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Effect of moisture on Electrical and Reliability Properties for Dense and Porous Low-*k* Dielectrics

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Introduction- As feature sizes of integrated circuits (ICs) continuously shrink to sub-micro, interconnect resistance-capacitance (RC) delay begins to dominate overall device speed in copper/low-*k* metallization. To decrease RC delay time, interconnection resistance has been reduced by using copper (Cu) instead of aluminum, while interlayer capacitance has been lowered by replacing conventional silicon dioxide SiO_2 (k~4.0) with low-*k* materials (k < 4.0) [1-3]. During interconnect integration, wet processes, such as polymer removal, electrochemical plating (ECP), and chemical mechanical polish (CMP), are indispensible steps. In such conditions, low-*k* materials have to deal with the moisture. Therefore, it is of importance to study the influence of moisture on the low-*k* dielectrics [4-6]. This work investigates the impact of the moisture on the physical, electrical properties, and reliability of the low-*k* films. Different low-*k* materials with and without porogen were tested in order to find out the moisture adsorption mechanism within the low-*k* dielectric. The content of moisture on the low-*k* material related to the dielectric reliability was also examined.

Experimental- 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 (PECVD). The porous low-*k* films were deposited from diethoxymethylsilane (DEMS) and alpha- terpiene (ATRP) as a matrix and porogen precursor, respectively. A small amount of oxygen was also introduced as an oxidant. After deposition, UV curing was performed to remove the organic porogen to form the porous low-*k* materials. The dense low-*k* materials were also deposited in the same system without introducing porogen precursor. The basic properties of both low-*k* films are listed in Table I.

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). The dielectric constant (k) was measured at 100 Hz from Metal-insulator-silicon (MIS) structure (Aluminum/low-*k*/*p*-Si).The current-voltage (*I-V*) and dielectric breakdown measurements were performed at room temperature (25°C) on MIS structures. Electromigration test structure of 250 μm length and 0.1 μm width was fabricated using Cu double-layered dual damascene interconnect.

Results and discussions- Figure 1 (a) presents the FT-IR absorption spectra for the porous low-*k* films before and after moisture treatment. As shown, absorption bands resulting from H-O-H bonds at 3200~3400 cm^{-1} are observed after moisture treatment, and the intensity of H-O-H bonds seems to increase with increasing the immersion time as shown in the inset of Fig.1 (a). To further understand the moisture uptake in the dense and porous low-*k* films, the dependence of the intensity of H-O-H bonds on the moisture immersion time for both low-*k* films is shown in the Fig. 1 (b). The vertical axis shows the normalized peak intensities of H-O-H bonds calculated from the peak area relative to Si-O-Si bonds in the FT-IR spectrum. As shown, the peak intensities of H-O-H bonds increases with increasing the moisture exposure time and reach saturation after 24 hr exposure. Moreover, the porous low-*k* films show a higher moisture-uptake behavior in comparison to the dense low-*k* films. This indicates that the pore in the porous low-*k* films contribute to the moisture-uptake. For both low-*k* films, a higher moisture-uptake is observed at 85°C conditions. Therefore, we use 85% humidity and 85°C temperature as the moisture treatment condition in the following study.

Water contact angle (WCA) measurements were performed to check the low-*k* films' hydrophilization after the moisture test. For as-deposited low-*k* films, a larger WCA (~90°) was observed in the porous low-*k* films, indicating that this porous low-*k* film seems to be hydrophobic. Moreover, the WCA value deceases with moisture immersion time, suggesting that the porous low-*k* film tends to be water-uptake. As shown, the variation in WCA is larger for moisture treatment at 85°C, which is consistent with the FT-IR result. However, in the case of the dense low-*k* films, different WCA trends with the moisture exposure time were observed in two moisture exposure temperatures. At 85°C moisture test condition, the WCA value is slightly increased with increasing the moisture immersion time, which is a unique behavior. The root cause is not clear and is needed to further investigate.

Figure 3 (a) and (b) show the elastic modulus (E) and hardness (H), respectively, as functions of the moisture exposure time for both low-*k* films. To avoid the substrate effect on the low-*k* films, the films with thicknesses greater than 600 nm was used for the nanoindentation measurements. A shown, the elastic modulus and hardness slightly increases with increasing the moisture immersion time for the porous low-*k* films. This trend is similar to the result reported by L. Broussous et al [8]. However, in the dense low- *k* films, the mechanical strength remained unchanged even 168 hr moisture immersion time. This result indicates that moisture-uptake in the porous low-*k* film improve its mechanical strength in the low-*k* film. Furthermore, the moisture seems to absorb on the pore wall surface [4].

Figure 4 shows the variation of the dielectric constant (k value) of the low-*k* films as a function of the moisture immersion time. The dielectric constant of the low-*k* films was estimated from accumulation capacitance of the MIS structure. As shown, the dielectric constant increases with increasing the moisture immersion time for both low-*k* films, and saturated as the immersion time reaches 24 hr. This increasing k value can be attributed to the incorporation of water, which has a large dielectric constant of 70~80. Moreover, a larger increase in the k value for the porous low-*k* films, which correlates well with a higher O-H bonding in the low-*k* films. To understand the desorption behavior of the absorbed moisture, the moisture-uptake sample (168 hr) was annealed in N_2 atmosphere at 400°C, and then measure the k value again. The measured k values are displayed in the inset of Fig.4. The k value can be reduced by a thermal annealing; however, the k value can not recover to the original value as the fresh low-*k* film, which is slightly higher. This result implies that some absorbed water, which is physically absorbed in generally [8], can be removed by annealing at 400°C. While, the chemically absorption water or with a higher bonding energy is rarely removed by a 400°C annealing.

Figure 5 shows the leakage current at 2 MV/cm of low-*k* films as a function of the moisture immersion time. These measurements were also performed on the MIS structures. As shown, a slightly increase in the leakage current was found only in the porous low-*k* films, but this increment is minor after 168 h moisture immersion. Additionally, the breakdown voltage is also unchanged in split of the moisture treatment time. Some works reported that the moisture in the low-*k* film increases the leakage current, however, the used test structures were line-to-line serpentine structures, which the interface are the main leakage path [9]. Therefore, the moisture in the interface acts as the leakage path, leading to an increased leakage current. In this study, MIS structures were used to detect the leakage current. Therefore, the bulk low-*k* film, instead of the interface, determines the leakage performance. Owing to a small ratio of the moisture within the low-*k* film relative to the bulk low-*k* film, the effect of the moisture is negligible, leading to a comparable performance in the leakage current.

To investigate the effect of the moisture on the low-*k* dielectric's long term reliability, time-dependent-dielectric breakdown (TDDB) was performance to measure the dielecitic breakdown times. Figure 6 shows the cumulative probability of TDDB results for the porous low-*k* films with various moisture immersion times. As shown, the lifetime degrades about ten times and slightly decreases with increasing the moisture immersion time. As also shown in Fig. 6, for 168 hr moisture-immersion sample with performing a thermal annealing at 400 C for 1h, the lifetime is increased as compared to that without a thermal annealing. However, the TDDB performance only partly be restored, which is still worse than that of the fresh sample. This also demonstrates that a annealing in N_2 gas can desorb partial absorbed moisture, and some chemically absorbed moisture can not be removed, which negatively influences the TDDB performance.

Figure 7 presents the cumulative failure distribution of electromigration (EM) lifetime for typical Cu interconnect lines. The moisture treatment was performed before Cu interconnect deposition. The cumulative failure distribution is plotted by measurement of 30 sample's failure time using lognormal distribution [10]. For both low-*k* materials, the lifetime was degraded for samples with moisture immersion. The degradation is significant for the porous low-*k* films. This deceased EM lifetime is presumably caused by the oxidized Cu surface, which failure mode is on the Cu interface demonstrated by scanning electron microscopy (SEM) analysis (not shown). This degradation Cu interface was oxidized by the diffused moisture from the neighboring low-*k* dielectrics as apply the electrical field to the dielectrics (EM stress). Similar to TDDB results, the thermal annealing can restore the EM performance. However, this recover can return to the same level as the pristine film, which is different from the TDDB behavior. It is believed that the chemically absorbed moisture can not be removed by a 400°C annealing and remains within the low-*k* films. However, this absorbed moisture is trapped in the low-*k* films and can not move during EM testing. Therefore, the measured EM failure time is not impacted by this absorbed moisture.

Conclusions- The influence of moisture on the properties of the dense and porous low-*k* films is investigated in this study. 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 on the porous low-*k* dielectrics. A higher temperature anneals at 400°C is needed to decompose physically-adsorbed water, which is benefit to restore reliability performance. On the other hand, the chemically-adsorbed moisture seems to be difficult to be removed by a 400°C annealing, causing a degraded 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.

References

[1] A. Grill, *Annu. Rev. Mater. Res.* **39** (2009) 49.
[2] K. Maex, M. R. Baklanov, D. Shamiryan, F. Lacopi, S. H. Brongersma, Z. S. Yanovitskaya, *J. Appl. Phys.* **93** (2003) 8793.
[3] T. Furusawa, D. Ryuzaki, R. Yoneyama, Y. Homma, and K. Hinode, *J. Electrochem. Soc.* **148** (2001) F175.
[4] Y. Uchida, S. Hishiya, N. Fujii, K. Kohmura, T. Nakayama, H. Tanaka, T. Kikkawa, *Microelec. Eng.* **83**, 112 (2006).
[5] H. Aoki, d. Watanabe, R. Moriyama, M. K. Mazumder, N. Komatsu, C. Kimura, and T. Sugino, *Dimond & Related materials*, **17**, 628 (2008).
[6] A. A. Kumbhar, S. K. Singh, and R. O. Dusane, *Thin Solid Films*, **501**, 329 (2006).
[7] L. Broussous, G. Berthout, D. Rebiscoul, V. Rouessac, and A. Ayral, *Microelec. Eng.* **87**, 466 (2010).
[8] E.G. Linigera, T.M. Shawa, S.A. Cohena, P.K. Leungb, S.M. Gatesa, G. Bonillaa, D.F. Canaperib, and S. Papa Rao *Microelec. Eng*. **92**, 130 (2012).
[9] A. V. Varaigar, S. G.. Mhaisalkar, and A. Krishnamoorthy, *Microelec. Reliab*. **44**, 745 (2004).
[10] S. Yokogawa and H. Tsuchiya, *Jpn. J. Appl. Phys.* **44**, 1717 (2005).

Table I: Film properties of the dense and porous low-*k* materials

Sample	Precursor	UV curing	Dielectric constant (k)	Breakdown electric filed (MV/cm) at 25°C	Porosity (%)	Pore size (nm)
Dense low-*k*	DEMS+O_2	No	3.02	9.8	N/D	N/D
Porous low-*k*	DEMS+O_2+ATRP	Yes	2.56	6.9	15	1.35

N/D= not detected

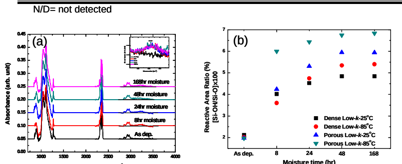

Figure 1: (a) FT-IR spectra of low-*k* films after various moisture immersion times. (b) Relative OH-bonding absorbance intensity.

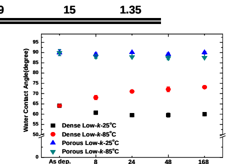

Figure 2: Water contact angle of low-*k* films after various moisture immersion times.

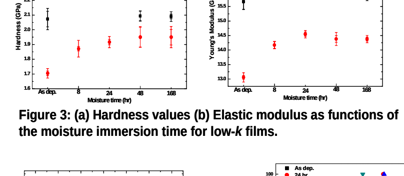

Figure 3: (a) Hardness values (b) Elastic modulus as functions of the moisture immersion time for low-*k* films.

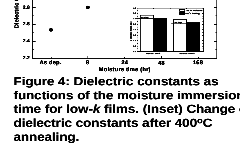

Figure 4: Dielectric constants as functions of the moisture immersion time for low-*k* films. (Inset) Change of dielectric constants after 400°C annealing.

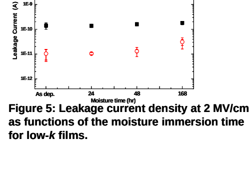

Figure 5: Leakage current density at 2 MV/cm as functions of the moisture immersion time for low-*k* films.

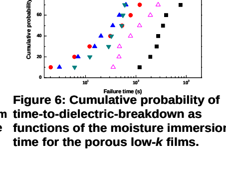

Figure 6: Cumulative probability of time-to-dielectric-breakdown as functions of the moisture immersion time for the porous low-*k* films.

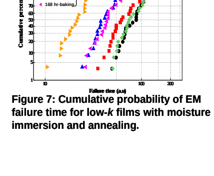

Figure 7: Cumulative probability of EM failure time for low-*k* films with moisture immersion and annealing.