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Recovering Dielectric Loss of Low Dielectric Constant Organic Siloxane during the Photoresist Removal Process

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The interaction between low dielectric constant (low-*k*) hybrid organic siloxane polymer (HOSP) and O_2 plasma ashing has been investigated. O_2 plasma ashing is commonly performed to remove the photoresist (PR) during integrated circuit fabrication. However, dielectric loss usually occurs in the HOSP films during the PR removal process. In order to eliminate dielectric loss originating from an O_2 plasma attack, hexamethyldisilazane (HMDS) treatment is proposed to repair the damage in the HOSP film. HMDS can react with Si-OH bonds and reduce moisture uptake. Moreover, the leakage current and the dielectric constant is decreased significantly when damaged HOSP film undergoes HMDS treatment. For this reason, HMDS treatment is a promising method to apply to the photoresist removal.

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As the device dimensions continue to shrink to 0.25 μm and below, the interconnect delay becomes a limiting factor for increasing device speed. Since the *RC* delay is a product of the resistance in the metal interconnect (*R*) and the capacitance between the metal lines (*C*), incorporating new materials of low resistivity and low permittivity into interconnect fabrication can effectively reduce this time constant.[1,2]

In order to decrease the resistance (*R*), copper has recently been introduced as an interconnect metal, due to its high electrical conductivity. In addition, the low dielectric constant (low-*k*) materials are also proposed for decreasing the parasitical capacitor for future integrated circuit (IC) applications.[3-9] One of the promising low-*k* dielectrics, a spin-on deposition hybrid organic siloxane polymer (HOSP) is a strong candidate. The HOSP is derivative of SiO_2, in which one of the four oxygen atoms bonded to every silicon atom is replaced by hydrogen and methyl groups. In addition, the HOSP has a low dielectric constant of about 2.5 so that it has a high evaluation in ultralarge scale integration (ULSI) applications.

However, photoresist stripping is an indispensable step in integration processing. The dielectric properties of the HOSP films will degrade after photoresist stripping.[10,11] As a result, hexamethyldisilazane (HMDS) treatment is proposed for improving the quality of the HOSP film after photoresist stripping. Furthermore, electrical measurements and material analyses have also been used to evaluate the HOSP film during the photoresist stripping process.

Experimental

The wafers were coated with the HOSP solution at a rotation of 500 rpm for 5 s, and the sequential spin was at 2500 rpm for 20 s. After the spin-coating process, the HOSP films were baked on a hot plate at 150, 200, and 350°C for 1 min, respectively. Finally, the resulting wafers were further processed by furnace curing at 400°C under nitrogen ambient for 1 h.

In this work, samples STD, A, and B were prepared. Sample STD was the as-cured HOSP film without any plasma treatment. Sample A was the HOSP film with O_2 plasma ashing for 1 min. Sample B was the O_2 plasma-treated HOSP film (sample A) after having undergone an HMDS atmosphere at 80°C for 15 min. Afterward, aluminum were deposited on samples STD, A, and B as the top electrode to manufacture the metal insulation semiconductor (MIS) structure.

The O_2 plasma ashing was carried out at a plasma-enhanced chemical vapor deposition chamber. The O_2 plasma was operated with a rf power of 200 W at a pressure of 300 mTorr. The flow rate was 700 sccm, and the operating temperature was kept at 300°C.

The chemical bonds of the HOSP films after different processes were investigated by Fourier transform infrared (FTIR) spectroscopy. The thickness of the HOSP films was measured by an N&K analyzer. The thermal desorption system spectrometer (TDS) was carried out to monitor the desorbed moisture from HOSP films. A Keithley model 82 C-V meter was used to measure the dielectric constant of HOSP films, and the capacitance-voltage (C-V) characteristics were measured at 1 MHz with an ac bias for high frequency. Finally, the current-voltage (I-V) characteristics were also measured using a MIS structure to evaluate the insulation property of HOSP films.

Results and Discussion

In the integrated processes, photoresist removal is an indispensable step. The photoresist removal is implemented conventionally by utilizing O_2 plasma ashing. Therefore, the impact of O_2 plasma ashing on the quality of HOSP film is investigated in this study. Figure 1 shows the thickness variation of HOSP film (sample STD) with O_2 plasma ashing for 1 to 9 min. The thickness of the HOSP film is decreased with an increase of the O_2 plasma treatment time. The film shrinkage is due to the damaged structure after the HOSP film undergoes the O_2 plasma ashing process. The FTIR spectra have confirmed our inference. Figure 2 shows the FTIR spectra of the HOSP film with O_2 plasma ashing for 1 to 9 min. The intensity of Si-OH bonds and H_2O is increased after O_2 plasma ashing. Furthermore, the intensities of Si-H, C-H, and $Si\text{-}CH_3$ peaks are decreased dramatically. During O_2 plasma ashing, the oxygen radicals can diffuse into the HOSP film to attack the functional groups and consequently a large amount of $Si\text{-}CH_3$ bonds and Si-H bonds are broken. This will cause the HOSP films to generate dangling bonds. The dangling bonds may be easily converted into Si-OH bonds when the dangling bonds are exposed to the environment. The Si-OH bonds in the damaged HOSP films often lead to moisture uptake with the result that the Si-OH bonds and H_2O signal appear in the FTIR spectra.

Figure 3 shows the leakage current density of the HOSP film with O_2 plasma ashing for 1 to 9 min. The leakage current is increased with the increase of the O_2 plasma treatment time. Furthermore, the dielectric constant is also increased with the increase of the O_2 plasma treatment time, as shown in Fig. 4. The dielectric loss

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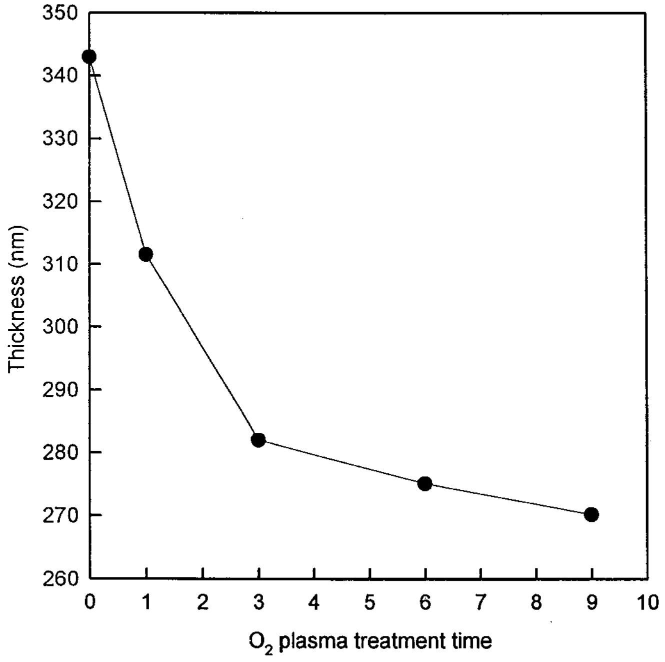

Figure 1. The thickness variation of HOSP films (sample STD) with O_2 plasma ashing for 1 to 9 min.

is due to the destruction of functional groups in the HOSP films after the O_2 plasma ashing process, which is consistent with the FTIR spectra in Fig. 2.

In order to overcome these issues, HMDS treatment has been developed to repair the damage originating from photoresist stripping in the HOSP film. Chemical HMDS treatment, $(CH_3)_3Si\text{-}NH\text{-}Si(CH_3)_3$, can react with Si-OH bonds caused by O_2 plasma ashing in the damaged HOSP film. The chemical reaction equation between the HMDS and Si-OH bonds is shown as follows[12]

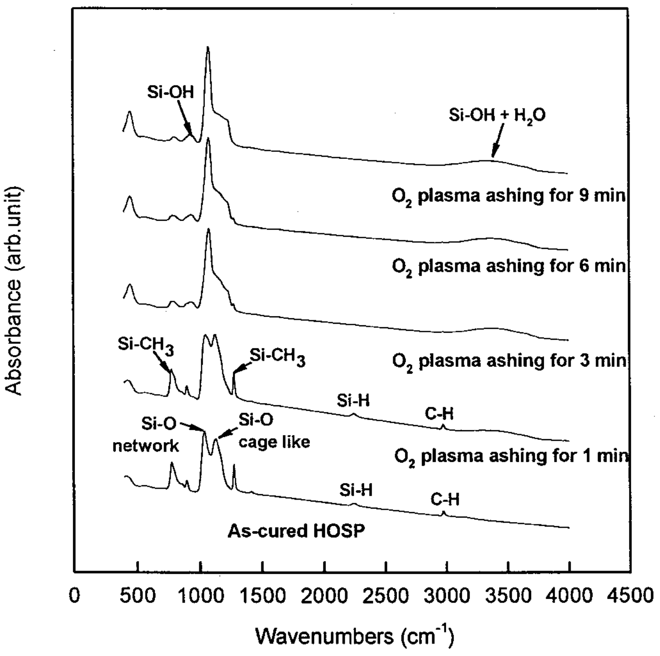

Figure 2. The FTIR spectra of HOSP films (sample STD) with O_2 plasma ashing for 1 to 9 min.

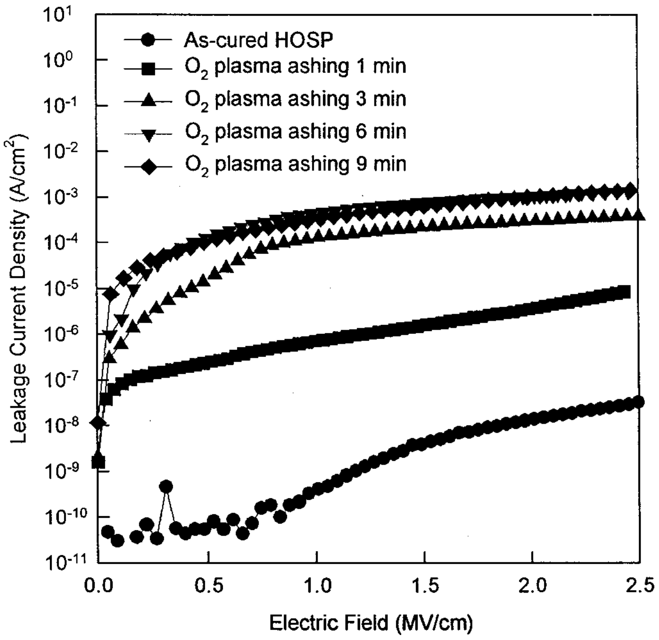

Figure 3. The leakage current density of HOSP films (sample STD) with O_2 plasma ashing for 1 to 9 min.

$$(CH_3)_3Si\text{-}NH\text{-}Si(CH_3)_{3(g)} + HO\text{-}Si\text{-}_{(s)} \rightarrow (CH_3)_3\text{-}Si\text{-}O\text{-}Si\text{-}_{(s)} + (CH_3)_3\text{-}SiNH_{2(g)} \quad [1]$$

$$(CH_3)_3\text{-}SiNH_{2(g)} + HO\text{-}Si\text{-}_{(s)} \rightarrow (CH_3)_3\text{-}Si\text{-}O\text{-}Si\text{-}_{(s)} + NH_{3(g)} \quad [2]$$

Figure 5 shows FTIR spectra of samples STD, A, and B. When sample A undergoes HMDS repair, the intensity of the Si-OH bonds and moisture decreases, as shown in sample B. These experimental

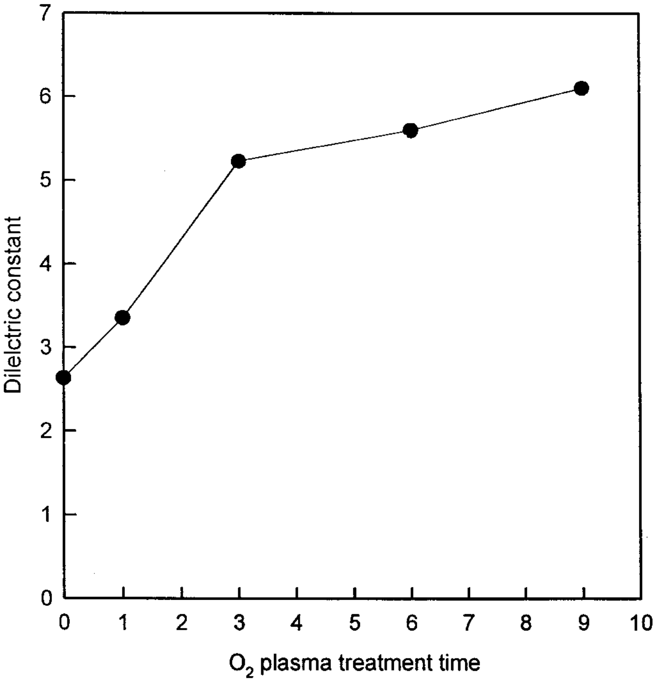

Figure 4. The dielectric constant of HOSP films (sample STD) with O_2 plasma ashing for 1 to 9 min.

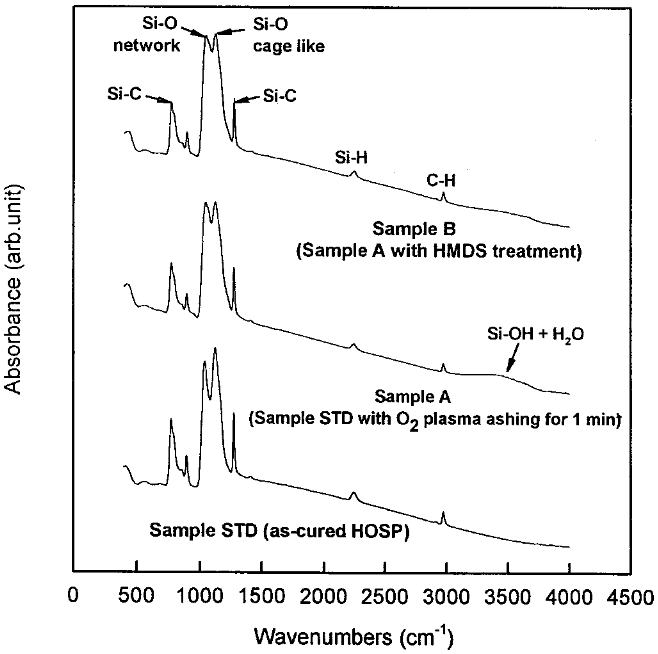

Figure 5. The FTIR spectra of sample STD, sample A, and sample B.

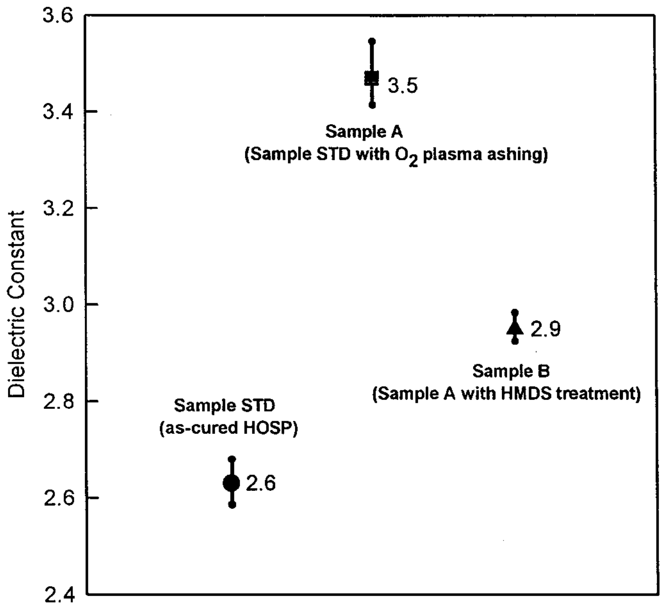

Figure 7. The dielectric constant of sample STD, sample A, and sample B.

results are consistent with our inference. The Si-OH bonds not only are decreased to repair the damaged HOSP film, but react with HMDS to form Si-OSi(CH_3)$_3$ bonds. The Si(CH_3)$_3$ bonds are hydrophobic so that the film surface can be made more hydrophobic by HMDS treatment.

The hydrophobic surface will reduce the moisture uptake. The TDS analysis also confirms our inference, as shown in Fig. 6. The moisture content of sample B is significantly lower than that of sample A. These results indicate that HMDS treatment of HOSP film can effectively enhance the resistance to moisture uptake, and for this reason the dielectric property of HOSP film will be maintained at an excellent level.

Figures 7 and 8 show both the dielectric constant and leakage current variations when HOSP film undergoes O_2 plasma ashing and HMDS treatment. The dielectric constant of HOSP will increase after O_2 plasma ashing, whereas it will decrease after sequential HMDS treatment. The dielectric constant of sample STD increases from 2.6 to 3.5 after O_2 plasma ashing, as shown in sample A. After sequential HMDS treatment, the dielectric constant reduces to 2.9, as shown in sample B.

Moreover, the leakage current density increases significantly when sample STD undergoes O_2 plasma ashing, as shown in sample

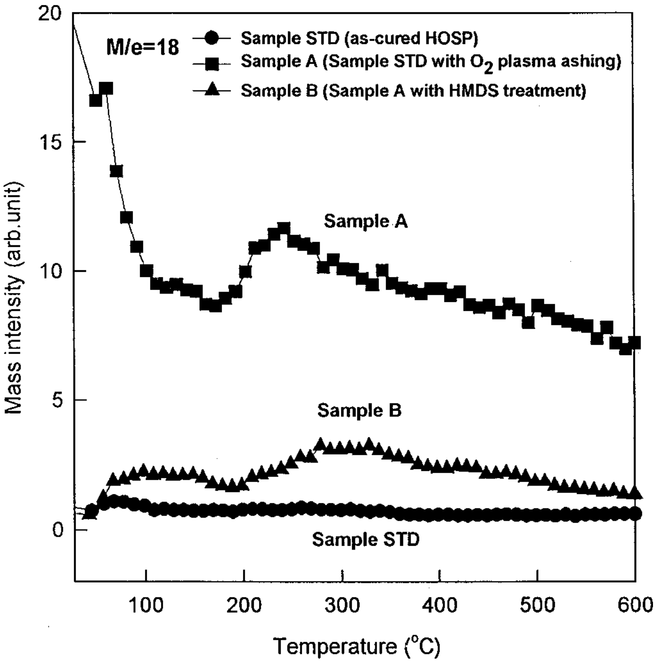

Figure 6. The temperature dependence of moisture desorption of sample STD, sample A, and sample B.

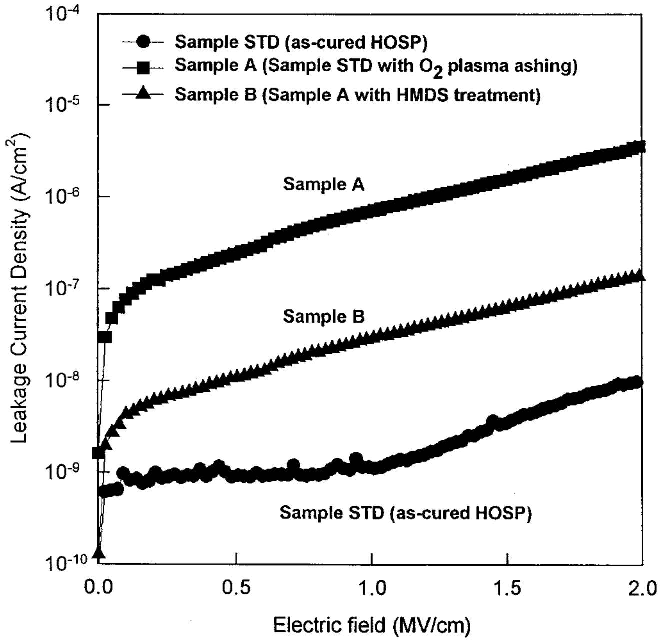

Figure 8. The leakage current density of sample STD, sample A, and sample B.

A. After further HMDS treatment, the leakage current density is decreased by a factor of 1-2, as shown in sample B. This indicates that HMDS can repair the damaged structure in the HOSP film and reduce both the leakage current density and dielectric constant after the photoresist removal process.

Conclusions

In this study, HMDS treatment is applied to HOSP films. The HMDS treatment can eliminate the Si-OH bonds in the damaged HOSP film, transforming more hydrophobic surfaces. This can reduce moisture uptake in the HOSP film so that the leakage current and dielectric constant will decrease. Material analyses verified our interpretation. The Si-OH bounds are decreased significantly in the FTIR spectra when the damaged HOSP film undergoes HMDS treatment. In addition, TDS analysis also shows that the moisture uptake can be reduced after HMDS treatment and as a consequence the dielectric properties will be maintained in excellent condition. As a result, HMDS treatment is a promising method for repairing the dielectric loss to the HOSP film in the photoresist removal process.

Acknowledgments

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