



Effect of moisture on electrical properties and reliability of low dielectric constant materials



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ABSTRACT

The effect of absorbed moisture on the electrical characteristics and reliability of low dielectric constant materials (low-*k*) was investigated in this study. The experimental results reveal that porous low-*k* dielectrics absorb more moisture than dense low-*k* dielectrics. This absorbed moisture degrades the electrical performance and reliability of both classes of low-*k* dielectrics. Annealing at a higher temperature of 400 °C is required to decompose the physically-adsorbed moisture and thereby restore reliability performance. However, the chemically-adsorbed moisture seems to be difficult to remove by annealing at 400 °C, causing a degraded TDDB performance.

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1. Introduction

Low-*k* materials with dielectric constant (*k*) less than 4 as an interlayer dielectric with copper (Cu) interconnects displays significant advantages for interconnect resistance–capacitance (RC) delay improvement, crosstalk-noise minimization, and power consumption reduction for the continuous scaling of advanced integrated circuits [1–4]. Cu interconnects were adopted to replace conventional aluminum (Al) lines to reduce the resistance by about 30% [5]. The low *k* materials which incorporate low polarizability Si–F or Si–C bonds replaces Si–O bonds can reduce the dielectric constant to as low as 2.8, which is benefit for the capacitance between Cu interconnects reduction [6,7].

To further reach the desired reduction in RC delay for 32 technology node and beyond, low-*k* materials with *k* value of 2.5 or lower is required according to “International Technology Roadmap for Semiconductors” [8]. To obtain the low-*k* materials with a lower *k* value, the common strategy is introducing the porogen into the film and then the porogen is removed by thermal treatment or ultraviolet (UV) light radiation to produce the empty pore. The *k* value of the produced porous low-*k* materials can be further reduce to below 2.8, depending on the porosity of the film because the relative permittivity of empty pore is about 1.0 [9–11].

However, the integration of the porous low-*k* materials into Cu interconnects is extremely challenging because various technological process steps such as polymer removal, electrochemical plating, and chemical mechanical polish [12–14]. In these processes, low-*k* materials have to deal with the moisture and may induce water uptake. Moreover, the adsorbing amount becomes significant for the porous low-*k* materials due to the existence of open pores at the surface. Therefore, it is of importance to study the influence of moisture on the properties of low-*k* dielectrics.

This study investigated the impact of moisture on the physical and electrical properties as well as the reliability of low-*k* dielectrics. Different low-*k* dielectrics with and without porogen were tested in order to find out the moisture adsorption mechanism. The relationship between the moisture content of low-*k* material and the dielectric reliability was also studied.

2. Experiments

The as-deposited porous low-*k* material is a SiCOH film, deposited on a *p*-type (100) silicon substrates by plasma-enhanced chemical vapor deposition. The porous low-*k* dielectrics were deposited from diethoxymethylsilane and alpha-terpiene as a matrix and porogen precursor, respectively. A small amount of oxygen was also introduced as an oxidant. The deposition temperature, pressure, and power were 300 °C, 7.5 torr, and 600 W, respectively. After deposition, UV curing with 200–450 nm wavelength was

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performed to remove the organic porogen. The dense low-*k* dielectrics were also deposited in the same system without introducing porogen precursor. The resulting thickness is about 300 nm. The dielectric constants are ~2.54 and 3.02 for the porous and dense low-*k* materials.

For the moisture reliability test, the porous and dense low-*k* materials (blanket wafer) were immersed in humidity system of 85% humidity at 25 °C and 85 °C for 8–168 h. The chemical structure of low-*k* materials before and after moisture test was investigated by Fourier transform infrared spectroscopy (FT-IR) (Bio-Rad Win-IR PRO). Al metallization with 120 nm thick were thermally evaporated on the low-*k* dielectric films through the showdown mask to produce Metal–insulator–silicon (MIS) structure (Al/low-*k*/p-Si), as shown in Fig. 1, to measure electrical properties. The dielectric constant (*k*) was measured at 100 Hz. The current–voltage (*I*–*V*) and dielectric breakdown measurements were performed at room temperature (25 °C). Electromigration (EM) test structure of 250 μm length and 0.1 μm width was fabricated using Cu double-layered dual damascene interconnect. More details on test structure fabrication and EM characterization can be found elsewhere [15].

3. Results and discussion

Fig. 2(a) presents the FT-IR absorption spectra of porous low-*k* dielectrics before and after moisture treatment. As shown, absorption bands resulting from Si–OH bonds at 3200–3400 cm⁻¹ are observed after moisture treatment, and the intensity of the Si–OH bonds increased with moisture immersion time, as shown in the inset in Fig. 2(a). To further compare the uptake of moisture by dense and porous low-*k* dielectrics, Fig. 2(b) plots the dependence of the intensity of the signals from the Si–OH bonds on the moisture immersion time for both classes of low-*k* dielectrics. The vertical axis represents the peak intensities of Si–OH bonds normalized to those of Si–O–Si bonds in the FT-IR spectrum. The peak intensities of Si–OH and Si–O–Si bonds were calculated from the peak area. As indicated, the peak intensity of Si–OH bonds increases with the duration of exposure to moisture and reaches saturation after 24 h of exposure. Moreover, porous low-*k* dielectrics show a higher moisture-uptake behavior than dense low-*k* dielectrics, indicating that the pores in the porous low-*k* films contribute to the uptake of moisture. For both classes of low-*k* dielectrics, more moisture is taken up at 85 °C than at 25 °C. Therefore, moisture treatment at 85% humidity and 85 °C was performed in this study.

Water contact angle (WCA) measurements were performed to evaluate the hydrophilization of low-*k* films after the moisture

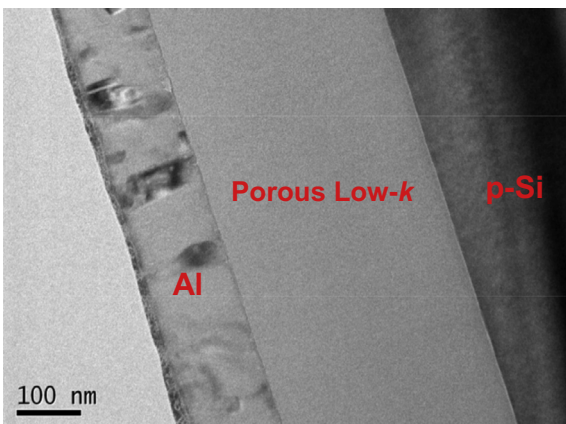


Fig. 1. Image of Al/porous low-*k*/p-Si stacked structure.

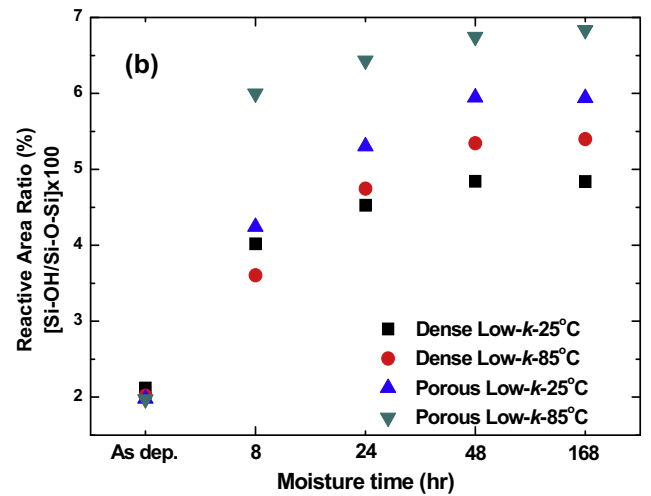
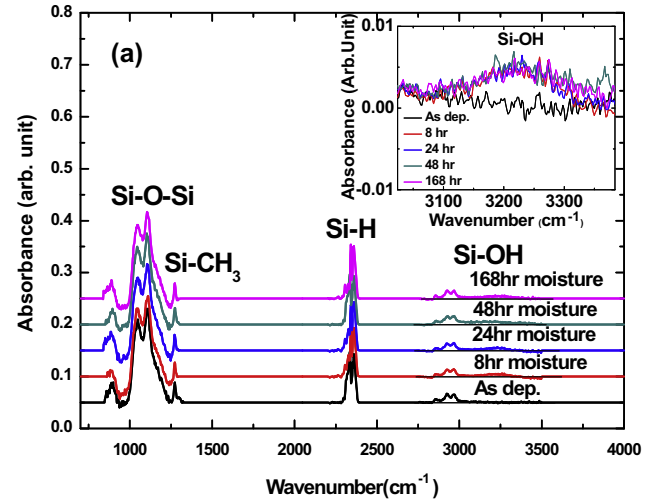


Fig. 2. (a) FT-IR spectra of low-*k* films after various moisture immersion times. (b) Relative Si–OH bonding absorbance intensity.

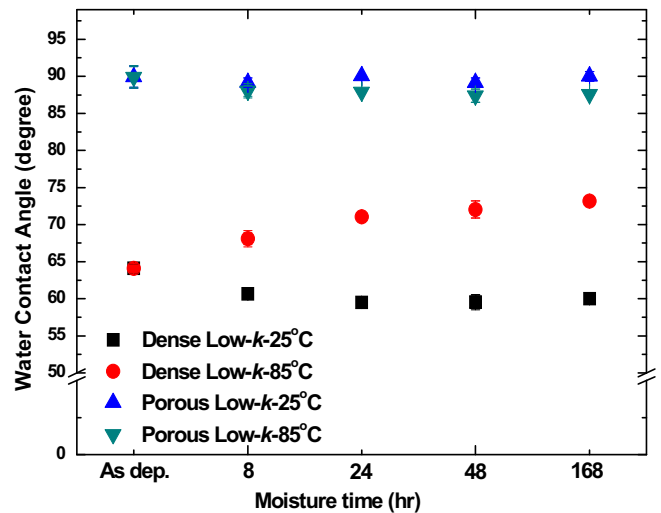


Fig. 3. Water contact angle of low-*k* films after various moisture immersion times.

test. The result is shown in Fig. 3. For as-deposited low-*k* dielectrics, porous low-*k* films had a larger WCA (~90°) than dense low-*k* dielectrics, indicating that porous low-*k* films were

hydrophobic. Moreover, the WCA value decreased as the moisture immersion time increased, suggesting that the porous low- k dielectric tended to take up water. Additionally, the variation in the WCA value is larger at a moisture treatment temperature of 85 °C. This result is consistent with the FT-IR results. However, dense low- k dielectrics exhibited a different variation of WCA value with the moisture exposure time at two moisture exposure temperatures. In the moisture test at 85 °C, the WCA value slightly increased with the moisture immersion time. The root cause of this unique behavior is unclear and further study is required.

Fig. 4(a) and (b) plot the hardness (H) and elastic modulus (E), respectively, as functions of the moisture exposure time for both low- k dielectrics. To avoid the substrate effect on the low- k dielectrics, nanoindentation measurements were made on films with thicknesses greater than 600 nm. As shown, the hardness and elastic modulus of the porous low- k films slightly increased with the moisture immersion time. This trend is similar to that reported by Broussous et al. [16]. However, the mechanical strength of dense low- k films remained constant even after 168 h of immersion in moisture. This result reveals that moisture-uptake in the porous low- k film can improve its mechanical strength, suggesting that the moisture seems to be absorbed on the surfaces of the walls of the pore within the low- k film [12].

Fig. 5(a) shows the dielectric constant (k value) variation of low- k dielectrics as a function of moisture immersion time. The

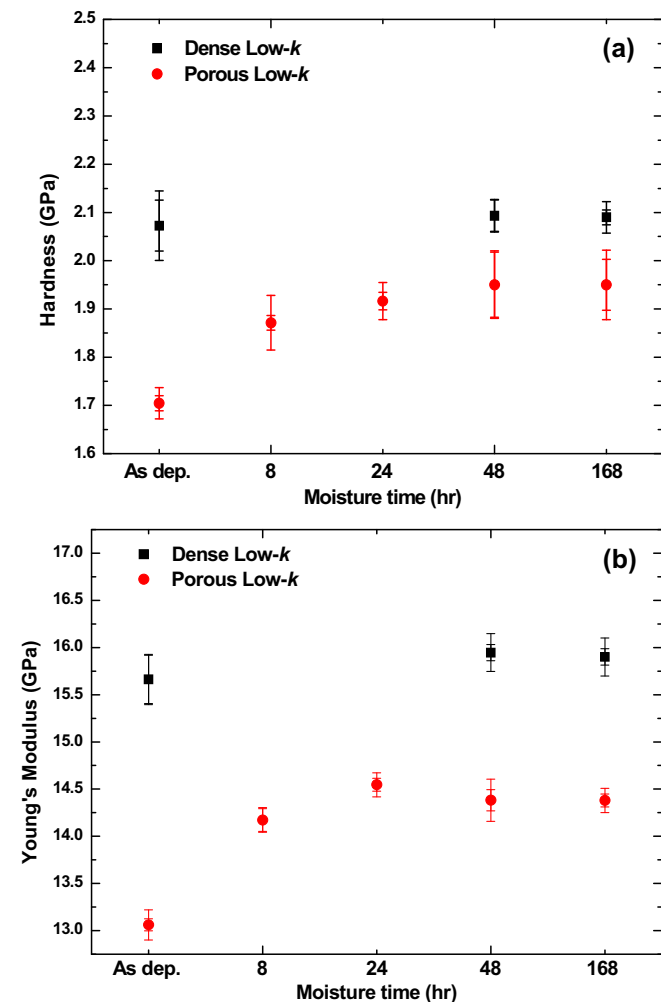


Fig. 4. (a) Hardness values (b) Elastic modulus of low- k films as functions of the moisture immersion time.

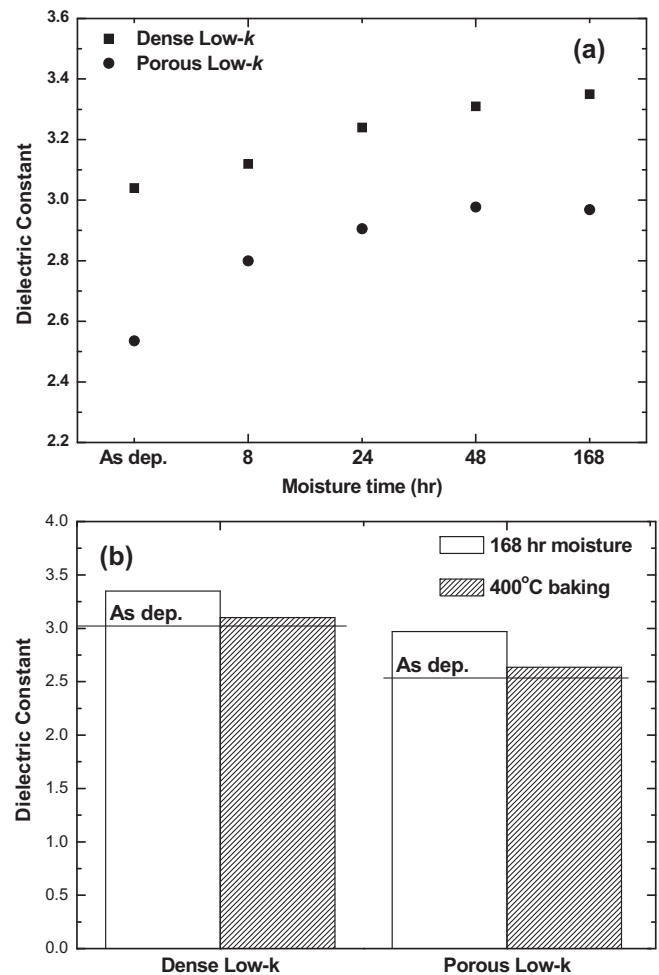


Fig. 5. (a) Dielectric constants of low- k films as functions of the moisture immersion time. (b) Change of dielectric constants after 400 °C annealing.

dielectric constant of the low- k films was estimated from the accumulation capacitance of the MIS structure. The thickness of the low- k dielectric in the MIS structure was approximately 300 nm. As shown, for both porous and dense low- k films, the dielectric constant increased with the moisture immersion time and saturated when the immersion time reached 24 h. This increase in k value can be attributed to the incorporation of water, which has a large dielectric constant of 70–80. Additionally, the larger increase in k value for the porous low- k films was observed, which is strongly related to higher Si–OH bonds. To understand the desorption behavior of the absorbed moisture, the moisture-uptake sample (168 h) was annealed in an N_2 atmosphere at 400 °C, and then the k value was measured again. Fig. 5(b) presented the measured k values. The k value can be reduced by thermal annealing, but it cannot be recovered to the original k value of the pristine low- k dielectrics. Rather the k value that is obtained by recovery is slightly higher. This result reveals that some absorbed moisture, which is physically-absorbed in generally [17], can be removed by annealing at 400 °C whereas the chemically-absorption moisture or absorbed water with a higher bonding energy is unlikely to be removed by a 400 °C annealing.

Fig. 6 plots the leakage current of low- k dielectrics at 2 MV/cm as a function of the moisture immersion time. These measurements were also performed on the MIS structures. As shown, the leakage current of the dense low- k dielectrics remained unchanged when they were immersed in moisture. The porous low- k dielectrics exhibited a slight increase in the leakage current, but even

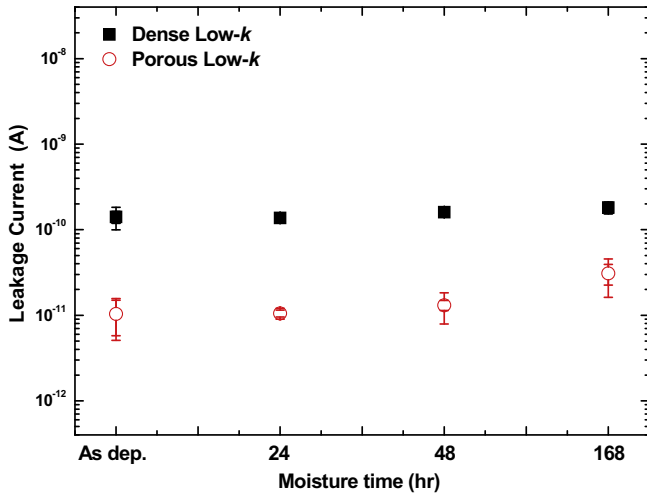


Fig. 6. Leakage current density of low-k films at 2 MV/cm as functions of the moisture immersion time.

after 168 h of immersion in moisture, this increment is still small. Additionally, the breakdown voltage is independent of the moisture treatment time. Some works have reported that the moisture in a low-k film increases the leakage current, but the test structures were line-to-line serpentine structures, in which the interface was the main leakage path [18]. Therefore, the moisture in the interface acted as the leakage path, increasing the leakage current. In our study, the leakage current was detected in the MIS structures. Hence, the bulk low-k film, rather than the interface, determines the leakage current performance. The small ratio of the moisture content within the low-k film relative to the bulk low-k film makes the effect of the moisture negligible, so the leakage current performance is comparable for the pristine and moisture-uptake low-k dielectrics.

To study the effect of the moisture on the long term reliability of the low-k dielectrics, time-dependent-dielectric breakdown (TDDB) performance was determined by measuring the dielectric breakdown times. Fig. 7 plots the cumulative probability distribution of TDDB lifetimes for the porous low-k films with various moisture immersion times. As shown, the lifetime is reduced by

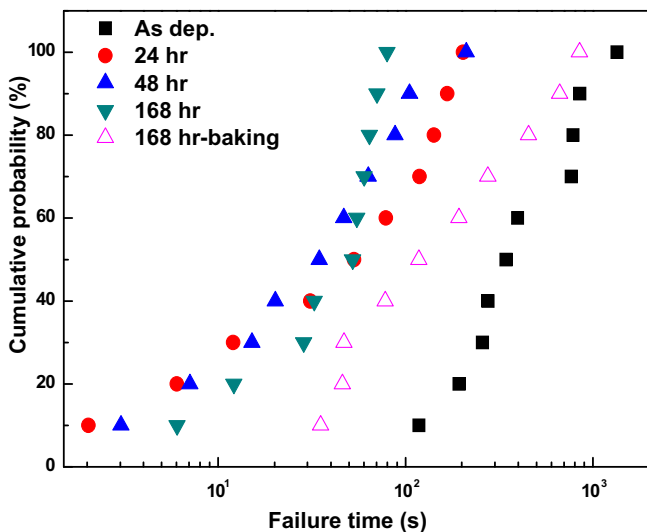


Fig. 7. Cumulative probability of time-to-dielectric-breakdown of porous low-k films as functions of the moisture immersion time.

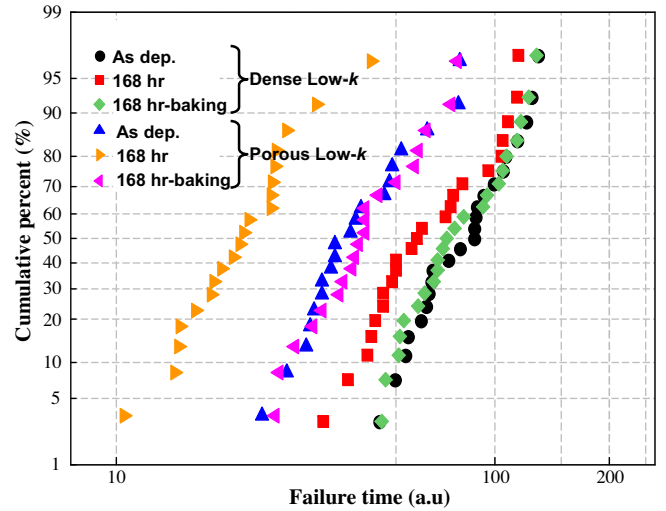


Fig. 8. Cumulative probability of EM failure time of low-k films with moisture immersion and annealing.

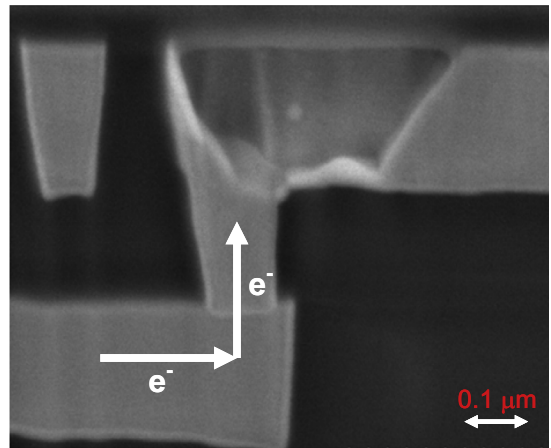


Fig. 9. SEM image of moisture-uptake sample after EM failure.

a factor of approximately ten for the moisture-uptake sample and slightly decreases as the moisture immersion time increases. As also presented in Fig. 6, the sample that was immersed in moisture for 168 h and then thermally annealing at 400 C for 1 h had a longer lifetime than that without thermal annealing. However, its TDDB performance was only partially restored, being poorer than that of the fresh sample. This result also demonstrates that annealing in N₂ gas can desorb partially absorbed moisture, and that some of the chemically-absorbed moisture cannot be removed, negatively influencing the TDDB performance.

Fig. 8 presents the cumulative failure distribution of EM lifetimes for typical Cu interconnect lines. The moisture treatment was performed before the Cu interconnect was deposited. The cumulative failure distribution was plotted by measurements of the failure times of 30 samples using lognormal distribution [19]. Immersion in moisture reduced EM lifetimes of both low-k materials. For the porous low-k films, this degradation is significant. The failure mode is on the Cu interface which is identified by scanning electron microscopy, as displayed in Fig. 9. Moreover, EDX line scan indicates that the Cu sample with moisture immersion of 168 h shows higher oxygen concentration at the Cu interface than the sample without moisture immersion by about 2.2 times. Therefore, we can postulate that the reduction in EM lifetime is caused by the oxidized Cu surface. The Cu interface was oxidized by the moisture

that diffused from the neighboring low- k dielectrics when the electrical field was applied to the dielectrics (EM stress). Consistent with low- k dielectric TDDB results, thermal annealing can restore EM performance. However, differing from the TDDB behavior, this EM performance recovery is complete, which EM lifetime is comparable with that of the pristine film. The chemically-absorbed moisture is believed not able to be removed by annealing at 400 °C and to remain within the low- k films. It is thus trapped in the low- k films and cannot move during EM testing. Therefore, the measured EM failure time is not affected by this chemically-absorbed moisture.

4. Conclusions

The influence of absorbed moisture on the properties of dense and porous low- k dielectrics was studied in this work. We found that moisture has a negative impact on low- k film's properties, including electrical characteristics and reliability performance. Moreover, these degradations are becoming more serious for porous low- k dielectrics. Annealing at a high temperature of 400 °C is required to decompose the physically-adsorbed moisture, which is benefit to restore reliability performance. On the other hand, the chemically-adsorbed moisture seems to be difficult to remove by annealing at 400 °C, degrading TDDB performance. Consequently, propose a new method to remove the chemically-adsorbed moisture in the low- k dielectrics is essential for promising better Cu/low- k integrity.

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