

# An Advanced Remote-Plasma Assisted Ozone-Ethylene Radical (OER) Process for Cu-SiO<sub>2</sub> Hybrid Bonding Yield Enhancement

Tatsunori Shino  
MEIDEN NANOPROCESS  
INNOVATIONS, INC.  
Chiba, Japan  
shino-t@npi.meidensha.co.jp

Mariappan Murugesan  
NICHe, Tohoku University  
Sendai, Japan  
muruges@bmi.niche.tohoku.ac.jp

Kiyoharu Mori  
NICHe, Tohoku University  
Sendai, Japan  
k.mori@bmi.niche.tohoku.ac.jp

Bungo Tanaka  
Graduate School of Biomedical  
Engineering  
Tohoku University  
Sendai, Japan  
b-tanaka@lbc.mech.tohoku.ac.jp

Eitaro Toyama  
MEIDEN NANOPROCESS  
INNOVATIONS, INC.  
Chiba, Japan  
toyama-e@npi.meidensha.co.jp

Tetsuya Nishiguchi  
MEIDEN NANOPROCESS  
INNOVATIONS, INC.  
Chiba, Japan  
nishiguchi-t@npi.meidensha.co.jp

Takafumi Fukushima  
Graduate School of Engineering  
Graduate School of Biomedical  
Engineering  
Tohoku University  
Sendai, Japan  
fukushima@lbc.mech.tohoku.ac.jp

**Abstract**—The Ozone-Ethylene Radical generation technology (OER) process generates large amounts of electrically neutral OH radicals by mixing an unsaturated hydrocarbon gas with a highly concentrated ozone gas under dust- and water-free conditions. Here, we examined the potential of using the OER process as a pretreatment to activate chip surfaces before hybrid bonding. Through real-time semi-quantitative radical concentration measurement, we confirmed that a large amount of OH radicals can be supplied to the surface of a bonding substrate placed in a custom-made vacuum chamber by mixing highly concentrated (>80%) ozone gas and ethylene gas under optimized process conditions. We also confirmed that the OER process is suitable as a pretreatment before hybrid bonding in the sense that both dielectric layer hydrophilization for strong adhesive bonding and a negligibly small Cu-Cu interface resistance are satisfied simultaneously. A connection test using a daisy chain of 5000 Cu electrodes assembled after OER pretreatment and hybrid bonding showed that overall interface resistance was as small as that afforded by a conventional citric acid hydration process. In addition, for surfaces for which OER is less effective at activation compared with plasma treatment (i.e., that of silicon thermal oxide films), sequential treatment with a mild remote plasma followed by OER works well for producing reliable, strong hybrid bonding. In summary, because the OER process is plasma- and water-free, the use of OER pretreatment not only simplifies the overall hybrid bonding process but also provides an interface with improved reliability.

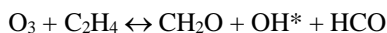
**Keywords**—hybrid bonding, surface modification, hydration, hydrophilic, surface activation, ozone, hydroxyl radical

## I. INTRODUCTION

Hybrid bonding is a means of heterogeneously stacking chips at a very fine interconnection pitch to produce three-dimensional integrated technologies at low temperatures. To achieve reliable hybrid bonding where the surfaces of both the

dielectric layer and metal pads are involved in adhesion, a multistage process is usually used that involves surface activation by plasma treatment, surface hydration and cleaning (e.g., rinsing with deionized water), and finally high-temperature annealing with the two activated surfaces aligned face to face for dehydration condensation. The initial hydrophilic treatment is most often accomplished by using a plasma, but this can cause oxidation of the metal surface and the generation of contamination through sputtering of the metal and sticking of the metal particles to the dielectric surface and to the walls of the process chamber [1]. To avoid these issues, a hydrophilic plasma treatment method has been proposed in which a low-power nitrogen plasma is used instead of a moderate-power oxygen or argon plasma [2]. However, even when a low-power plasma is used, incorporation of excess water molecules from the rinsing step into the plasma-treated surfaces, as well as imperfect removal of metal particles generated during the plasma treatment, means that the post-dehydration anneal requires a high temperature, is time-consuming, and results in unreliable hybrid bonding because the excess water molecules incorporated into the bonding surfaces act as desorption sites and create voids that degrade bond strength. Thus, a dust- and water-free hybrid bonding process is needed.

Here, we examined the use of our Ozone-Ethylene Radical (OER) process as a dust- and water-free hydrophilic treatment method for use in hybrid bonding. The OER process is a surface treatment that utilizes the OH radicals that are generated when a high-concentration (>80%) ozone gas and an unsaturated hydrocarbon gas (ethylene gas in this case) are mixed. The OH radicals are formed via the following reaction pathway, which has a relatively large branching fraction (e.g., 15%) at room temperature [3]:



OH radical is a very strong oxidizing agent, second only to fluorine, which has allowed the OER process to be used previously for photoresist removal [4]. When a silicon dioxide ( $\text{SiO}_2$ ) thin film meets OH radicals at room temperature, the OH radicals react directly with the silicon dangling bonds at the film surface to form Si-OH bonds. In the case of contact between silicon dangling bonds and water molecules, this reaction rarely occurs at room temperature because of the high activation energy required to form the Si-OH bond [5]. However, the surface of  $\text{SiO}_2$  thin films contains a low density of dangling bonds, and the OER process itself doesn't have enough energy to induce dangling bond formation. We therefore developed a sequential pretreatment process that involves initial treatment of  $\text{SiO}_2$  thin film with a remote mild plasma to increase the density of dangling bonds followed by hydrophilic OER treatment. Because this approach does not involve any direct plasma treatment or a rinsing with water to achieve the optimal density of dangling bonds at the bonding surfaces, the hybrid bonding process remains free of dust and excess water.

## II. EXPERIMENTAL

### A. OER process monitoring

A quartz crystal microbalance (QCM; NIHON DEMPA KOGYO CO., LTD.) sensor was used to monitor in real-time the amount of OH radicals generated during the OER process. This type of monitoring has been used previously to quasi-quantitatively monitor the concentration of atomic oxygen via the variation of oscillation frequency caused by etching of a polyimide film deposited on the sensor's surface [6]. The QCM sensor used in the present study was a twin-QCM (TQCM) sensor that contained a detection electrode and a reference electrode (Fig. 1). By measuring the frequency difference between the detection electrode and the reference electrode, the quantity of OH radical precisely proportional to the amount of radical impinging onto the film surface was determined by canceling the local temperature fluctuation brought about by chemical reactions at the sensor surface and by the gas flow. Since the OH radicals are far more reactive than other generated radicals such as ozone, atomic oxygen, hydroperoxyl radical ( $\text{HO}_2$ ) and hydrogen peroxide ( $\text{H}_2\text{O}_2$ ) [7], the generated amount of OH radical can be discussed based on the measured oscillation frequency shift.

Fig. 2(a) shows an overview of the OER process setup and OH radical monitoring system. Highly concentrated (>80%) ozone gas was produced by using a Pure Ozone Generator (MEIDEN NANOPROCESS INNOVATIONS, INC.) The OER chamber was equipped with a customized gas dispersion head that supplied OH radicals to the sample surface without loss by recombination of short-lived OH radicals with ambient molecules or atoms before arriving at the sample surface. To examine how addition of ethylene gas to the ozone gas during OER treatment and how the concentration of ozone affected the

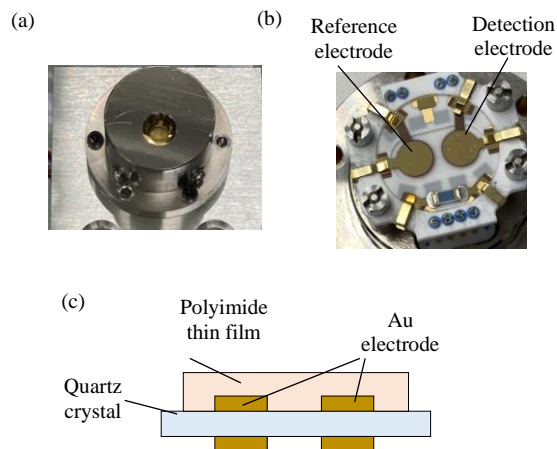


Fig. 1. (a, b) Photographs of the twin-quartz crystal microbalance sensor unit with and without its cover. (c) Diagram showing a cross-sectional view of the sensor chip. The electrodes were 4 mm in diameter, and the polyimide thin film was 5.4  $\mu\text{m}$  thick.

amount of OH radicals produced, the process conditions were tuned and compared.

### B. OER treatment, hybrid bonding, and electrical resistance measurement

To investigate the effect of OER treatment on copper oxidation, electrical measurements were performed using a daisy-chain layout consisting of  $5\text{ }\mu\text{m} \times 5\text{ }\mu\text{m}$  Cu electrodes each with a thickness of 1.5  $\mu\text{m}$  and set on top and bottom chips embedded in an  $\text{SiO}_2$  matrix. Test element group patterns were formed at the wafer level on a 12" wafer using square chips with sides of 6 mm and 7 mm for the top and bottom chips, respectively. The chips were subjected to OER treatment by placing them in the treatment chamber into which highly concentrated ozone (>80%, 200 sccm) and ethylene (40 sccm) gases were introduced for 1 min under a vacuum of less than 100 Pa. One day after the treatment, the top and bottom chips were temporarily flip-chip bonded at room temperature under 10 N applied pressure for 1 min in the ambient clean-room air. The bonded chips were then loaded into a wafer bonder for permanent bonding under an  $\text{N}_2$  atmosphere for 2 h at 400°C with an applied pressure of 500–1000 N/chip. For comparison, we also prepared samples that were similarly bonded after citric acid pretreatment instead of OER pretreatment. Electrical resistance measurements were performed on 5000  $\mu$ -junctions using the four-probe approach.

### C. Contact angle measurement

To quantitatively evaluate the hydrophilic property of the treated surfaces, water contact angles were measured. Samples of non-alkali glass, bare silicon wafer, and silicon wafer coated with an  $\text{SiO}_2$  thin film were subjected to OER treatment for 1 min. For comparison and to evaluate the effectiveness of treatment with a remote mild plasma for increasing the surface energy (hydrophilic property) and density of dangling bonds

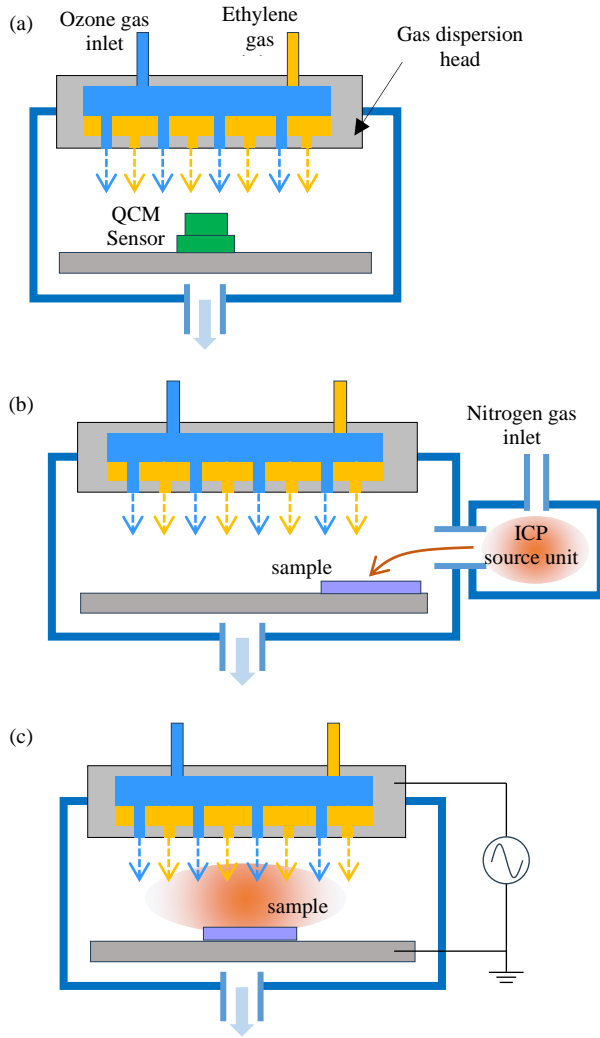


Fig. 2. Schematic view of the Ozone-Ethylene Radical treatment chamber equipped (a) with a quartz crystal microbalance (QCM) sensor for in-situ, real-time radical generation monitoring, or with (b) an inductively coupled plasma (ICP) as a remote plasma source or (c) a capacitively coupled plasma (CCP) as a direct plasma source, both for enhancement of surface activation

within the topmost few nanometers of the surface, we subjected an  $\text{SiO}_2$  thin film to inductively coupled plasma (ICP) processing. Fig. 2(b) shows the experimental setup. An ICP source unit (SEMI-KLEEN; PIE Scientific, LLC) was attached to the OER processing chamber to create a system that can perform both remote plasma processing and OER processing. The remote plasma was activated under a nitrogen gas pressure of 200 Pa at an output power of 150 W for 8 min. During the treatment, a weak remote plasma and reactive radicals were generated and allowed to contact the sample film. The contact angle was compared between thermal oxide films subjected only to the plasma treatment and those sequentially exposed to the plasma and the OER treatments.

#### D. Bond strength measurement

A blade insertion test was conducted to compare the strength of the bonds produced by remote plasma treatment, OER treatment, or their combination. In addition, capacitively coupled plasma (CCP) activation, which also generates ions and electrons in addition to electrically neutral radicals, was used to investigate the influence of reactive species generated by the plasma on bond strength. Fig. 2(c) shows the experimental setup. The test sample was a silicon wafer coated with a thermal oxide film, bonded one day after treatment, and annealed at  $300^\circ\text{C}$  for 1 h. This direct plasma treatment was performed under a nitrogen gas pressure of 500 Pa and an output power of 375 W for 30 s.

### III. RESULTS AND DISCUSSION

#### A. OER process

Fig. 3 shows the frequency shift of the TQCM sensor when ethylene gas was introduced to the flow of ozone gas in the treatment chamber at room temperature. No frequency shift was detected in the absence of ethylene, irrespective of the concentration of ozone used. However, when ethylene was added to highly concentrated ( $>80\%$ ), but not low concentration ( $\sim 20\%$ ), ozone gas, a marked increase in frequency was observed. These findings indicate that the effectiveness of the OER process to deliver OH radical is dependent on a high ozone concentration, and that in the absence of ethylene, even when the concentration of ozone is high, the generation of reactive species like OH radicals is negligible at room temperature. These findings also indicate that even when the number of ozone molecules supplied to a surface is kept constant, the large number of  $\text{O}_2$  molecules present (up to four times as many in the case of  $\sim 20\%$  ozone) prevents the locally generated OH radicals from arriving at the sample surface, probably via recombination of OH with  $\text{O}_2$  or other ambient molecules and atoms. Together, these results demonstrate that OER treatment using a highly concentrated ozone gas can deliver a large number of OH radicals to a sample surface.

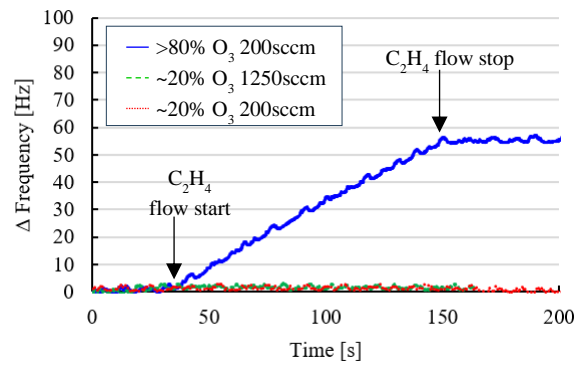


Fig. 3. Frequency shift of the twin-quartz crystal microbalance sensor during Ozone-Ethylene Radical treatment. The ozone gas flow rates are indicated in the legend. The ethylene ( $\text{C}_2\text{H}_4$ ) gas flow rate was 40 sccm for all conditions.

### B. OER treatment, hybrid bonding, and electrical resistance

After the flip-chip bonding was complete (see EXPERIMENTAL), alignment accuracy was confirmed by using an infrared microscope; the alignment accuracy was within 1–2  $\mu\text{m}$  for both the citric acid and OER processing (data not shown). Fig. 4 shows cross-sectional scanning electron microscopy images of a hybrid bonded interface after OER treatment. The images demonstrate that a void-free Cu-Cu bonding interface was obtained between the top and bottom chips, and that single-crystal Cu was formed during the annealing process for permanent bonding.

Fig. 5 shows the current (I)–voltage (V) characteristics of a daisy chain of 5000 Cu  $\mu$ -joints. The resistance was comparable between the citric acid treatment and the OER treatment. The resistance deduced from the I–V data was around 33–34  $\text{m}\Omega/\mu\text{-joint}$ , including the metal wiring line resistance. Since the resistance of the metal per Cu  $\mu$ -joint is around 30  $\text{m}\Omega/\mu\text{-joint}$ , the resistance at the bonding interface was around 3–4  $\text{m}\Omega/\mu\text{-joint}$ . This result indicates that OER treatment suppresses oxidation of the outermost Cu surface and avoids incorporation of particles and dust from the neighboring dielectric layer and the constituent materials of the processing chamber, both of which lead to increased interface resistance.

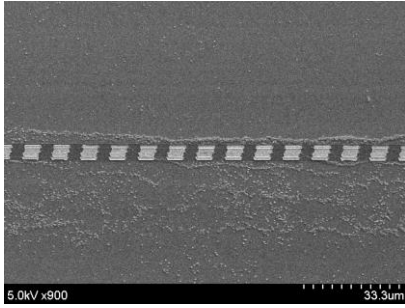


Fig. 4. Cross-sectional scanning electron micrographs of a hybrid bonded interface with a pitch of 8  $\mu\text{m}$ .

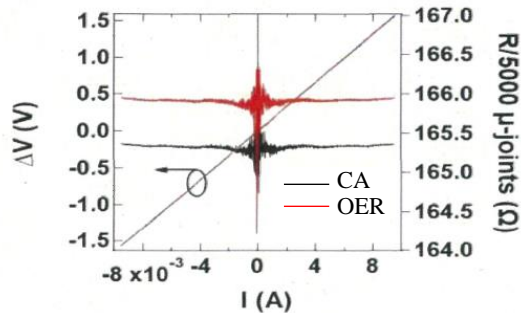


Fig. 5. Current (I)–voltage (V) characteristics of 5000 Cu  $\mu$ -joints ( $5 \times 5 \mu\text{m}^2$ ) in daisy-chain configuration: citric acid treatment (black) and Ozone-Ethylene Radical treatment (red).

### C. Contact angle

Table I shows the results of the contact angle measurements. The contact angles of the surfaces of the alkali-free glass and bare silicon wafer were markedly reduced by OER treatment alone. However, the contact angle of silicon thermal oxide film was not reduced to the same extent. This suggests that surfaces with imperfections such as defects and dangling bonds can be modified by the OH radical produced by OER treatment, whereas surfaces with few imperfections and strong stable bonds such as Si-O are modified much less. When the thermal oxide film surface was subjected to remote plasma treatment alone, the contact angle was decreased to less than  $5^\circ$ , which indicates that this treatment induced the formation of dangling bonds and new unstable bonds such as Si-N (shown schematically in Fig. 6). Thus, sequential OER treatment after mild remote plasma surface activation may be an effective method for surface OH termination without the need for treatment with a strong, direct plasma.

TABLE I. CONTACT ANGLE ON SUBSTRATES WITH/WITHOUT SURFACE TREATMENTS.

	<i>Alkali-free glass</i>	<i>Si wafer</i>	<i>Thermally oxidized Si wafer</i>
<i>No treatment</i>	33.7°	47.1°	54.1°
<i>OER</i>	<5°	<5°	21.4°
<i>Remote plasma</i>	-	-	<5°
<i>Remote plasma + OER</i>	-	-	<5°

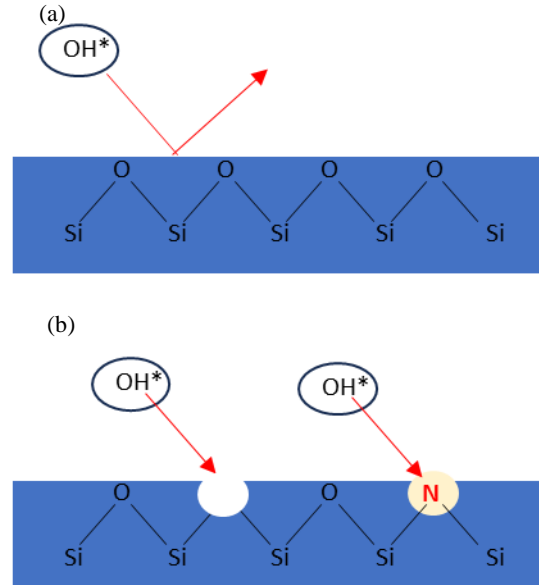


Fig. 6. Schematic diagram of a model of OH radical treatment. (a) In a thermal oxide film with few dangling bonds, OH radicals do not react. (b) Plasma treatment increases the number of dangling bonds and surface nitridation sites, which react with OH radicals.

#### D. Bond strength

Table II summarizes the results of the bond strength measurements. Continuous remote plasma + OER treatment afforded bonds with the highest strength. This is thought to be due not only to effective modification by OH groups, but also to the fact that hybrid bonding was achieved without the incorporation of excess water. In addition, the OER treatment was performed while the surface remained in an active state without being exposed to the atmosphere, allowing for modification by OH groups at high density. Overall, direct plasma treatment afforded weaker bonds compared with remote plasma treatment, despite the direct treatment having a higher output. This is potentially because the plasma source for the direct treatment was located in the same processing chamber as the base material, which would allow etching to occur within the chamber during plasma generation, resulting in the generation of dust and particles that prevented strong bond formation.

TABLE II. BOND STRENGTH OF HYBRID-BONDED CHIPS AFTER REMOTE OR DIRECT PLASMA OR OER TREATMENTS.

	<i>Plasma</i> [J/m <sup>2</sup> ]	<i>Plasma</i> + H <sub>2</sub> O [J/m <sup>2</sup> ]	<i>OER</i> [J/m <sup>2</sup> ]	<i>Plasma</i> + <i>OER</i> [J/m <sup>2</sup> ]
<b>Remote</b>	1.44	1.37	1.31	1.51
<b>Direct</b>	1.05	1.37	1.05	1.37

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#### IV. CONCLUSIONS

Here, we examined the potential for using our OER process as a pretreatment for improved hybrid bonding. Initial experiments showed that the OER process produces OH radicals only when a highly concentrated ozone gas is used and that the amount of radical irradiation is very easy to control. When we investigated the properties of the hybrid bonding obtained after OER treatment by using 5000  $\mu$ -joint test element groups, we found that oxidation of Cu due to the OER treatment did not pose a problem in terms of increased electrical resistance. Contact angle measurements suggested that hydrophilization by OER is very effective for surfaces with many dangling bonds, but less so for surfaces with few dangling bonds, such as silicon thermal oxide films. However, when OER was performed after introducing dangling bonds by using plasma or ion beam treatments, better modification by OH groups was achieved. These findings suggest that OER treatment alone may be sufficient for hydrophilization of chemical vapor deposition films, such as SiCN films, because they are characterized by a high density of dangling bonds [5]. The strongest hybrid bonds were obtained by sequential treatment with ICP remote plasma and OER, and these bonds were stronger than those produced with plasma and water treatment, suggesting that the increased bond strength is a result of the OER process being dust- and water-free. Thus, we conclude that the OER process is a potentially useful pretreatment to facilitate improved hybrid bonding.

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