S0013-4651(99)10-093-4 CCC: $7.00

Using NH_3 Plasma Treatment to Improve the Characteristics of Hydrogen Silsesquioxane for Copper Interconnection Application

Kow-Ming Chang, I-Chung Deng,* Sy-Jer Yeh, and Yao-Pin Tsai

Department of Electronic Engineering and Institute of Electronics, National Chiao Tung University and National Nano Device Laboratory, Hsinchu, Taiwan

Hydrogen silsesquioxane, a material with low dielectric constant, can successfully suppress Cu diffusion without using a barrier metal by implementing a NH_3 plasma treatment. Lower leakage current and better barrier capability can be achieved by hydrogen silsesquioxane film after NH_3 plasma treatment. Having been treated with different plasma exposure times, this film can still maintain its original dielectric constant with few changes. The decrease in leakage current with increasing exposure time can be attributed to the following mechanisms: dielectric film becomes denser, dangling bonds are passivated, nitride film is formed on the hydrogen silsesquioxane, and the bulk damage of hydrogen silsesquioxane is annealed out. A thin layer of nitride formed on the dielectric is the cause for having better capability. The thickness of the nitride layer on hydrogen silsesquioxane is about 35 nm, and it can prevent the Cu diffusion/migration into the underlying dielectric. The role of our nitride film is to act as a passive diffusion barrier.

Manuscript received October 24, 1999.

The increase of resistance-capacitance (RC) time delays resulting from the smaller feature size devices fabricated on large dies, longer transmission lines, and more closely spaced interconnects will continue to bring further challenges in the semiconductor industry. Device integrated with lower dielectric constant material and lower resistance Cu film is capable of improving its performance and reducing the interconnection delay. Currently, Cu and hydrogen silsesquioxane (HSQ) are the leading candidates for metal and dielectric, respectively. However, the diffusivity of Cu in HSQ is rather high. The degradation and transport of copper is through its oxidation and diffusion/migration of ions. Cu interconnects need a barrier layer around them to prevent the diffusion into the interlayer dielectric. The diffusion of Cu will cause the dielectric to fail; namely, it can lead to a significant increase in leakage current. The goal of this work is to reduce the diffusion of Cu into the dielectric.

The HSQ has the following characteristics: carbon free, reflowability, low dielectric constant, and a good gap-filling capability. If we want to replace the commonly used SiO_2 with the organic low-*k* material, a number of process compatibility and reliability issues have to be addressed. Among them, the most important ones include electrical characteristics, thermal properties, and moisture absorption. Various materials have been studied as diffusion barriers between Cu and SiO_2 interface. The conductive barriers Ta, Ti, W, and their alloys such as TiN, TiW, WN, TaSi, and TaSiN were investigated successfully.[1,2] However, the barrier metal-free structure can specially reduce the resistance in fine patterns.[3,4] An excellent barrier capability is obtained by forming a thin barrier layer of SiON on the surface of SiOF film.[3] Gardnes *et al*.[5] also demonstrated that using a thin SiN film as a barrier layer was better than using a refractory metal in lowering device RC delay time.

Flowable oxide (FOx-16), a type of spin-on HSQ, is a low-*k* material used in this study. It is shown that the H_2 annealing and H_2 plasma treatment of low-*k* materials are capable of reducing the device's leakage current.[6] However, their barrier capability against Cu is still unsatisfactory. A thin nitride film formed on the surface of HSQ by NH_3 plasma treatment can result in very successful results. In other words, the capability of suppressing Cu using an additional plasma treatment is much better than the as-cured sample.

Experimental

A dilute fluid of HSQ (FOx-16:FOx-1 = 1:3) was spun on (100) 4-7 Ω-cm p-type Si wafers. Its thickness was approximately 100 nm after curing at 350°C for 60 min. The process steps used in this study are listed as follows:

* Electrochemical Society Student Member.

1. An 100 nm HSQ was spun on the Si substrate.
2. HSQ was treated with a NH_3 or H_2 plasma by plasma enhanced chemical vapor deposition (PECVD) technique. The substrate temperature was 300°C, the pressure was 40 Pa, the flow rate for NH_3 or H_2 was 300 sccm, and the RF power was 300 W.
3. A Cu film of 200 nm was deposited on the different samples by sputtering and then formed a metal oxide semiconductor (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 the material. The atomic concentrations of Cu ion in HSQ film were examined by secondary ion mass spectrometry (SIMS). The percentage of nitrogen in HSQ is measured by X-ray photoelectron spectroscopy (XPS) technique. The dielectric constant was calculated from capacitance-voltage (C-V) plots using MOS structure. The leakage current was measured by precision semiconductor parameter analyzer (HP 4156A).

Results and Discussion

Figures 1a and b show the FTIR spectra of cured FOx-16 after NH_3 and H_2 plasma treatment with different exposure times. These figures indicate that the HSQ structure starts to convert to Si-O stretch network structure after its being treated by NH_3 or H_2 plasma, *i.e.*, HSQ film becomes denser after plasma treatment. The high density of this HSQ structure implies that it has larger refractive index and dielectric constant. The dielectric constant varies with different plasma exposure times as shown in Fig. 2. The initial as-cured value of HSQ is 2.7, and it increases slightly as the exposure time increases. This result agrees with the fact that the HSQ film becomes denser after plasma treatment. The slightly higher dielectric constant implies that the thin nitride film was formed only on the surface of SOG after NH_3 plasma treatment.

SIMS analysis shows that the thickness of nitride film is about 35 nm on the surface of HSQ after NH_3 plasma treatment for 10 min as shown in Fig. 3a. The nitride film is the best material to be used as a barrier to guard against the impurity diffusion/migration. Loke *et al*.[7] showed that Cu^+ penetration can be prevented by 75 nm nitride layer. As shown in Fig 3b, the HSQ film demonstrated an obvious improvement after its being treated by NH_3 plasma for 10 min. From this figure, we found that copper can diffuse into the as-cured HSQ at 500°C. On the other hand, after NH_3 plasma treatment for 10 min, the HSQ film demonstrated better characteristics than the as-cured sample. In addition, the Cu depth profile of an as-cured sample is almost the same as the one having a 500°C anneal-

S0013-4651(99)10-093-4 CCC: $7.00

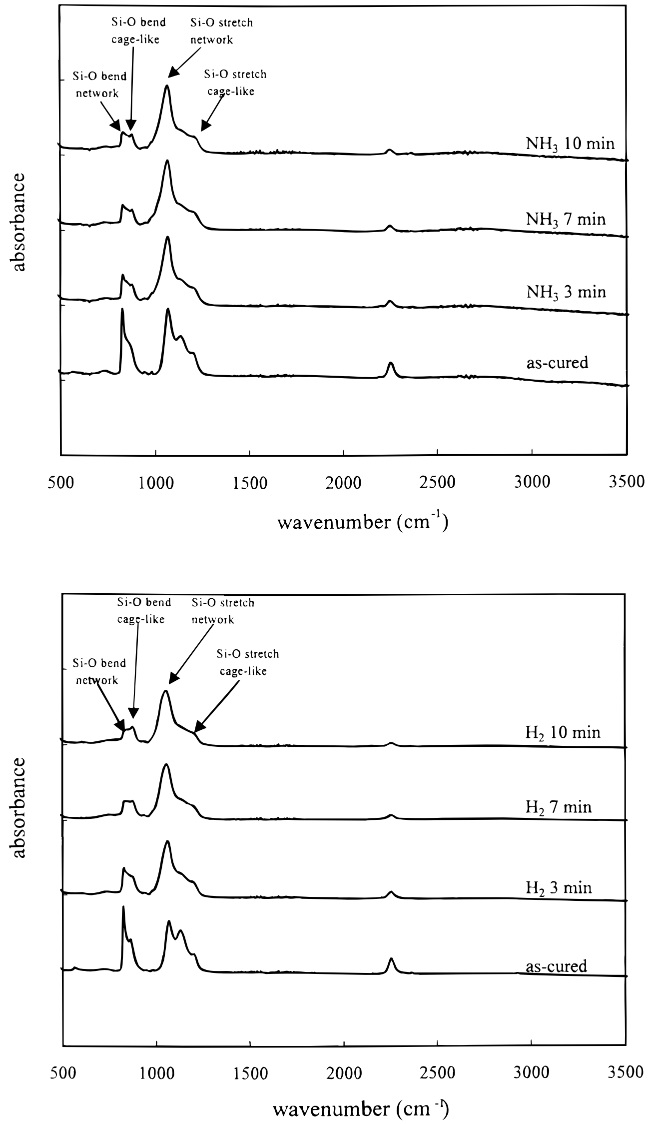

Figure 1. FTIR spectra of cured HSQ after (a, top) NH_3 plasma treatment, (b, bottom) H_2 plasma treatment for different exposure times.

ing for 60 min. This directly proves that the NH_3 plasma-treated HSQ has successfully blocked the Cu diffusion. From XPS analysis, we found a strong peak of N_{1S} at 398 eV and a weak peak of N_{1S} at

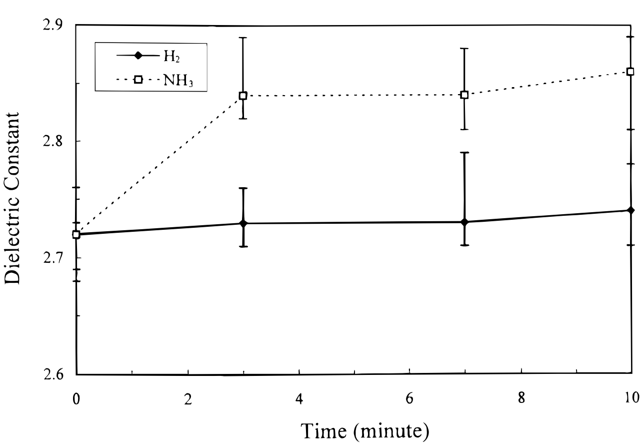

Figure 2. The variation of dielectric constant after different plasma treatment conditions.

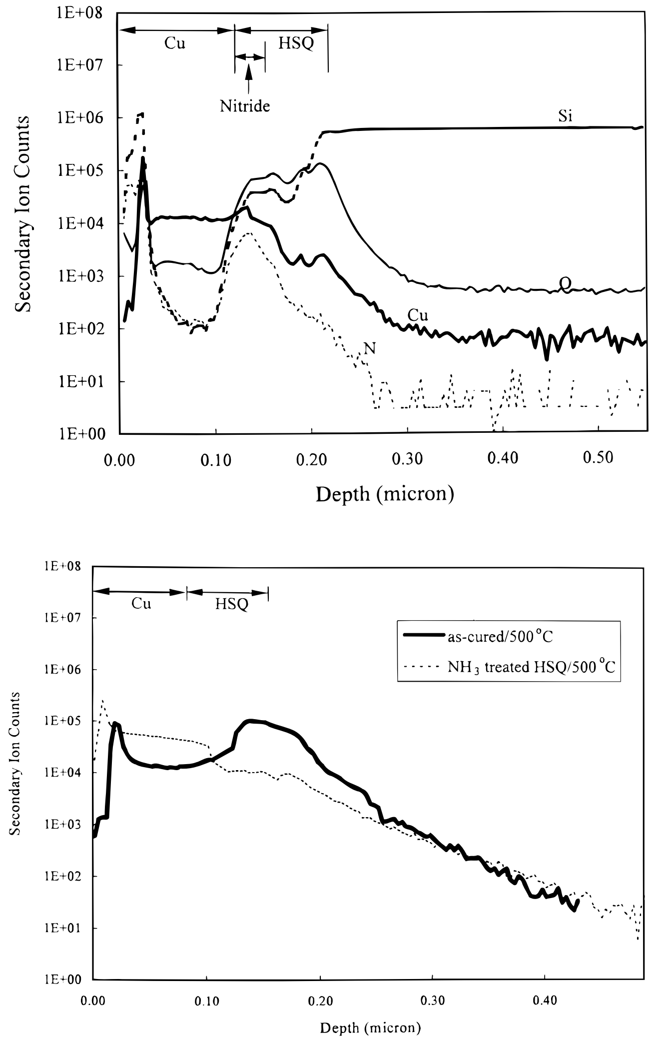

Figure 3. (a, top) SIMS depths profile of as-cured HSQ. (b, bottom) Comparing the Cu penetrated into HSQ after annealing at 500°C for 60 min.

403.5 eV as shown in Fig. 4. The lower binding energy of N_{1S} is attributed to the electron transfer from Si to nitrogen atom. In other

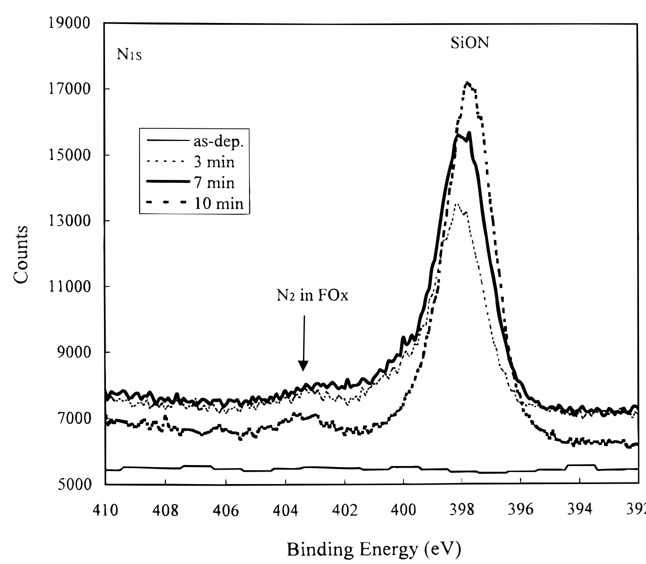

Figure 4. N_{1S} XPS spectra of HSQ after NH_3 plasma treatment for different exposure times.

S0013-4651(99)10-093-4 CCC: $7.00 © The Electrochemical Society, Inc.

Table I. The composition percentage of the surface of FOx with NH_3 plasma treatment for different times.

Time \ Element	O_{1S} (%)	N_{1S} (%)	C_{1S} (%)	Si_{2P} (%)
No plasma	47.066	0	9.377	43.557
3 min	39.214	12.825	13.435	34.526
7 min	30.423	21.369	12.117	34.241
10 min	27.006	23.182	14.099	35.713

words, the role of our nitride should act as a passive diffusion barriers.[8,9] The passive barrier is considered to be probably the best diffusion barrier.[10] It causes a significant improvement in the dielectric characteristics. Figure 4 shows that the strength of N_{1S} peak increases with increasing the plasma treatment time. The percentage of nitrogen atoms in HSQ film also increases with increasing the NH_3 plasma treatment time as shown in Table I. The increasing percentage of nitrogen atoms implies that the barrier effect is improved after longer plasma treatment time. The percentage of nitrogen atoms increases rapidly first and then reaches to a saturation point after a 7 min NH_3 plasma treatment. The nitrogen concentration only increases 2% between 7 and 10 min NH_3 plasma treatment.

Figure 5a shows the leakage current density of MOS capacitors. A decrease in leakage current after NH_3 plasma treatment can be observed. The leakage current decreased further with increasing plasma exposure time. This result is similar to the samples after H_2 plasma treatment in Fig. 5b. The reasons for reducing the leakage current can be attributed to the following: (*i*) the HSQ film becomes denser after plasma treatment; (*ii*) the passivated dangling bonds in the SOG cause a decrease in leakage current with increasing plasma exposure time. Hydrogen being passivated plays a major role of passivation; while the previous work[6] found an increase in leakage current after N_2 plasma treatment; (*iii*) thin nitride film of 35 nm on the HSQ can effectively block the electrical field which could otherwise induce Cu ion drifting into the HSQ; (*iv*) the plasma damage is only on the surface of the HSQ film and the damage in the bulk of HSQ film is annealed out during plasma treatment.

Figures 6a and b reveal the leakage current for both as-cured HSQ film and its having been treated by NH_3 plasma, respectively. In Fig. 6a, the capacitor remained intact up to 400°C annealing for 60 min. This arises from the fact that the damage in HSQ is annealed out after annealing at 400°C comparing with the HSQ at room temperature of which it has a higher leakage current. The capacitor suffered significant degradation with high leakage current after annealing at 500°C for 60 min. After NH_3 plasma treatment shown in

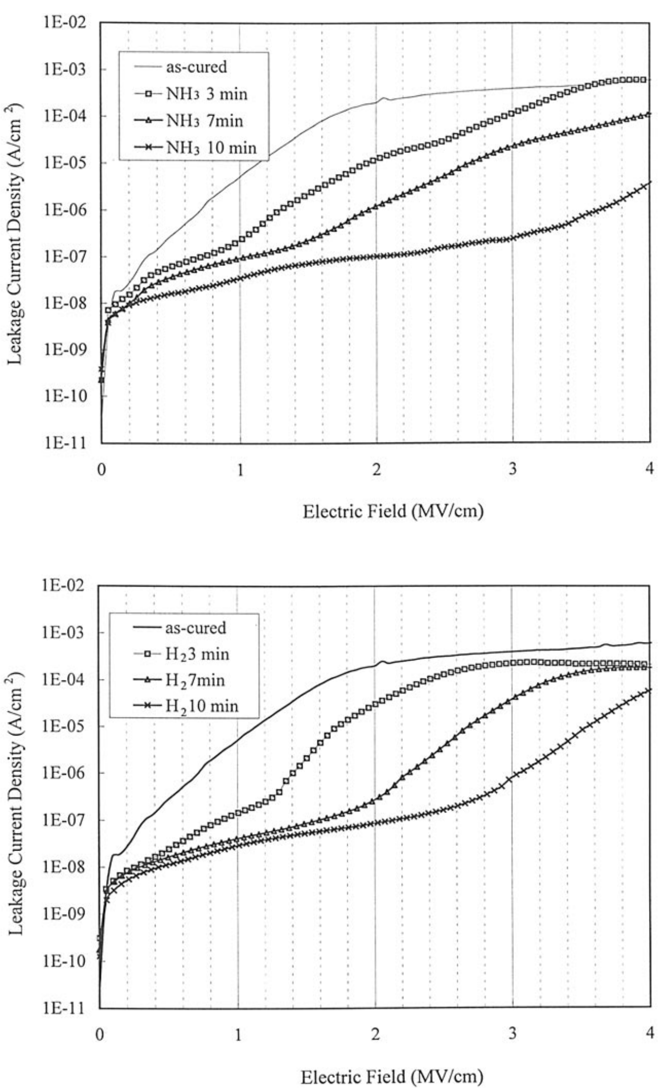

Figure 5. The leakage current density of HSQ after (a, top) NH_3 plasma treatment, (b, bottom) H_2 plasma treatment for different exposure times.

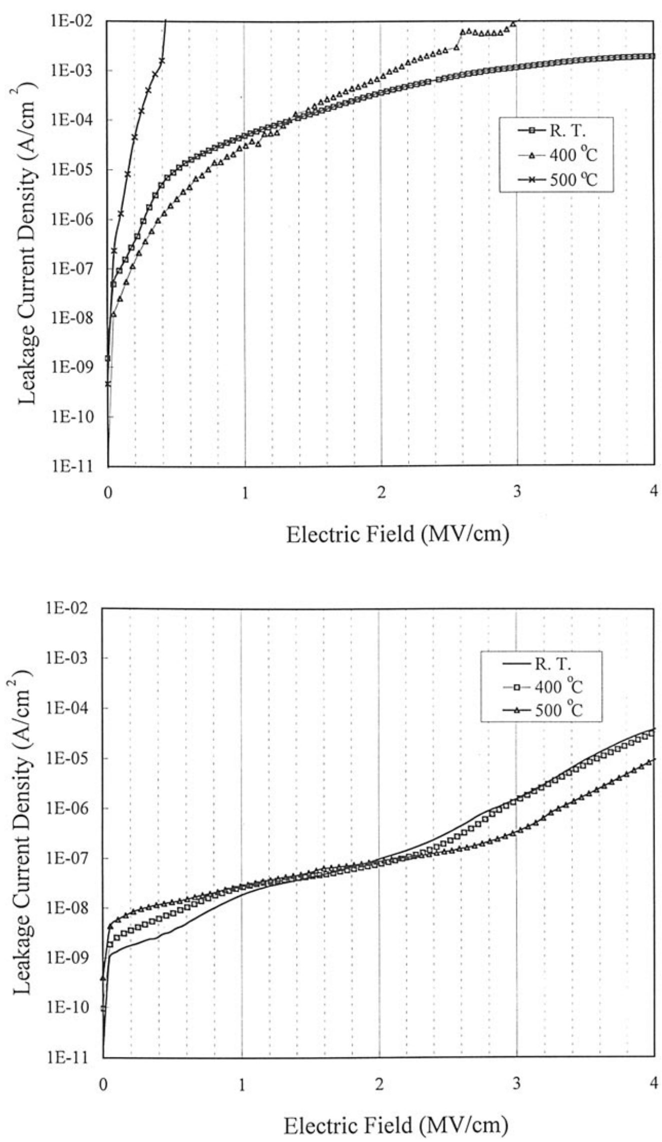

Figure 6. The leakage current density of (a, top) as-cured HSQ and (b, bottom) NH_3 plasma-treated HSQ after annealing at 400 and 500°C for 60 min.

S0013-4651(99)10-093-4 CCC: $7.00 © The Electrochemical Society, Inc.

Fig. 6b, the leakage current level is of three orders lower than those of as-cured samples at 1 MV/cm electric field. Even after annealing at 500°C for 60 min the leakage current density remains almost the same as the as-treated samples.

Figure 7a shows the breakdown electric field (E_{BD}) distribution of the samples with Cu gate after NH_3 and H_2 plasma treatments. HSQ shows a great improvement of breakdown voltage after NH_3 plasma treatment. We also measured the electric field of the Al gate as shown in Fig 7b. In this case, all of the samples show the same level of breakdown electric field. As the electrode was replaced by Cu, the as-cured sample demonstrated significant degradation. Therefore, Cu is expected to be a major cause of leakage current. The formation of a nitride film on the surface of SOG results in a higher breakdown voltage and better barrier capability.

The time to failure (TTF) stress can be used as an indicator to examine the barrier quality. The effect of electric field on copper transport was conducted when the temperature was measured at 150°C. As shown in Fig. 8, the initial decrease in the leakage current is similar to the samples of Cu on oxide or nitride.[11,12] This decrease in leakage current is due to the injection of mobile ions of Cu into the dielectric. The injection of ions leads to the charge buildup in the dielectric and to oppose further injection. It can be seen that the leakage current reduces continuously until it balances with the electron injection from the back-side electrode. In Fig. 8, it was found that the SOG sample with a NH_3 plasma treatment shows a better integrity than the as-cured one after TTF stress test. After applying four times the magnitude of the electric field to the NH_3 plasma-treated sample, its TTF time is still much longer than those of the as-cured and H_2 plasma-treated ones. Finally, at the breakdown stage, the NH_3 plasma-treated sample shows an abrupt breakdown without a gradual increase in leakage current, which is similar to oxynitride in the other reports.[5] The "self-healing" phenomena (the leakage current spikes up and down) are sometimes observed in TTF testing. These phenomena are due to the nonuniform diffusion of copper.[11] Based on the above data, the NH_3 plasma treatment is an excellent method for improving the quality of HSQ.

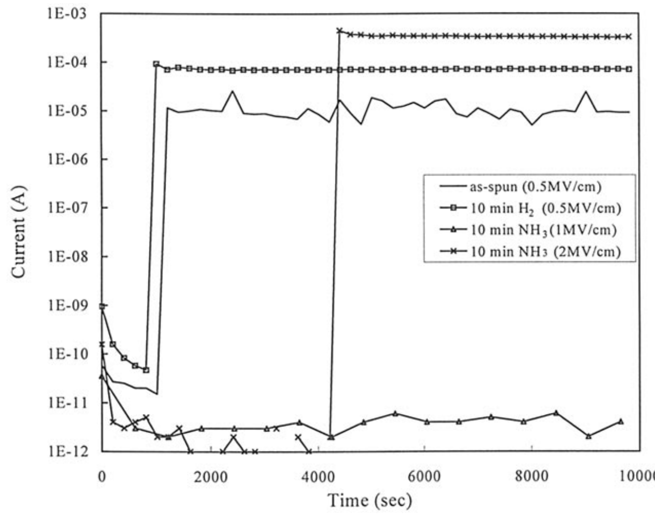

Figure 8. Influence of time to failure of Cu/HSQ/Si structure after different plasma treatment conditions.

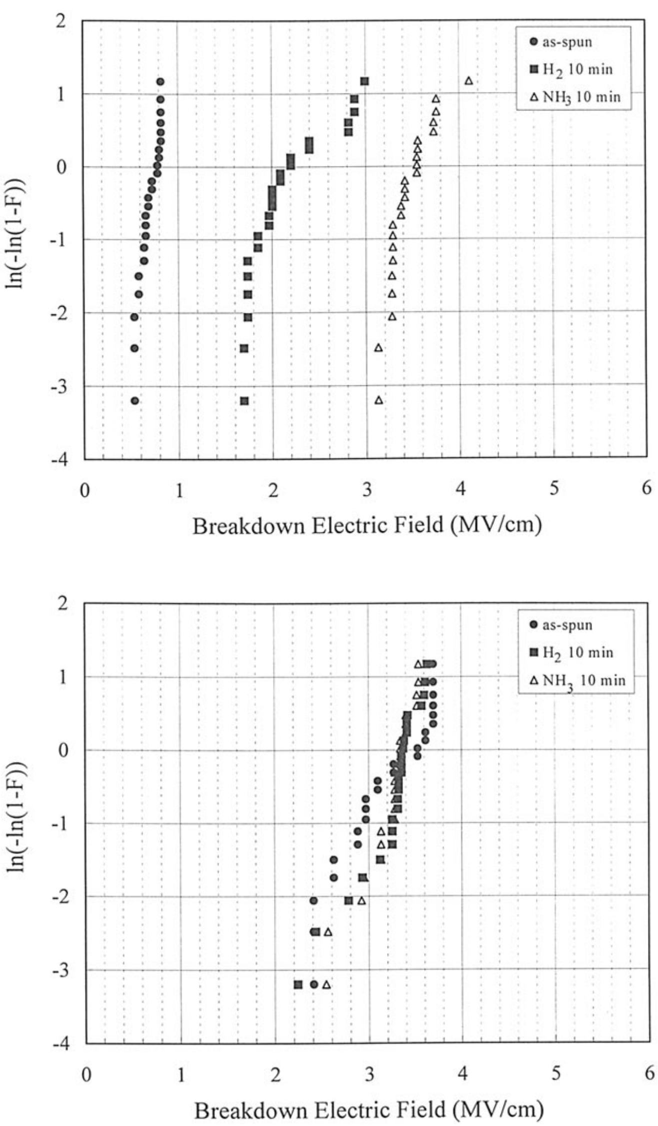

Figure 7. Weibull plot of (a, top) Cu/HSQ/Si and (b, bottom) Al/HSQ/Si structures' breakdown electric field (E_{BD}) distribution after different plasma treatment conditions.

Conclusion

NH_3 plasma treatment provides an efficient method for improving the quality of FOx-16, a flowable low-*k* material. After NH_3 plasma treatment, the leakage current shows three orders of magnitude lower than that of as-cured sample at an electric field of 1 MV/cm. We have found that FOx-16 has capabilities for preventing Cu diffusion after its being treated by NH_3 plasma. This was due to a 35 nm nitride film formed on the HSQ surface and the overall dielectric constant was not changed. This nitride film offers a dramatic improvement in terms of barrier characteristics. After annealing in NH_3 ambient at 500°C for 1 h, no increase in leakage current was observed in the Cu/HSQ/Si structure. The function of nitride film acts as passive diffusion barriers. This thin nitride film can also improve the breakdown voltage of HSQ. As the experimental results indicate, the NH_3 plasma treatment is an excellent approach for improving the characteristics of HSQ.

Acknowledgments

This work is supported by the National Science Council under grant NSC88-2215-E-009-046.

National Chio Tung University assisted in meeting the publication costs of this article.

Reference

1. Y. S. Diamand, A. Dehhia, D. Hofstetter, and W. G. Goldham, in *Proceedings of the VLSI Multilevel Interconnection Conference, VMIC*, p. 109 (1991).
2. S. Hirao, M. Satake, H. Kamada, M. Sekiguchi, T. Tamaki, and S. Mayumi, in Symposium on VLSI Technology, Digest of Technical Papers, p. 57 (1997).
3. K. Mikagi, H. Ishikawa, T. Usami, M. Suzuki, K. Inoue, N. Oda, S. Chikaki, I. Sakai, and T. Kikkawa, *Tech. Dig. Int. Electron Devices Mtg.*, p. 365 (1996).
4. G. M. Adema, L. T. Hwang, G. A. Rinne, and I. Turlik, *IEEE Trans. Comp., Hybrids, Manuf. Tech.*, **16**, 53 (1993).

S0013-4651(99)10-093-4 CCC: $7.00 © The Electrochemical Society, Inc.

5. D. S. Gardner, J. Onuki, K. Kudoo, Y. Misawa, and Q. T. Vu, *Thin Solid Films*, **262**, 104 (1995).
6. P. T. Liu, T. C. Chang, S. M. Sze, F. M. Pan, Y. J. Mei, W. F. Wu, M. S. Tsai, B. T. Dai, C. Y. Chang, F. Y. Shih, and H. D. Huang, *Thin Solid Films*, **332**, 345 (1998).
7. A. L. S. Loke, J. T. Wetzel, C. Ryu, W. J. Lee, and S. S. Wong, in Symposium on VLSI Technology, Digest of Technical Papers, p. 26 (1998).
8. M-A. Nicolet and M. Bartur, *J. Vac. Sci. Technol.*, **19**, 786 (1981).
9. M. Nagai and K. Kishida, *Appl. Surf. Sci.*, **70/71**, 759 (1993).
10. S. Wolf, in *Silicon Processing for the VLSI Era*, Vol. 2, p. 123, Lattice Press, Sunset Beach, CA (1990).
11. G. Raghavan, C. Chiang, P. B. Ander, S. M. Tzeng, R. Villasol, G. Bai, M. Bohr, and D. B. Fraser, *Thin Solid Films*, **262**, 168 (1995).
12. M. Vogt, M. Kachel, M. Plotner, and K. Drescher, *Microelectron. Eng.*, **37/38**, 181 (1997).