

Amorphous-Carbon Barrier against Moisture for Copper Metallization and Effects of CF₄ Plasma Treatment

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Abstract

The moisture barrier properties of amorphous-C (a-C) layer for Cu metallization in long-term storage is investigated under the temperature humidity storage (THS) as a low-temperature coating compatible with device fabrication processes. Depth profiles by XPS demonstrate the excellent barrier properties of a-C layer to prevent Cu oxidation, and the efficiency is comparable to the stacked graphene with large-grain size deposited at a high-temperature. In addition, CF₄ plasma treatment is considered to be a potential method to improve the barrier efficiency by forming C–F bonds in the a-C layer.

1. Introduction

Cu metallization has been widely used in LSIs, such as memories. An important requirement of these devices is to increase the reliability of long-term storage. A critical reliability risk of Cu metallization, such as pads, for long-term storage is oxidation from moisture in the environment [1].

In our previous work, we reported the moisture barrier properties of large-grain graphene [2, 3], and accidentally, we also found that some areas of a-C dominant structure without graphene seem to be a potential barrier against moisture [2]. Moreover, fluorine plasma treatment is expected as a potential method to improve the moisture barrier performance of a-C layer by forming C–F bonds.

In this paper, we investigated the moisture barrier properties of a-C with various thicknesses on the Cu film surface and then characterized their efficiency by X-ray photoelectron spectroscopy (XPS) depth profiling. In addition, the effects of CF₄ plasma treatment on the a-C are studied to improve the performance of the thinner a-C layer.

2. Experimental Methodology

Fabrication of a-C/Cu sample

100-nm-thick Cu film was prepared on SiO₂/Si substrate by DC magnetron sputtering at 200°C to complete the Cu grain growth. Then, a-C film with different thicknesses (15, 10, and 5 nm) was deposited from a graphite target using RF magnetron sputtering at room temperature.

Test and analysis methods

After sample preparations, a primary investigation was carried out to characterize the a-C film by XPS. The THS test under the condition of 85°C/85% RH was performed to accelerate the Cu-oxidation for 50 h. XPS depth profiles of C, Cu, and O atomic concentration were acquired by etching the

sample surface every 50 s until the Cu surface was exposed.

CF₄ plasma treatment

Typical 15-nm-thick a-C samples were exposed to CF₄ plasma with the forward power of 30W at 0.1 Torr for various durations (1, 3, and 5 min). The primary optimization of conditions was made to increase the intensity of C–F bond with remaining the a-C layer after the plasma process. Then, THS testing and XPS depth profiling are also performed to investigate the effects of CF₄ plasma treatment.

3. Results and Discussion

Characteristic of a-C layer coated on Cu surface

Fig. 1 shows the typical C 1s spectrum of sputtered a-C. It shows the a-C is composed of mainly sp² bonds (~80%) along with sp³ bonds, whose peaks are located at 284.5 and 285.5 eV, respectively [4]. After 50h of THS test, the depth profiles (Fig. 2) show that the Cu oxidation decreases as the a-C thickness increases, where the O atoms in Cu₂O and CuO bonds which located at 530.3 and 529.7 eV were counted as the O content. The dominant structure of Cu-oxides for a-C/Cu is a low oxidation state (Cu₂O), besides that is a high oxidation state (CuO) for the Cu surface without a-C barrier as shown in Fig. 3.

Characteristic of a-C layer with CF₄ plasma treatment

Fig. 4 shows the (a) F 1s and (b) C 1s spectra by XPS after the CF₄ plasma treatment on 15-nm-thick a-C for 1 to 3 min. After the treatment, C–F bonds were formed as shown in Fig. 4. Longer processes than 1 min show the additional peak of Cu–F bonds located around 683 to 685eV, and it indicates that the a-C layer was etched by CF₄ plasma and Cu was partially fluorinated. The depth profile after 1 min plasma (Fig. 5) also shows the reduced a-C thickness after plasma comparing to that without plasma (Fig. 2a).

Comparison of moisture barrier efficiency

The maximum O/Cu ratios of Cu without a-C, with a-C, and with a-C exposed to CF₄ plasma for 1 min are compared along with that of the Cu surface with double layer graphene (DLG) which we reported previously [3], in Fig. 6. Comparing the O/Cu ratios between with and without a-C barrier, the ratios reduced drastically with a-C, indicating that a-C layers can prevent Cu from oxidation. The efficiency of a-C barrier was degraded with reducing the a-C thickness. For the a-C with CF₄ plasma treatment for 1 min, the O/Cu ratio is almost same as that of 15-nm-thick a-C in spite of the reduced thickness by plasma etching. It suggests that an appropriate CF₄ plasma treatment might potentially improve the efficiency of

a-C barrier.

Comparing the efficiency of a-C barriers with that of DLG [3], it is surprising that the O/Cu ratios of a-C/Cu with and without CF₄ plasma treatment are quite close to that of DLG-coated Cu sample. These results demonstrate that 15-nm-thick a-C layer and the thinner a-C layer after CF₄ plasma treatment can be a practical moisture barrier to protect Cu surface.

4. Conclusions

This work demonstrates the moisture barrier properties of a-C layer deposited on Cu film by sputtering. 15-nm-thick a-C layer was found as an excellent barrier to obstruct the penetration of moisture by showing the same O/Cu ratio as that of the DLG-coated Cu surface. In addition, appropriate CF₄ plasma treatment was found to induce C–F bonds in a-C and it is expected to improve the barrier efficiency of a-C. Since the low process temperature is compatible with device fabrication, the a-C barrier will be a practical method to improve the reliability of Cu metallization in long-term storage.

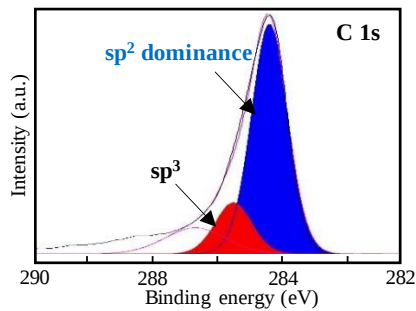


Fig. 1. C 1s spectrum of sputtered a-C, indicating a sp² dominant structure of deposited a-C.

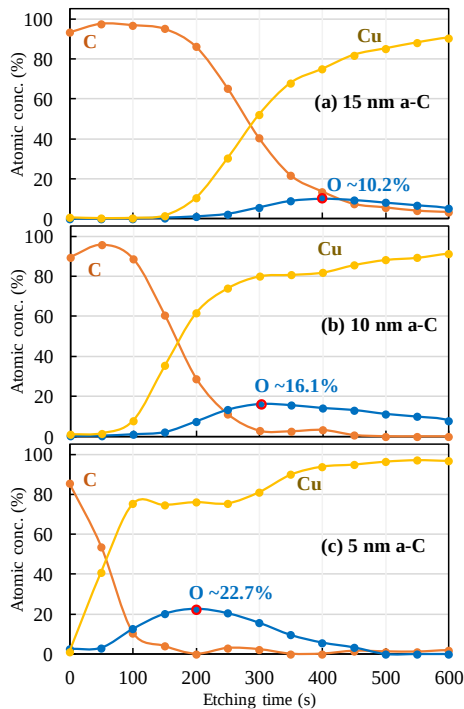


Fig. 2. Depth profiles for (a) 15 nm, (b) 10 nm, and (c) 5 nm a-C/Cu.

Acknowledgements

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References

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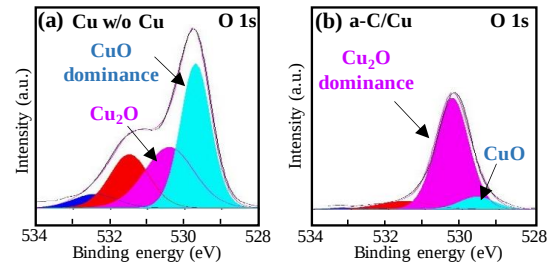


Fig. 3. O 1s spectra of Cu (a) without a-C and (b) with a-C layer.

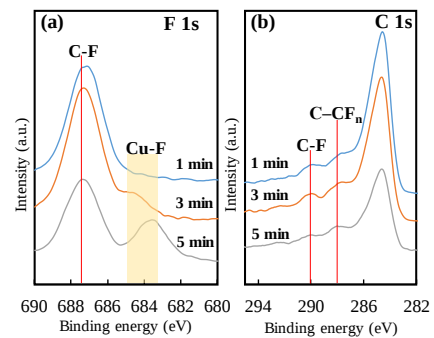


Fig. 4. (a) F 1s and (b) C 1s spectra of a-C with CF₄ plasma treatment.

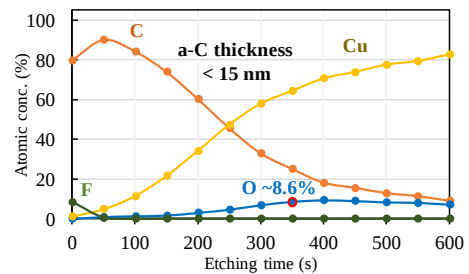


Fig. 5. Depth profiles of a-C/Cu after 1 min CF₄ plasma treatment.

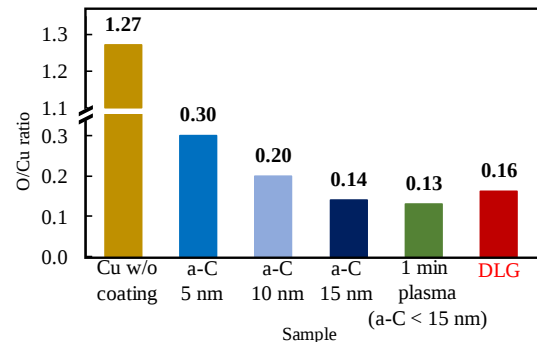


Fig. 6. Comparison of moisture barrier efficiency between a-C barriers and that of DLG [3] after 50h of THS test.