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# Novel post CMP cleaning using buffered HF solution and ozone water

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## Abstract

Post chemical mechanical polishing (CMP) cleaning is a key process for copper (Cu) CMP in dual damascene interconnection technology. During the post CMP cleaning, it is an important issue to minimize organic and Cu contamination residues on the dielectric surface. This study proposed a novel post CMP cleaning using HAL buffer hydrofluoric (BHF) solution and ozone ($O_3$) water cleaning. The performance of the proposed cleaning technology was investigated and compared to conventional citric solution cleaning, which is currently used in post Cu CMP cleaning. From roughness, contamination residues and electrical characteristics, the proposed cleaning technology showed better performance than citric solution cleaning did. This excellent cleaning performance is attributed to the surface etching and contamination elimination effect of HAL BHF solution and $O_3$ water. Based on the experimental results, the proposed cleaning technology is feasible and superior to the conventional post CMP cleaning.

*Keywords:* BTA; Buffered HF; Cu; Ozone water; Post CMP cleaning

## 1. Introduction

Ultra-large-scale integration (ULSI) requires dimension scaling of device and interconnection. Unfortunately, intrinsic properties of the materials currently used for interconnection, such as resistivity and electromigration performance, cannot fit the optimal scaling. This problem explains the growing interest in copper (Cu) as a replacement for conventional aluminum (Al) based alloys. Compared to aluminum and aluminum alloys, Cu has low resistivity (1.7 μΩ cm) and high melting point (1085 °C) meaning good electromigration resistance and reliability. Accordingly, Cu interconnection can be expected to have lower delay and higher reliability than aluminum interconnection of the same dimensions. Chemical mechanical polishing (CMP) is the most popular technology for fabricating Cu interconnections. CMP process requires the action of metal etching and passivating with an abrasive material [1]. Cu CMP has many advantages including surface planarization, reduced process steps and thermal budget, etc. [2,3]. However, it will induce metal and organic contamination residues on the dielectric material surface. A major reliability issue is dielectric degradation caused by Cu-ion drift. Because of its quick diffusion through $SiO_2$ and Si, and the formation of acceptor and donor levels within the forbidden band-gap, Cu needs a suitable cleaning after the CMP process. Besides, benzotriazole (BTA, $C_6H_5N_3$) is frequently used to

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reduce the etching rate and thus avoid isotropic etching on the Cu surface and ensure good surface planarization. However, BTA is a type of organic contamination which degrades the subsequent process integration. The greatest challenge to the post Cu CMP cleaning is the removal of residual Cu and BTA contamination from the inter-metal dielectric (IMD) and Cu surface.

Cu CMP is a complicated process and it will induce many unwanted effects such as polishing damage, slurry residue, etc. To simply investigate the influence of Cu and BTA contaminations, the intentionally contaminated method using $CuSO_4$ and BTA solutions were adopted, and the CMP process was not performed to exclude other factors. In this work, a buffer hydrofluoric (BHF) cleaning solution HAL 4006 and HAL 4025 were used to reduce Cu and BTA contaminations on the IMD surface. The step following HAL BHF cleaning was ozone ($O_3$) water immersion, which effectively removed the surfactant in the HAL BHF solution and performed further cleaning. Effects of the cleaning solution on roughness, Cu and BTA removal were studied and analyzed. Finally, the electrical characteristics of the MOS capacitor using the novel cleaning technology were also investigated and discussed.

## 2. Experiment

The novel post CMP cleaning technology includes two steps, namely, HAL BHF solution dipping and $O_3$ water immersion. This study used two kinds of HAL BHF solution: HAL 4006 and HAL 4025. The composition of HAL 4006 is 0.2% HF and 40% $NH_4F$, plus surfactant, while the HAL 4025 is 0.7% HF and 40% $NH_4F$, plus surfactant. Conventional cleaning, 0.5% citric solution cleaning, was also used for comparison. The $O_3$ water included the concentrations of 10 and 15 ppm. To simulate the exposed wafer surface after CMP process, dielectric and Cu layer were deposited on p-type Si(1 0 0) wafers with resistivity of 15–25 Ω cm. For the dielectric layer sample, the wafers were cleaned with RCA initial cleaning, and then 2000 Å TEOS oxide was deposited on the Si wafer by LPCVD. And for the Cu layer sample, a two-layer Cu/Ta structure with thickness 2000 Å/1000 Å was sputtered on the Si wafer with pre-deposited 2000 Å TEOS oxide. Two types of contaminations occurred during the CMP process including metal (Cu) and organic (BTA) contamination. To simulate the metal and the organic contaminations during the CMP process, wafers were immersed in 10 ppm

Table 1
Experimental procedures

| Experiments | Cleaning Method | Contamination | Cleaning | | LPD (Å) |
|---|---|---|---|---|---|
| | | | Step 1 | Step 2 | |
| Roughness analysis | HAL 4006 | None | HAL 4006 (5 min) | – | – |
| | HAL 4025 | | HAL 4025 (5 min) | – | – |
| | Citric | | 0.5% Citric solution (5 min) | – | – |
| Cu and BTA contamination analysis | DI Water | (1) Cu, (2) BTA | DI Water (10 min) | – | – |
| | HAL 4006 | | HAL 4006 (5 min) | 10 or 15 ppm $O_3$ water (10 min) | – |
| | HAL 4025 | | HAL 4025 (5 min) | 10 or 15 ppm $O_3$ water (10 min) | – |
| | Citric | | 0.5% Citric solution (5 min) | – | – |
| Electrical characteristics (MOS capacitor) | Control | – | – | – | 950 |
| | HAL 4006 | (1) Cu, (2) BTA | HAL 4006 (5 min) | 10 or 15 ppm $O_3$ water (10 min) | 950 |
| | HAL 4025 | | HAL 4025 (5 min) | 10 or 15 ppm $O_3$ water (10 min) | 950 |
| | Citric | | 0.5% Citric solution (5 min) | – | 950 |
| | DI Water | | DI Water (10 min) | – | 950 |

$CuSO_4$ and 0.005 M BTA solutions for 10 min, respectively. Table 1 lists the detailed experimental procedures conducting roughness, metal and organic contamination analysis and electrical characterization. Surface roughness was measured using the atomic force microscopes (AFM) and the measured area was 5 μm × 5 μm. Cu contamination was determined by total reflection X-ray fluorescence spectrometry (TRXRF), and BTA contamination was measured by thermal desorption system–atmospheric pressure ionized mass spectrum (TDS–APIMS). Moreover, MOS capacitor was used to study the effects of contamination on device characteristics and the performance improvement after novel cleaning technology. To prevent the out-diffusion and cross-contamination of Cu and BTA at high temperature furnace oxidation, the MOS capacitor with room temperature liquid-phase deposition silicon dioxide (LPD_$SiO_2$) as gate insulator [4] was used to investigate the cleaning efficiency of different cleaning solutions. Firstly, a thin layer of native oxide, which serves as the growing basis of LPD_$SiO_2$, was formed on Si wafer using 10 ppm $O_3$ water oxidation. The Cu and BTA contamination were contaminated as mentioned above before gate insulator deposition. After 950 Å LPD_$SiO_2$ depositions, the aluminum gate electrode was deposited and patterned to finish the MOS capacitor. Fig. 1 shows the fabrication process flow of MOS capacitor. The diameter of MOS capacitor was 400 μm. Through the MOS capacitor, the leakage current density, breakdown field and charge to breakdown ($Q_{bd}$) characteristics were analyzed. The leakage current density was measured at 2 MV/cm, and the $Q_{bd}$ was measured using voltage-ramp method with

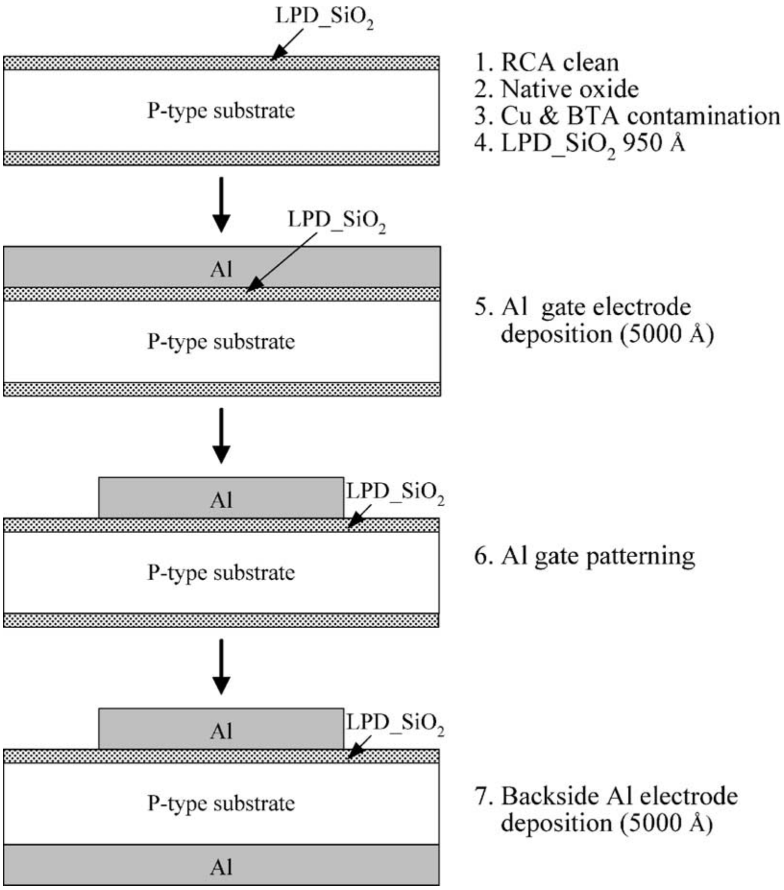

Fig. 1. Fabrication process flow of LPD MOS capacitor.

negative bias ramps from −30 to −75 V on the front side Al gate electrode. All these parameters were measured with HP4156C semiconductor parameter analyzer.

## 3. Results and discussion

### 3.1. Analysis of pre- and post-cleaning surface roughness

Oxide roughness is well known to be important in the control of leakage current and breakdown field. If the post-cleaning oxide surface is rough, then the local electrical field enhancement due to sharp curvature will degrade the leakage current and breakdown performance. Roughness performance of the HAL BHF solution and the conventional 0.5% citric solution cleaning were compared. Fig. 2 shows the TEOS oxide and Cu surface roughness after cleaning with different solutions. The roughness result of AFM measurement is the average value ($R_a$) within 5 μm × 5 μm area, and the resolution is 0.01 nm. Roughness of the pre-cleaning TEOS oxide and Cu are 0.555 and 2.971 nm, respectively. The roughness of the TEOS oxide surface after cleaning with HAL 4006, HAL 4025 and 0.5% citric solution are 0.380, 0.358 and 0.565 nm, respectively, as shown in Fig. 2(a). Furthermore, the roughness of Cu surface after cleaning with HAL 4006, HAL 4025 and 0.5% citric solution cleaning are 1.034, 0.896 and 1.407 nm, respectively, as shown in Fig. 2(b). From the experimental results, HAL 4006 and HAL 4025 solution cleaning improved the surface roughness of TEOS oxide and Cu, and also showed better performance than 0.5% citric solution cleaning. Hydrofluoric acid can slightly etch the oxide and Cu surfaces, and the surfactant in HAL 4006 and HAL 4025 solutions helps to smooth the surface during the cleaning process. Because of the lack of surfactant, 0.5% citric solution cleaning cannot achieve better roughness performance than HAL BHF solution.

### 3.2. Analysis of residual Cu and BTA contaminations pre- and post-cleaning

The greatest challenge in the post Cu CMP cleaning is the removal of residual Cu and BTA contamination from the IMD surface. To overcome this problem, three types of chemical solutions were tested, including HAL 4006, HAL 4025 and 0.5% citric solution. Besides, $O_3$ water was used to eliminate surfactant residue and enhance the cleaning efficiency. The cleaning performance of all methods was compared to that of simple deionized (DI) water cleaning. Fig. 3 compares the residual Cu contamination on the TEOS oxide surface after cleaning with these solutions. After dipping with HAL 4006 and HAL 4025 solutions and following the immersion of 10 ppm $O_3$ water, Cu contamination are $1.543 \times 10^{10}$ and $2.246 \times 10^{10}$ atoms/cm$^2$, respectively. In the case of 0.5% citric solution cleaning, the residue of Cu contamination is $3.437 \times 10^{10}$ atoms/cm$^2$. Moreover, the pre-cleaning level of contamination is at the order of $4.93 \times 10^{12}$ atoms/cm$^2$. HAL 4006 and HAL 4025 solution clearly showed the better cleaning ability than 0.5% citric solution for removing of Cu impurity on oxide surface. The removal of Cu contamination can be attributed to the oxide surface etching by HAL BHF solution. Another possible reason may be the metal oxidation by $O_3$ water, which makes the contamination soluble in water.

Fig. 4 illustrates the analysis of residual BTA contamination on the oxide surface after cleaning with different solutions. After cleaning with HAL BHF solution and 15 ppm $O_3$ water, BTA contamination on the TEOS oxide surface was significantly reduced in comparison with DI water cleaning only and 0.5% citric solution cleaning. Compared to the Cu contamination cleaning, HAL 4006 and HAL 4025 solutions are more effective than 0.5% citric solution to remove BTA residue on the oxide surface. Thus, the above experimental results suggest that both Cu and BTA can be removed effectively by the proposed cleaning technique.

### 3.3. Electrical characterization of MOS capacitor pre- and post-cleaning

Although the cleaning solutions can influence surface roughness conditions, the roughness of LPD_SiO$_2$ is believed not to influence electrical characteristics. Because the LPD_SiO$_2$ is deposited on the thin native oxide after cleaning, the surface roughness is less obvious. This section will mainly focus on the cleaning efficiency of Cu and BTA contaminations.

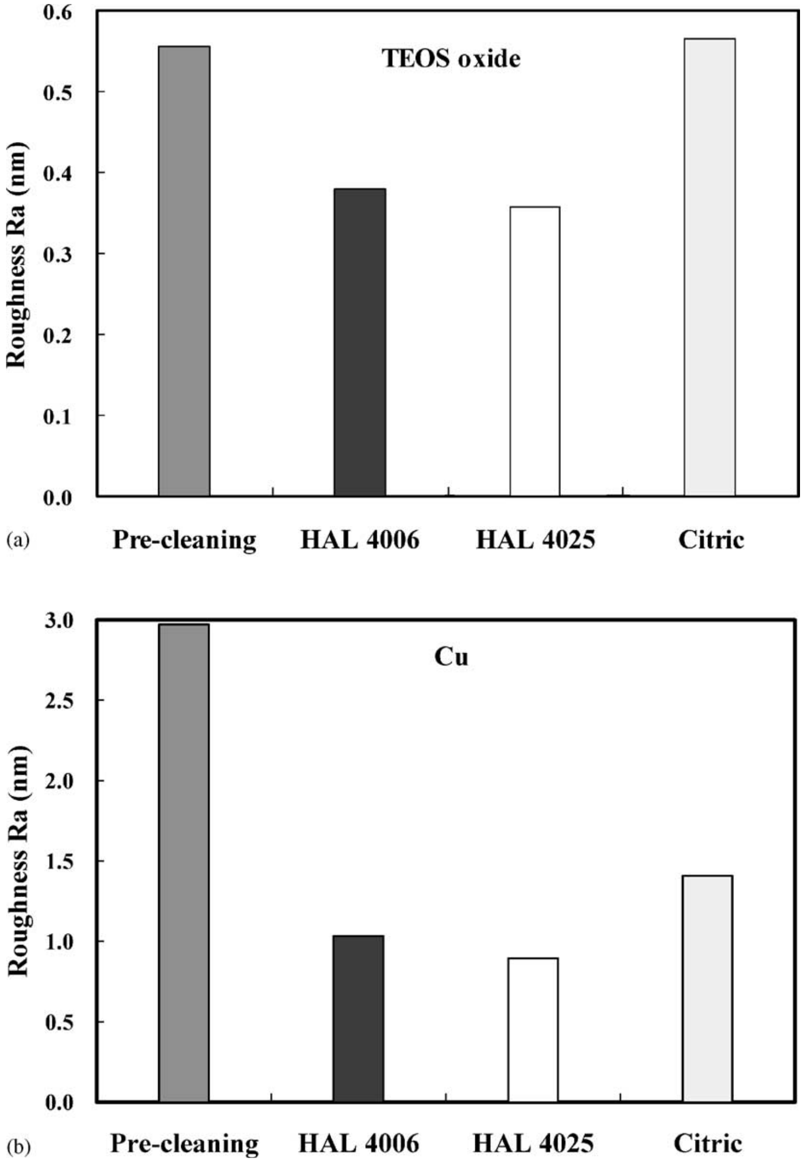

Fig. 2. AFM roughness analysis of: (a) TEOS oxide; and (b) Cu surface after different cleaning.

Fig. 5 displays the electrical characteristics of the LPD MOS capacitor after contamination with Cu and subsequent cleaning. Fig. 5(a) illustrates that the samples with HAL 4006 and HAL 4025 solution cleaning have leakage current density as low as $10^{-8}$ A/cm$^2$. On the contrary, the 0.5% citric solution cleaning shows wide leakage current distribution compared to HAL BHF solution cleaning, and consequently has poor electrical performance. Fig. 5(b) is the breakdown field distribution. The samples with HAL 4006 and HAL 4025 solution cleaning showed higher breakdown field than those with 0.5% citric solution cleaning. Also, the breakdown field of samples with DI water cleaning significantly dropped to around 4 MV/cm. With the aid of HAL BHF solution, the breakdown field can be raised to around 6–7 MV/cm. The experimental results revealed that cleaning with HAL BHF solution was superior to that with 0.5% citric solution. Oxide

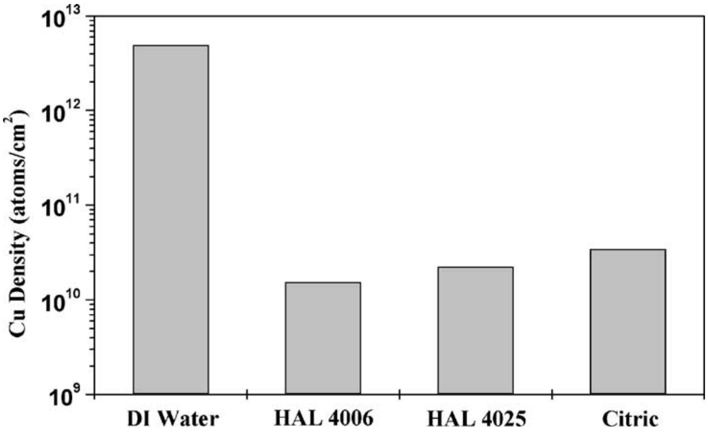

Fig. 3. TRXRF analysis of Cu contamination on TEOS oxide surface after different cleaning.

breakdown characteristic is a critical indicator of thin gate oxide integrity [5]. The charge to breakdown ($Q_{bd}$) characteristic has been considered an effective test to reveal thin oxide reliability problems during process development and manufacturing. Fig. 5(c) illustrates the weibull plot of $Q_{bd}$ for all cases. Notably, the $Q_{bd}$ value for samples with HAL 4006 and HAL 4025 solution cleaning were higher than those with 0.5% citric solution cleaning. Fig. 6 displays the electrical characteristics of LPD MOS capacitor after

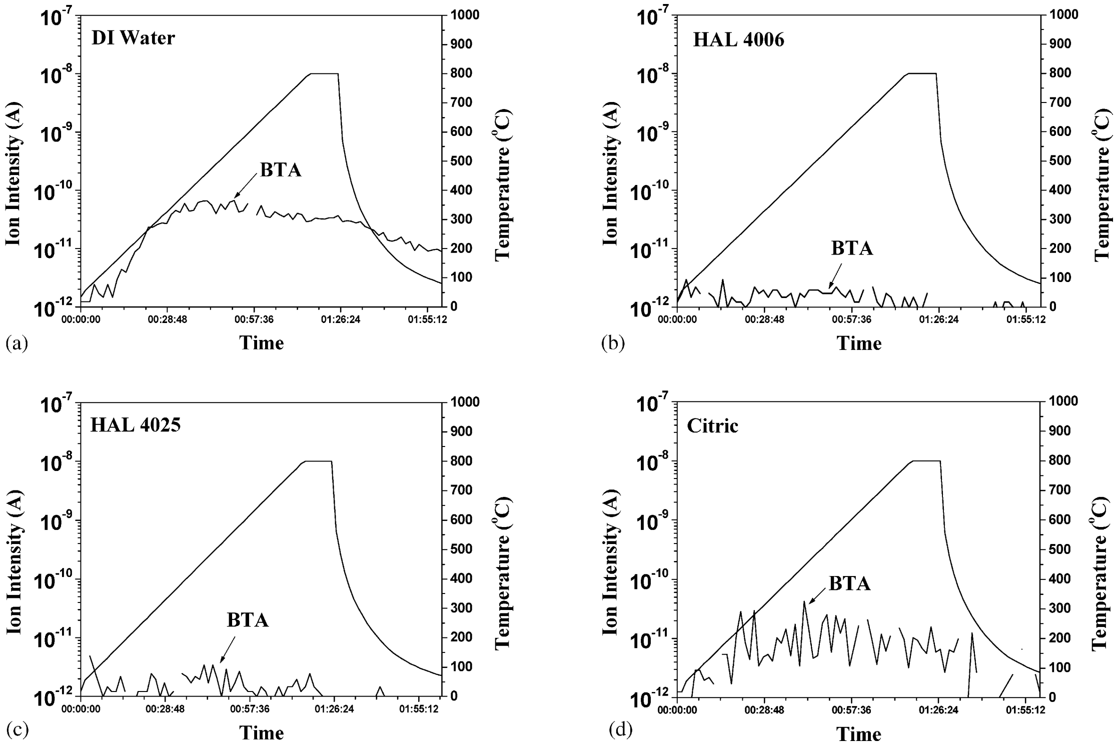

Fig. 4. TDS–APIMS analysis of BTA contamination on TEOS oxide surface after different cleaning: (a) DI water; (b) HAL 4006; (c) HAL 4025; and (d) citric solution.

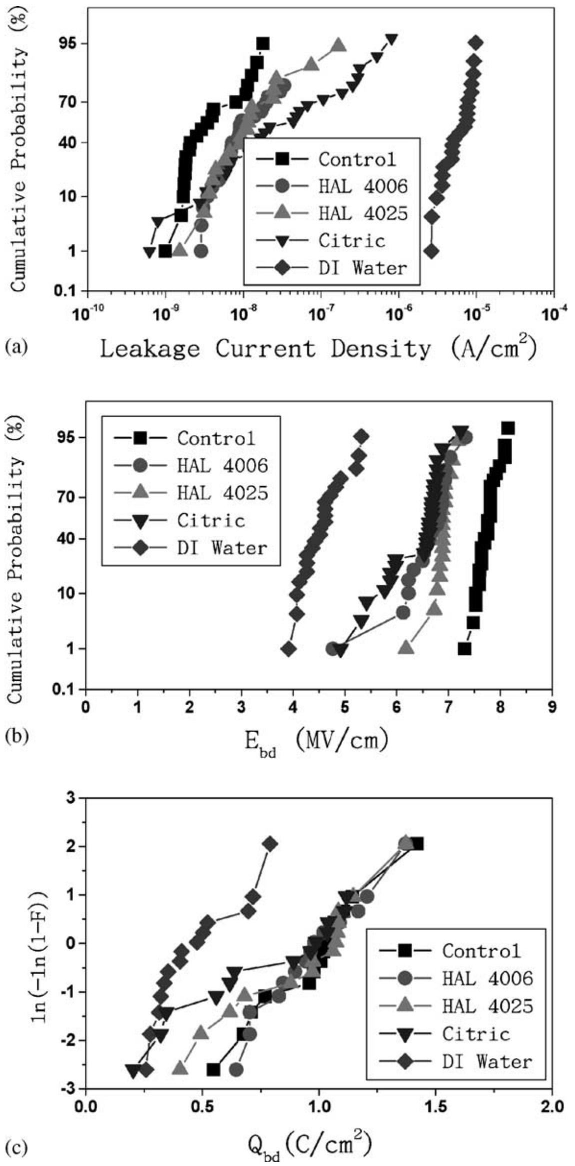

Fig. 5. Electrical characteristics of LPD MOS capacitor after contaminating with Cu and subsequent cleaning: (a) leakage current density distribution; (b) breakdown field distribution; and (c) $Q_{bd}$ weibull plot.

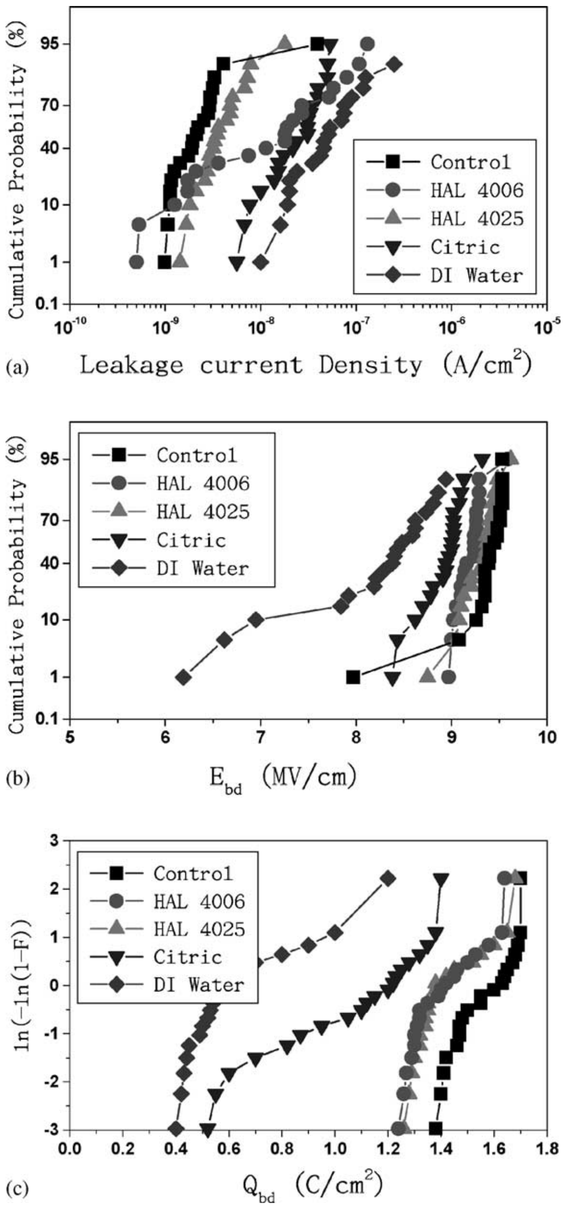

Fig. 6. Electrical characteristics of LPD MOS capacitor after contaminating with BTA and subsequent cleaning: (a) leakage current density distribution; (b) breakdown field distribution; and (c) $Q_{bd}$ weibull plot.

contaminating with BTA and subsequent cleaning. Fig. 6 shows similar results to Fig. 5. Again, the samples with HAL 4006 and HAL 4025 solution cleaning exhibited better performance than 0.5% citric solution cleaning. Owing to the cleaning efficiency of HAL BHF solution and the $O_3$ water, the ultra-thin contaminated oxide film on the surface is etched and cleaned away. Consequently, the Cu and BTA contaminations are removed from the wafer surface. The reliability and integrity of the gate oxide thus increase with reducing contamination on the wafer surface.

## 4. Conclusion

A novel cleaning technology consisting of HAL BHF solution and subsequent $O_3$ water cleaning was proposed here. From AFM investigation, the HAL BHF solution showed better smoothness than conventional 0.5% citric solution cleaning on the Cu and IMD surfaces. Regarding the reduction of the Cu and BTA contamination on the IMD surface, the HAL BHF solution was found to have the lowest contamination residue on the oxide surface. Finally, electrical characterization of LPD MOS capacitor was performed pre- and post-cleaning. The LPD MOS capacitor using HAL BHF solution plus $O_3$ water cleaning after 10 ppm $CuSO_4$ and 0.005 M BTA contamination were found to show the best electrical characteristics. This phenomenon indicates that defects, traps and organic impurities all of which are related to reliability problems, are reduced after cleaning with HAL BHF solution. The high cleaning performance can be attributed to: (1) surface smoothing by surfactant in HAL BHF solution; (2) etching effects of BHF; and (3) cleaning efficiency of $O_3$ water. From the experimental results, it is concluded that HAL BHF and $O_3$ water can effectively remove Cu and BTA contamination during post CMP cleaning.

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