Characterization of Ozone-Ethylene Radical Pretreatment for Hybrid Bonding without Water Rinsing Processes

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***Abstract*— An Ozone-Ethylene Radical (OER) generation technology can produce a highly active oxidizing agent of OH radicals by mixing an unsaturated hydrocarbon gas with a highly concentrated ozone gas. The OH radicals given by the OER treatment are expected to be used as a prospective surface hydrophilization technique without water rinsing. In this study, we investigate the effectiveness of the surface treatment technology OER on hybrid bonding with thermally grown SiO_2, CVD-SiCN, and PVD-Cu thin films by water contact angle (WCA), AFM, and XPS. N_2 plasma activation is also used before the OER treatment for comparison. OER drastically reduces the WCA of the SiCN thin films compared to the SiO_2 thin film. The AFM analyses found that the surface roughness of the dielectric films is kept after the OER treatment, whereas OER slightly increases the surface roughness of Cu. XPS results suggest that the OER treatment acts on the SiO_2 nitrided by N_2 plasma to form Si-OH, and in addition, $Cu(OH)_2$ becomes dominant after OER processing. On the other hand, hydrophilic Cu_2O mainly occupies the Cu surface before the OER treatment. Furthermore, the OER treatment on SiCN enhances oxygen composition, suggesting that OER yields more Si-OH groups by OH radicals. These results indicate that OER is a useful pretreatment method for hybrid bonding.**

Keywords—hybrid bonding, surface modification, hydrophilic, pretreatment, ozone, hydroxyl radical

I. INTRODUCTION

3D stacking is an advanced packaging technology that vertically integrates IC chips and interconnects in layers with short Cu-TSVs. Thus, 3D stacking with the TSVs has attracted much attention to overcoming performance and power consumption issues compared to conventional planar 2D packages. Cu-TSV and solder micro-bumps with underfill are currently used for high-bandwidth memory (HBM), but thermal management is a big concern. There is a growing interest in hybrid bonding, which allows simultaneous bonding of dielectric and metal layers, decreasing thermal resistances and increasing energy-efficient performance (EEP) in addition to fine-pitch interconnect density.

Hybrid bonding is achieved by the thermal diffusion bonding of Cu and the covalent bonding of dielectrics such as SiO_2 and SiCN. The Cu surface should be oxide-free because oxidation of the Cu surface limits Cu-Cu interdiffusion and raises electrical resistance. In addition, it is important to terminate the SiO_2 surface with high-density OH groups because Si-OH groups are polar and can form strong hydrogen bonding networks even at room temperature. The covalent bonds can be formed at relatively low annealing temperatures. To create such a reliable bonding interface, surface cleaning (e.g., wet etching with citric acid/water) and plasma irradiation are often used to activate the surface and remove contaminants and oxidized layers. However, suppose excess water is chemically and physically adsorbed on the surface of SiO_2 during the rinsing process. In that case, high-temperature annealing is needed to remove the water uptake completely, and consequently, void formation from the water molecules is restricted at the bonding interface. Therefore, a water-free pretreatment of surface hydrophilization is required.

Here, we apply Ozone-Ethylene Radical (OER) to hybrid bonding. The OER process is a dust-free and water-free surface treatment method using OH radicals generated by mixing high-concentration (>80%) ozone and an ethylene gas [1]. Since OH radical is a strong oxidizing agent, second only to fluorine, it is expected to react with SiO_2 dangling bonds given by N_2 plasma treatment to form Si-OH and remove organic contamination. Therefore, we investigate the effectiveness of the water-free pretreatment technology OER on hybrid bonding.

II. EXPERIMENTAL

A. Materials.

We characterize SiO_2, SiCN, and Cu thin films for hybrid bonding using OER. The SiO_2 film was formed on Si wafers by thermal oxidation with a thickness of 100 nm. The Cu film was formed on Si wafers by magnetron sputtering with a thickness of 500 nm. The SiCN film was formed by a plasma-enhanced chemical vapor deposition (PECVD) process with a thickness of 100 nm. The source gases were NH_3 and $Si(CH)_4$; the deposition temperature was 350°C.

B. Pretreatment

The OER treatment was performed for 1 min for each sample. In addition to a single OER treatment, we employed plasma processing with conventional surface activation for comparison. Considering plasma damages from the direct plasma treatment and particle generation due to sputtering, we used a remote inductively coupled plasma (ICP) process. N_2 was used as the plasma source, and the plasma was run for 8 min at 150 W of RF power under a pressure of 250 mTorr. Since dangling bonds formed by the plasma process were expected to react with active OH groups generated by the OER treatment to form Si-OH bonds, a two-step N_2 plasma/OER surface treatment was also compared.

C. Measurement

To measure the effect of several surface treatments. The physical and chemical structures were investigated before and after the pretreatment. The water contact angle (WCA) was used to evaluate surface hydrophilicity in a sessile drop mode quantitatively. Surface morphology was measured by atomic force microscopy (AFM), and the surface chemical states were measured by X-ray photoelectron spectroscopy (XPS). The SiO_2 and Cu thin films were calibrated to center the C 1s peak at 284.6 eV.

III. RESULTS AND DISCUSSION

A. Water Contact Angle (WCA)

Table I and Fig. 1 show the results of WCA measurements. The WCA drastically decreased from 54.3° to 25° for SiO_2 and from 71.5° to 6.5° for SiCN with a single OER treatment. These suggest that the OER treatment formed Si-OH bonds. SiCN has many dangling bonds, so it can be said that OER treatment works more effectively [2]. The contact angle of Cu decreased from 48.6° to 39.5° before and after the OER treatment, comparable to that of remote N_2 plasma. These results confirm that the OER treatment is a useful method of surface hydrophilization, especially for SiCN (and SiO_2), which is used in hybrid bonding.

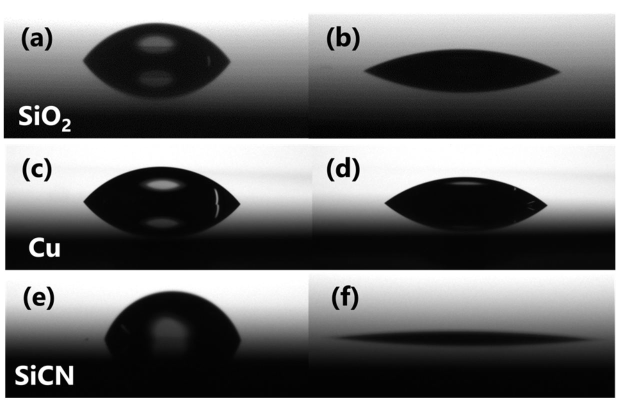

Fig. 1. WCA measurements of SiO_2 (a)(b), Cu (c)(d), and SiCN (e)(f) before (left) and after (right) OER treatment.

TABLE I. WATER CONTACT ANGLE (WCA) ON SUBSTRATE BEFORE AND AFTER SURFACE PRETREATMENT.

Water contact angle[°]	SiO_2	Cu	SiCN
No treatment	54.3	48.6	71.5
OER	25.0	39.5	6.5
Remote plasma	<5	39.2	5.8
Remote plasma + OER	<5	39.9	5.6

TABLE II. SURFACE ROUGHNESS RQ ON SUBSTRATE BEFORE AND AFTER SURFACE PRETREATMENT.

Surface roughness [nm]	SiO_2	Cu	SiCN
No treatment	0.16	7.2	0.25
OER	0.18	11.5	0.25
Remote plasma	0.18	10.1	0.26
Remote plasma + OER	0.20	11.3	0.26

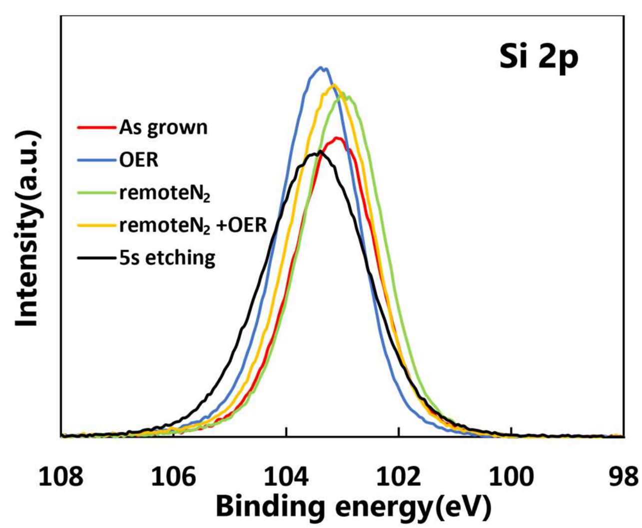

Fig. 2. XPS spectra of Si 2p for SiO_2 before and after various surface treatments.

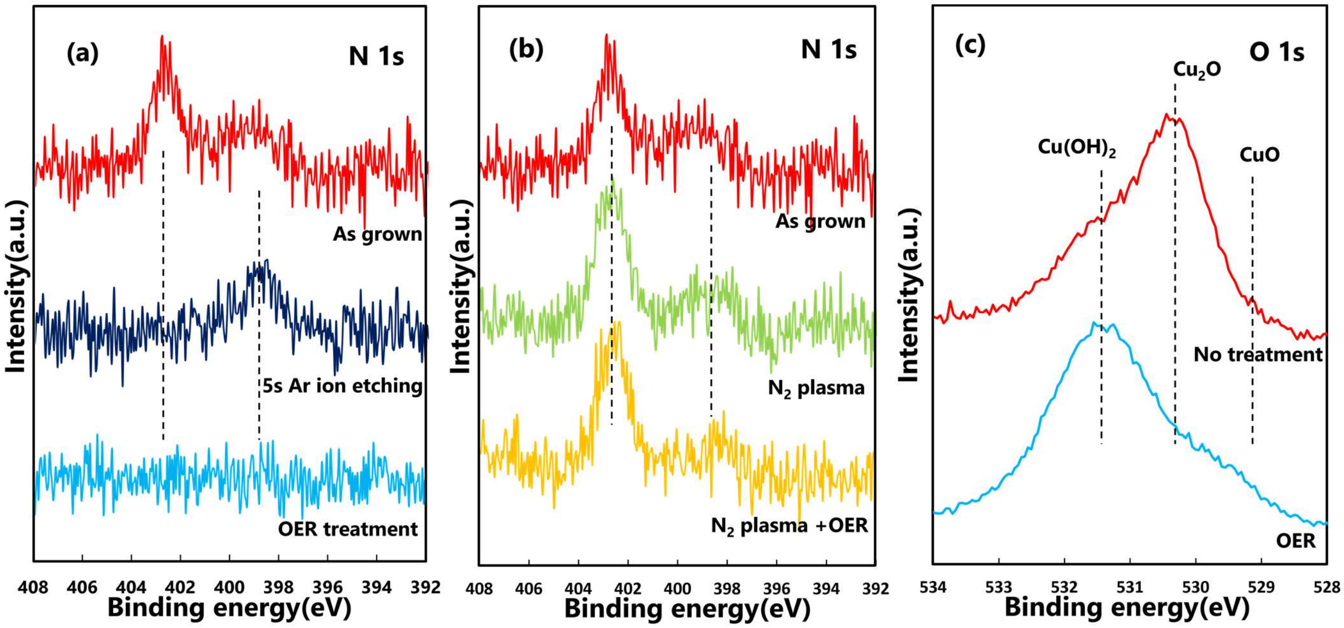

Fig. 3. XPS spectra of N 1s for SiO_2 before and after several surface treatments (a)(b) and O 1s for Cu before and after OER treatment (c). Cu spectra are normalized for comparison.

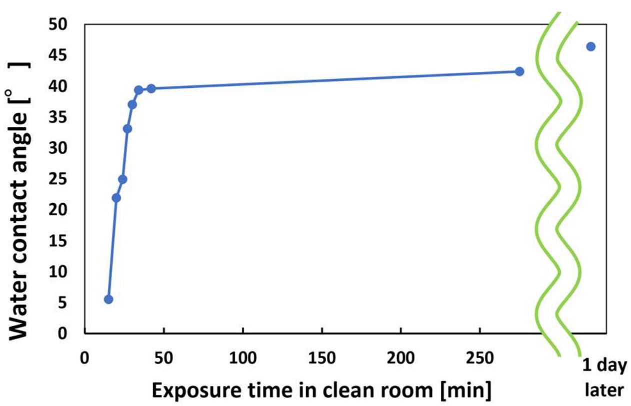

Fig. 4. The evolution of the water contact angle in cleanroom ambient after Cu deposition by PVD.

B. Surface Roughness

In direct plasma processes, the wafer surface is physically modified by ion bombardment, resulting in surface damage and/or roughened surfaces. As a result, the surface roughness of SiO_2 and SiCN increases slightly, almost negligible, before and after the three types of surface treatment, confirming that the remote plasma does not roughen the surface. While the surface roughness of Cu increased, the results were comparable to those obtained with remote N_2 plasma. As mentioned above, it is confirmed that the OER treatment and remote N_2 plasma processing can perform damage-free pretreatment without roughening the surfaces.

C. X-ray photoelectron spectroscopy (XPS) analyses

Figs. 2 and 3 (a) (b) show the XPS spectra of Si 2p and N 1s for SiO_2 before and after the several surface treatments. The Si 2p spectra of as-grown SiO_2 and OER-, N_2 plasma-, and the two-step (N_2+OER) treatments are shown in Fig. 2, where the peaks centered at 103.1, 103.4, 103,1, and 103.2 eV with FWHMs are 1.78, 1.69, 1.76, and 1.78, respectively. Two peaks are also observed in the N 1s spectrum in Fig. 3(a) and (b) at 399.5 and 402.5 eV, which are attributed to NSi_3 and $NSiO_2$, or NO_3 bonds, respectively [3].

The peaks at 402.5 eV disappear after 5-sec etching with an Ar ion gun, confirming that the peaks are not present in the entire film but only in the topmost layer. As shown in Fig. 3, OER-treated thin films show the disappearance of the two peaks at 399.5 and 402.5 eV. Nitrogen has a lower electron affinity than oxygen, and thus, the peak of the Si-N bond appears on the low energy side in the Si 2p spectra. It is considered that the bond between N and Si is broken by the OER treatment, which causes a slight decrease in the FWHM of the Si 2p peak. However, in the combination of N_2 plasma with OER, the reduction of the N 1s peak is less pronounced, and further investigation is needed to elucidate this phenomenon.

The measured O 1s spectra of Cu before and after OER treatment are shown in Fig. 3 (c), where the Cu peaks consist of CuO, Cu_2O, and $Cu(OH)_2$, corresponding to 529.3, 530.3, and 531.4 eV, respectively [4]. The main peak of Cu before the surface treatment is centered on Cu_2O, whereas after the OER treatment, the main peak is $Cu(OH)_2$, and the spectra have a sub-peak with a gradual shoulder on the low-energy side. Fig. 4 shows the time-dependent change of WCA on a PVD-Cu film in a cleanroom after sputtering. The quick increase in the WCA of the Cu layer suggests that the reaction with O_2 and water in the air oxidizes the Cu. OH radicals reacted with this oxidized Cu to form $Cu(OH)_2$. Since $Cu(OH)_2$ is hydrophilic with OH groups, the WCA of $Cu(OH)_2$ will decrease. $Cu(OH)_2$ has oxygen, but a dehydration reaction occurs first between the Cu-OH structures at low temperatures at the bonding interface:

$$Cu - OH + HO - Cu \rightarrow Cu - O - Cu + H_2O$$

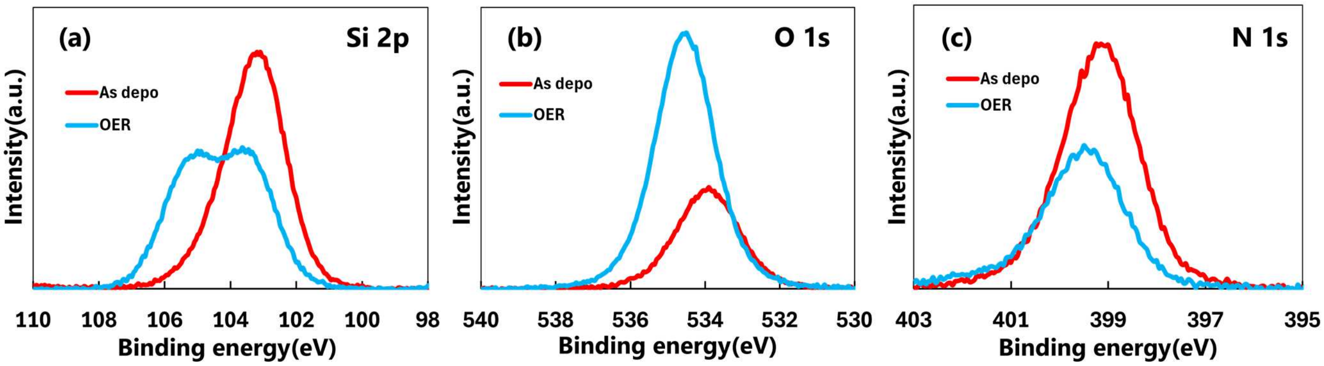

Fig. 5. XPS spectra of Si 2p (a), O 1s (b), N 1s (c) for SiCN before and after OER treatment.

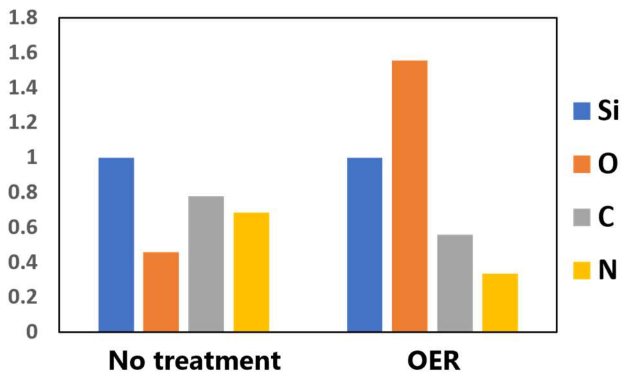

Fig. 6. Chemical composition of a SiCN film (normalized by Si atomic %).

During heating and annealing at 200°C, dehydration occurs, and Cu and O are diffused. This behavior makes the bonding interface low oxygen and is expected to provide good bonding strength and electrical properties [5].

Fig. 5 shows the Si 2p, O 1s, and N 1s spectra of SiCN, where the SiCN spectra are not charge-corrected and are therefore considered to be shifted toward higher energies. In the Si 2p spectra, a main peak at 103.1 eV is observed, whereas the OER treatment results in two peaks at 103.5 and 105.5 eV, which are considered to be the Si-N and Si-O peaks. Fig. 6 shows the change in chemical composition before and after OER treatment. Normalized by Si atomic %. The large increase in oxygen content after OER treatment suggests the formation of Si-OH bonds by reaction with OH radicals in the OER treatment. This result also supports the significant decrease in the WCA of SiCN after OER processing.

IV. Conclusions

In this study, we employed OER treatments used for hybrid bonding and verified whether the OER could provide advantageous surface modification. WCA measurements showed that OER alone could improve the hydrophilicity, and the hydrophilicity of SiCN was drastically decreased from 71.5° to 6.5°, which means the reaction of the OH groups with dangling bonds. The AFM results showed that OER and remote N_2 plasma could be applied to the surface pretreatment without surface roughness. While the surface roughness of Cu increased, the results were comparable to those obtained with remote N_2 plasma. The XPS measurements of SiO_2 showed that the N 1s spectral peak in SiO_2 disappeared by OER treatment. Cu_2O was a dominant composition before OER treatments, whereas $Cu(OH)_2$ was another dominant one after pretreatment. As for the SiCN thin film, the OER treatment efficiently increased the hydrophilicity of the surface by forming $Cu(OH)_2$, whereas after the OER treatment, the Cu surface was hydrophobic before pretreatment due to rapid reactions with O_2 and H_2O in the air. In addition, it was confirmed that the OER treatment resulted in a SiCN film with a high oxygen content. This result is consistent with the WCA measurement, implying that the OH groups act on the dangling bonds of SiCN and Si-N and Si-C to introduce more Si-OH groups. From these findings, we conclude that the OER treatment is an effective surface pretreatment method for hybrid bonding.

Acknowledgment

This work was performed at Tohoku University's Micro/Nano-machining Research and Education Center (MNC) and Jun-ichi Nishizawa Research Center. This work was also supported through the activities of VDEC, The University of Tokyo, in collaboration with Cadence Design Systems.

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