

Heat, moisture and chemical resistance on low dielectric constant (low- k) film using Diethoxymethylsilane (DEMS) prepared by plasma enhanced chemical vapor deposition

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Abstract

Resistance of low dielectric constant (low- k) dielectrics, deposited using Diethoxymethylsilane (DEMS) precursor and helium (He) carrier gas with or without oxygen (O_2) reaction gas, against heat, moisture stress and chemical treatment is clarified. The low dielectric constant organosilicate glass (OSG) films deposited using DEMS and O_2 is shown to be the most reliable: the dielectric constant are stable even after a heating test at 700 °C and a pressure cooker test (PCT) for 168 h. This stability is high enough to ensure the low- k properties throughout fabricating multilevel interconnects and long-term reliability after the fabrication. This is due to the stability of Si-CH₃ bonds and more Si-C-Si- bonds, which has high degree of cross-linking. However, the degradation of the dielectric constant occurs after O_2 plasma ashing process. The nitrogen plasma treatment is proposed to prevent the damage from O_2 attack in the low- k films deposited using DEMS precursor.

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1. Introduction

As minimum device features shrink below 180 nm, the increase in propagation delay, the resistance and capacitance delay (RC) of the interconnect has become a limiting factor in ultra-large scale integration (ULSI) device performance. Since RC delay is a product of the resistance in the metal interconnect (R) and the capacitance between the metal line (C), incorporating copper (Cu) wiring and low- k dielectric to replace the conventional AlCu/SiO₂ into interconnect technology can effectively reduce the RC delay [1–3].

Various low dielectric constant materials have been proposed to decrease the time delay caused by capacitance. Recently, organosilicate glass (OSG), deposited by Plasma-Enhanced Chemical Vapor Deposition (PECVD) using various organo-precursors, such as Methylsilane (MS),

Tetramethylsilanetetrasiloxane (TOMCATS) and Diethoxymethylsilane (DEMS), is the most promising low- k dielectric candidate [4–8]. Among these precursors, DEMS precursor is a strong candidate based on the excellent film properties. DEMS (H-Si(CH₃)(OC₂H₅)₂)-based low- k films not only have a lower dielectric constant ($k=2.8-3.0$) but also have a greater hardness (higher cross link) as it contains an O/Si ratio of 2:1 in the precursor produced optimum films [9].

However, during the interconnect fabrication process, thermal cycle and photoresist stripping are the indispensable steps. Therefore, the physical (thickness and refractive index) and electrical properties (dielectric constant and leakage current) of the low- k interconnect dielectric are needed to be resistance against heat, moisture, and chemical stress in order to prevent the degradation during the interconnect fabrication process. Furthermore, to ensure the high reliability performance of the high-speed ULSI, the moisture resistance is essential to avert moisture penetrating from the outside the package [10–12].

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In this work, the stability of the low- k films deposited using DEMS precursor against heat, moisture and chemical stresses is clarified. The low- k films prepared using DEMS or DEMS/O₂ reactant gas are submitted to reliability tests to distinguish the stability divergence for the effect of the addition of O₂. Furthermore, the electrical measurements and material analyses have also been used to evaluate the low- k film before and after the reliability tests.

2. Experimental

2.1. Material prepared

All thin film deposition was performed on an Applied Materials Producer system with a 200 mm Producer chamber. The thin films were deposited on p-type (100) silicon substrates by radio frequency (13.56 MHz) PECVD with Diethoxymethylsilane (DEMS, CVD precursor) carried to the reaction chamber in the vapor phase by inert helium (He) gas. The chamber pressure and RF power were maintained at 800 Pa and 700 W, respectively, throughout the deposition process. The deposition temperature and He flow were kept 400 °C, and 150 sccm, respectively. The DEMS flow rate was fixed at 1500 mg and oxygen (O₂) flow was varied from 0 to 250 sccm (herein the O₂/DEMS ratio was 0–0.175).

2.2. Reliability test

To determine the thermal stability, the films were annealed for 1 h in a nitrogen ambient at temperatures ranging from 400 to 800 °C. Moreover, to mimic the thermal stresses encountered during Cu interconnects fabrication process; thermal annealing at 425 °C in nitrogen ambient for 1 h was performed 7 times. For the humidity test, a pressure cooker test (PCT) was carried out at 120 °C, 100% relative humidity, and 2 atmosphere pressure for 168 h. To test the impact of O₂ plasma on the film properties, the as-deposited DEMS-based films were exposed to O₂ plasma environment in a cathode-coupled rf asher. The pressure and RF power were 10 mTorr and 200 W, respectively, and the process time was set at 60 s.

2.3. Analysis method

The low- k films were analyzed for thickness and refractive index (RI, at 633 nm) by reflectometer (SCI FilmTek) and/or ellipsometer (Nano-Spec[®]9100) before and after stressing. The thickness change is defined herein as

$$\text{Thickness change (\%)} = \frac{\text{THK}_{\text{stressing}} - \text{THK}_{\text{As.dep.}}}{\text{THK}_{\text{As.dep.}}} \times 100\%$$

where THK_{stressing} and THK_{As.dep.} represent the measured thickness after stressing and as-deposition, respectively.

Fourier transform infrared (FT-IR) measurements were operated in the absorbance mode on a Bio-Rad Win-IR PRO FT-IR spectrometer with wave number ranging from 400 to 4000 cm⁻¹. FT-IR was performed at a resolution of 4 cm⁻¹, each spectrum being the average signal over 32 scans with the background corrected to a silicon reference. The dielectric constant (k) and leakage current density were measured by a SSM Inc. mercury probe cyclic voltammeter (CV) system at 1 MHz frequency. The k value was obtained from the average of 9 sites measurement.

3. Results and discussions

The dependence of the stress behavior of the as-deposited DEMS-based low- k films as a function of the O₂/DEMS ratio was investigated. The intrinsic stress of DEMS-based low- k films becomes more tensile as the O₂ flow rate is increased. Furthermore, thermal stability had been evaluated by stress/temperature analysis. Fig. 1 shows the stress hysteresis curves of the low- k films with polymerization of DEMS and oxidation of DEMS and O₂. It reveals that the stress shift between the first thermal cycle and the second cycle was suppressed for the low- k films prepared by DEMS and O₂. Minimal change in stress is observed for

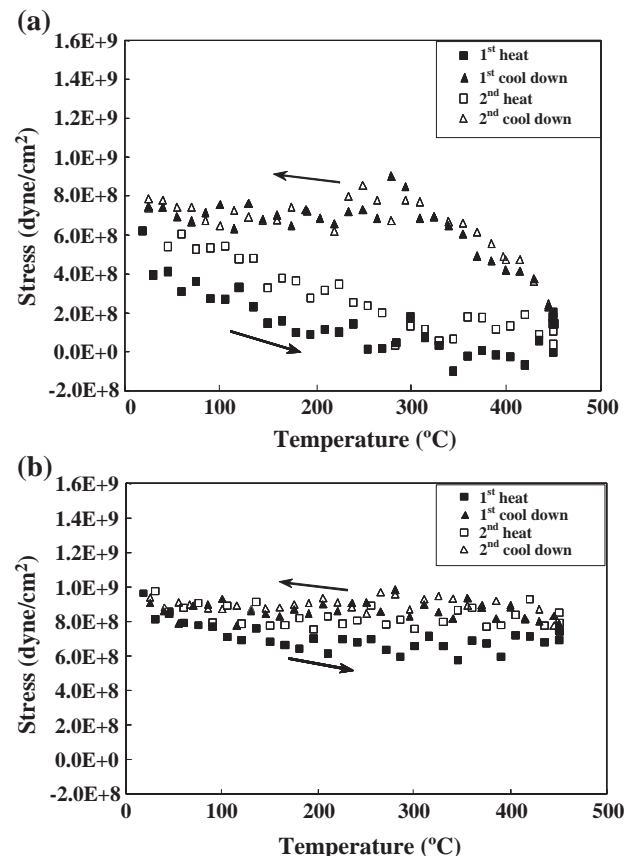


Fig. 1. The stress-hysteresis of DEMS-based low- k films prepared by (a) O₂/DEMS=0; (b) O₂/DEMS=0.05.

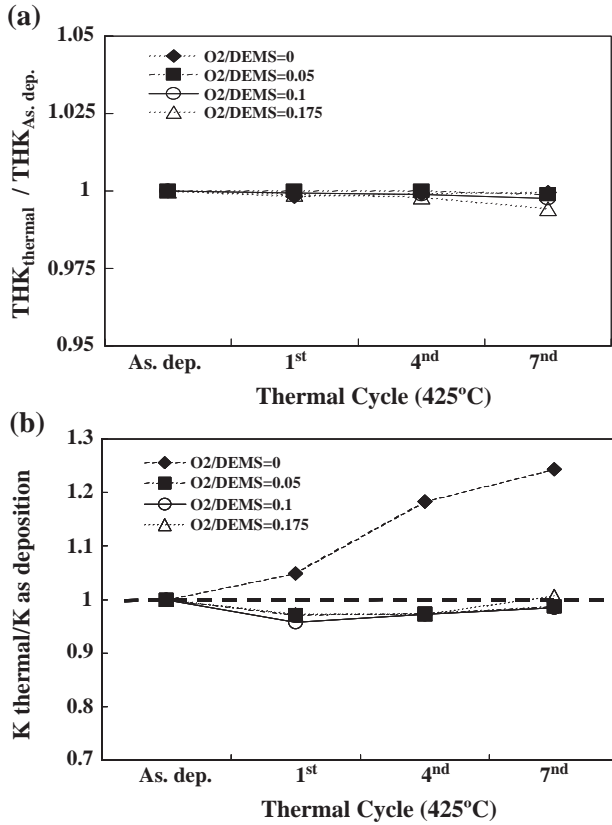


Fig. 2. The film properties change of DEMS-based low-*k* films after 7 times 425 °C thermal annealing (a) thickness; (b) dielectric constant.

low-*k* films deposited using DEMS and O₂. The shift magnitude is 2.0E7 dyn/cm², significantly smaller than that with pure DEMS deposition (3.0E07 dyn/cm²). This result implies that the low-*k* films deposited using DEMS and O₂ have better thermal stability.

In the Cu integration processes, there are at least 7–8 layers interconnect dielectric deposition with the deposition temperature of around 400 °C. The dependence of the heating cycles on the degradation of the thickness and dielectric constant of DEMS-based low-*k* films with various O₂/DEMS ratios are compared in Fig. 2(a) and (b), respectively. For DEMS-based low-*k* films, the thickness remains constant after performing 425 °C annealing cycling, independent of O₂/DEMS ratios shown in Fig. 2(a). This implies that low-*k* films deposited using DEMS precursor has a higher bonding strength when subjected to the heating tests related to other OSG films prepared by other precursors [13–15]. On the other hand, it can be seen from Fig. 2(b) that the dielectric constant change of low-*k* films with DEMS/O₂ was found to behave differently to that with DEMS only. The dielectric constant of the low-*k* films deposited only using DEMS gradually increase with increasing the heating cycles of 425 °C. In contrast, as O₂ was incorporated into the reaction, the dielectric constant of DEMS-based low-*k* films almost retains constant, even after the seven cycles of the 425 °C heating test. To further

investigate the heating resistance of DEMS-based low-*k* films, different heating temperatures, ranging from 400 to 800 °C, were performed. The influence of the heating temperatures on the change in the thickness and the dielectric constant of DEMS-based low-*k* films are shown in Fig. 3(a) and (b), respectively. Similar to other OSG low-*k* films using other precursors [14,15], the dielectric constant of the low-*k* films deposited using DEMS or DEMS/O₂ maintain a stable value (*k*=2.8–3.2) at temperatures up to 600 °C. Moreover, the dielectric constant of low-*k* films deposited only using DEMS degrade to 3.6 as the heating temperature is increased to 700 °C and sharply increases to 5.0 as the temperature increases to 800 °C. On the other hand, the dielectric constant of low-*k* films deposited using DEMS/O₂ does not degrade until the annealing temperature is increased to 800 °C. This indicates that DEMS-based low-*k* films with O₂ as an oxidant gas have a superior thermal resistance compared to those deposited only using DEMS precursor. This result seems to imply that low-*k* films deposited using DEMS and DEMS/O₂ have different bonding structures, which exhibits

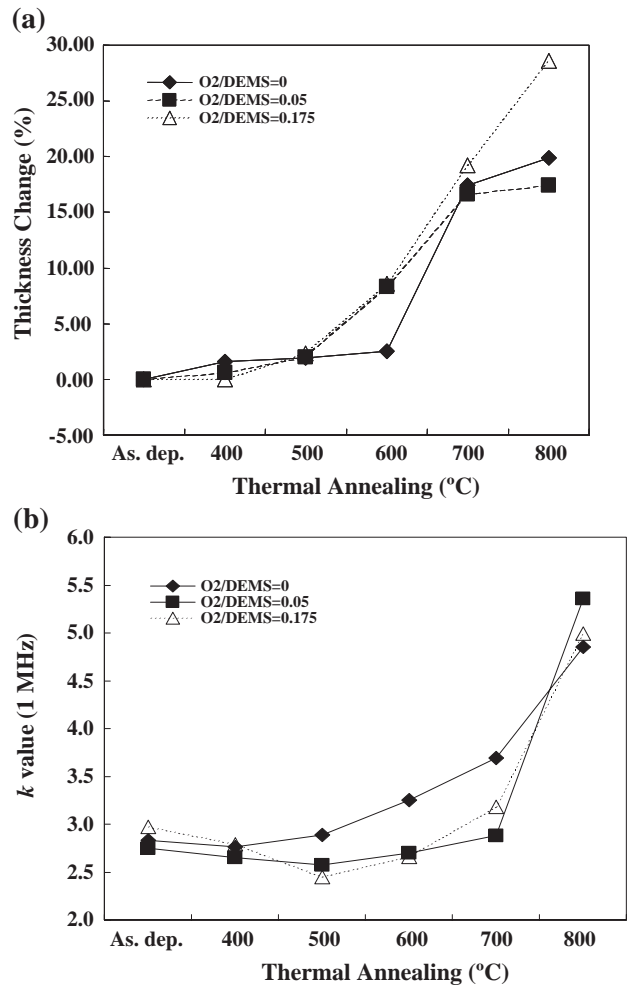


Fig. 3. The film properties of DEMS-based low-*k* films after thermal tests with temperature ranging from 400 to 800 °C (a) thickness; (b) dielectric constant.

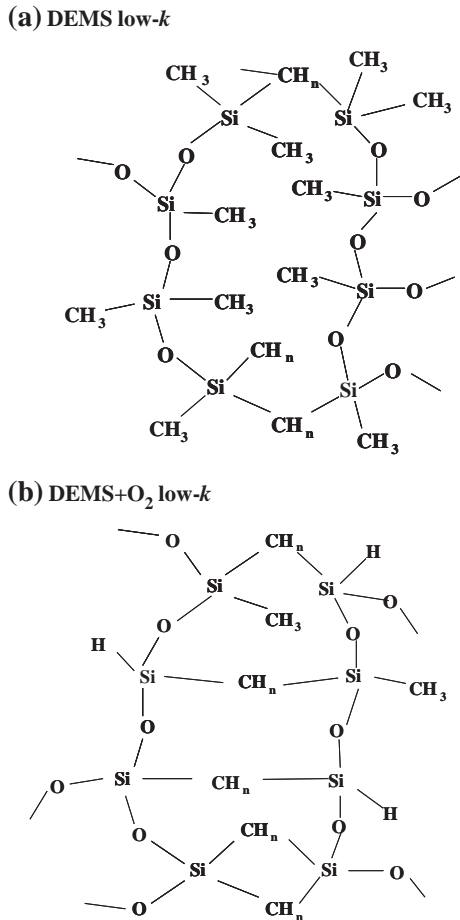


Fig. 4. Schematics of the chemical bonding structure (a) DEMS; (b) DEMS+O₂.

a different thermal resistance. To further investigate the difference in the bonding structure for these low-*k* films, FTIR and X-ray Photoemission spectroscopy (XPS) analyses were conducted depicted in the previous report [9,13]. The low-*k* films deposited using only DEMS precursor have more $-\text{CH}_3$ terminal bonds and less $\text{C}-\text{Si}_{4-x}\text{H}_x$ ($x < 2$) bonds. In contrast, the deposited low-*k* films contain more $\text{C}-\text{Si}_{4-x}\text{H}_x$ ($x < 2$) bonds to form a cross-linking structure and more Si-H terminated bonds as O₂ gas was added to the reaction. The speculated schematics of the low-*k* film chemical bonding structures deposited using (I) DEMS, (II) DEMS/O₂ are shown in Fig. 4. Furthermore, it is worth to note that the dielectric constant of DEMS-based low-*k* films deposited using DEMS/O₂ further decrease after the annealing process with temperature below 600 °C. The decreasing dielectric constant could be attributed to the desorption of the small amount water in the film and rearrangement of the amorphous structure during annealing. It was observed from FTIR spectra that no significant change in the concentration of the C-H bond and Si-CH₃ bond was observed, which are thermally stable up to 600 °C. We believe that the decreasing dielectric constant of low-*k* films deposited by DEMS/O₂ was a result of the

formation of open ring structures in the films caused by the loss of water and CH_x organic materials during annealing at 400–600 °C. Since the thermal resistance of Si-CH_x-Si bonds is lower than Si-CH₃, the Si-CH_x-Si bonds were converted to CH_x organic materials and desorbed during 400–600 °C annealing. This is positive to reduction the dielectric constant, but is negative to the thickness stability. As the annealing temperature is increased to 700 °C, the Si-CH₃ absorbance peak dramatically decreases and there is an increase in the oxide character of the film, and a loss of methyl groups after the annealing process as shown in Fig. 5. Interestingly, the enhancement in Si-O characteristics is less for the low-*k* films deposited using DEMS/O₂ film, which also showed much smaller increases in the dielectric constant. This suggests that the Si-CH₃ bonding did not decompose until the thermal temperature above 700 °C. In addition, low-*k* films deposited only using DEMS, where Si is bonded with multi-methyl group ($-\text{CH}_3$) bonding would degrade easily during the higher temperature annealing.

The change in the dielectric constant of DEMS-based low-*k* films under the moisture stress test in terms of O₂/DEMS ratios is shown in Fig. 6. It indicates a slightly increase in the refractive index and the dielectric constant after a 168 h PCT for two different deposition conditions. Compared to low-*k* films deposited using 3MS as precursor [13], low-*k* films deposited using DEMS as precursor shows a better moisture resistance, implying that this film has a surface hydrophobic property as a result of more $-\text{CH}_3$

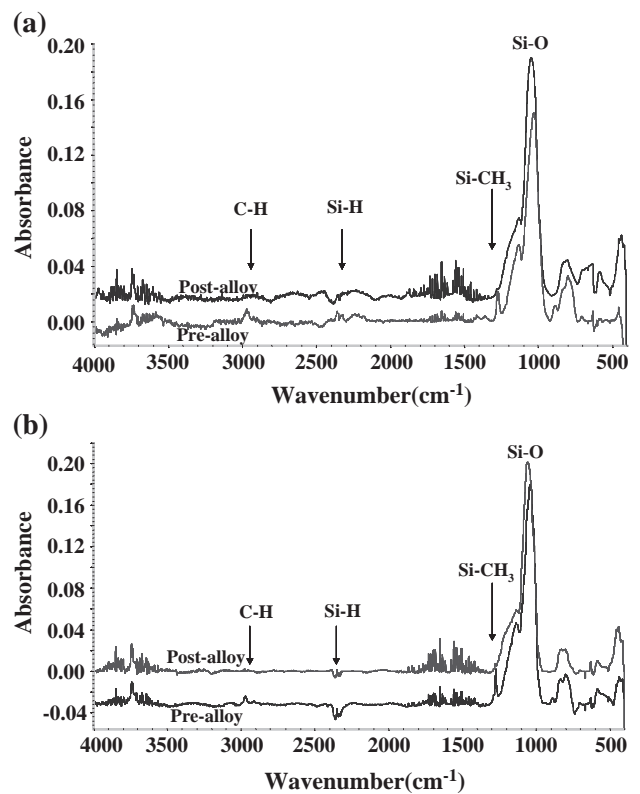


Fig. 5. FTIR spectrum change of DEMS-based low-*k* films after 700 °C thermal annealing (a) DEMS; (b) DEMS+O₂.

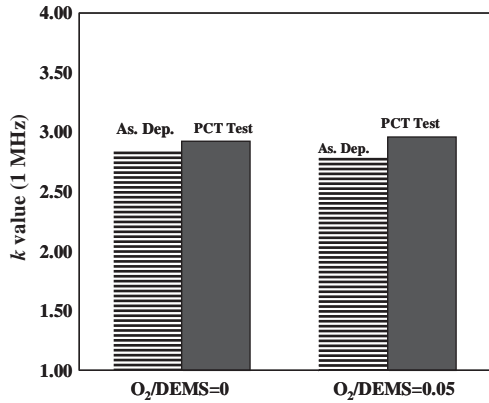


Fig. 6. The dielectric constant change of DEMS-based low-*k* film after 168 h PCT test.

terminal bonds. Additionally, the dielectric constant of low-*k* films deposited only using DEMS precursor increases to 2.93 from 2.86, which is slightly lower than that prepared by DEMS/O₂ with a dielectric constant of 2.96. More surface hydrophobic -CH₃ bonds in low-*k* films prepared using DEMS precursor hinders the moisture penetrate into the film, causing this divergence. More interesting to note, the stress of the low-*k* films tends to decline to neutral value after the moisture test. Furthermore, Thermal Desorption Spectrum (TDS) analysis indicated that the H₂O peak was observed at about 250 °C and the desorption amount of H₂O was greater for the low-*k* films prepared using DEMS/O₂ reaction. These results imply that the deposited low-*k* film still contains moisture in terms of physical absorption and low-*k* films produced only using DEMS precursor have better moisture resistance.

In the interconnect integration fabrication, the ILD layer etching and photo-resist stripping processes are indispensable steps. Fig. 7 shows the etching rate of DEMS-based low-*k* film as a function of O₂/DEMS ratios, performed using Ar/C₅F₈/N₂ gas. The etching rate of DEMS-based

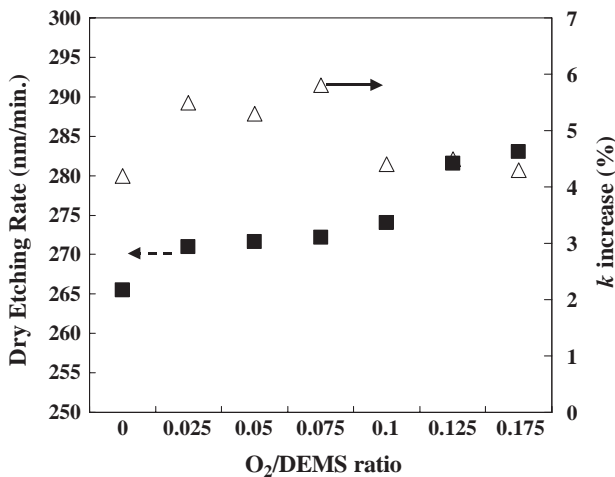


Fig. 7. The dry etching rate and dielectric constant change of DEMS-based low-*k* films as a function of the O₂/DEMS ratio.

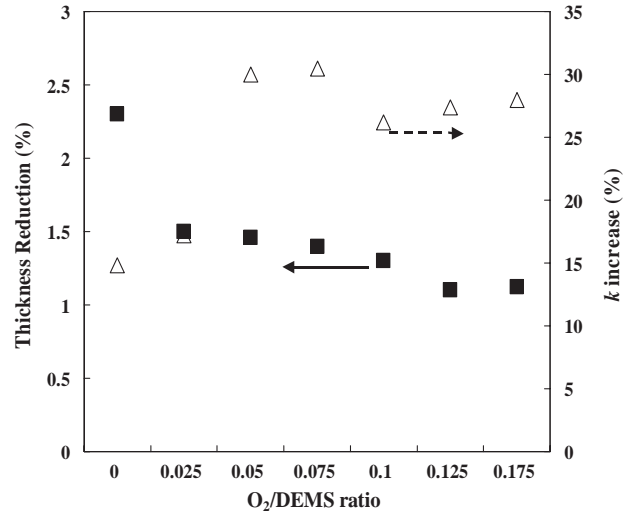
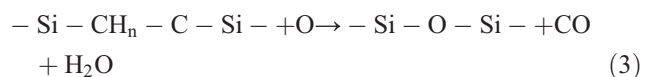
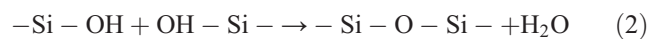
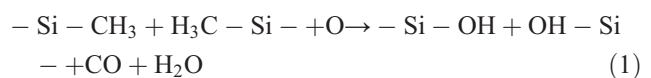


Fig. 8. The thickness and dielectric constant change of DEMS-based low-*k* films after O₂ plasma ashing as a function of the O₂/DEMS ratio.

low-*k* films slightly increases with increasing the O₂/DEMS ratio. The higher etching rate for DEMS-based low-*k* films with a higher O₂ flow rate is suspected to porosity structure in the low-*k* film; that is, the film is less dense (refractive index is lower for DEMS-based low-*k* films with a higher O₂ flow rate). On the other hand, the increase of the dielectric constant for post-etching DEMS-based low-*k* films is less than 6%. This indicates that low-*k* film deposited by DEMS and O₂ gas can efficiently withstand the treatment of the etching chemical gas.

In conventional photo-resist stripping step process, O₂ plasma ashing is commonly implemented because of its better efficiency in removing the polymer. However, all porous low-*k* films would suffer a degradation of the dielectric constant after exposing O₂ plasma ashing process [16]. Therefore, the effect of O₂ plasma ashing on low-*k* films prepared by DEMS or DEMS/O₂ was investigated in this study. Fig. 8 shows the change of thickness and the dielectric constant of DEMS-based low-*k* film as a function of the O₂/DEMS ratio. The thickness reduction can be negligible since the maximum thickness reduction is about 2.5%, which occurred on the low-*k* films deposited only using DEMS precursor. Additionally, the thickness reduction is less 1% for low-*k* films deposited using DEMS/O₂ reactant. A plausible explanation is that terminated methyl groups in DEMS-based low-*k* films are oxidized in the O₂ plasma condition, in line with the following Eqs. (1)–(3):



The forming $-\text{Si}-\text{O}-\text{Si}-$ bonds are almost as dense as $-\text{Si}-\text{C}-\text{Si}-$ as the bond length of $\text{Si}-\text{O}$ is similar to that of $\text{Si}-\text{C}$ bonds. As a result, the thickness change under O_2 oxidation can be negligible, which may account for the lower reduction in the DEMS/ O_2 reaction because the low- k films deposited using DEMS/ O_2 contains more $\text{Si}-\text{C}-\text{Si}$ bonds.

In contrast to the thickness reduction, the degradation in the dielectric constant of low- k films deposited using DEMS/ O_2 gas becomes serious as O_2 flow rate is increased. On the other hand, low- k films deposited only using DEMS gas show a lower change in the dielectric constant. This is expected to the increased $\text{Si}-\text{H}$ bonds in the deposited low- k films with a higher O_2 flow rate. Exception of the above oxidation, O_2 plasma treatment has also been found to result in dangling bonds arising from the enhanced breaking of $\text{Si}-\text{H}$ bonds by oxygen radicals. The reaction of $\text{Si}-\text{H}$ and oxygen radicals can be expressed as the following Eq. (4). The resulting OH bonding increases the dielectric constant.



Therefore, low- k films deposited using DEMS/ O_2 gas are needed to further improve its O_2 plasma ashing resistance when we consider it as the inter-layer dielectric.

To solve the dielectric constant degradation issue for the deposited low- k films, the dielectric constant of DEMS-based low- k films with post O_2 plasma treatment was measured after dry etching method, as shown in Fig. 9. The purpose of dry etching is to remove the dense layer, which is oxidized on the top of low- k film during the O_2 plasma ashing process. As can be seen, after the dry etch, the dielectric constant of the low- k films deposited using DEMS or DEMS/ O_2 reduced to about 3.3, which is close to the original as-deposition value. It clearly shows that the low- k film inside is not degraded during the O_2 ashing process. SEM also displays the distinct two-layers inside the low- k film after the O_2 plasma ashing. The depth of the oxidation film increases with increasing O_2 exposure time. This dense

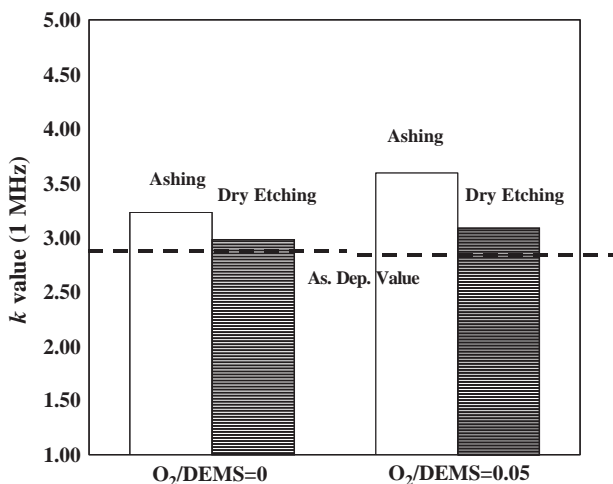


Fig. 9. The dielectric constant change of DEMS-based low- k films by removing the surface layer.

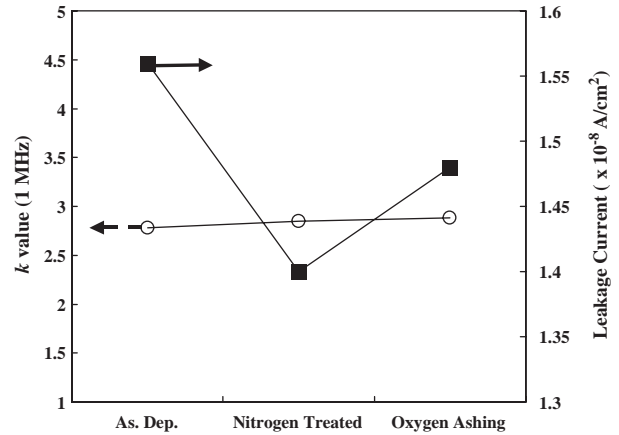


Fig. 10. The change in dielectric constant and leakage current at 2 MV/cm of the nitrogen treated low- k films after O_2 plasma ashing.

surface can be removed by sputter etching method prior to the metal deposition in the practical fabrication process. As a result, control of the O_2 plasma time and pre-sputter etching process is a feasible method in recovering the low- k film dielectric constant. Another approach to alleviate dielectric constant degradation is using NH_3 or N_2 plasma treatment on the as-deposited low- k films. This N_2 plasma treatment would induce the N atom doping in low- k films and replace the $\text{Si}-\text{H}$ bonds to form a thin $\text{Si}-\text{N}$ layer on the film surface. The dielectric constant of low- k films prepared by DEMS/ O_2 is slightly increased from 2.78 to 2.86 after N_2 plasma treatment. The new forming layer can effectively impede the O_2 plasma ashing attack for the low- k films. Fig. 10 shows the leakage current density at 2 MV/cm and dielectric constant of the N_2 plasma treated low- k films before and after being exposed to the O_2 plasma treatment. The leakage current density remains at a stable value of about $1.40\text{E}-8 \text{ A/cm}^2$ at 2 MV/cm, which is slightly lower than the as-deposited low- k film ($1.65\text{E}-8 \text{ A/cm}^2$ at 2 MV/cm) due to the formation of $\text{Si}-\text{N}$ bonds. In addition, the dielectric constant of N_2 plasma-treated low- k films deposited with 0.05 ratios of O_2/DEMS maintains the stable value when compared to the films without N_2 plasma treatment. This result indicates this functional group produced by N_2 plasma treatment ensures that the low- k films have a superior electrical performance to against O_2 plasma ashing damage.

4. Conclusion

The resistance of the organo-silicate glass low- k film deposited using DEMS and various O_2 flow against heat, moisture stress and chemical test for was investigated. Low dielectric constant organo-silica-glass film deposited using DEMS and O_2 is shown to be the most reliable. The dielectric constants are stable even after a heating test at 700°C and a pressure cooler test for 168 h, and are superior to other PECVD low- k films deposited using other precursors.

This excellent stability ensures the low- k film deposited using DEMS is suitable for application as multilevel interconnects, showing long-term reliability after fabrication. However, the O₂ plasma ashing process leads to a dielectric degradation in deposited low- k films during photoresist removal processing. A N₂ plasma treatment is proposed as a method of preventing the damage from an O₂ plasma attack on the low- k films deposited using DEMS/O₂ gas.

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