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A Novel Pretreatment Technology for Organic Low-Dielectric Material to Suppress Copper Diffusion and Improve Ashing Resistance

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A new novel pretreatment technology for integration of organic low-dielectric material in copper interconnects for ultralarge scale integration applications is developed. Using NH_3 plasma treatment, two extremely important advantages were achieved in spin-on organic polymer (SOP), including the reduction of copper diffusion and the improvement of ashing resistance. A copper/SOP/Si capacitor structure is used to study the electrical characteristics of SOP film after ashing treatment or postanneal. Higher barrier capability and better ashing resistance can be achieved by the SOP layer after NH_3 plasma treatment. After annealing at 500°C for 60 min, secondary ion mass spectroscopy depths profile shows that the Cu atoms do not penetrate into the SOP when they are pretreated by NH_3 plasma. Furthermore after the ashing step, the carbon atoms in the SOP film almost remain the same when they are pretreated by NH_3 plasma. On the other hand, the concentration of carbon in as-cured SOP is no longer seen. The reason of improving ashing resistance and better barrier capability was due to the organic polymer film rearranging to form a carbon-containing silicon nitride film.

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There are many techniques for achieving low dielectric materials. These materials can be deposited on the substrate either by spin-on or by chemical vapor deposition (CVD). Spin-on materials have several advantages different from those of CVDs, such as better gap filling capability, better planarization, lower cost, and easier use. The most studied low-*k* materials are fluorinated SiO_2 and inorganic spin-on-glass (SOG). Fluorinated SiO_2 has a dielectric constant of 3.1, but it does not meet the need of subquarter micrometer technologies. Inorganic SOG contains much silanol (Si-OH), and tends to crack due to large shrinkage during curing steps.[1,2] The organic SOP results in several beneficial film properties, *e.g.*, low dielectric constant, decreased silanol content low moisture absorption, increased crack resistance, and excellent planarization.

Currently, Cu and spin-on organic polymer (SOP) are the leading candidates for metal and dielectric materials. Device integration with lower dielectric constant material and lower resistance Cu film is capable of improving its performance and reducing the interconnection delay.[3-5] The major drawback of the next generation of Cu interconnects is the fast diffusion speed in the traditional oxide layer and in the low dielectric constant materials.[6,7] A thin barrier metal is inserted between the Cu and the dielectric layer, which is a conventional method for blocking Cu diffusion. This barrier metal-free structure[6,8,9] for SiON interlevel dielectrics has been proved to be an effective block for Cu diffusion and reduction of resistance-capacitance (RC) delay time. The other problem with organic SOP materials is the oxygen plasma stripping photoresist process,[10,11] which causes significant damage to organic low dielectric material, thus limiting its interlevel dielectric application. NH_3 plasma treatment can effectively improve the barrier effect against Cu and the ashing resistance at the same time. This method brought many good results with the exception of a little higher dielectric constant and leakage current than as-cured samples.

In this study, a carbon-containing silicon nitride was achieved by NH_3 plasma exposed to organic SOP film. This layer has shown a much greater improvement in the barrier effect and in ashing resistance.

Experimental

The organic SOP (Allied Signals X-720) was spun on (100) 4-7 Ω cm p-type Si wafers. It is based on methyl(CH_3) phenyl(C_6H_5) silsesquioxane. The thickness of SOP is approximate 200 nm after curing at 400°C for 60 min. The process steps used in this study are

1. A 200 nm SOP was spun on Si substrate.
2. SOP was treated with NH_3 plasma by plasma-enhanced chemical vapor deposition (PECVD) technique. The substrate temperature is 300°C, the pressure is 40 Pa, the flow rate of both NH_3 and H_2 is 300 sccm, and the rf power is 300 W.
3. The ashing treatment was performed by a barrel reactor asher with oxygen plasma. The pressure is 0.5 Torr, the rf power is 100 W, the rf frequency is 13.56 MHz, and the exposure time is 10 min.
4. The Cu film of 200 nm was deposited on the different samples by sputter and then formed an metal insulator semiconductor (MIS) capacitor structure.

Several different measurement techniques were used to measure the as-deposited and annealed samples. Fourier transform infrared (FTIR) spectroscopy was used to help us understand the molecular structure of material. The atomic concentrations of Cu ion in the SOP film were examined by secondary ion mass spectrometry (SIMS). The percentage of nitrogen in SOP was measured by X-ray photoelectron spectroscopy (XPS) technique. The dielectric constant was calculated from the capacitance-voltage (C-V) plots using MIS structure. The leakage current was measured by precision semiconductor parameter analyzer (HP 4156A).

Results and Discussion

Figure 1 shows the FTIR spectra of SOP after different curing temperatures. When cured above 500°C, the spectra indicate that the peaks of organic groups such as Si-CH_3 and Si-C_6H_5 get lower with increasing temperature and even disappear at 700°C. The organic groups started to be decomposed at 500~600°C,[12,13] curing at 400°C seems not to cause a change of Si-C content in the SOG film. This figure also indicates that the cage-like structure starts converting to network structure at 600°C, and it shows a near-stoichiometric SiO_2 after curing at 700°C for 1 h. The low dielectric constant properties are related to the cage-like structure in the SOP film and disappear after annealing at high temperatures. Figure 2 shows that the thickness of the SOP film started to shrink significantly after curing at 600°C for 1 h. This is consistent with the organic group that started to decompose in the temperature range of 500~600°C as shown in Fig. 1. The shrinkage of X-720 SOP is very small when anneals are below 500°C, which implies that this organic SOP has the advantages of better planarization and higher cracking resistance.

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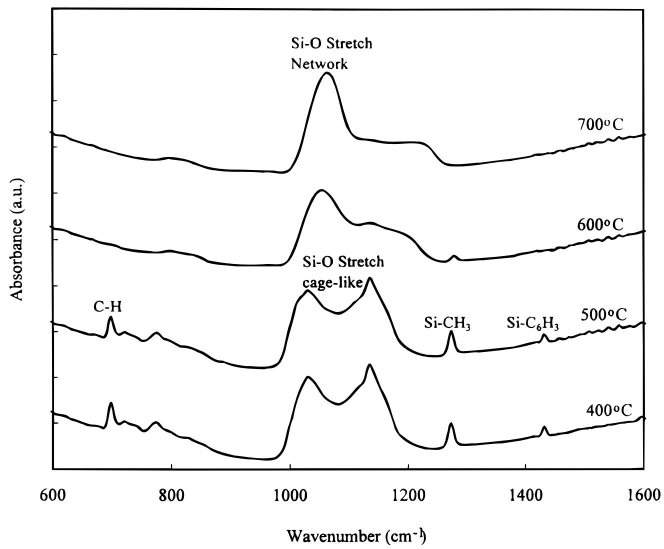

Figure 1. FTIR spectra of the cured SOP after thermal treatment at different temperatures for 1 h.

In the integrated circuit process, photoresist stripping (ashing) by using oxygen plasma is inevitable. Organic SOP will suffer rapid oxidation during the ashing step. Furthermore, the carbon content in the organic SOP will be removed. Figure 3a shows the FTIR spectra of the as-cured MSQ film after ashing for different times. The organic groups in this film gradually disappeared with increasing ashing time. The disappearance of cage-like structure correlated well with the shrinking of film thickness and the increase of dielectric constant. The silanol (Si-OH) peak was also present at 928 cm^{-1} which implied an increase in the absorption of moisture in the SOP film. The presence of silanol and water was undesirable and would cause reliability problems, such as poisoning via hot carrier degradation. Figure 3b shows that the FTIR spectra of the H_2 plasma pretreatment sample reveal the same results as the as-cured one. The organic group in the SOP film also decomposed after the ashing step. This indicated that the H_2 plasma do not improve the characteristics of ashing resistance. In Fig. 3c, however, the organic SOP can effectively increase the ashing resistance of the SOP after an NH_3 plasma treatment for 10 min. The spectra of organic SOP remain unchanged after an ashing treatment for 10 min.

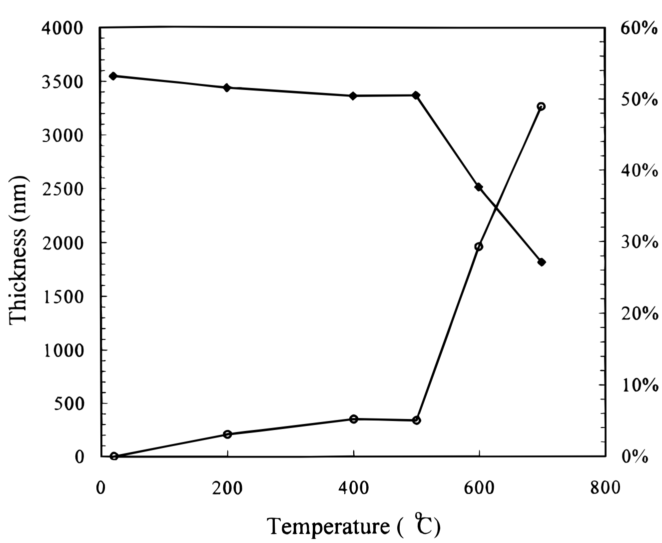

Figure 2. The thickness variation of SOP film after annealing at different temperatures for 1 h.

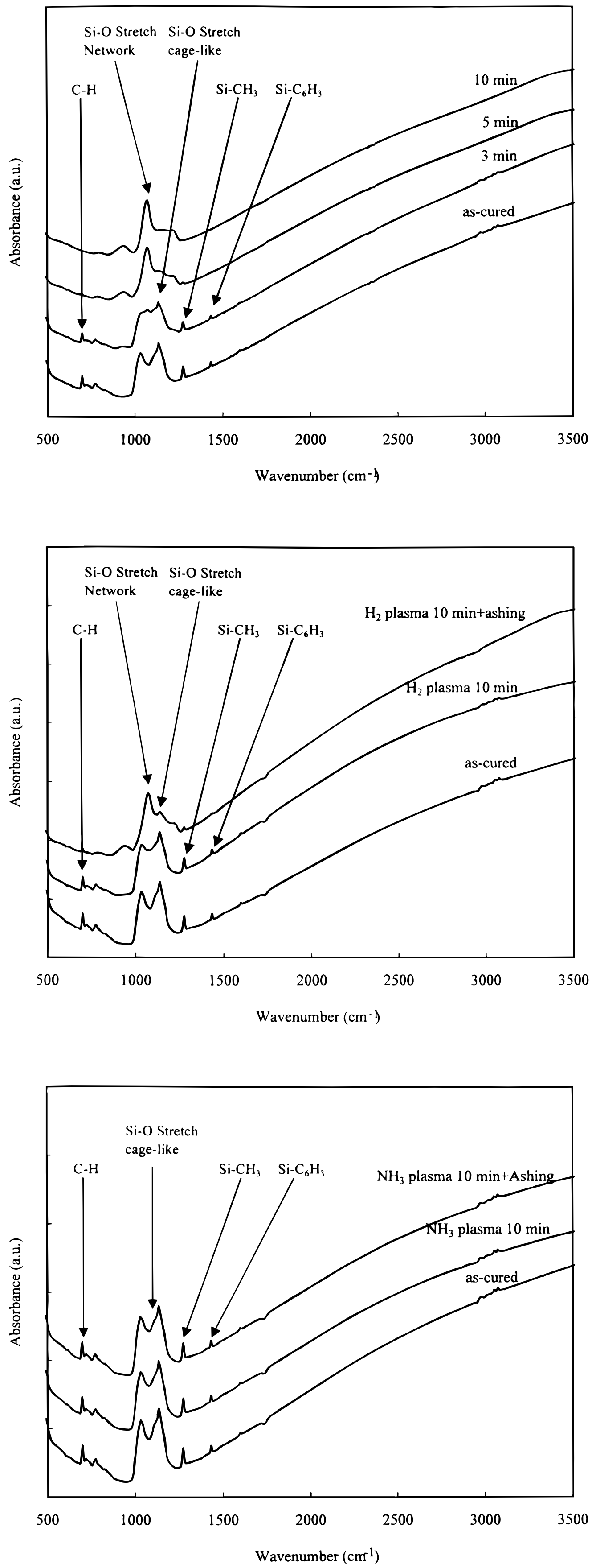

Figure 3. FTIR spectra of (a, top) as-cured SOP after ashing for different times, (b, middle) NH_3 plasma pretreated SOP after ashing for 10 min, (c, bottom) H_2 plasma pretreated SOP after ashing for 10 min.

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Figure 4 shows the X-ray photoemission spectroscopy (XPS) spectra of carbon in organic SOP film under different conditions before and after ashing treatments. The carbon peak of C_{1S} at 284.8 eV is not found in the XPS spectra of the as-cured and H_2 plasma treated samples. It coincides with those of the organic groups removed during the ashing step as shown in Fig. 3a and b. After NH_3 plasma treatment, the carbon content almost remains unchanged, and a new peak of N_{1S} was observed at 400 eV. The incorporation of nitrogen atoms increases with increasing exposure time. The N_{1S} peak implies that a nitride layer of SiCON is formed after NH_3 plasma treatment. This nitride layer plays a major role in improving the ashing resistance.

The formation of nitride film also improves the electrical characteristics of SOP. Figure 5a shows the leakage current density of the as-cured MIS capacitors. It shows a three orders increase in leakage current after the ashing step. Comparing the H_2 and NH_3 plasma-treated samples, in Fig. 5b and c, the sample with pretreated SOP by H_2 plasma shows an increase of leakage current, which is smaller than that of the SOP layer after NH_3 plasma treatment. However, the leakage current of the NH_3-plasma treated sample after ashing plasma exposure is better than the others. Although the sample of SOP after NH_3 plasma treatment reveals a little higher leakage current and dielectric constant than that of SOP after H_2 plasma treatment, the NH_3 plasma can effectively improve the ability of resisting the ashing oxygen plasma. After the ashing step, the NH_3 pretreated sample had a one order lower leakage current than that of the H_2 plasma-treated sample. Figure 5c also demonstrates that only the sample with 20 min NH_3 plasma pretreatment shows no leakage current degradation after the ashing step. The dielectric constant of this sample is 2.85. However, more plasma exposure time results in a higher dielectric constant and higher leakage current. Even though the ashing step causes more damage on the surface of the NH_3 plasma sample pretreated for 10 min, the 20 min NH_3 plasma pretreated sample shows the same leakage current level after the ashing step. Thus, the sample of pretreated by NH_3 plasma for 10 min demonstrated better characteristics than the others. Therefore, we chose this condition to study its characteristics further.

After annealing at 350 and 400°C for 60 min, as shown in Fig. 6, we compare the leakage current density of Cu/as-cured SOP/Si structure with the Cu/SOP/Si structure in which SOP film was exposed in NH_3 plasma for 10 min. This figure shows that the SOP after NH_3 plasma treatment has a lower leakage current than the others. This phenomenon implies that the formation of nitride film can effectively improve the barrier effect against Cu diffusion. Moreover, after annealing at 350°C for 60 min, the NH_3 plasma-treated SOP sample shows a lower leakage current than the as-treated one. This is due to fact that the damage in SOP is annealed-out after the annealing treat-

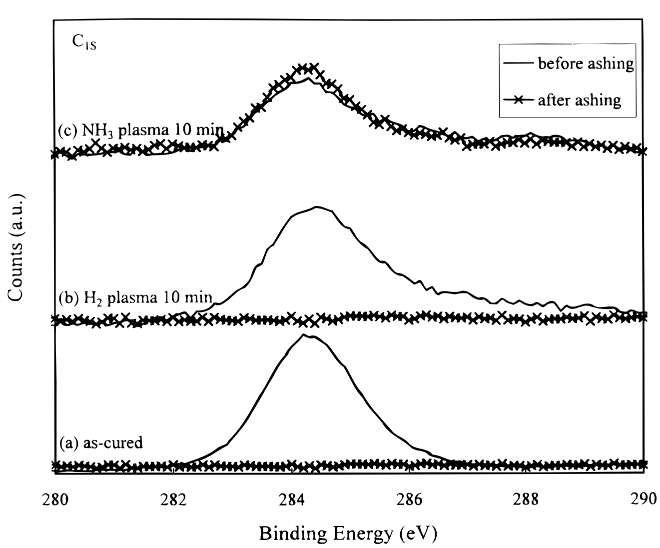

Figure 4. C_{1S} XPS spectra of (a) as-cured SOP, (b) H_2 plasma pretreated SOP, and (c) NH_3 plasma pretreated SOP before and after ashing treatments.

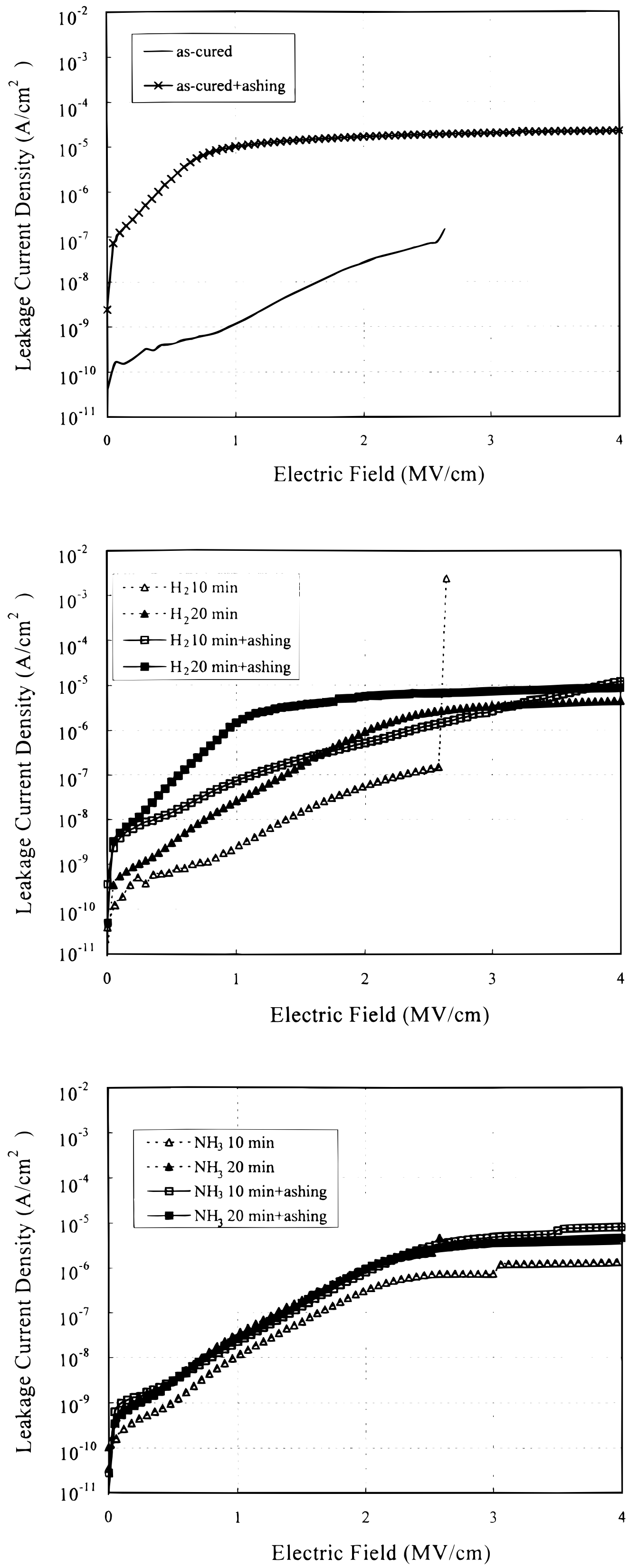

Figure 5. Comparing the leakage current density of (a, top) as-cured SOP, (b, middle) H_2 plasma pretreated SOP, and (c, bottom) NH_3 plasma pretreated SOP before and after ashing treatments.

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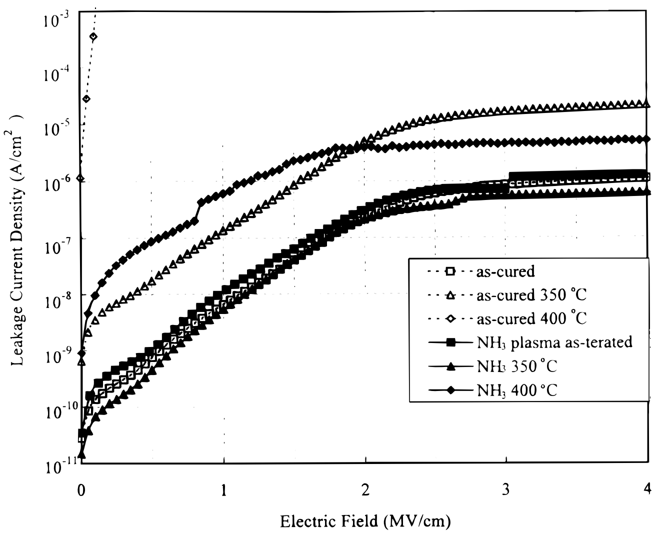

Figure 6. The leakage current density of as-cured SOP and NH_3 plasma pretreated SOP samples after annealing at 350 and 400°C for 1 h.

ment. Figure 7 compares the Cu depth profile of the as-cured SOP and NH_3 treatment SOP after annealing at 400°C for 1 h. The results show an obvious improvement after NH_3 treatment. Comparing samples with differently treated conditions above, only the sample with NH_3 plasma treatment successfully blocks the Cu diffusion.

Figures 8a and b indicate the electrical breakdown field (E_{BD}) distributions of the as-cured samples and NH_3 plasma-treated samples after annealing at various temperatures, respectively. The SOP layer shows a great improvement of breakdown voltage after the NH_3 plasma treatment. In Fig. 8a, the as-cured SOP sample shows a significant degradation in breakdown field after postannealing at 350°C for 60 min. We suggested that the degradation of breakdown field was due to Cu atoms diffusing into SOP film through thermal excitement. In the case of the samples treated by NH_3 plasma, it shows an improvement in electrical breakdown field after postannealing at 350°C. The difference between the as-cured and the NH_3-treated samples is a layer of carbon-containing silicon nitride film on the surface of SOP after the NH_3 plasma treatment. It is very clear that the higher breakdown field is attributed to the SOP film which becomes denser and damage in the SOP film was annealed out after postannealing.

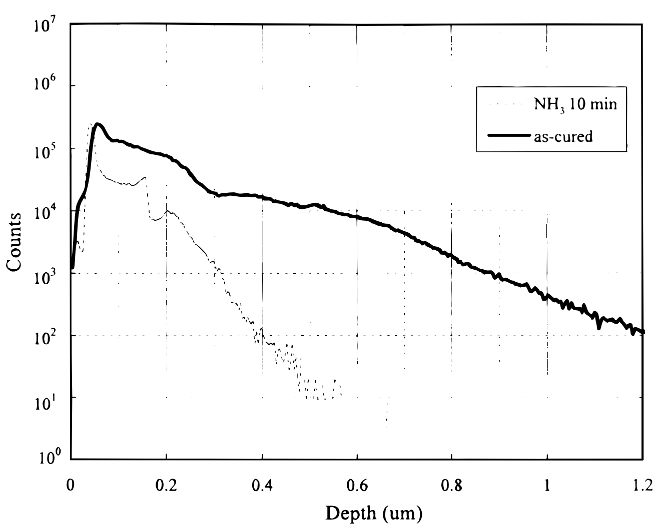

Figure 7. Comparing the Cu depth profiles of as-cured and NH_3 plasma pretreated SOP samples after annealing at 400°C for 1 h.

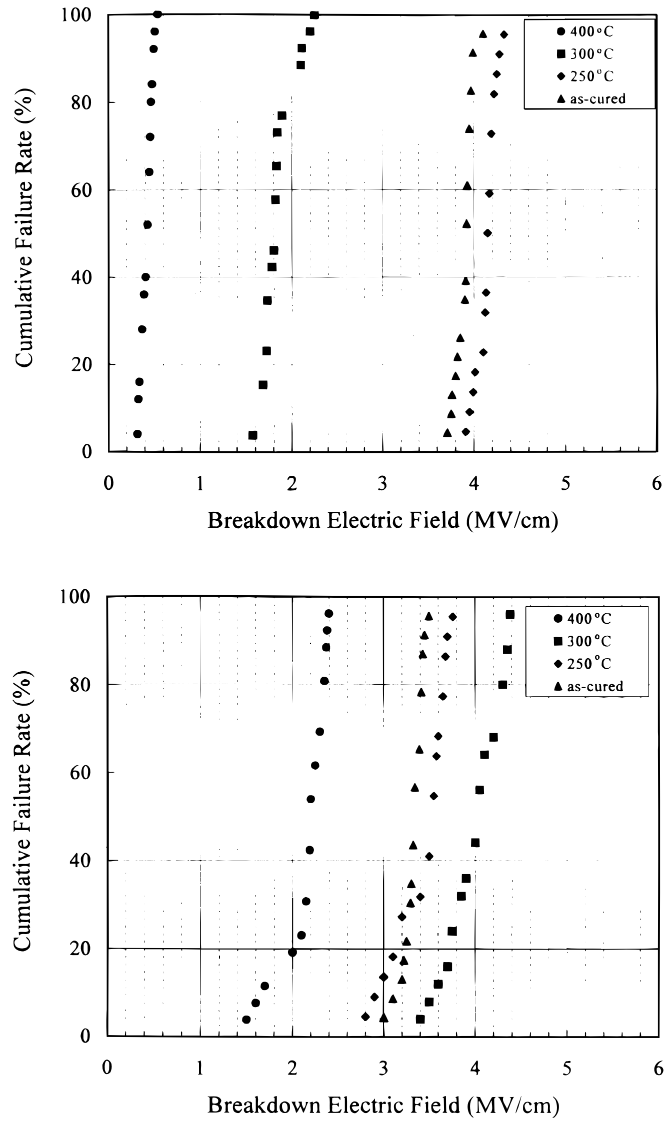

Figure 8. Weibull plot of electrical breakdown field (E_{BD}) distributions for (a, top) as-cured SOP, (b, bottom) NH_3 plasma pretreated SOP as capacitor dielectric layers after different thermal treatment conditions.

Figure 9 shows the influence of the time to failure (TTF) of Si/SOP/Cu capacitors that can be used as indicators of barrier quality. The effect of the electric field on copper transport is also shown for different samples when the temperature was measured at 150°C. In this figure of the TTF stress of SOP, it was found that the sample after NH_3 plasma treatment showed much greater improvement than the as-cured sample. Even if we applied four times the electric field to the NH_3 plasma sample, it still showed about four times longer TTF time than the as-cured sample. The NH_3 plasma-treated sample shows a "self-healing" phenomena (the leakage current spikes up and down) which are sometimes observed in TTF testing. These phenomena are due to nonuniform diffusion of copper.[14] Based on these measured data, the NH_3 plasma treatment is an excellent method for improving the quality of SOP.

Conclusion

The NH_3 and H_2 plasma treatments were studied to improve the quality of carbon containing organic low dielectric materials (*e.g.*, X-720), a spin-on low-*k* material. The NH_3 plasma treatment provides an efficient method for improving the ashing resistance and the blocking of Cu diffusion. On the other hand, this film does not achieve any notable improvement after it is treated by H_2 plasma. The X-720 film also shows a small thickness shrinkage after the cur-

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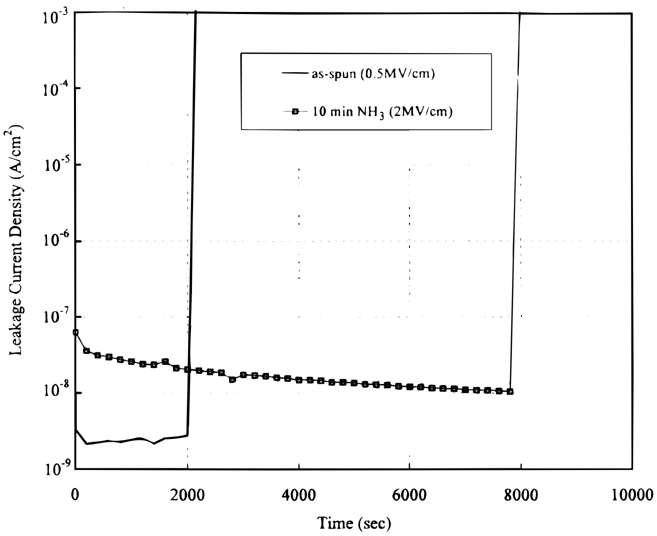

Figure 9. Influence of time to failure of Si/SOP/Cu capacitors after NH_3 plasma pretreatment for 10 min.

ing step. From the electrical measurements and SIMS and XPS analyses, we found that the characteristics of X-720 demonstrated a dramatic improvement after NH_3 plasma treatment. These improvements are due to a nitride film formed after the NH_3 plasma treatment. From the experimental results, the NH_3 plasma treatment is an excellent approach for improving the characteristics of X-720.

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