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JINYONG SHIM^{1†}, JINHYUN LEE^{1†}, BONGYOUNG YOO^{1*}

SELECTIVE Cu ELECTRODEPOSITION ON MICROMETER TRENCHES USING MICROCONTACT PRINTING AND ADDITIVES

Selective deposition was performed on a micrometer trench pattern using a microcontact printing (μ CP) 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 μ CP 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 μ CP method was performed in a glove box to achieve effective inhibition.

Keywords: μ CP, 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 (μ CP) 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 μ CP process was conducted by fabricating planar polydimethylsiloxane (PDMS) that transferred the alka-

nethiol 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 μ CP 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 $10 \times 10 \text{ mm}^2$. The SAMs solutions

¹ HANYANG UNIVERSITY, DEPARTMENT OF MATERIAL SCIENCE & CHEMICAL ENGINEERING, ANSAN, KOREA

* Corresponding author: byyoo@hanyang.ac.kr

† These authors contributed equally to this work



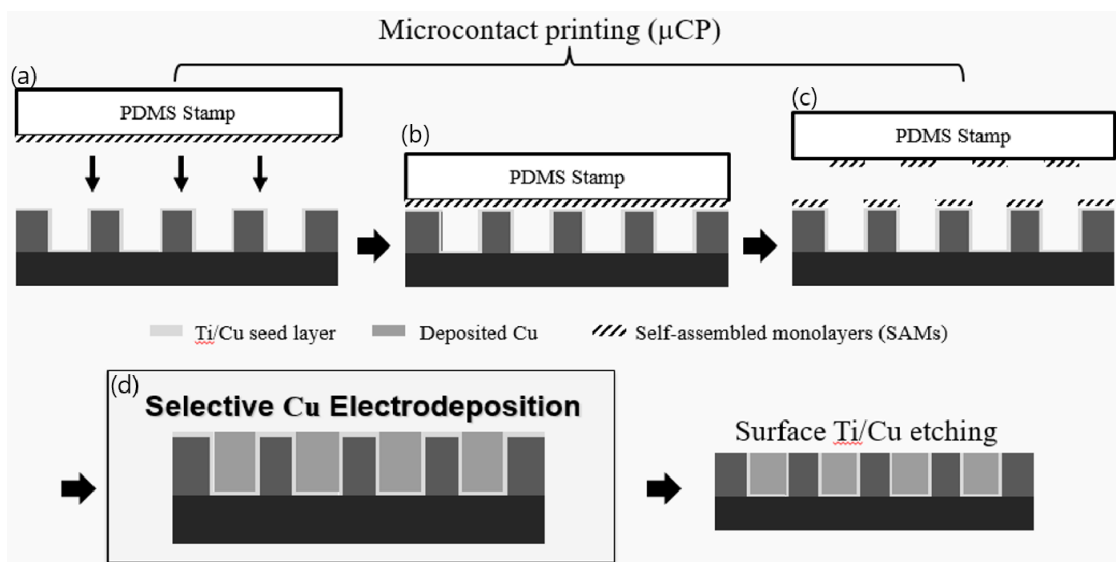


Fig. 1. A schematic diagram of the microcontact printing (μ CP) process. (a) Before stamping, (b) during stamping, (c) after stamping and SAMs formed only on the top surface of the patterns. (d) Selective Cu electrodeposition after the micro-contact printing (μ CP) process

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 $12 \times 12 \text{ mm}^2$ and sampled by attaching a silicon tape that exposed only $10 \times 10 \text{ mm}^2$ of the wafer. PDMS was cut to $10 \times 10 \text{ mm}^2$, and the PDMS was soaked in the SAMs solution for 12 hours and dried in the desiccator.

Figure 1 shows the scheme of the μ CP 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 μ CP process was completed (Fig. 1(d)). All electrochemical analyses were conducted by a potentiogalvanostat (VersaSTAT3, AMETEK Co.). The three electrode system consisted of a planar or patterned wafer, Pt-plated Ti plate ($20 \times 130 \text{ mm}^2$), 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 μ CP to confirm the effect of inhibiting Cu deposition on the patterned wafer by applying $-350 \text{ mV}(\text{Ag}/\text{AgCl})$.

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 $-0.10 \text{ V}(\text{vs. Ag}/\text{AgCl})$. 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

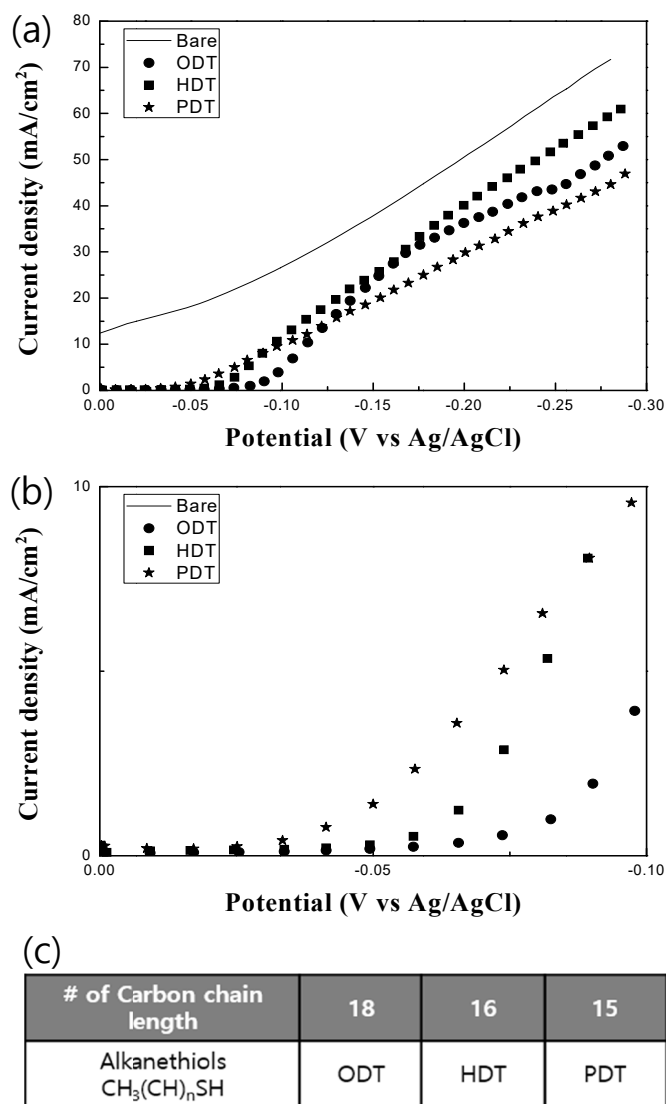


Fig. 2. LSV analysis. (a) LSV analysis according to the length of the carbon chain, (b) enlargement of the 0.00 to -0.10 V section. (c) Abbreviation for alkanethiols by carbon chain length

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 μ CP process. For this reason, we conducted an experiment in a glove box to minimize the oxidation. All steps, including making the solution and the μ CP 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 μ CP process in the glove box effectively applied SAMs to the top surface of the patterns only.

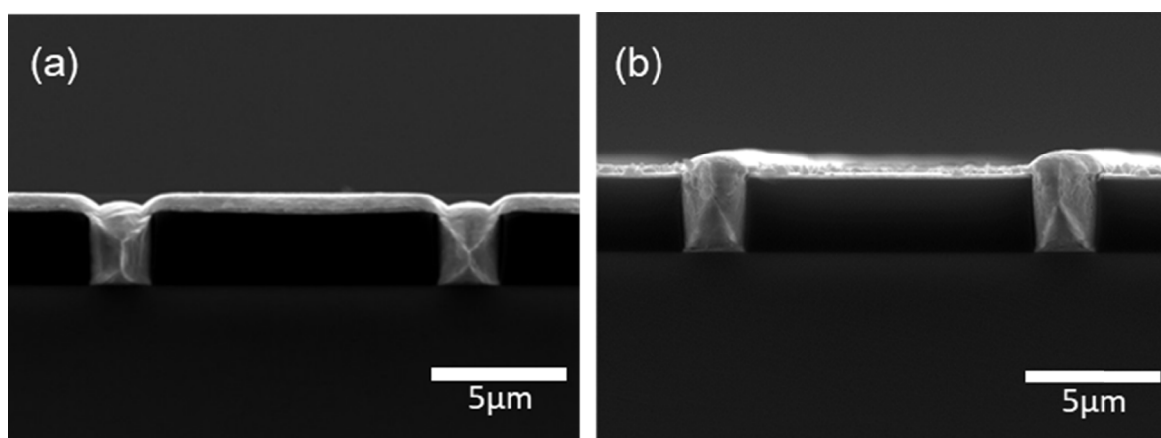


Fig. 3. SEM images of the cross-section of (a) the trench deposition with only additives without the microcontact printing (μ CP) process and (b) the trench after an additive and microcontact printing (μ CP) process

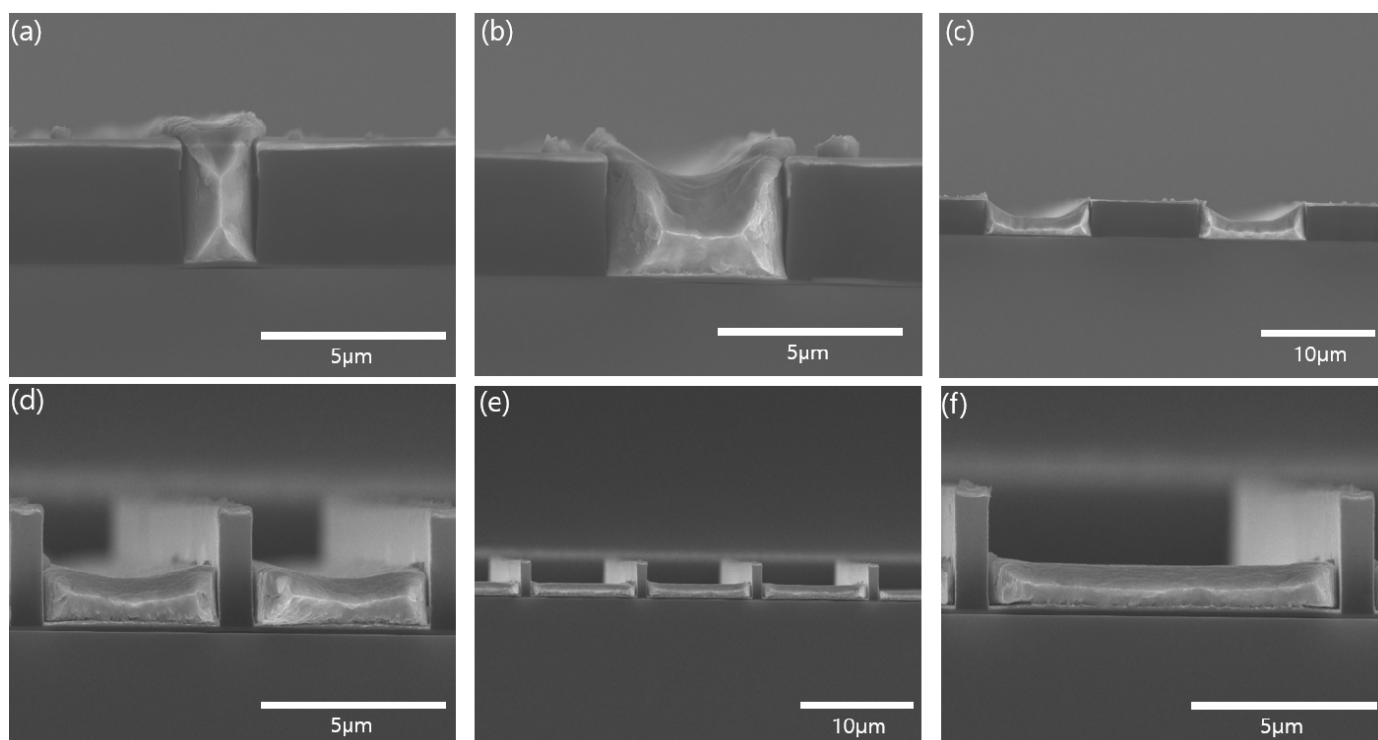


Fig. 4. SEM images of (a-f) the cross-section of the trench deposition with only additives without the microcontact printing (μ CP) process in the glovebox

4. Conclusions

In this study, the characteristics of the SAMs were measured according to the carbon chain length by electrochemical analysis. A μ CP process was applied to minimize Cu overburden. However, the Cu substrate and SAMs can be easily oxidized in air. For a more effective μ CP 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 μ CP process can replace the costly CMP process. This study shows the feasibility of improving the function of the RDL process and reducing future costs.

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