Chapter 5

Electrical and Physical Characteristics Improvement of Low-K Dielectric by NH3 Plasma Pre-treatment

5.1 Introduction

In wireless communication applications, the operation speed of the active devices could be dominant items, which limited the circuit capability. With the enlarging complex of the integrated circuit, longer interconnection lines associated with larger parasitic capacitance could be created and this could become another speed limiting issue in SOC design. As the length of metal interconnect increases and the distance between two interconnect wiring decreases, the performance of ULSI circuits is increasingly limited by the resistance of interconnects and the capacitance of layer-to-layer and line-to-line. The multiplication of resistance and capacitance (RC delay), AC power (CV^2f), and cross talk are increasingly serious as IC technology scaling down [1-5].

Recently, spin-on low dielectric constant (low-k) materials are considered as candidates for the next generation of interlevel dielectric (ILD) and intermetal dielectric (IMD) films in the interconnect structure of integrated circuits. However, the dielectric constant of spin-on low-k materials was inversely related to the thermal stability. In the privous report [6,7], the organic groups start to be decomposed at the temperature of 500℃. The other problem is a serious degradation occurrence caused by O_2 plasma-treated to spin-on organic low-k film [8,9], which is a conventional photoresist stripping method. These problems will harm the device characteristics during post process steps, specially, in the Cu metallization. The degradation and the transport of copper is through its oxidation and diffusion/migration of ions by thermal excited, that means a significant increase in leakage current). Typically, Cu interconnects need a layer of refractory metal as a diffusion barrier layer around them to prevent its diffusion into the interlayer dielectric [10-12]. However, the interconnects with barrier metal around them shows higher RC delay time [3-5]. In lowering device RC delay time, a novel barrier metal-free structure was suggested [10,11,13].

In order to prevent the degradation of ashing damage and of Cu diffusion, before copper film deposition, a pre-treatment (e.g. plasma treatment and ion implantation) is needed to improve the characteristics (including leakage current density, breakdown field and barrier effect etc.) of spin-on low-k materials. In this work, we have successfully investigated a pre-treatment of NH_3 plasma to spin-on low-k films, and then an oxynitride layer was formed on the surface of spin-on low-k dielectric films. This oxynitride film own an excellent barrier capability against ashing plasma damage and Cu diffusion. So this dielectric layer did not need a barrier metal for the prevention of Cu diffusion. A barrier metal-free structure was formed by using NH_3 plasma-treated dielectric layer in the Cu metallization.

5.2 Experiments

The X-720, based on methyl(CH_3) phenyl(C_6H_5) silsesquioxane, was spun on (100) 4-7 Ω-cm p-type Si wafers with a thickness, which is about 200 nm after curing at 400℃ for 60 min. After curing step, X-720 film was treated with a NH_3 or H_2 plasma by plasma enhanced chemical vapor deposition (PECVD) technique. The substrate temperature was 300℃, the pressure was 40 Pa, the flow rate for NH_3 or H_2 was 300 sccm respectively, and the RF power was 300 W. Finally, the Cu film of 200 nm was deposited on the different samples by sputtering and then formed a MOS capacitor structure.

Several different measurement techniques were used to measure the various properties of all as-deposited and annealed samples. Fourier transform infrared (FTIR) spectra can help us understand the molecular structure of material. The percentage of nitrogen concentration in X-720 film was measured by x-ray photoelectron spectroscopy (XPS) technique. Dielectric constant was calculated from capacitance-voltage (C-V) plots using MIS structure. The leakage current was measured by precision semiconductor parameter analyzer (HP 4156A).

5.3 Results and Discussions

O_2 plasma treatment is a conventional method to remove organic photoresist after dry or wet etching. However, the curve (b) in Fig. 5.1 demonstrated that the low dielectric materials become to absorb moisture (Si-OH bonds was observed) after O_2 plasma treatment. H_2 and NH_3 plasma treatment were used to attempted to resolve this problem during ashing step. However, only the NH_3 plasma-treated low-k film, curve (d) in Fig. 5.1, did not detect any moisture absorption after O_2 plasma ashing for 10 min. We found that the low-k materials have excellent capability against O_2 plasma damage when given a pre-treatment to low-k materials. In this figure, we also found that the organic groups of as-cured sample and H_2 plasma-treated sample were decomposed after ashing step, i.e. loss the properties of low-k material. After O_2 plasma treatment for 10 min, only NH_3 plasma-treated sample remains the same spectra.

Figure 5.2 shows the comparison of the thickness and dielectric constant variation of different samples after ashing treatment for 10 min. In this figure, a 50% shrinkage in the thickness of as-cured low-k film was observed after exposed in ashing plasma for 10 min. The decrease in low-k film is inverse proportion to the O_2 plasma exposure time. The large shrinkage of the film is due to rapid oxidation in ashing step. The dielectric constant of as-cured sample shows large increase after ashing step. We suggested that the increase in dielectric constant is due to the generation of silanol (Si-OH) and the degradation of film's properties during oxygen plasma treatment (as shown in Fig. 5.1). The thickness of film after NH_3 plasma treatment almost keeps the same (less than 1%) after ashing step. Obviously, a great improvement in the shrinkage resistance is obtained after giving a NH_3 plasma pre-treatment to the low-k film. We believe that the NH_3 plasma causes a thin nitride film on the surface of low-k film, which can resist oxygen plasma damage.

XPS spectrum of low-k film reveals a new N_{1S} peak at 400 eV after NH_3 plasma treatment for 10 min as shown in Fig. 5.3. The incorporation of nitrogen atoms increases with the increase of the exposure time. It implies that the nitrogen atoms are doped into low-k film and formed a carbon-contained SiO_XN_Y layer by NH_3 plasma treatment. Figure 5.4 shows the enlarged XPS spectra of C_{1S} peak in different conditions before and after ashing treatments. In Fig. 5.4 (a), we found a strong peak of C_{1S} at 284.8 eV and a weak one at higher binding energy (288 eV). This weak peak of C_{1S} may be attributed to the electron transference which is from nitrogen to carbon atoms. In other word, this carbon-contained SiO_XN_Y layer (about $20\overset{o}{A}$ thick) should act as a passive diffusion barrier[14,15]. This layer can cause a significant improvement in the ashing resistance. After ashing treatment for 10 min, as shown in Fig. 5.4 (b), the carbon peak of C_{1S} at 284.8 eV is not found in the XPS spectra of the as-cured and the H_2 plasma-treated samples, i.e. organic groups were removed during the ashing step. NH_3 plasma-treated low-k film shows the carbon content almost remains unchanged. It proved that the passivation layer of carbon-contained silicon nitride film prevented the occurrence of damage in the O_2 plasma.

Figure 5.5 (a) shows the different X-720 films before and after ashing treatment. Figure 5.5 (b) shows the sample of as-cured X-720 film after ashing treatment for 10 min. The seam between two metal lines was observed everywhere. It coincided with the shrinkage of as-cured X-720 film after ashing step, as shown in Fig. 5.2. The seams imply that the organic content in the X-720 film was removed by oxygen plasma ashing. On the other hand, the NH_3 plasma-treated film did not cause any significant changes in the properties of X-720 film. In the figure 5.5 (c), we did not observe any seam between two metal lines. This phenomenon proves that the NH_3

plasma treatment provides an efficient method to improve the quality of carbon-contained organic low dielectric materials.

An MIS structure was used to judge the leakage current density of X-720 film, as shown in Fig. 5.6. The as-cured sample reveals 3-4 orders degradation in leakage current after ashing treatment. This significant degradation is due to the organic groups of X-720 film is removed during oxygen plasma in ashing step. H_2 and NH_3 plasma was used to attempte to improve the resistance against oxygen plasma degradation. However, the H_2 plasma-treated film did not show sufficient improvement in ashing resistance. Though giving H_2 plasma treatment to X-720 film for 10 min, it still shows 2-3 orders degradation in leakage current after ashing step. In the case of NH_3 plasma-treated sample, it only shows 1-2 order increase in leakage current after ashing treatment for 10 min. Figure 5.6 indeed demonstrated that the NH_3 plasma treatment can effectively improve the ability of resisting the ashing oxygen plasma during the photoresist stripping step.

After annealing at 350℃ and 400℃ for 60 min, as shown in Fig. 5.7, we compared the leakage current density of Cu/as-cured X-720/Si structure with the Cu/X-720/Si structure which X-720 film was exposed in NH_3 plasma for 10 min. An excess advantage of blocking Cu diffusion in low-k materials was also achieved after NH_3 plasma pre-treatment. Some authors [16] proved that the low-k film showed lower leakage current after H_2 plasma pre-treatment in Al electrode capacitor. However, the H_2 plasma-treated film also did not achieve sufficient improvement in Cu electrode capacitor (not show here). X-720 film after NH_3 plasma treatment, as shown in Fig. 5.7 (b), again shows lower leakage current than the others. This phenomenon is also due to nitride film on the surface of X-720 after NH_3 plasma treatment, which can effectively improve the barrier effect against Cu diffusion.

Figure 5.8 shows the weibull plot of electrical breakdown field distributions for X-720 film as the dielectric layer in MIS capacitors. This figure reveals that the X-720 film after NH_3 plasma treatment has better electrical breakdown field distributions. The as-cured X-720 sample shows a serious degradation of breakdown after post-annealing at 350℃ for 60 min. This degradation was due to Cu atoms diffusing into X-720 film through thermal excitement. On the other hand, the NH_3 plasma-treated X-720 film reveals a significant improvement even after post-annealing at 350℃ for 60 min. It implies that nitride film on the surface of X-720 film can effectively improve the barrier effect against Cu diffusion. The prior results show an obvious improvement in the characteristics of X-720 film after NH_3 treatment.

5.4 Conclusion

NH_3 plasma treatment provides an efficient method to improve the quality of carbon-contained organic low dielectric materials, e.g., X-720, a spin-on low-k material. From the electrical characteristics, FTIR and XPS analyses, we have found that X-720 demonstrated a great improvement of blocking Cu diffusion and of ashing resistance after NH_3 plasma treatment. It is due to a carbon-contained silicon oxynitride film was formed on the surface of X-720 film, and the function of this layer acts as a passive diffusion barrier. Although the NH_3 plasma-treated sample reveals great improvement in the properties of ashing resistance and blocking Cu diffusion, it still need further improvement in the barrier characteristics against Cu diffusion at higher annealing temperatures. The further study, improving the barrier effect against Cu without changing its dielectric constant, is going.

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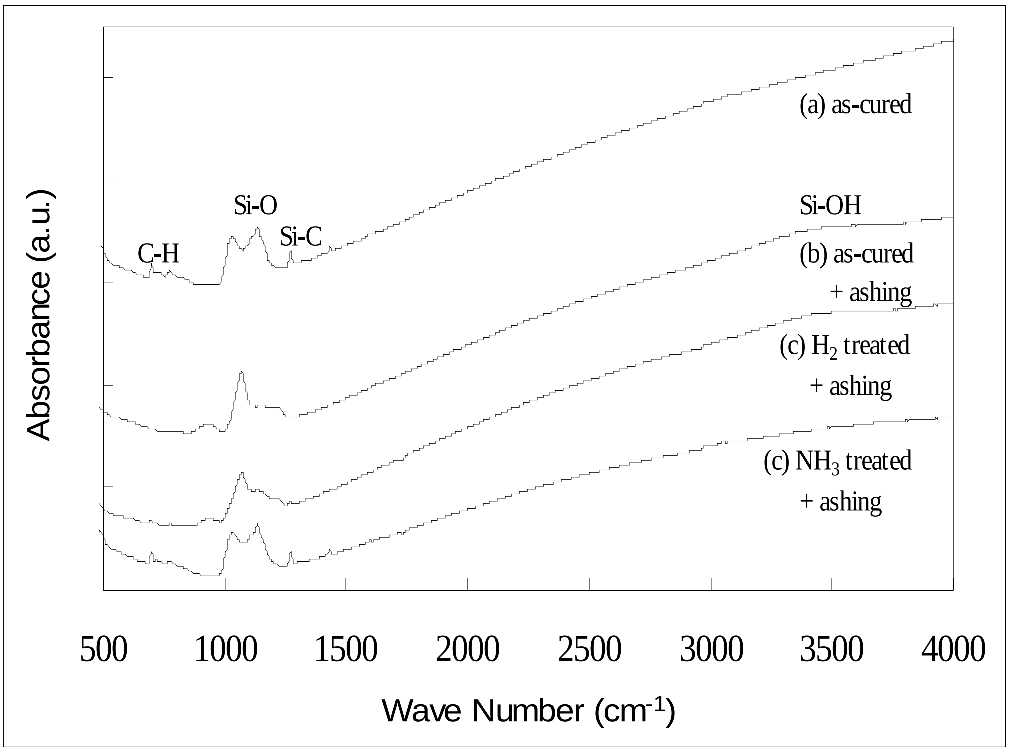
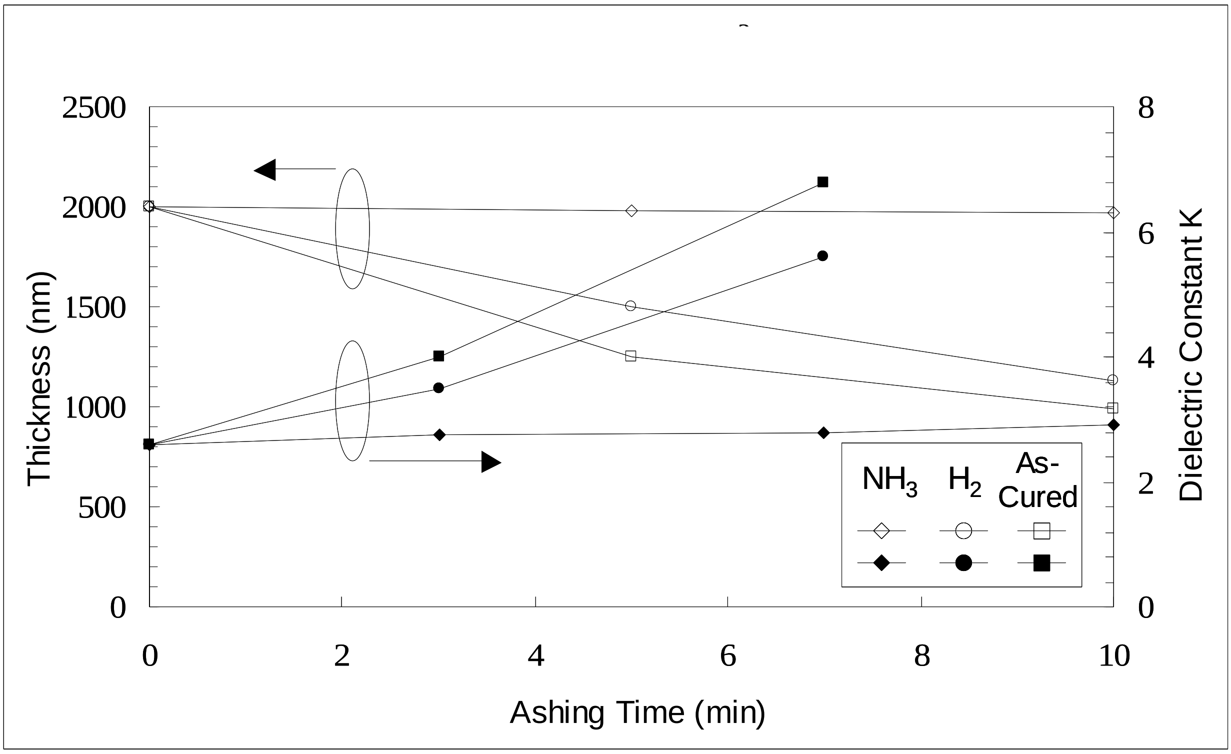
Figures and Tables in Chapter 5



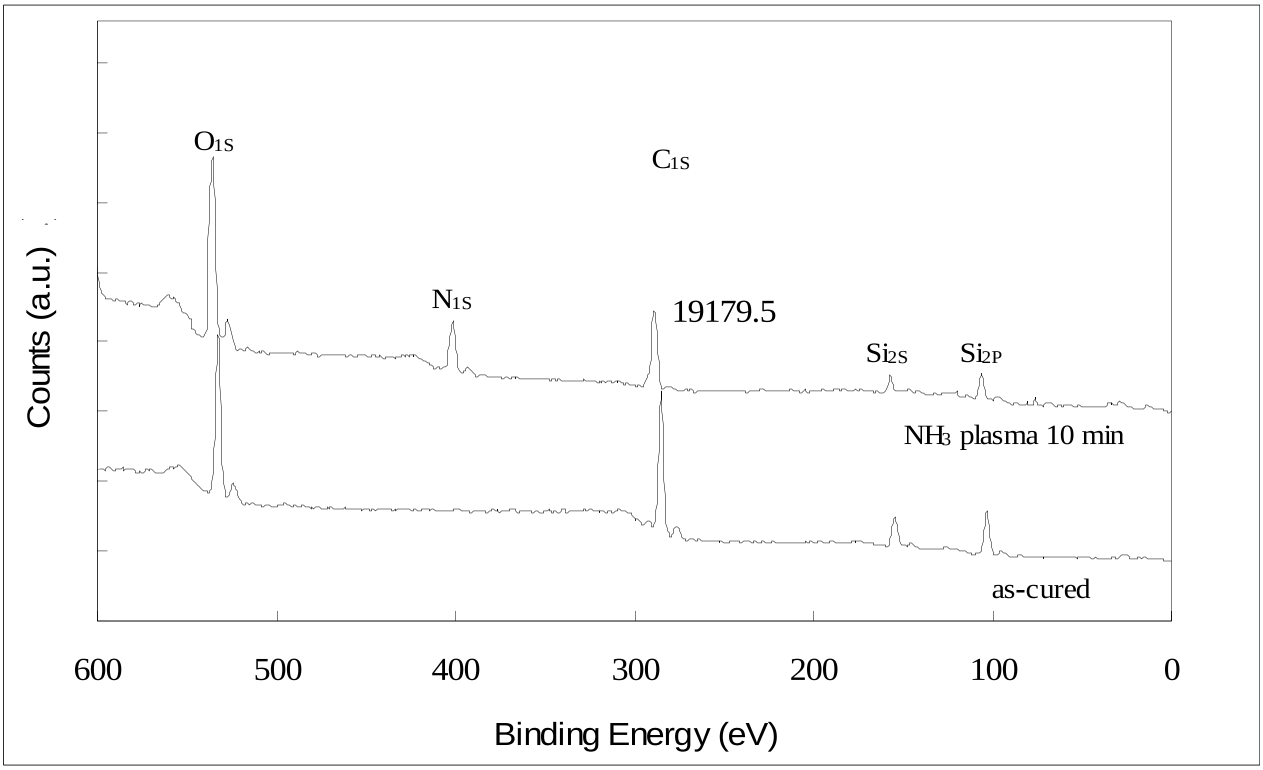
FTIR spectra of the different pre-treated X-720 films after O_2 plasma treatment (ashing) for 10 min.

Figure 5.1.1



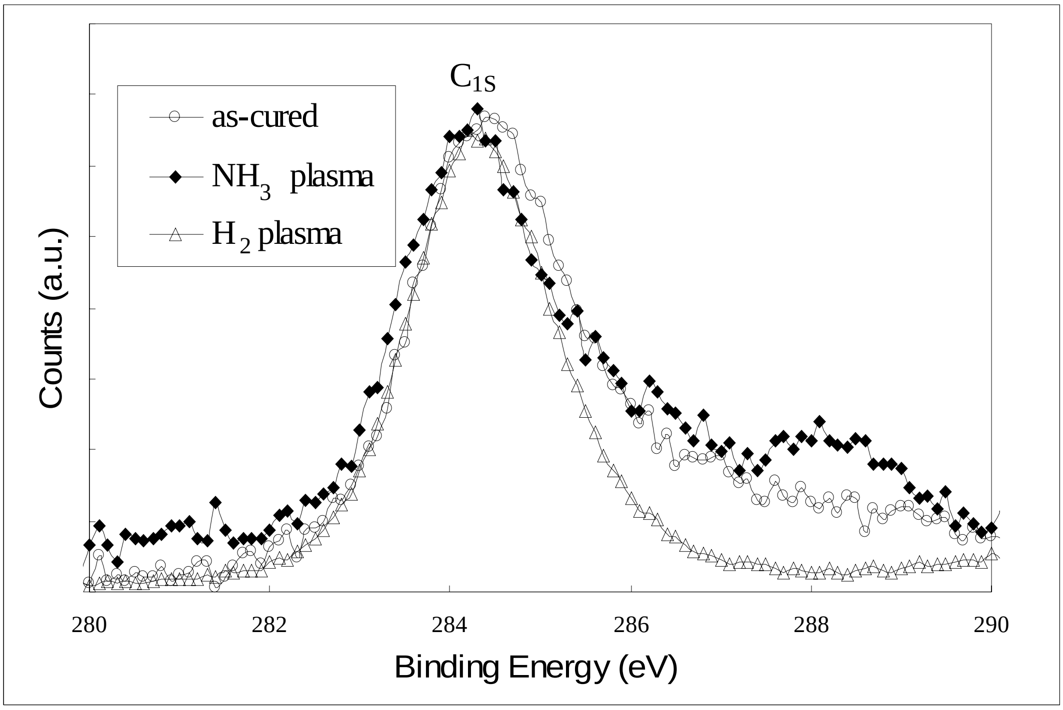
The thickness and the dielectric constant variation of the different pre-treated X-720 films after O_2 plasma treatment (ashing) for 10 min.

Figure 5.1.2



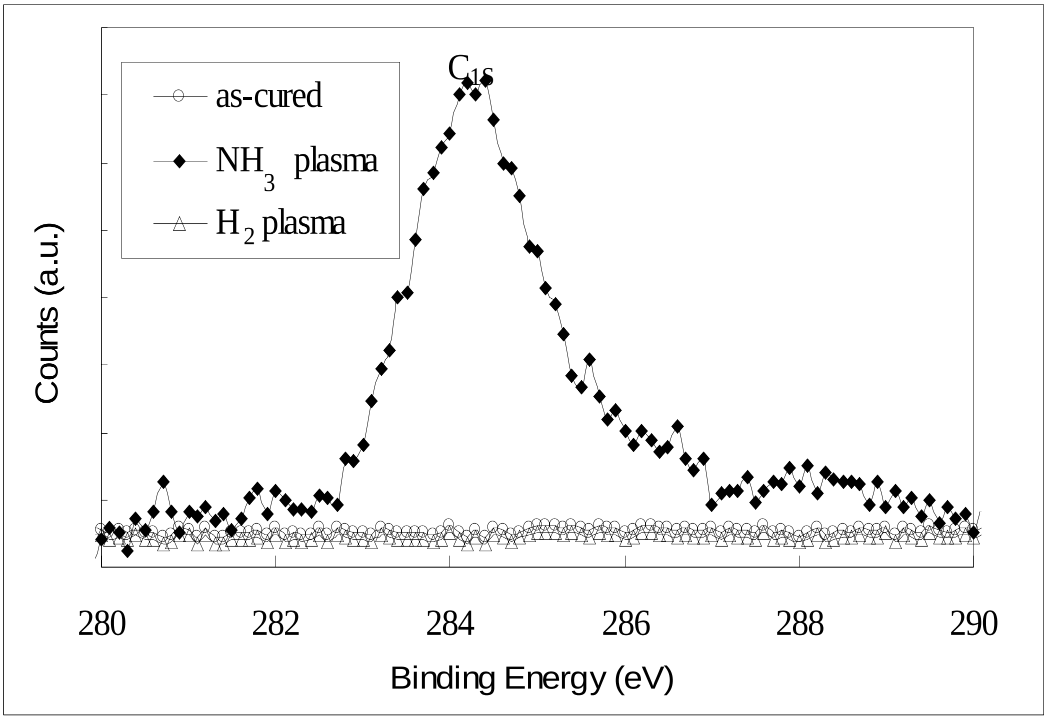
XPS spectra of the X-720 film before and after NH_3 plasma pre-treatment.

Figure 5.1.3



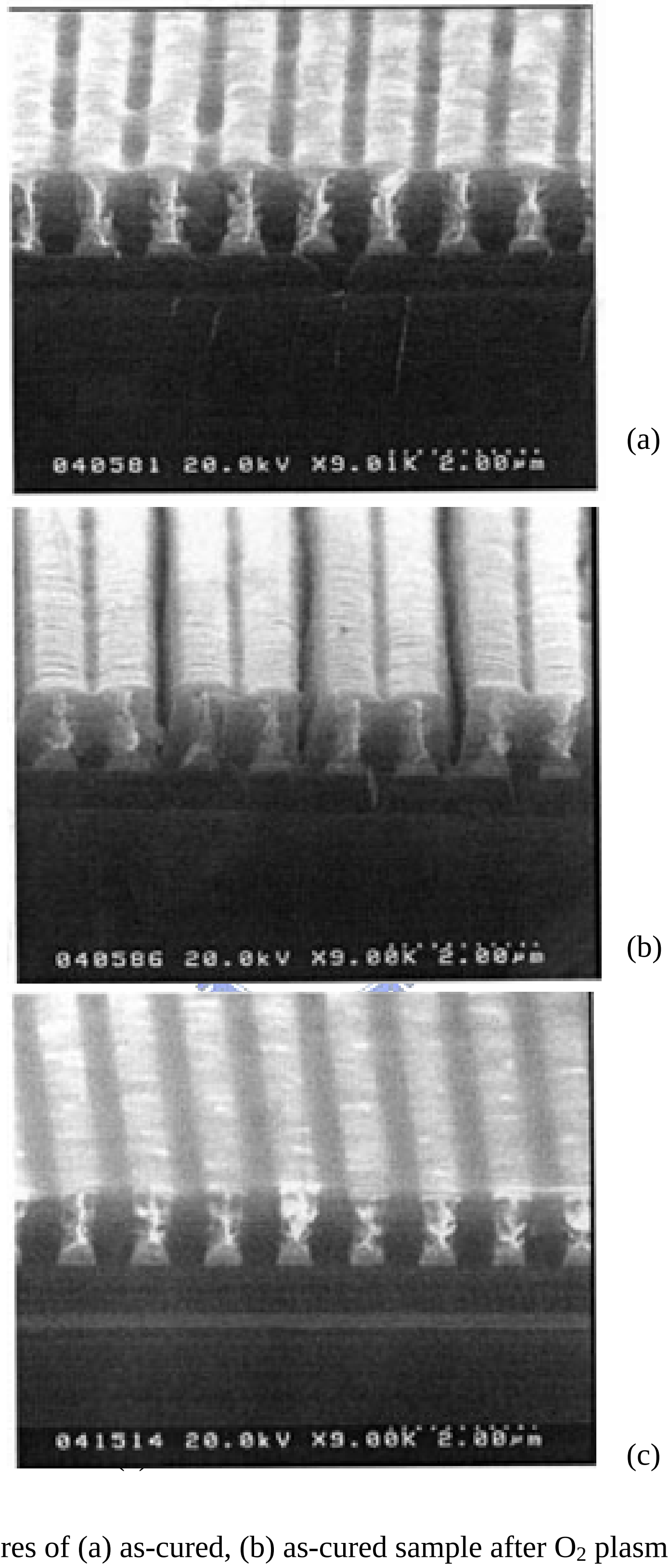
4 C_{1S} XPS spectra of the different pre-treated X-720 films (a) before and (b) after O_2 plasma treatment (ashing) for 10 min.

Figure 5.1.4 (a)



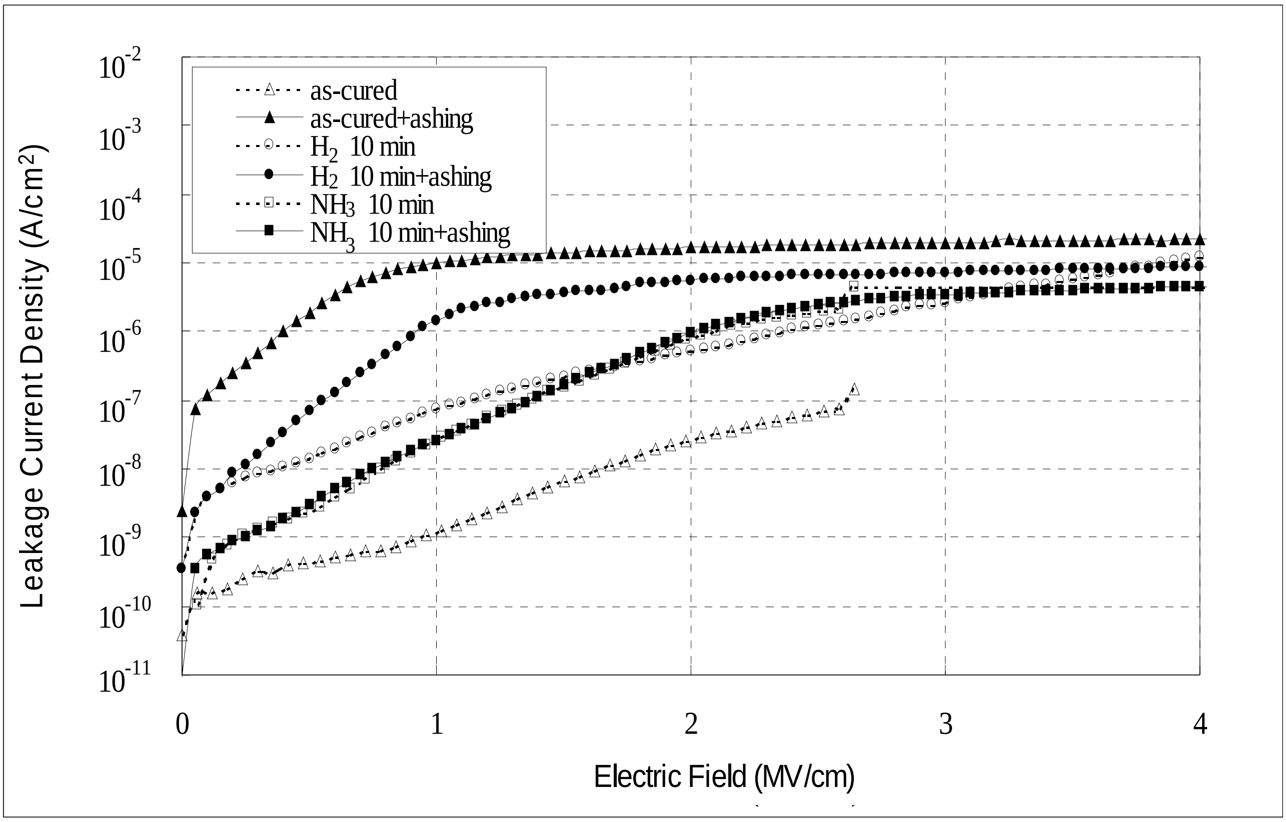
The SEM pictures of (a) as-cured, (b) as-cured sample after O_2 plasma treatment (ashing) for 10 min, (c) NH_3 plasma pre-treated sample after O_2 plasma treatment (ashing) for 10 min.

Figure 5.1.4 (b)



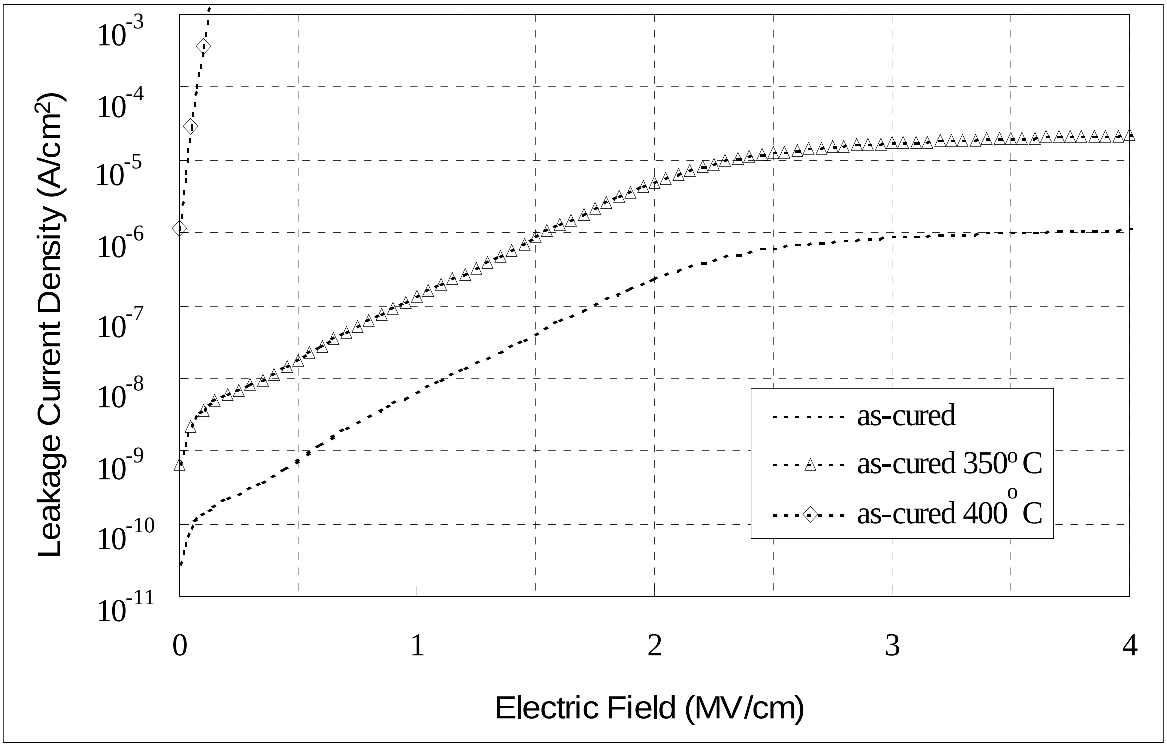
The SEM pictures of (a) as-cured, (b) as-cured sample after O_2 plasma treatment (ashing) for 10 min, (c) NH_3 plasma pre-treated sample after O_2 plasma treatment (ashing) for 10 min.

Figure 5.1.5



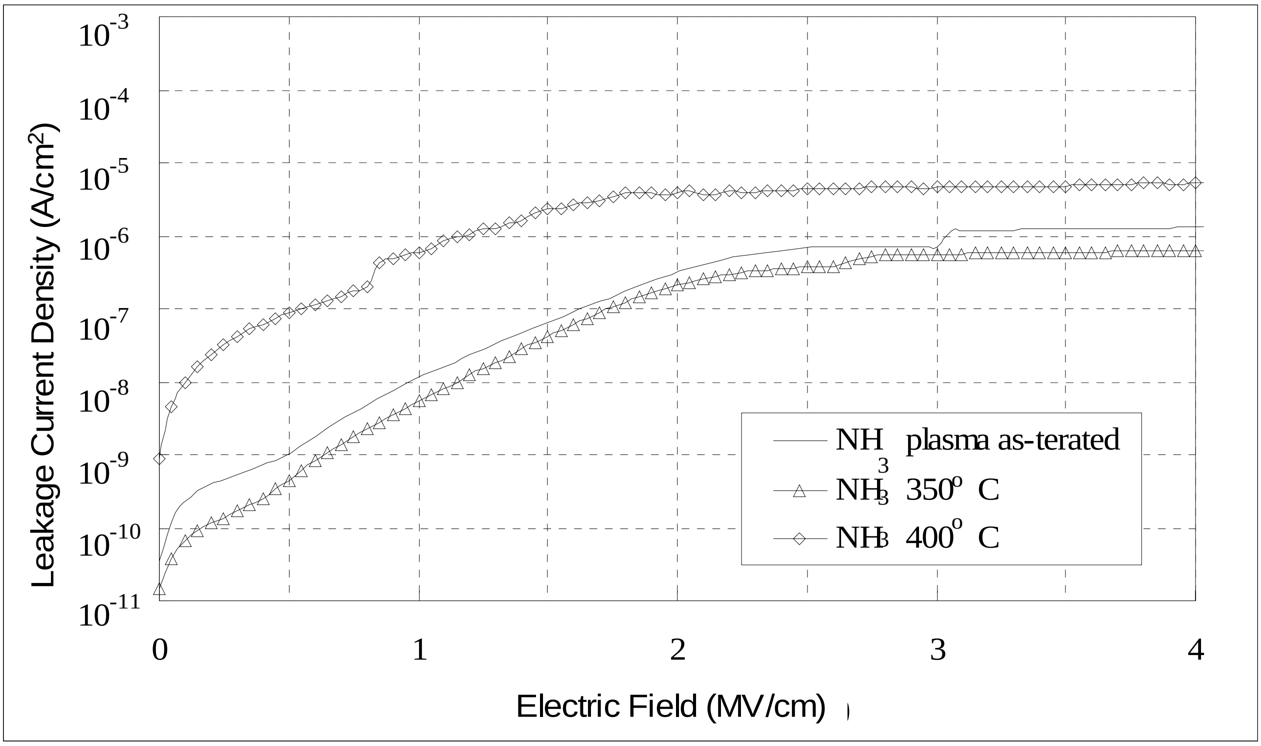
Comparing the leakage current density of the different pre-treated X-720 samples before and after O_2 plasma treatment (ashing) for 10 min.

Figure 5.1.6



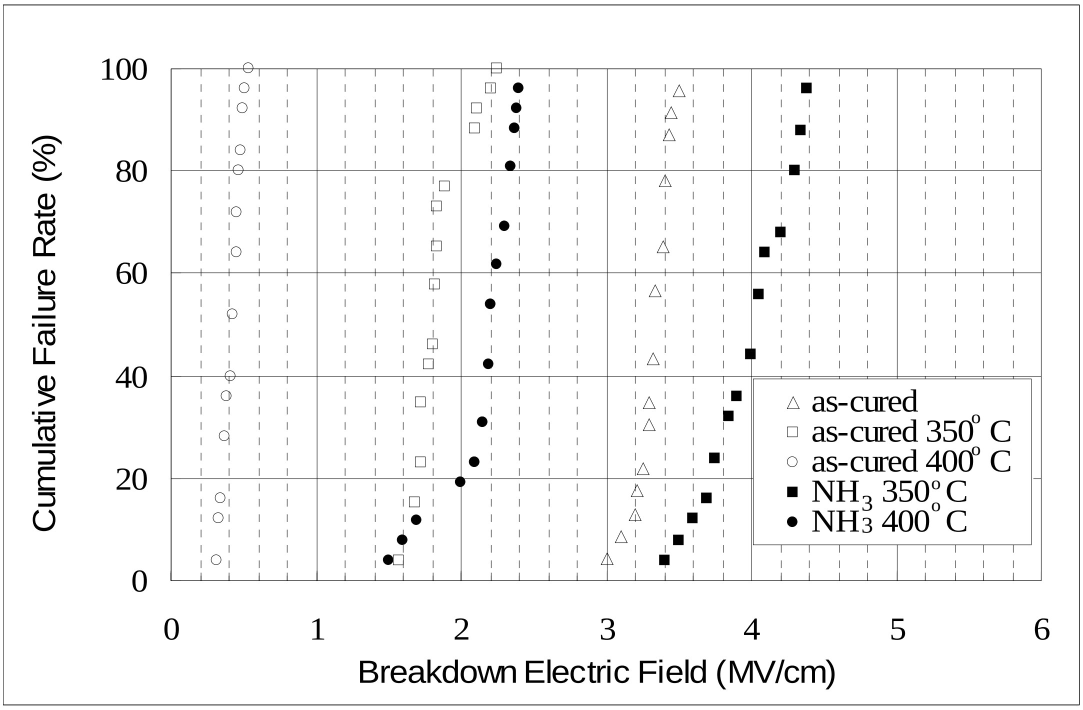
The leakage current density of as-cured X-720 samples after annealing at 350℃ and 400℃ for 1 hour.

Figure 5.1.7 (a)



The leakage current density of NH_3 plasma pre-treated X-720 samples after annealing at 350℃ and 400℃ for 1 hour.

Figure 5.1.7 (b)



Weibull plot of electrical breakdown field (E_{BD}) distributions for as-cured and NH_3 plasma pre-treated X-720 films as the capacitor dielectric layers after different thermal treatment conditions.

Figure 5.1.8