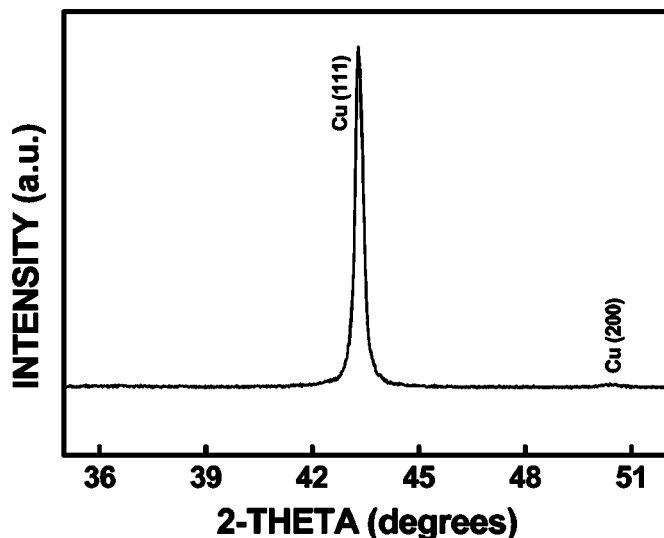
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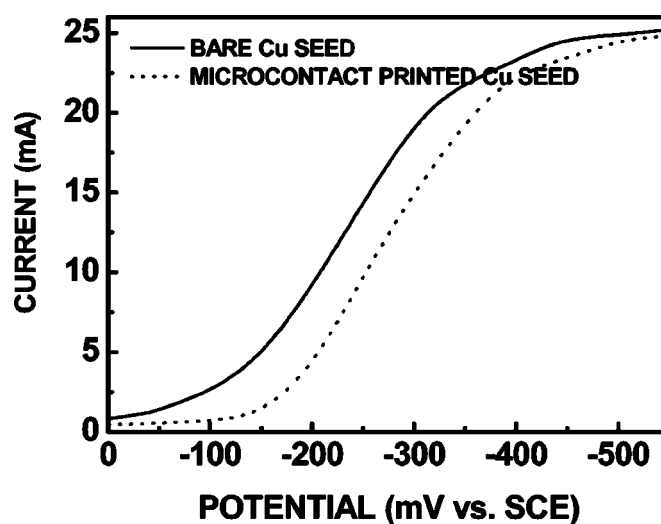


**Figure 1.** Schematic procedure of  $\mu$  CP and subsequent selective damascene Cu electrodeposition.

to the unwanted surface during printing are known to be possible.<sup>19</sup> Similarly, SAMs on the top of trenches may diffuse into the inside of the trench; thus, the sidewall near the top had no deposits, and the filling had a round profile as shown in Fig. 5b. The small figure in Fig. 5b was a SEM image of the Cu deposit when contact time was increased up to 30 s. As expected, there was almost no deposit along the sidewall near the top of the trench due to the extended diffusion

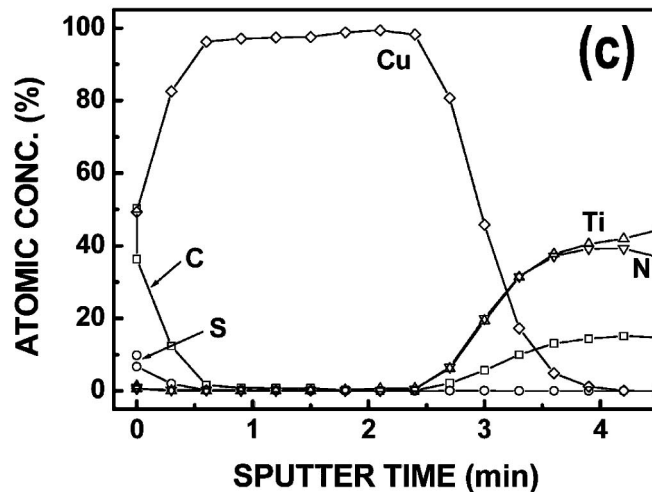
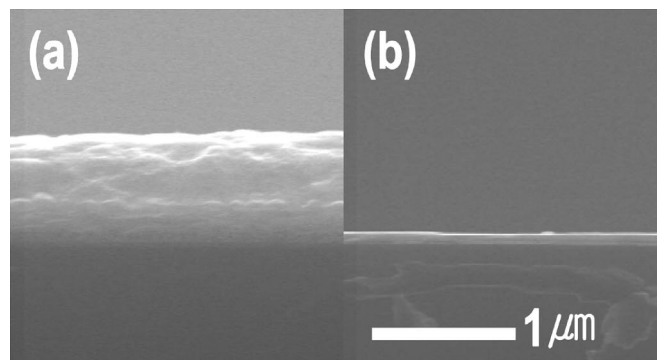


**Figure 2.** XRD analysis of PVD Cu seed layer.

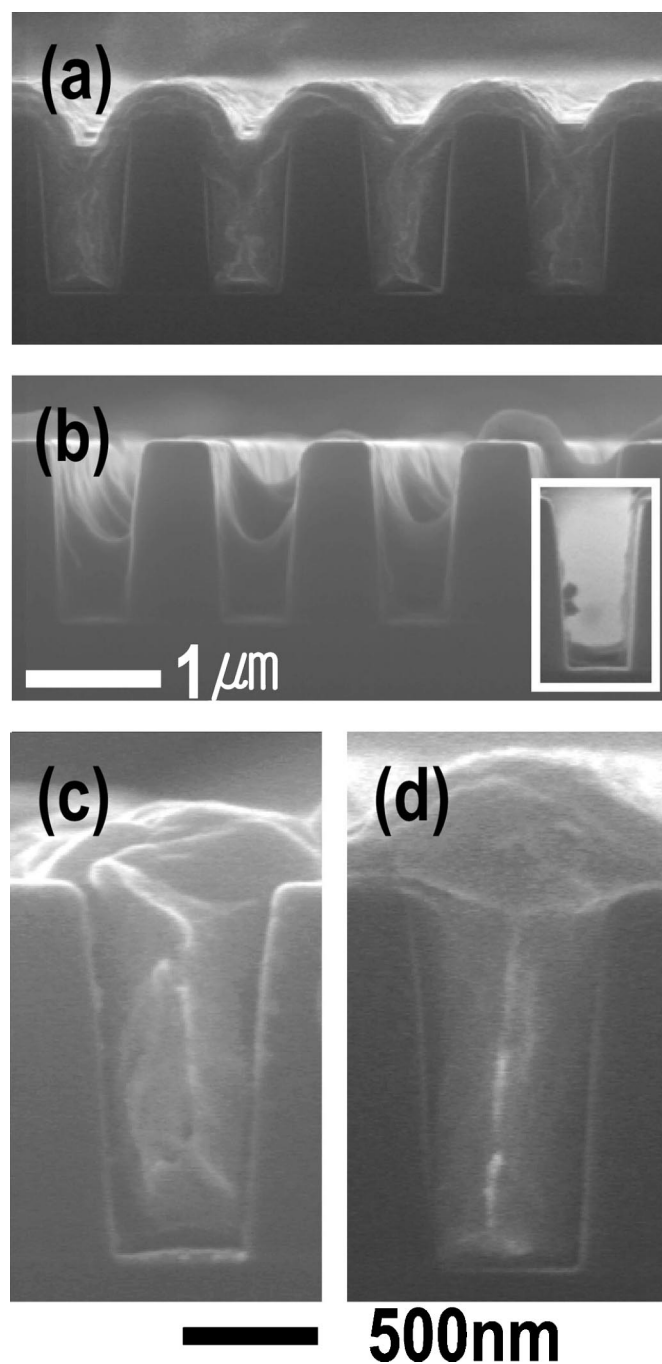


**Figure 3.** Linear sweep voltammogram of Cu electrodeposition on bare and 5 s microcontact printed Cu surface. Rotation speed of 0.2 cm<sup>2</sup> Cu electrode and scan rate were 300 rpm and 20 mV/s, respectively.

of SAMs during the increased contact time. After the deposition was complete, the formation of bump was observed in either case (Fig. 5c and d), which was conclusive evidence of superfilling. Nonetheless, the bump formation mechanism seemed to be different for each case. The growth inhibition on top of the trench made the deposit grow continuously from the trench bottom to the surface normal



**Figure 4.** Cross-sectional FESEM images of electrodeposited Cu films at -140 mV for 200 s (a) on bare Cu seed, (b) on 5 s microcontact printed Cu seed, and (c) AES analysis of sample (b).



**Figure 5.** Cross-sectional FESEM images of electrodeposited Cu films (a) at  $-250$  mV for 250 s using three-additive system, (b) at  $-140$  mV for 100 s using 5 s  $\mu$  CP, (c) at  $-140$  mV for 150 s using 5 s  $\mu$  CP, and (d) at  $-250$  mV for 300 s using three-additive system, respectively. Inset: in (b) presents the Cu electrodeposit at  $-140$  mV for 150 s using  $\mu$  CP with increased contact time of 30 s. Additives used for (a) and (d) are 50  $\mu$  M SPS, 88  $\mu$  M PEG, and 1 mM NaCl.

direction in the case of filling via  $\mu$  CP as shown in Fig. 5c. On the other hand, the bump was formed as a result of bottom-up acceleration by accumulated organic accelerators inside of the trench<sup>3-6</sup> in the case of the additive-based superfilling shown in Fig. 5d. These results demonstrated that  $\mu$  CP could be a successful and simple method for damascene Cu filling, comparing favorably with the organic additive system without the complex reaction, impurity, and maintenance problems of organic additives.

### Conclusions

This study demonstrated that  $\mu$  CP could be applied to trench-selective Cu superfilling. Below a certain potential, SAMs of 1-decanethiol on the Cu surface can successfully suppress current flow through the interface of Cu/H<sub>2</sub>SO<sub>4</sub> electrolyte and inhibit deposition. When applied to a damascene structure, deposits can be void/seam-free through  $\mu$  CP and bumps can occur after deposition is completed, a match for the three-additive system. Surface diffusion of 1-decanethiol molecules, which is an important factor in the shape of the deposits, is strongly dependent on contact time.

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