Superconformal copper filling of a nano-scale trench by nucleation suppression at the trench entrance during metal organic chemical vapor deposition

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A B S T R A C T
Superconformal filling of copper (Cu) into the nano-scale SiO2 trench was investigated by controlling the nucleation and growth conditions during the metal organic chemical vapor deposition of Cu. Inductively coupled H2/Ar plasma pretreatment of the Ru-deposited trench pattern with a substrate biasing prior to deposition led to suppression of Cu nucleation on the top and entrance areas of the trench. In turn, Cu grows preferentially inside the trench. Controlled nucleation by plasma pretreatment enabled the achievement of superconformal Cu gap filling of sub-60 nm trenches without voids. Suppression of nucleation was attributed to deposition of sputtered silica (Si)-containing species on the top and entrance areas of the trench from the quartz window of the plasma reactor.

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1. Introduction

Electrochemical deposition (ECD) has generally been used in filling both trenches and ultra-large scale integration (ULSI) interconnects with copper (Cu) due to the advantages in cost, process temperature, and gap-filling properties. The conventional ECD process requires the formations of barrier and Cu seed layers prior to ECD [1,2]. As the feature sizes of devices approached 22 nm and greater, the ECD process demands thinner barrier/seed layers to minimize the increase in interconnect resistance. This requires superior gap-fill performance due to barrier/seed overburden caused by an increased aspect ratio in the Cu line [2,3]. Furthermore, the thickness ratio of the barrier and seed layers relative to that of the Cu line continues to increase. Thus one-step direct filling, which does not require a Cu seed layer, could be beneficial for Cu interconnect formation. To fill the nano-scale trench directly without the need for a seed layer or generation of voids and seams after filling, a superconformal or bottom-up filling process utilizing chemical vapor deposition (CVD) is required.

For direct one-step superconformal filling of a trench by Cu, catalyst-enhanced chemical vapor deposition (CECVD) has attracted significant attention. CECVD has the capability of direct gap filling without a seed layer, and superconformal filling prevents overhang formations at the tops of the trenches [4]. For CECVD, adsorbed iodine atoms on the Cu layer aid in Cu nucleation and accelerate deposition. The iodine adatoms floating down from the sidewall of the trench gradually gather onto the bottom during deposition. The unequal concentration yields different Cu growth rates at the bottom and entrance areas of the trench. Eventually, the Cu growth rate of the bottom overtakes those of the sidewall and top, leading to superconformal filling [5]. However, there is some probability of iodine incorporation into the growing Cu films during CECVD, which can lead to corrosion of the Cu line [4,6].

The motivation of this work is to examine non-iodine-based catalysts for superconformal filling using CVD. Furthermore, we aimed to minimize the growth rate of Cu at the entrance area of the trench by suppressing the local nucleation rate so that overhang formation is inhibited. As a result, conformal deposition of Cu can be obtained. For superconformal filling, the Cu deposition rate at the entrance area should be slower than that of the bottom [5,7]. If not, Cu will cover the entire trench, and overhang will occur. It is known that an excess of hydrogen can act like a suppressor, inhibiting the surface reaction of Cu precursors by filling the vacant sites of a surface [8]. In this study, hydrogen inductively coupled plasma (ICP) was applied to investigate the possibility of using hydrogen plasma pretreatment to differentially control the Cu nucleation rates at the entrance and bottom of the trench. We used a metal organic CVD (MOCVD) system specially designed for generating hydrogen ICP with capabilities for in-situ plasma pretreatment and Cu deposition. To selectively suppress Cu nucleations at the top and entrance of the trench over those of the bottom of the trench, we treated the Ru-deposited trenches with hydrogen ICP. The selective pretreatment protected the trenches from overhang formation, which could result in superconformal filling.

Our experimental results, however, showed that a very small amount of the ultra-thin SiO2-like layer, rather than adsorbed hydrogen, acted as the primary suppressor for nucleation on the Ru surface. The
suppression layer that formed on the entrance and top of the trenches reduced the nucleation and growth rate of the Cu layer, which led to superconformal filling of the nano-scale SiO$_2$ trench.

2. Experimental

Blanket Ru (20 nm)/TiN (50 nm)/SiO$_2$ (100 nm)/Si wafer samples were prepared for measurements of Cu deposition rate and analysis of deposited Cu layer morphologies. The Ru and TiN layers were used as a glue layer and diffusion barrier, respectively. These layers were prepared using an atomic layer deposition (ALD) process. For trench structure, a 10-nm-thick Ru layer was uniformly formed by ALD on a patterned SiO$_2$ trench with a gap width of 70–140 nm and depth of 300–320 nm.

Copper deposition was conducted in a cold-wall vertical-type MOCVD system combined with an ICP source and a substrate heater for in-situ plasma pretreatment and Cu deposition. During the plasma pretreatment process, the substrate was not allowed to be heated. The pretreatment was conducted in Ar (10 SCCM)/H$_2$ (90 SCCM) plasma at an operating pressure of 15 mTorr and a top electrode power of 500 W. Argon gas in the hydrogen plasma pretreatment was added for effective plasma initiation.

(Hfac) Cu (DMB) [(hexafluorooracetylacetonate) Cu (3, 3-dimethyl-1-butene)] (Quleap Co., Korea) was used as a Cu metal organic (MO) precursor. The (hfac) Cu (DMB) precursor was vaporized in a bubbler and then transported through a delivery line into the chamber, using Ar (100 SCCM) as a carrier gas. The temperatures of the bubbler and the line were maintained at 41 °C and 70 °C, respectively. Copper was deposited for 5–13 min at a process pressure of 0.4 Torr, and the substrate temperature was in the range of 120–150 °C.

The deposited Cu films were evaluated using field emission scanning electron microscopy (FE-SEM, JEOL JSM-7500F) to measure film thickness and nucleation density. An X-ray diffractometer (XRD, Bruker AXS D8 Discover) was used to analyze the microstructures of the deposited Cu thin films. The elements in the Cu film at the interface of the Cu and Ru layer were analyzed using an X-ray photoelectron spectrometer (XPS, ESCA 2000) and an Auger electron spectrometer (AES, PHI 700). For AES analysis, the plasma pretreatment was conducted on the blanket Ru substrate. Then, Cu was additionally deposited onto the pretreated Ru surface by DC magnetron sputtering in a separate sputter deposition system to improve the reliability of the analysis.

3. Results and discussion

Plasma pretreatment was conducted by varying the treatment time from 60 to 150 s. Copper was deposited on both the untreated Ru and plasma-treated Ru surfaces for comparison. Fig. 1 shows the top-view of FE-SEM images of Cu films grown on the Ru surfaces with different treatment times. As shown in Fig. 1, copper nucleation was suppressed more as the plasma pretreatment time increased to 120 s [Fig. 1(b)] and 150 s [Fig. 1(c)] compared to that with no treatment [Fig. 1(a)]. Copper grains on the Ru surface that had received no treatment were uniform and connected to each other, while on the plasma-pretreated Ru surfaces they were large and more disperse. For the sample treated for 120 s [Fig. 1(b)], the Cu grain size and layer thickness were decreased significantly compared to those of Cu grown without pretreatment [Fig. 1(a)]. For the sample treated for 150 s [Fig. 1(c)], the Cu grains, which were about half the size of the sample pretreated for 120 s [Fig. 1(b)], were more uniform. As the plasma pretreatment time increased, Cu islands were formed instead of a continuous Cu film, and the grain sizes decreased even further. These results imply that Cu nucleation was suppressed by plasma pretreatment, and that suppression of nucleation was enhanced at longer treatment times. The effect of longer plasma pretreatment on the grain size of Cu films grown on the planar Ru films in this experiment implies that the Cu growths on the top and entrance areas of a trench structure can be suppressed, as shown in Figs. 4 and 5. Due to the difficulty in reaching H radicals and ions inside the trench, however, nucleation of Cu inside the trench will be less affected.

The chemical binding states of the pretreated Ru substrate were examined using XPS measurement in order to understand why Cu nucleation was suppressed on the plasma-pretreated Ru surfaces. The wide-scan XPS spectra obtained from the samples with and without treatment for 120 s are shown in Fig. 2, where it is illustrated that the
The intensity of the Ru 3d5/2, Ru 3d3/2, Ru 3p3/2, and Ru 3p1/2 peaks weakened after plasma pretreatment, while the Si 2s and Si 2p peaks appeared, and the intensity of the O 2s peak increased [Fig. 2]. The results indicate that there existed a significant chemical change on the Ru surface after plasma pretreatment, and there is a possibility for formation of a SiOx-like layer on treated Ru surfaces. Formation of a SiOx-like layer on the pretreated Ru surface is presumably attributed to sputtering of sputtered silica (Si)-containing species from the quartz window of the plasma reactor.

To confirm the possibility of SiOx-like layer formation, the surface of the Ru layer was also investigated by AES depth profiling. For reliable analysis, surface of the pretreated Ru layer was sputter-deposited by a 60-nm-thick Cu layer in a separate DC magnetron sputter deposition system with no Si-containing chamber materials. The pretreatment was conducted in Ar (10 SCCM)/H2 (90 SCCM) plasma for 120 s at an operating pressure of 15 mTorr and a top electrode power of 500 W. Slight increases in the silicon and oxygen peak intensities were observed around a 60 nm depth, as shown in Fig. 3, indicating a relatively small amount of a SiOx-like layer. Under a certain condition, Cu nucleation was also suppressed on the Ru layer pretreated by Ar plasma only, which confirms the formation of a SiOx-like layer on treated Ru surfaces by sputtering of sputtered silica-containing species from the quartz window of the plasma reactor. The high concentrations of carbon and oxygen seem to be caused by contamination from air.

The gap-filling process by Cu MOCVD was carried out after the pretreatment of the ALD Ru layer that was deposited onto the SiO2 trench. The pretreatment time was varied from 120 to 150 s. For comparison, Cu was deposited onto the sample without plasma pretreatment, as shown in Fig. 4(a). The widths and aspect ratios of the trenches in Fig. 4(a), (b), and (c) were 121 nm and 3:1, 89 nm and 3.5:1, and 108 nm and 3:1, respectively. The image in Fig. 4(a) shows that Cu was not uniformly deposited in the wider trench compared to...
the Cu-filling capabilities shown in Fig. 4(b) and (c). The relatively large Cu grains deposited onto the top of the trench and near the entrance were likely to lead to the formation of voids and overhangs. The results in Fig. 4(a) imply that it is crucial to suppress Cu nucleation on the top surface and near the entrance of the trench in order to achieve superconformal filling.

As the plasma pretreatment time increased to 120 s [Fig. 4(b)] and 150 s [Fig. 4(c)], copper nucleation was gradually suppressed at the entrance and top areas of the trench. Voids in both Fig. 4(b) and (c) were observed inside the trenches even though Cu nucleation was heavily suppressed on the top of the trench. For the sample with a treatment time of 120 s [Fig. 4(b)], the Cu at the bottom of the trench was filled with voids due to faster Cu growth near the middle of the sidewall than at the bottom of the trench. The aspect ratio of the trench in Fig. 4(b) is greater than that in Fig. 4(c). This result indicates that a pretreatment time greater than 60 s is needed to suppress Cu nucleation near the entrance and to prevent void formation inside the trench. Copper was deposited in the trench after the treatment time of 150 s [Fig. 4(c)], having an aspect ratio similar to that of the wider trench in Fig. 4(a), without blocking near the lower entrance of the trench. As the plasma pretreatment time increased, Cu in the trench nearly achieved superconformal filling. The results supported a possibility for achieving superconformal filling when Cu growth is effectively suppressed near the lower entrance of the trench.

To further enhance the gap filling of the trench, power was applied at the bottom of the substrate holder during the plasma pretreatment. The trench was treated with hydrogen ICP for 120 s without substrate biasing and then with a DC self-bias voltage \( V_{dc} \) of \(-50 \) V for 30 s [Fig. 5(a)]. Copper gap filling was conducted for 13 min at a substrate temperature of 120 °C. Superconformal Cu filling was achieved for the Ru-deposited trench with a width of \~120\,nm and height of \~330\,nm, as shown in Fig. 5(a). The thick Cu layer that formed on the top of the trench seemed to be caused by connected Cu pillars from inside the trench. For the Ru-deposited trench with a width of \~70\,nm (opening 50 \,nm) and a height of \~280\,nm, the trench was pretreated with direct plasma for 90 s without substrate biasing and then with substrate biasing at a \( V_{dc} \) of \(-50 \) V for 60 s [Fig. 5(b)]. The trench was filled superconformally with 50-nm-thick Cu without a seam or void, as shown in Fig. 5(b). The upper Cu layer on the Ru surface was thinner than that observed in Fig. 5(a) owing to the strengthened suppressions of Cu nucleation and growth. The results imply that the suppression ability relied on the treatment time of the applied substrate bias. It is assumed that the substrate bias gives SiO\(_x\)-like particles a higher directionality toward Ru trenches rather than random motion. As a result, SiO\(_x\)-like particles can more deeply penetrate into the trench, extending the suppression layer to the middle of the trench. The introduction of substrate bias led to a more efficient superconformal gap filling of the nano-scale trenches.

4. Conclusions

Copper nucleation was effectively suppressed by hydrogen plasma pretreatment and could be controlled with treatment time and substrate biasing. The chemical binding states of treated Ru surface
examined using XPS and AES measurements showed that a SiO$_x$-like layer was formed on the Ru surface. As a result, Cu nucleation on the top of the trench was heavily suppressed, and Cu was filled conformally as the plasma pretreatment time increased. The introduction of substrate bias during plasma pretreatment led to a more effective superconformal filling. Even for a 50-nm-wide trench, Cu could be filled superconformally without voids when the substrate biasing time was increased. Since the SiO$_x$-like layer affects the electrical properties of integrated Cu interconnect lines, assessment of the electrical properties of filled Cu is needed in future studies.

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