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The Novel Improvement of Low Dielectric Constant Methylsilsesquioxane by N_2O Plasma Treatment

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The organic silsesquioxane, methylsilsesquioxane (MSQ), has a low dielectric constant because of its lower film density compared to thermal oxide. However, the quality of MSQ film is degraded by the damage of oxygen plasma and hygroscopic behavior during photoresist stripping. In this work, we studied the N_2O plasma treatment for improving the quality of MSQ. The leakage current of MSQ decreases as the N_2O plasma treatment time is increased. The dielectric constant of N_2O plasma-treated sample remains constant (~2.7). In addition, the thermal stability of MSQ film can be enhanced. The role of N_2O plasma is to convert the surface layer of organic MSQ into inorganic type by decomposition of the alkyl group and thus form a passivation layer. The inert passivation layer enhances the resistance to moisture uptake and O_2 plasma attack. Therefore, N_2O plasma-treatment greatly improves the quality of low *k* MSQ film and removes the issue of photoresist stripping in the integrated process.

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As the critical dimension of integrated circuits is scaled down, the linewidth and spacings between metal interconnects are made smaller. A larger portion of the total circuit transmission time (*i.e.*, RC delay) will be due to parasitic resistance and capacitance of the interconnects and the interconnect becomes a bottleneck in improving the chip performance such as the operating speed and power consumption.

To address these issues, copper with its relatively low resistivity and interlayer dielectric films with lower dielectric constants have been proposed. These interlayer dielectric films can be either organic or inorganic materials, and can be deposited by either chemical vapor deposition (CVD) or spin-on glass (SOG) techniques.[1-3] SOG materials have been widely used as an interlayer dielectric in multilevel interconnect architectures because of their process simplification (lower cost) and good local planarization capabilities. Inorganic SOGs such as hydrogen silsesquioxane (HSQ), aerogels, and xerogels (which have hydrophobic pores) have been developed by introducing the Si-H group and by film formation through controlled gelation. Most of the Si-H groups in HSQ tend to decompose into Si-OH groups due to moisture and temperatures exceeding 400°C. [4] Many theories on the issues of HSQ film have been proposed.[5,6] The aerogel films have a dielectric constant of 1.3 to 2.0,[7] and the xerogel films have a dielectric constant of 1.3 to 2.5.[8] These dielectric films show very low dielectric constants due to the high porosity of the internal structure. Nevertheless, these materials easily absorb moisture which increases the dielectric constant. It seems that the procedure of film formation has limited applicability at present. On the other hand, an organic SOG, methylsesquioxane (MSQ), which has a dielectric constant of ~2.7, is available from Allied Signal, Inc., designated as T-18™. It has been developed by increasing the number of the Si-methyl groups which causes the film density to decrease[9] and lower film polarization resulting in a low *k*. In addition, this class of dielectrics, when compared to other organic polymers, appears to have higher resistance to harsh chemicals used in postetch cleaning and chemical mechanical polishing (CMP) processing.[10] Faced with the same issues of organic low *k* materials, however, the quality of MSQ film is degraded by the damage from oxygen plasma and hygroscopic behavior during photoresist stripping.[11] This instability is one of the major problems in using MSQ as a low *k* material.

In this work, we have studied how the N_2O plasma post-treatment can improve the quality of MSQ film. Properties of post-treated MSQ film were evaluated by electrical measurements as well as chemical composition analyses. In addition, the effect of O_2 plasma ashing was investigated to understand the impact of integrated processes on the dielectric film quality.

Experimental

The unpatterned silicon wafers were coated with a single layer of MSQ film, and baked sequentially on a hot plate at 180°C for 2 min and 250°C for 1 min. The resulting wafers were treated by furnace curing at 400°C for 30 min. The as-spun film thickness is about 620 nm. After 250°C baking, the film thickness is reduced to 545 nm. Finally, film thickness is increased to about 565 nm after a curing process. For each condition, film stress, shrinkage, refractive index, and Fourier transform infrared (FTIR) absorption measurements were carried out. In this experiment, two types of samples are prepared. The standard (std) sample was the as-cured MSQ film. Sample A3, sample A6, and sample A9 were the as-cured MSQ films with N_2O plasma post-treatment for 3, 6, and 9 min, respectively. All of the samples were annealed at a temperature range of 400-520°C for investigating the thermal stability of the MSQ film. In addition, the O_2 plasma treatment was applied to all the samples for investigating the impact to the MSQ film during the photoresist stripping. The plasma-enhanced (PE)-CVD chamber was used for various plasma treatments. Each of plasmas was operated at a pressure of 300 mTorr, and with a rf power of 200 W. The flow rate for each of these gases was 300 sccm, and the temperature of chamber was kept at 300°C. Metal insulator semiconductor (MIS) capacitors were manufactured by sputtering aluminum onto all the samples as the top electrode. A Keithley model 82 CV meter was used to measure the dielectric constants of MSQ films. The capacitors were measured at 1 MHz with an ac bias for high frequency C-V curves. Leakage current-voltage (*I-V*) characteristics of MSQ were measured by an HP4145B semiconductor parameter analyzer.

Results and Discussion

Figure 1 shows the Fourier transform infrared (FTIR) spectra of MSQ before and after a series of baking and curing steps. After 180 and 250°C baking, H-OH peak intensities were reduced due to the evaporation of organic solvent. The intensity of Si-O peak signal is decreased, and the Si-O-Si peak intensity is increased. After a 400°C

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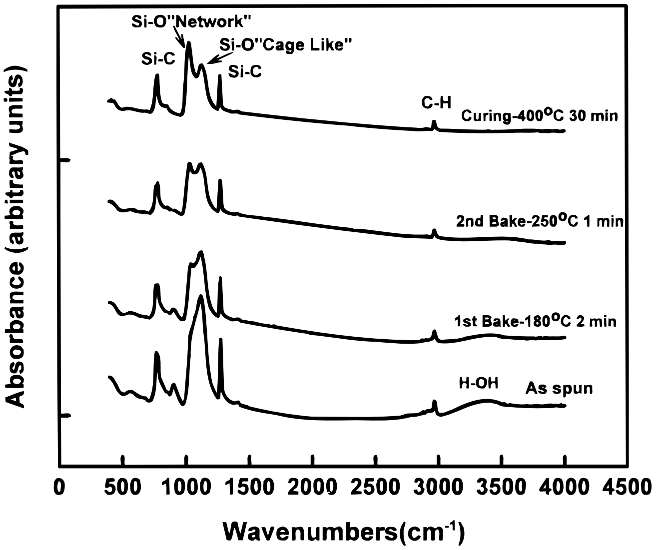

Figure 1. FTIR spectra of MSQ before and after a series of bake and curing steps.

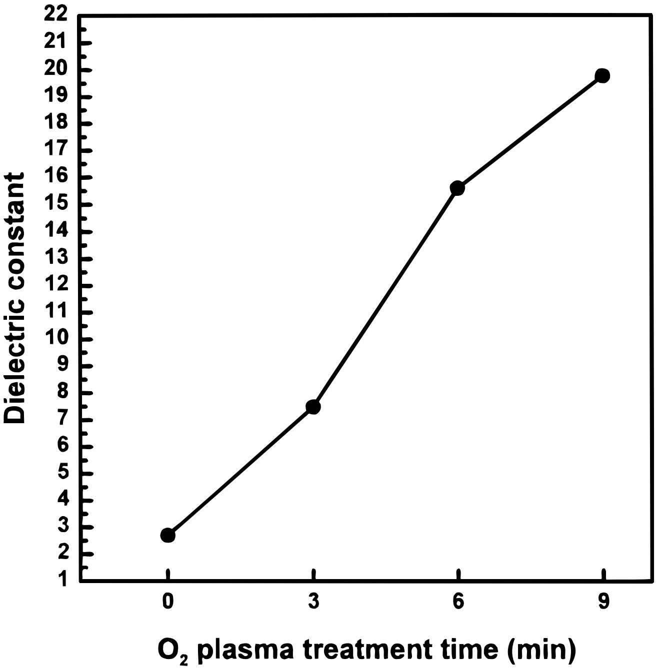

Figure 3. The dielectric constant of sample std with O_2 plasma treatment as a function of the treatment time.

curing, the peak signal of H-OH bonds were totally removed and a sharp significant Si-O-Si peak appeared. It was shown clearly that a large amount of Si-O bonds are cross-linking into Si-O-Si bonds, forming a more porous network structure.[12]

In the integrated processes, photoresist stripping was conventionally implemented by O_2 plasma ashing to remove organic elements. The impact of O_2 plasma on the quality of MSQ film is not negligible. Figure 2 shows the leakage current density of sample std after the O_2 plasma treatment at 300°C for 3 to 9 min. The leakage current dramatically increases with the increasing duration of the O_2 plasma treatment. In addition, the dielectric constant of MSQ largely increases as O_2 plasma time is increased, as shown in Fig. 3. These results are due to the conversion of the Si-CH_3 bonds into Si-OH bonds when O_2 plasma is applied to MSQ. Exposure to the O_2 plasma causes a large amount of the Si-CH_3 bonds to break, leaving a significant amount of dangling bonds in the film. Some of those dangling bonds formed Si-O bonds and others converted into Si-OH bonds. The film will absorb moisture leading to the increased leakage current and high dielectric constant. These results are consistent with Fig. 4, which shows FTIR spectra of sample STD with O_2 plasma treatments. In these spectra, the intensity of the Si-C and C-H bond signals are decreased dramatically and the intensity of the Si-OH bond signals increased when the MSQ was treated by O_2 plasma. The increase in the Si-OH bond signal has two possible

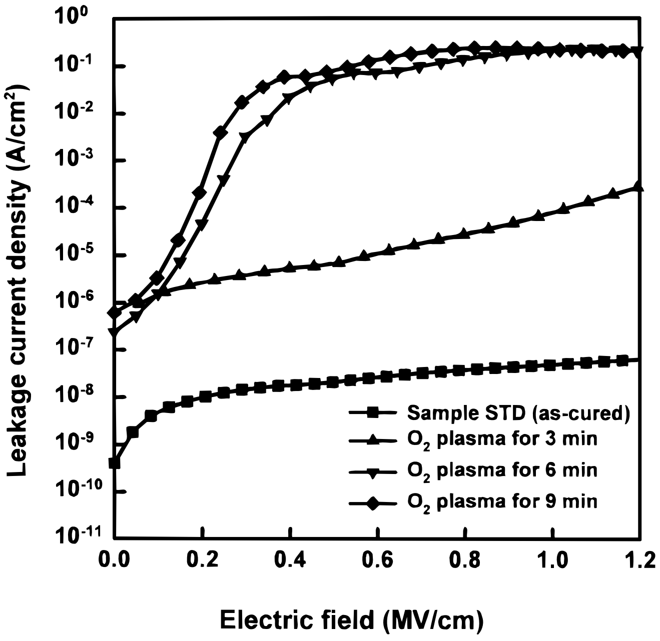

Figure 2. The leakage current density of sample std after the O_2 plasma treatment for 3 to 9 min.

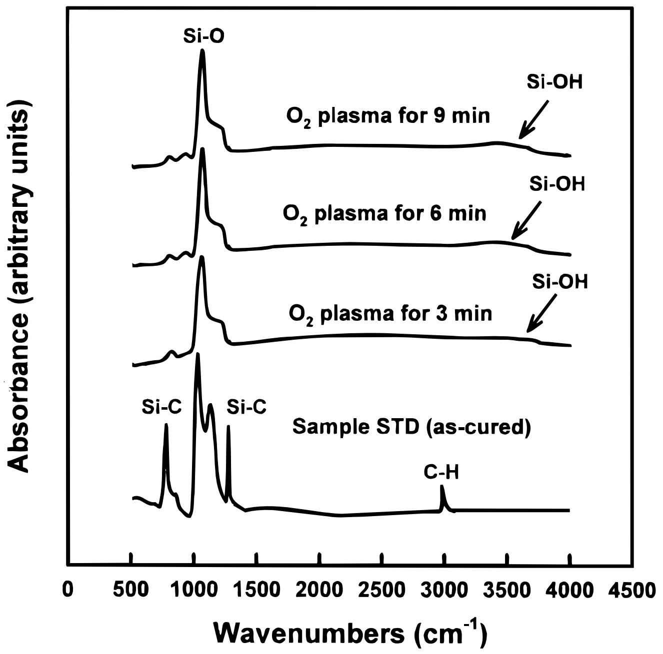

Figure 4. FTIR spectra of sample std with O_2 plasma treatment for 3 to 9 min.

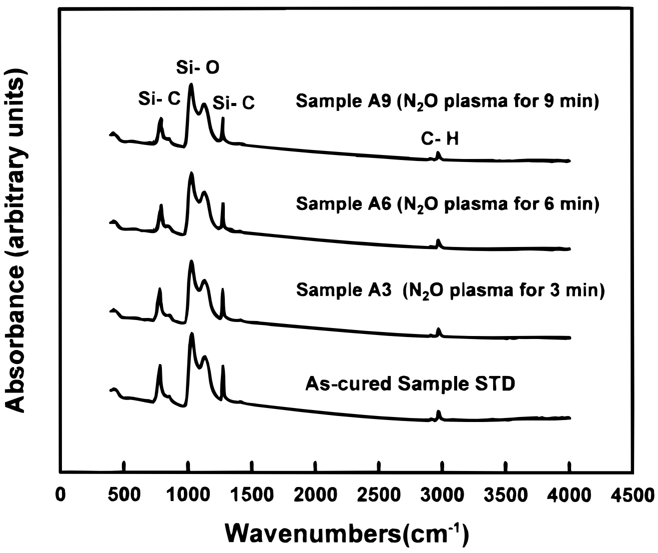

Figure 5. FTIR spectra of sample std, sample A3, sample A6, and sample A9.

causes. One is that when the O_2 plasma breaks Si-CH_3 bonds, MSQ film absorbs O radicals to convert Si-CH_3 bonds into Si-OH bonds for a period of bonding recombination time. The other is that the dangling bonds easily absorb moisture when the sample is exposed to the environment. As a result, the MSQ becomes unstable after O_2 plasma treatment. Both the leakage current and dielectric constant of MSQ will dramatically increase due to moisture absorption and dangling bond formation.

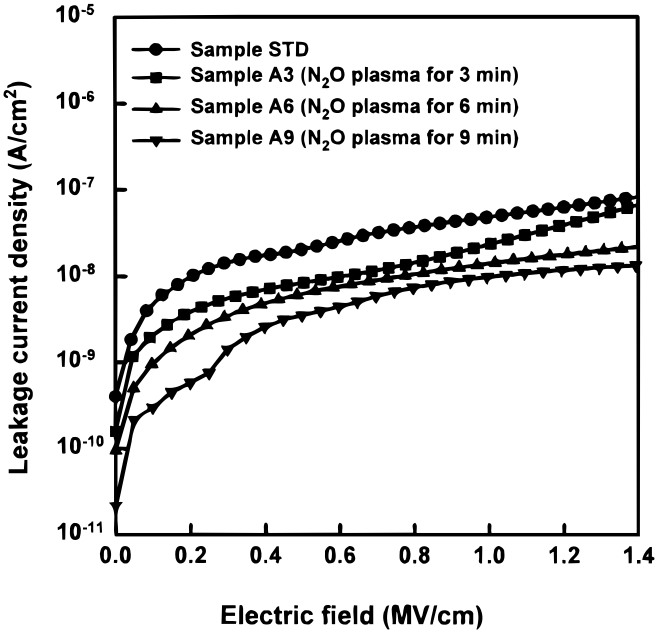

Figure 6. The leakage current density of sample std, sample A3, sample A6, and sample A9.

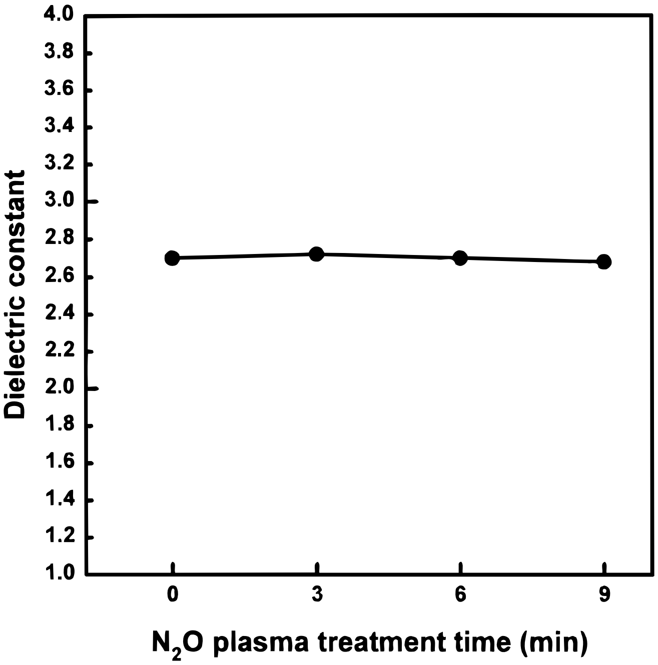

Figure 7. The dielectric constant of MSQ as a function of the N_2O plasma treatment time.

Figure 5 shows the FTIR spectra of MSQ films treated by the N_2O plasma for 3 to 9 min. The signal of Si-OH bonds is not observed. The intensity of Si-C and C-H bonds are slightly decreased, but still maintained at a high level within 9 min. The leakage current of sample std, sample A3, sample A6, and sample A9 are shown in Fig. 6. The leakage current of MSQ film decreases with increasing the N_2O plasma treatment time. Figure 7 shows the dielectric constant of MSQ as a function of the N_2O plasma treatment time. The dielectric constant remains stable (~2.7) for the treatment time from 3 to 9 min. Figure 8 shows both the leakage current density and dielectric constant of sample std, sample A3, sample A6, and sample A9 after annealing at 520°C for 30 min. The leakage current of MSQ film decreases with increasing N_2O plasma treatment time. In addition, the dielectric constant of MSQ film without N_2O plasma-treatment becomes very high (about 5.8) after annealing at 520°C for 30 min. However, the dielectric constant of MSQ film with N_2O plasma-treatment can remain very low. Both the leakage current and dielectric constant of N_2O plasma-treated MSQ film are still acceptable for interlevel dielectric (ILD) applications. Therefore, it clearly shows that the thermal stability of MSQ film can be promoted up to 520°C at least.

To study the resistance of MSQ film using N_2O plasma treatment to O_2 plasma attack, the O_2 plasma treatment is performed for sample std and sample A9. Figure 9 shows the leakage current density and dielectric constants of sample std and sample A9 both of which were treated by O_2 plasma for 3 min. Both the leakage current and dielectric constant of sample A9 are much lower than that of sample std. Figure 10 shows the FTIR spectra of sample std and sample A9 after experiencing O_2 plasma treatment for 3 min. The Si-C and C-H bonds dramatically decrease as well as the Si-OH bond appears in the spectrum of sample std after O_2 plasma treatment. However, the Si-C and C-H bonds of sample A9 still maintain a high level after exposure to O_2 plasma. Meanwhile, Si-OH bonds and H-OH bonds have not appeared in the FTIR of sample A9. Therefore, the N_2O plasma treatment is capable of enhancing the resistance of MSQ film to O_2 plasma attack.

An explanation of the above results is believed to be as follows: during the curing process, bonding destruction and recombination simultaneously occur. In addition, the distorted bonding structure of the MSQ film exhibits many imperfect bonding (*i.e.*, dangling bonds) which will result in unstable film. In our work the content of N_2O plasma can provide some oxygen atoms to break some weaker alkyl group bonding, and then *in situ* nitrogen atoms provide cover for the dangling bonds reducing the number of imperfect bonds and forming an inert passivation layer. Therefore, the instability of film structure bonding will be released, and the thermal stability of MSQ film is promoted. In addition, the inert passivation layer will protect

MSQ film from moisture uptake and oxygen plasma attack during photoresist stripping. Consequently, the resistance of MSQ film to oxygen plasma attack is significantly enhanced.

Conclusions

In this work, the effects of N_2O plasma treatment on MSQ films have been investigated. The quality of low dielectric constant MSQ films is significantly improved by N_2O plasma post-treatment. N_2O plasma converts the surface layer of organic MSQ into an inorganic type by decomposition of the alkyl group and, *in situ*, provides nitrogen to cover the imperfect bonds forming an inert passivation layer. The inert layer can enhance the resistance of MSQ film to moisture uptake and O_2 plasma attack during photoresist stripping. FTIR

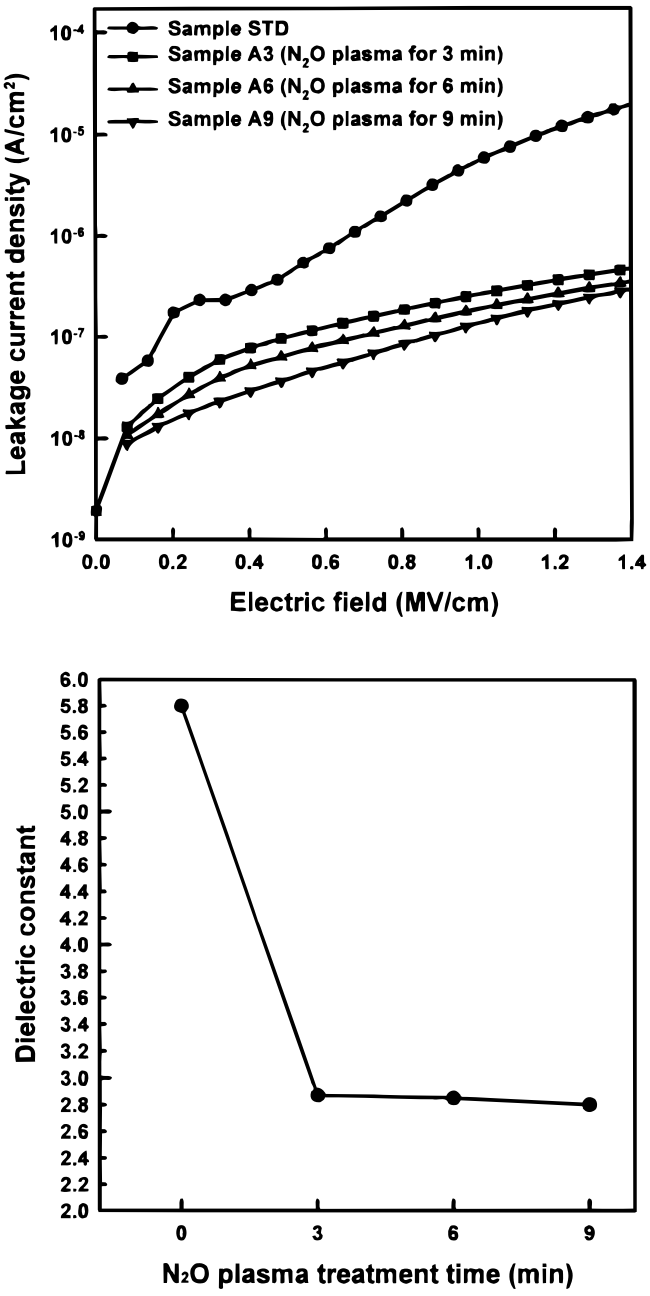

Figure 8. (a, top) The leakage current density of sample std, sample A3, sample A6, and sample A9 after annealing at 520°C for 30 min. (b, bottom) The dielectric constant of sample std, sample A3, sample A6, and sample A9 after annealing at 520°C for 30 min.

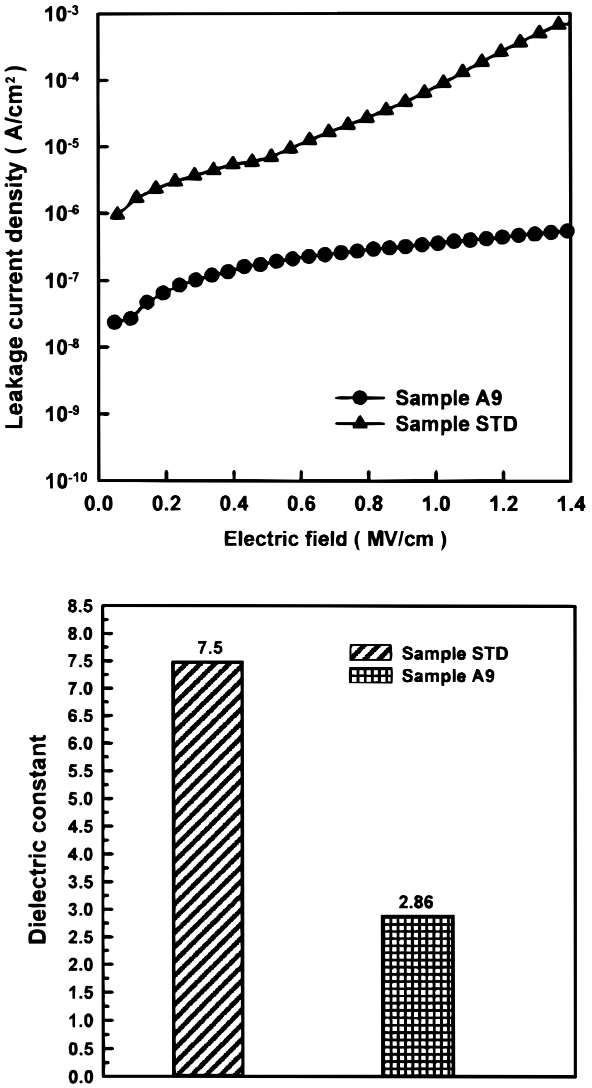

Figure 9. (a, top) The leakage current density of sample std and sample A9 with O_2 plasma treatment for 3 min. (b, bottom) The dielectric constant of sample std and sample A9 with O_2 plasma treatment for 3 min.

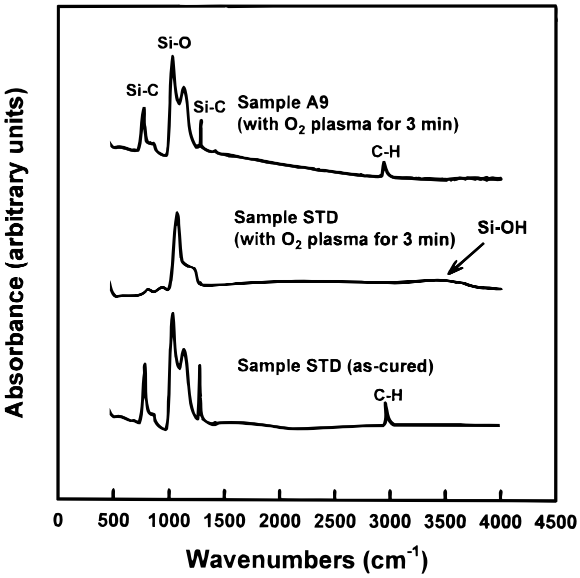

Figure 10. FTIR spectra of sample std and sample A9 with O_2 plasma treatment for 3 min.

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spectra are consistent with this inference. It was found that the signal of Si-OH bond did not appear when N_2O plasma-treated MSQ film was exposed to O_2 plasma ashing. This indicates that the N_2O plasma treatment does enhance the resistance of MSQ film to O_2 plasma attack during the photoresist stripping.

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