Arch. Metall. Mater. **66** (2021), 3, 741-744

DOI: 10.24425/amm.2021.136372

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SELECTIVE Cu ELECTRODEPOSITION ON MICROMETER TRENCHES USING MICROCONTACT PRINTING AND ADDITIVES

Selective deposition was performed on a micrometer trench pattern using a microcontact printing (μCP) process. Alkanethiols required for selective deposition were analyzed according to the carbon chain by linear sweep voltammetry (LSV). According to the LSV analysis, the effect of inhibiting Cu deposition depending on the length of the carbon chain was observed. During the Cu electrodeposition, the trench could be filled without voids by additives (PEG, SPS, JGB) in the plating solution. A μCP process suppressing the deposition of the sample was used for selective Cu electrodeposition. However, there was oxidation and instability of the sample and 1-hexadecanethiol in air. To overcome these problems, the μCP method was performed in a glove box to achieve effective inhibition.

Keywords: μCP, selective Cu deposition, RDL, overburden, SAM(alkanethiol), Additives

1. Introduction

The most important factor in the semiconductor industry is the densification of integrated circuit (IC) chips [1,2] to achieve more functionality in smaller chips. As a result, as the feature size decreases, the density of ICs has doubled and will continue to increase. However, density improvements in the packaging technology has been much slower than the increasing IC trend.

Semiconductor packaging technologies have been widely studied to overcome this I/O interconnection gap [3,4]. Recently, researchers have focused on a Fan-Out wafer level package (FOWLP) technology that maintains a high performance and reduces packaging costs. In the FOWLP process, the redistribution layer (RDL) rearranging I/O connections was fabricated by Cu electrodeposition [1,5,6]. During the Cu electrodeposition process, an undesired overburden deposition is formed on the patterns [6,7]. To eliminate the overburden, chemical mechanical polishing (CMP) has been used in the semiconductor industry. However, CMP increases the process cost [8,9]. The microcontact printing (μCP) process transfers self-assembled monolayers (SAM) to the top surface of the patterns, leading to a decrease in the process cost [10,11].

In this study, the μCP process was conducted by fabricating planar polydimethylsiloxane (PDMS) that transferred the alkanethiol molecules to the top surface of patterns [12]. Additionally, additives, such as an accelerator, suppressor, and leveler, were added to the $CuSO_4$ solution for bottom-up Cu filling [13]. The desorption behavior of the alkanethiol molecules was investigated by electrochemical analysis. The inside of the patterns was filled without void, while Cu was not deposited on the top of the patterns, which means that the μCP process can successfully achieve selective Cu deposition.

2. Experimental

The plating solution was comprised of ultrapure deionized water (18.63 MOhm), copper sulfate pentahydrate (YAKURY), 1 M hydrochloric acid (35%, DAEJUNG), and 0.58 M sulfuric acid (98%, DAEJUNG). The additives were 88 μM polyethylene glycol (PEG) 3400 (Sigma-Aldrich), 50 μM disodium 3, 3'-dithiobis(1-propanesulfonate) (SPS, WAKO), 40 ppm Janus Green B (JGB, TCI) in 50 ml of ultrapure deionized water (18.63 MOhm) as a stock solution.

PDMS (Sylgard 184 A and 184 B) was mixed for 10 minutes at a 10:1 volume ratio and placed in a petri dish with a flat bottom for polymerization at room temperature for 1 day. The hardened PDMS was cut to 10 × 10 mm^2. The SAMs solutions

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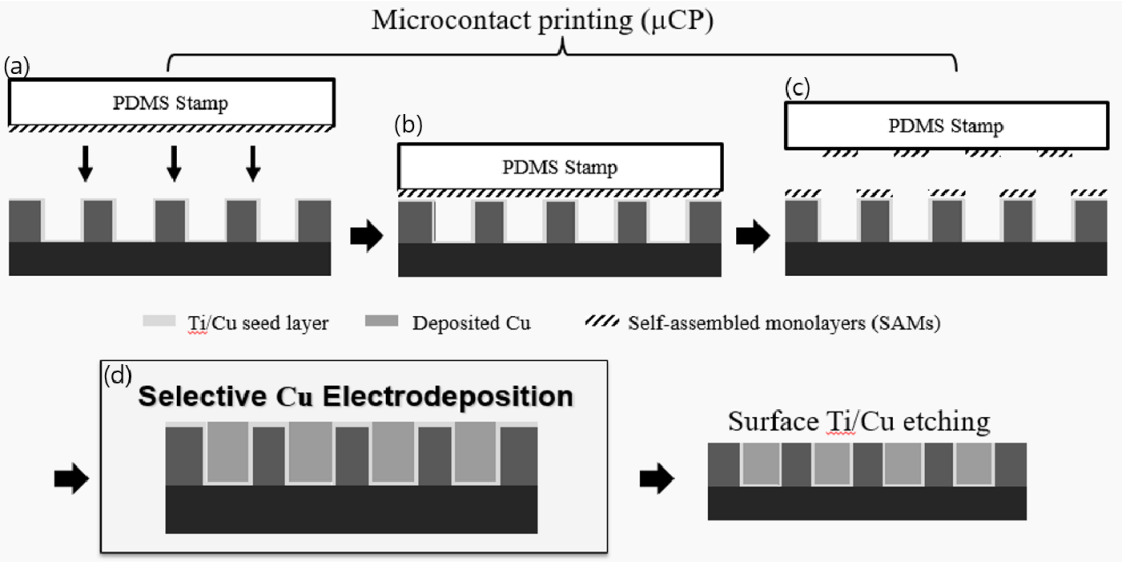


Fig. 1. A schematic diagram of the microcontact printing (μCP) process. (a) Before stamping, (b) during stamping, (c) after stamping and SAMs formed only on the top surface of the patterns. (d) Selective Cu electrodeposition after the micro-contact printing (μCP) process

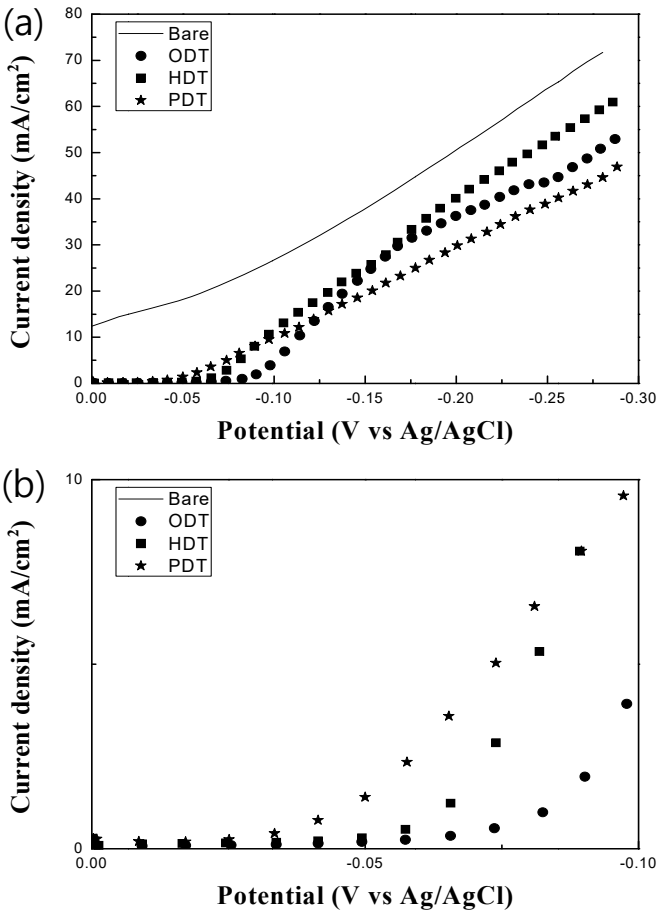
were prepared at 3-5 mM by adding 1-octadecanethiol (ODT, 98%, Sigma-Aldrich), 1-hexadecanethiol (HDT, 99%, Sigma-Aldrich), and 1-pentadecanethiol (PDT, 97%, Sigma-Aldrich). To prevent the oxidation of the SAMs, the SAM solutions were prepared in a glove box.

The patterned wafer was cut to 12 × 12 mm^2 and sampled by attaching a silicon tape that exposed only 10 × 10 mm^2 of the wafer. PDMS was cut to 10 × 10 mm^2, and the PDMS was soaked in the SAMs solution for 12 hours and dried in the desiccator.

Figure 1 shows the scheme of the μCP process. SAMs were transferred from PDMS to the patterned wafer Fig. 1(a), 1(b) and 1(c). Electrochemical plating was carried out as soon as the μCP process was completed (Fig. 1(d)). All electrochemical analyses were conducted by a potentio/galvanostat (VersaSTAT3, AMETEK Co.). The three electrode system consisted of a planar or patterned wafer, Pt-plated Ti plate (20 × 130 mm^2), and Ag/AgCl reference electrodes as the working, counter, and reference electrodes, respectively. All experiments were conducted at room temperature. Electrodeposition was conducted with and without μCP to confirm the effect of inhibiting Cu deposition on the patterned wafer by applying −350 mV(Ag/AgCl).

3. Results and discussion

Figure 2(a) and 2(b) show the linear sweep voltammetry (LSV) analysis according to the length of the carbon chain. Figure 2(c) shows the abbreviation of alkanethiols by the length of the carbon chain. Figure 2(b) is the enlargement part of Fig. 2(a) showing 0.00 V to −0.10 V(vs. Ag/AgCl). As shown in Fig. 2(a), when the potential was applied in the bare substrate, the current density linearly increased. However, the formation of SAMs on the sample using alkanethiols revealed a tendency to inhibit Cu deposition. As shown in Fig. 2, ODT was the most effective in suppressing Cu deposition. However, ODT was easily saturated



(c)

# of Carbon chain length	18	16	15
Alkanethiols $CH_3(CH)_nSH$	ODT	HDT	PDT

Fig. 2. LSV analysis. (a) LSV analysis according to the length of the carbon chain, (b) enlargement of the 0.00 to −0.010 V section. (c) Abbreviation for alkanethiols by carbon chain length

at room temperature. Therefore, HDT was selected for selective Cu electrodeposition.

As shown in Fig. 3(a), the inside of the patterns was filled by Cu without void, and Cu was also deposited on the top surface. Alternatively, as shown in Fig. 3(b), only the inside of the patterns was filled without void and Cu deposition on the top surface was greatly reduced because of the SAMs. HDT successfully suppressed the Cu deposition on the top surface of the substrate, though not completely. Because Cu is a metal that can be easily oxidized in air, Cu might be oxidized to copper oxide, inhibiting the binding between Cu and alkanethiols. Consequentially, the suppression of SAMs did not occur on the top surface because the inhibition ability of SAMs was degraded. This result matched the previous research on the oxidation of HDT [14,15].

To prevent the oxidation of HDT in air, an atmospheric condition without oxygen was required during the μCP process. For this reason, we conducted an experiment in a glove box to minimize the oxidation. All steps, including making the solution and the μCP process, were conducted in the glovebox, except for the electrodeposition of Cu. After removing the sample from the glovebox, the plating step was performed immediately.

As shown in Fig. 4, inhibition of HDT in the glove box improved performance on the top surface of the samples compared with Fig. 3. Based on these results, SAMs were transferred to the top of the patterns; however, they did not exist inside the patterns. Consequently, the μCP process in the glove box effectively applied SAMs to the top surface of the patterns only.

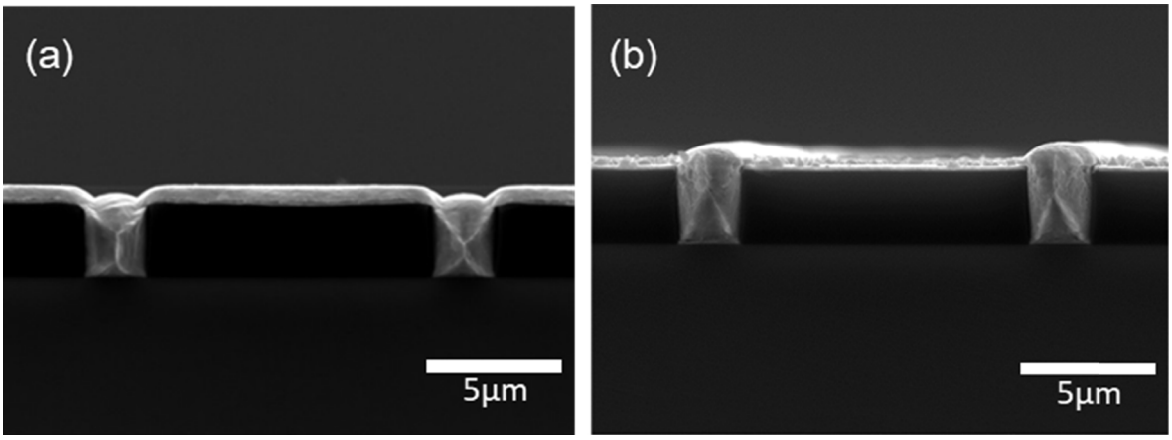


Fig. 3. SEM images of the cross-section of (a) the trench deposition with only additives without the microcontact printing (μCP) process and (b) the trench after an additive and microcontact printing (μCP) process

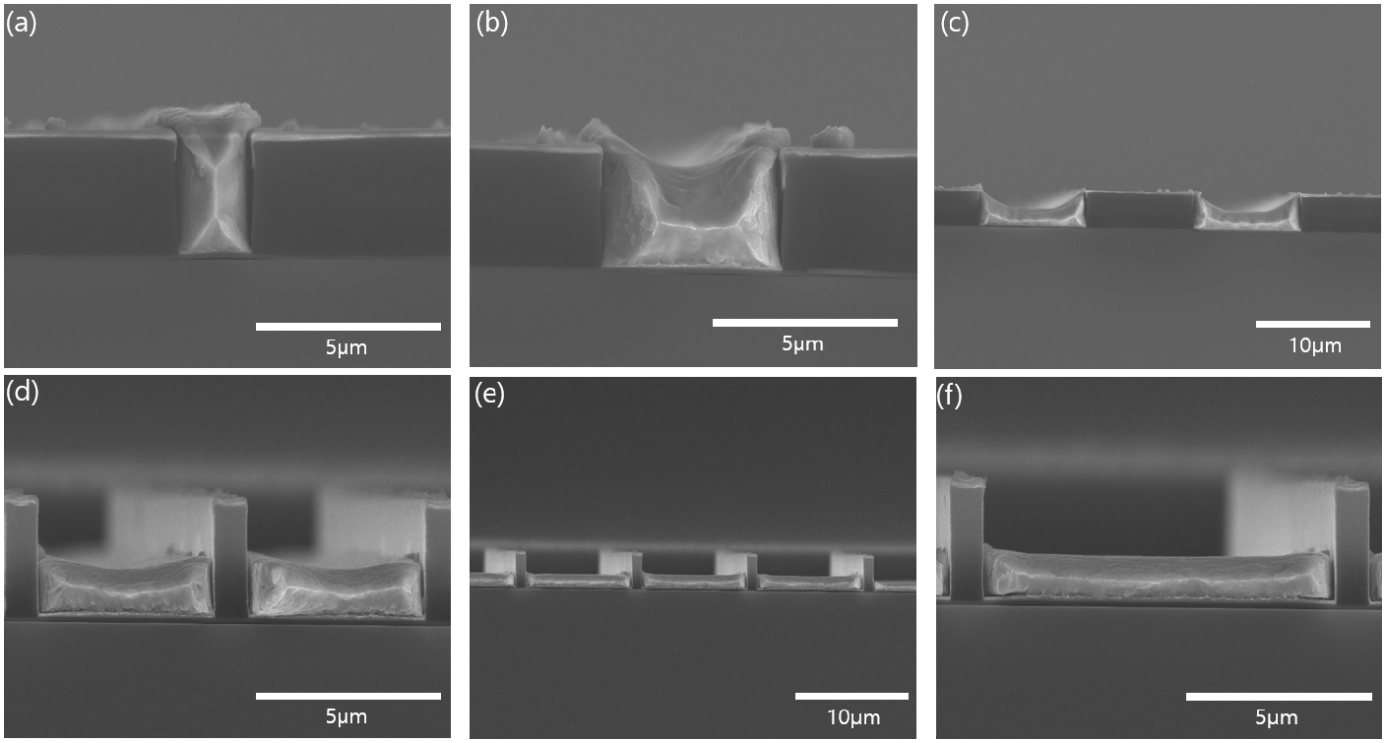


Fig. 4. SEM images of (a-f) the cross-section of the trench deposition with only additives without the microcontact printing (μCP) process in the glovebox

4. Conclusions

In this study, the characteristics of the SAMs were measured according to the carbon chain length by electrochemical analysis. A μCP process was applied to minimize Cu overburden. However, the Cu substrate and SAMs can be easily oxidized in air. For a more effective μCP process, the process was carried out in a glove box, which effectively suppressed the deposition of Cu on only the top surface of the patterns. As a result, the μCP process can replace the costly CMP process. This study shows the feasibility of improving the function of the RDL process and reducing future costs.

Acknowledgments

This research was supported by Basic Science Research Program through the National Research Foundation of Korea (NRF) funded by the Ministry of Science, ICT & Future Planning (No. 2015R1A5A1037548) and research was supported by the MOTIE (Ministry of Trade, Industry & Energy (No. 10067804) and KSRC (Korea Semiconductor Research Consortium) support program for the development of the future semiconductor device and work was supported by the Technology Innovation Program (20005011, Development of materials and process technology for highly luminance micro display with 2000 PPI resolution) funded by the Ministry of Trade, Industry & Energy (MOTIE, Korea).

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