Trimethylchlorosilane Treatment of Ultralow Dielectric Constant Material after Photoresist Removal Processing

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The dielectric properties of organic-porous silica films deteriorate after photoresist removal processing. O_2 plasma ashing has been commonly used to remove photoresist. Nevertheless, the O_2 plasma will destroy the functional groups and induce moisture uptake in porous silica films. In this study, trimethylchlorosilane (TMCS) is used to repair the damage to porous silica caused by the O_2 plasma ashing process. The leakage current and dielectric constant will decrease significantly after the TMCS treatment is applied to damaged porous silica. These experimental results show that the TMCS treatment is a promising technique to repair the damage to porous silica during photoresist removal processing.
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As ULSI (ultralarge-scale integration) circuits are scaled down to the deep submicrometer regime, interconnect delay becomes increasingly dominant over intrinsic gate delay. In order to reduce the resistance-capacitance delay time, using low dielectric constant (low-*k*) materials as intermetal dielectrics is one of the effective methods. In addition, the use of low-*k* dielectrics can also lower power dissipation and reduce cross talk noise.[1-3]

There are numerous low-*k* dielectric materials available with the dielectric constant in the range of 2.0-4.1.[4-10] Within many low-*k* dielectrics, nanoporous material is a promising candidate. It has become an important class of low-*k* materials because the incorporation of voids reduces the dielectric constant of the film by lowering the overall material density.[11-13] Organic porous silica (sample STD) one of the nanoporous materials, is a good candidate for ULSI applications because of the low dielectric constant of about 2.0. Therefore, integrating porous silica as an interlayer dielectric into multilevel interconnects has received much attention in recent years.

However, photoresist stripping is an indispensable step in integration processing. Photoresist removal is commonly implemented with O_2 plasma ashing. The dielectric properties of the porous silica will deteriorate during photoresist stripping processes.[14,15] For overcoming the process issue, we have studied the trimethylchlorosilane (TMCS) treatment to improve the quality of porous silica film. Electrical measurement and material analyses have been used to evaluate porous silica. In addition, O_2 plasma ashing has been investigated to realize the impact of integrated processes on the dielectric film quality.

Experimental

The porous silica films used ($CH_3SiO_{1.5}$) contain methyl groups. The material has been developed by increasing the number of the methyl group thus giving a hydrophobic surface and resulting in lower film polarity. In addition, the porosity (volume fraction of pores) of the silica is about 50% and this leads to a low dielectric constant; a value of $k = 1.9$ was achieved.

The unpatterned silicon wafers were coated with the porous silica solution at a rotational velocity of 3000 rpm for 20 s. Then, the sequential bake was in the furnace under nitrogen atmosphere. For the bake condition, the temperature was raised from room temperature to 425°C at a rate of 20°C/min. Finally, the resulting wafers were further processed by furnace curing at 425°C for 60 min.

In this work, samples STD, A, and B were prepared. Sample STD was the as-cured porous silica film without any plasma treatment. Sample A was the as-cured porous silica with O_2 plasma ashing for 30 s. Sample B was the O_2 plasma-treated porous silica (sample A) after undergoing TMCS atmosphere at 60°C for 15 min. Afterward, all of the samples were further processed by furnace curing at 400°C for 60 min. Finally, aluminum was 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 in a plasma-enhanced chemical vapor deposition (PECVD) chamber. The O_2 plasma was operated with an rf power of 200 W at a pressuse of 300 mTorr. The flow rate was 700 standard cubic centimeters per minute, and the operating temperature was kept at 300°C.

The TMCS treatment was performed by utilizing TMCS vapor to treat sample A in an oven. The TMCS vapor is generated by heating TMCS solution and the vapor is conveyed to the oven at 60°C. Moreover, the TMCS vapor treatment is carried out at a pressure of 760 Torr.

The chemical structure of the porous silica following different processing was investigated by Fourier transform infrared (FTIR) spectroscopy. The thickness of the porous silica was measured by an n & k analyzer. A Keithley model 82 cyclic voltammetry meter was used to measure the dielectric constant of porous silica, and the capacitance-voltage characteristic was measured at 1 MHz with an ac bias for high frequency. Finally, the current-voltage characteristic was also measured by using MIS structure to evaluate the insulation property of porous silica.

Results and Discussion

In the integrated processes, the photoresist removal is implemented conventionally by utilizing the O_2 plasma ashing to remove organic photoresist. However, porous silica has a large exposed-surface area. This will raise the opportunity of reaction between porous silica and the O_2 plasma when porous silica undergoes photoresist removal. Therefore, the impact of the O_2 plasma processing on the porous silica film must be investigated.

Figure 1 shows the FTIR spectra of sample STD after being subjected to O_2 plasma ashing for 30 to 90 s. The intensities of the Si-OH and H_2O (938, ~ 3400 cm^{-1}) signals increase when O_2 plasma ashing is applied to sample STD. Furthermore, the intensities of Si-C (847, 1277 cm^{-1}) peaks and C-H (2980 cm^{-1}) peak are decreased dramatically. This indicates that oxygen radicals can diffuse deeply into porous inner structure of organic silica to attack a large amount of Si-C and C-H groups. This will lead to a large
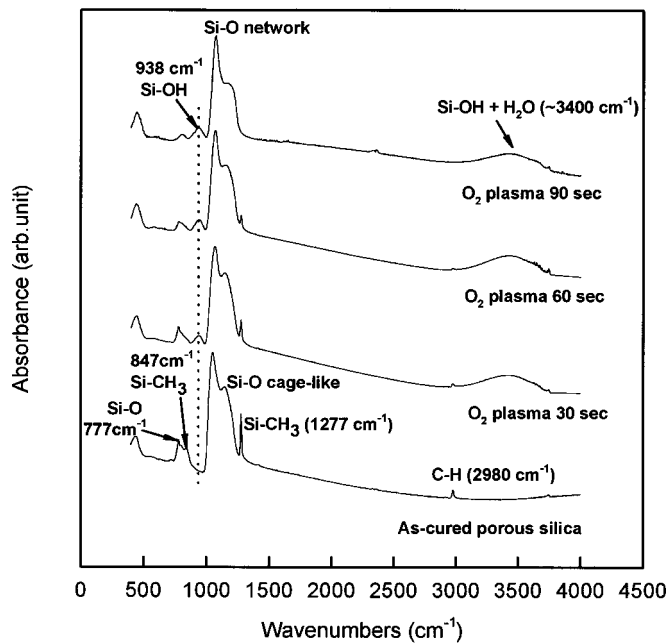
Figure 1. FTIR spectra of porous silica films (sample STD) after O_2 plasma ashing for 30 to 90 s.

Figure 3. The dielectric constant of porous silica films (sample STD) as a function of O_2 plasma ashing time.

number of Si-C and C-H bonds breaking, leaving many dangling bonds in the film. In addition, it is considered that two factors might cause an increase of the Si-OH groups. One is that when the O_2 plasma attacks the $Si-CH_3$ groups, porous silica immediately absorbs oxygen radicals to convert $Si-CH_3$ units to Si-OH groups. The other is that the dangling bonds in the porous silica absorb moisture immediately when the sample is exposed to the atmosphere. As a result, the functional groups in porous silica will be destroyed by the oxygen radical attack when the porous silica is exposed to O_2 plasma ashing. This will lead to the decreasing content of methyl
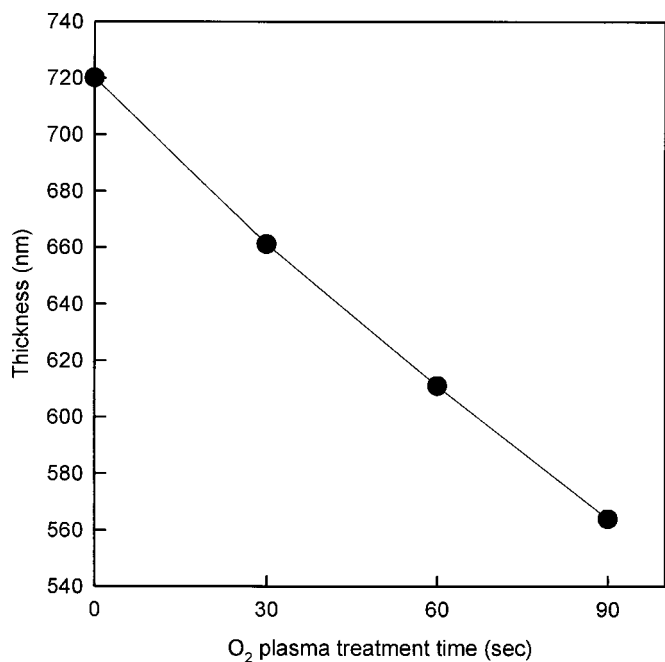
groups in porous silica so that the film thickness will decrease. The thickness variation has confirmed our inference. The thickness is decreased with an increase of the O_2 plasma treatment time, as shown in Fig. 2.

Porous silica with an excellent low-*k* property is due to the higher density of the functional group. Therefore, when the function groups decompose after O_2 plasma treatment, dielectric degradation of the porous silica will occur. Figure 3 shows the dielectric constant variation of sample STD as a function of O_2 plasma ashing time.

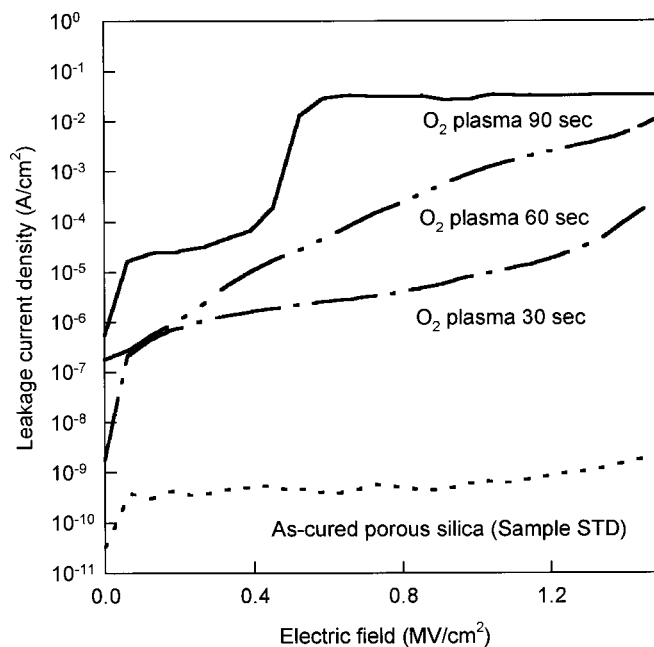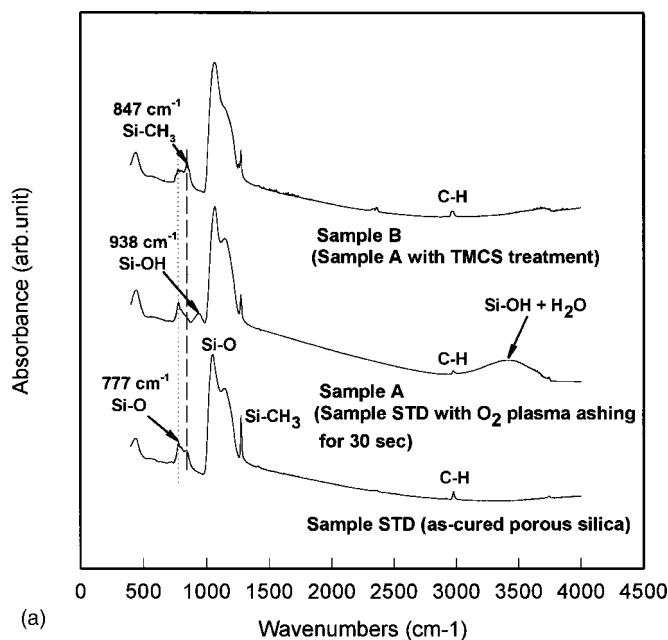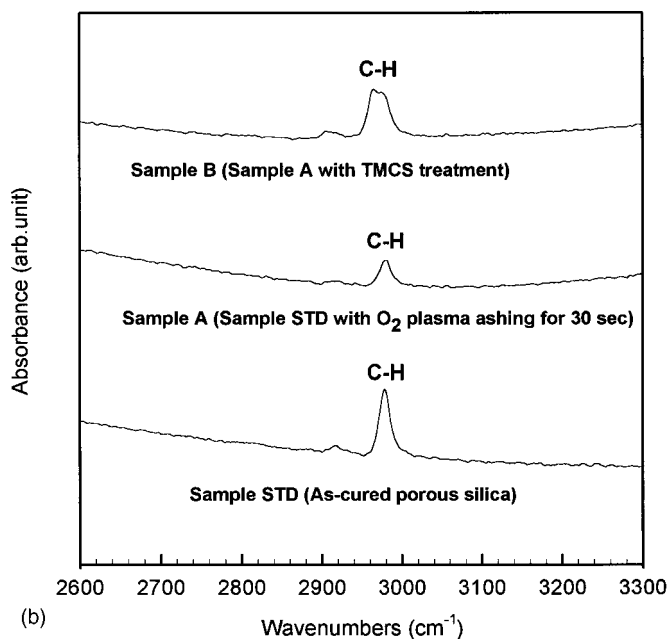**Figure 2.** The thickness variation of porous silica films (sample STD) with O_2 plasma ashing for 30 to 90 s.

Figure 4. The leakage current density of porous silica films (sample STD) after different O_2 plasma ashing times.
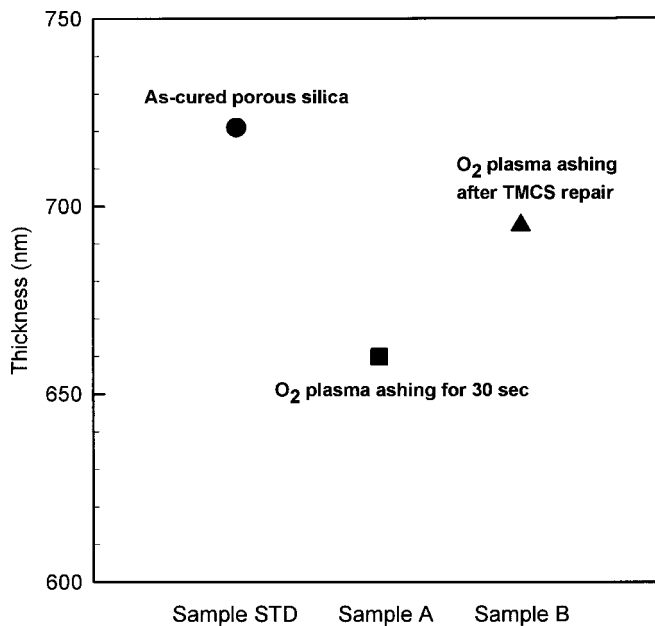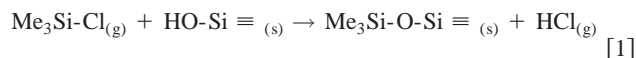
(a)

Figure 6. The thickness of sample STD, sample A, and sample B.

Figure 5a shows the FTIR spectra of samples STD, A, and B. In comparison with sample A (O_2 plasma-damaged porous silica), when sample A undergoes the TMCS treatment, the intensities of the IR bands from the Si-OH and moisture (938 and 3400 cm^{-1}) decrease significantly, as shown in the spectrum for sample B. Meanwhile, the intensity of the absorption band (847 cm^{-1}) increases, which is characteristic for the Si-C stretching and CH_3 rocking vibrations in trimethylsilyl groups. In addition, the intensity of the C-H groups increases when TMCS repair is carried out to the oxygen-exposed porous silica, as shown in Fig. 5a and b. These experimental results support our inference. The Si-OH groups are not only eliminated to repair the damaged porous silica, but are also undergoing reaction with TMCS, which form the Si-OSiMe$_3$
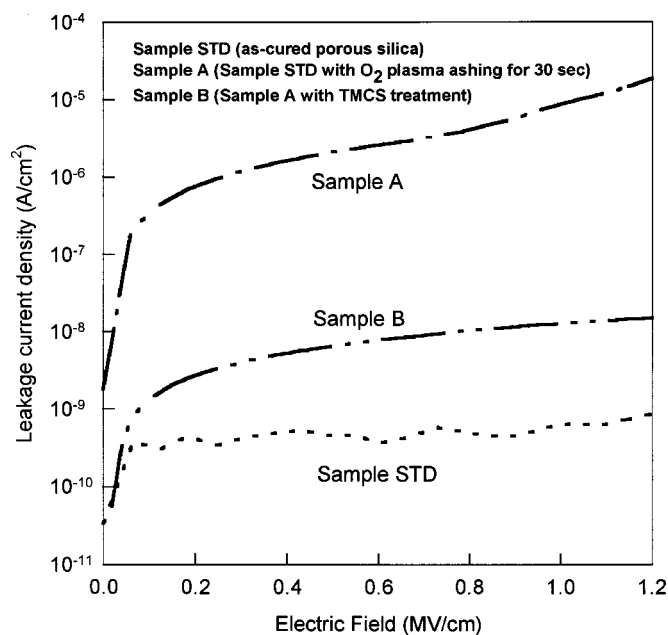

(b)

Figure 5. (a) The FTIR spectra of sample STD, sample A and sample B. (b) Enlargement of (a) ranging from 2600 to 3300 cm^{-1}.

The dielectric constant increases with an increase of the O_2 plasma treatment time. In addition, the leakage current also increases with an increase of the O_2 plasma treatment time, as shown in Fig. 4. These changes are due to the formation of the Si-OH groups in the porous silica, as proved by the FTIR data. The porous silica with the Si-OH groups will easily absorb moisture. The high polarity water molecules (dielectric constant ~78) present in the porous silica give rise to an increase of both leakage current and dielectric constant[16] (Fig. 3 and 4, respectively).

In order to overcome the process issue, trimethylchlorosilane (TMCS) is provided to repair the damaged porous silica. TMCS (Me$_3$Si-Cl) can eliminate the Si-OH groups via the reaction[17]

$$Me_3Si\text{-}Cl_{(g)} + HO\text{-}Si \equiv_{(s)} \rightarrow Me_3Si\text{-}O\text{-}Si \equiv_{(s)} + HCl_{(g)} \quad [1]$$

Figure 7. The leakage current density of sample STD, sample A, and sample B.
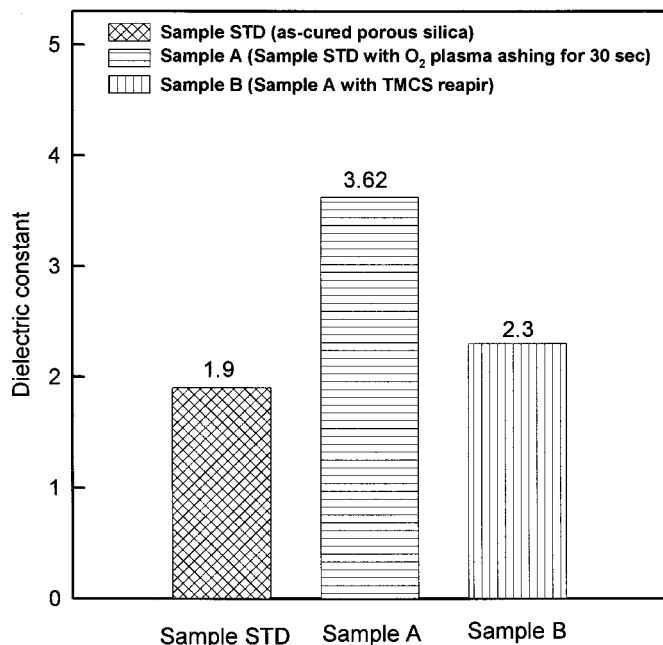
Figure 8. The dielectric constant of sample STD, sample A, and sample B.

groups. Since the SiMe$_3$ groups are hydrophobic, the TMCS treatment can change the film surface from hydrophilic to hydrophobic.

Figure 6 shows the thickness variation of porous silica with various process steps. The thickness decreases when porous silica undergoes O$_2$ plasma ashing. The decrease of thickness results from a drop of the methyl group content, caused by O$_2$ plasma ashing. However, the thickness of the damaged porous silica increases unexpectedly after TMCS treatment, as shown in Fig. 6. Two possible reasons may cause an increase of the thickness. One reason is that when TMCS reacts with Si-OH groups, it provides additional trimethylsilyl groups (-SiMe$_3$) to replenish the lost functional groups, caused by O$_2$ plasma ashing. The other reason is that some depositions of the TMCS species are on the surface of the damaged film. Therefore, the thickness of porous silica will increase after TMCS treatment.

Figure 7 shows the leakage current density of samples STD, A, and B. The leakage current density of sample A increases significantly when sample STD undergoes O$_2$ plasma ashing. After performing TMCS treatment, the leakage current density decreases by a factor of 2 to 3, as shown for sample B (Fig. 7). Moreover, the dielectric constant of as-cured porous silica increases after O$_2$ plasma ashing, whereas it decreases after sequential TMCS treatment, as shown in Fig. 8. The dielectric constant of sample STD increases from 1.9 to 3.62 after O$_2$ plasma ashing, as shown for sample A. After a sequential TMCS treatment, the dielectric constant is reduced to 2.3, as shown for sample B. The electrical properties indicate that the TMCS treatment can repair the damaged structure of the porous silica and reduce both the leakage current density and dielectric constant.

Conclusions

In this study, the TMCS treatment was applied to porous silica films to improve their quality deteriorated after O$_2$ plasma ashing process. TMCS repaired the damage caused by the O$_2$ plasma ashing. The Si-OH groups can be eliminated and transformed into Si-OSiMe$_3$ groups by TMCS treatment. The SiMe$_3$ groups possess hydrophobic properties and thus the surface of porous silica can be changed from hydrophilic to hydrophobic. Material analyses verified our interpretation. The content of the Si-OH groups decreases, whereas the content of the C-H groups increases when TMCS treatment is applied to the damaged porous films. In addition, a hydrophobic surface can also prevent moisture uptake so that the leakage current and the dielectric constant can be reduced significantly. Therefore, TMCS treatment is an effective method to repair the damage of porous silica caused by O$_2$ plasma ashing.

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