

The effect of ammonia plasma treatment on low-*k* methyl-hybrid-siloxane against photoresist stripping damage

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Abstract

The integration process, low-*k* hybrid-organic-siloxane-polymers (HOSP) and photoresist stripping process have been investigated. The dielectric properties of HOSP films are degraded after photoresist removal. This is because photoresist stripping processes destroy the functional groups and induce moisture uptake in HOSP films. In this study, NH₃-plasma treatment was used for HOSP films to form a thin nitrogen-containing layer, preventing HOSP films from O₂ plasma ashing and chemical wet stripper damage during photoresist removal. The leakage current is decreased significantly and the dielectric constant is maintained at a low value after photoresist removal. These experimental results show that NH₃ treatment is a promising technique to enhance the resistance of HOSP films to the photoresist stripping process. © 2001 Elsevier Science B.V. All rights reserved.

Keywords: Ammonia; Hybrid-organic-siloxane-polymer; Photoresist stripping

1. Introduction

As the critical dimension of integrated circuits is scaled down, the linewidth and spacings between metal interconnections are made smaller. A larger portion of the total circuit transmission time (i.e. RC delay) will be from parasitic resistance and capacitance of the interconnections. The interconnection becomes a bottleneck in improving the chip performance such as the speed and power consumption [1,2].

In order to decrease the resistance (*R*), copper has recently been introduced as the interconnect metal, due to its high electrical conductivity ($\sim 1.8 \mu\Omega\text{cm}$) compared with $3.0 \mu\Omega\text{cm}$ of Al. In addition, copper interconnect possesses a higher resistance to electromigration than Al wiring by one to two orders of magnitude.

Low dielectric constant (low-*k*) materials also are proposed to decrease the parasitic capacitor [3–9]. One

of many low-*k* dielectrics, a spin-on deposition hybrid-organic-siloxane-polymer (HOSP) is a promising candidate. The HOSP film is a derivative of SiO₂ in which one of the four oxygen atoms bonded to every silicon atom is replaced by hydrogen and methyl groups.

The HOSP is a SiO₂-based material, which is highly suitable for ULSI applications because of the low dielectric constant of approximately 2.5. Therefore, the integration of the HOSP films as an interlayer dielectric into multilevel interconnects has received much attention in recent years.

In integration processing, photoresist stripping is an indispensable step. The photoresist removal is commonly implemented with O₂-plasma dry ashing and wet stripper solution dipping. The dielectric properties of the low-*k* films may be degraded during photoresist stripping processes [10,11].

In this work, we studied the NH₃-plasma treatment to improve the quality of HOSP films. Electrical measurement and material analyses have been used for evaluation. In addition, O₂-plasma ashing and wet stripper

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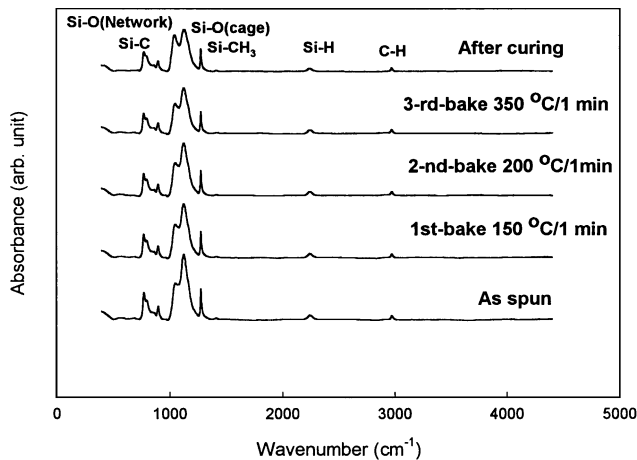


Fig. 1. FTIR spectra of HOSP films before and after a series of baking and curing steps.

dipping have been investigated to determine the impact of integrated processes on the dielectric film quality.

2. Experimental

The substrates used in the study were 4-inch p-type single crystal wafers (resistivity: 15–20 Ωcm) with (100) orientation. The wafers were coated with the HOSP methyl-hyrido-silsesquioxane (MHSQ) solution at rotational velocity 500 rev./min for 5 s for the first stage. Then, a second spinning stage was implemented at 2500 rev./min for 20 s. After the spin-coating process, the HOSP films were baked sequentially on a hot plate at 150°C, 200°C and 350°C for 1 min, respectively. It was followed by a furnace curing at 400°C under a nitrogen ambient for 1 h.

Four types of samples which were labeled as samples STD, NH-3, NH-6 and NH-9, respectively, were prepared. Sample STD was the as-cured HOSP film without any plasma treatment. Samples NH-3, NH-6 and NH-9 were the as-cured HOSP films with NH_3 plasma pre-treatment for 3, 6 and 9 min, respectively. Then, all types of samples were treated with O_2 plasma ashing for 3 min and wet stripper dipping at 60°C for 10 min, respectively.

The NH_3 plasma treatment was carried out in a plasma-enhanced chemical vapor deposition (PE-CVD) chamber. The NH_3 plasma was operated with a rf power of 200 W at a pressure of 300 mtorr. The flow rate was 700 sccm, and the operating temperature was kept at 300°C.

Metal insulation semiconductor capacitors (MIS) were manufactured by depositing aluminum onto the HOSP film as the top-electrode.

The chemical bonds of the HOSP films after different processes were investigated by Fourier transform infra-

red (FTIR) spectroscopy. The thickness of the HOSP films were measured by a n&k analyzer. The capacitance–voltage (C – V) characteristic was measured at 1 MHz with an AC bias for high frequency. A Keithley Model 82 CV meter was used to make the measurements on an electrode area of 0.0053 cm^2 . The current–voltage (I – V) characteristics were also measured using MIS structure to evaluate the insulation property of HOSP film.

3. Results and discussion

Fig. 1 shows the FTIR spectra of HOSP films before and after a series of baking and curing steps. After 150°C, 200°C and 350°C baking, the intensity of Si–O (cage) peak is decreased and Si–O–Si (network) peak intensity is increased. After 400°C curing, the network structure significantly appears. It clearly shows that a large amount of Si–O bonds cross-link into Si–O–Si bonds and form a more rigid network structure.

In integrated processes, photoresist removal is an indispensable step. The photoresist removal is implemented conventionally by O_2 plasma ashing and wet stripper solution treatment. Therefore, the impact of O_2 plasma ashing and chemical wet stripper on the quality of HOSP film was investigated in this study. Fig. 2 shows the FTIR spectra of the as-cured HOSP film before and after photoresist removal processes (i.e. O_2 plasma ashing and chemical wet stripping). The intensities of Si–OH and H–OH bonds were increased after photoresist stripping. Furthermore, the intensities of Si–H, C–H and Si– CH_3 peaks were decreased dramatically. These FTIR spectra results can be explained as follows.

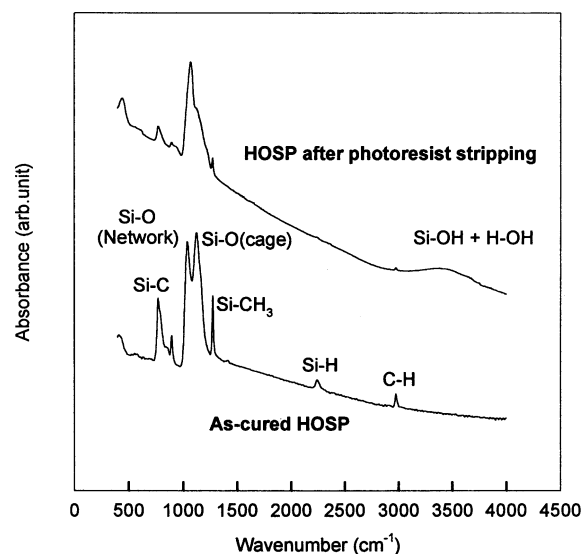


Fig. 2. FTIR spectra of HOSP films before and after photoresist stripping processes (O_2 plasma ashing and wet stripper dipping).

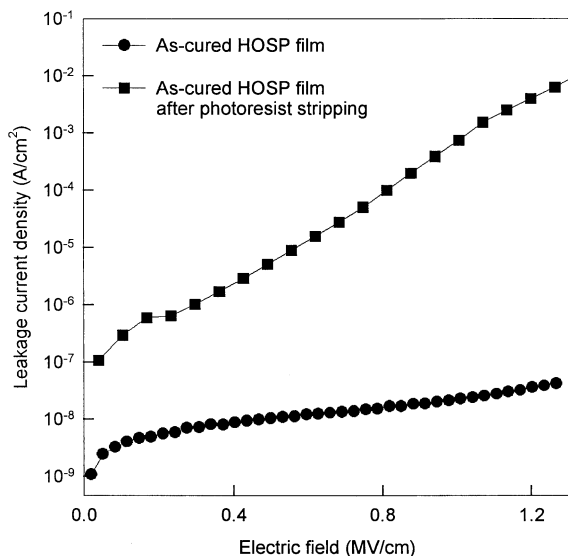


Fig. 3. The leakage current density of HOSP films before and after photoresist stripping processes.

During O₂ plasma ashing, O radicals react with functional groups of HOSP films, breaking Si-CH₃ bonds and Si-H bonds. This causes the HOSP films to generate dangling bonds. Sequentially, the high-alkalinity content of wet stripper solution (pH 12.6) leads to continuous hydrolysis reactions of HOSP films, forming even more dangling bonds in the HOSP films. The dangling bonds could easily react with hydroxide ions (OH⁻) in the wet stripper solution and form Si-OH bonds. These Si-OH bonds in the HOSP films lead to moisture uptake. Therefore, the Si-OH bond and H-OH bond signals appear in the FTIR spectra.

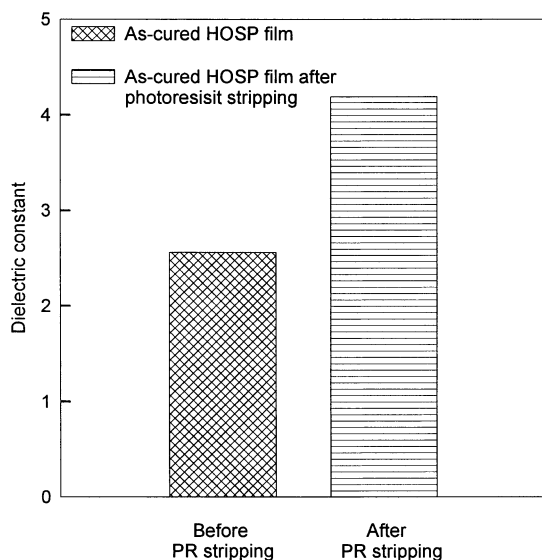


Fig. 4. The dielectric constant of HOSP films before and after photoresist stripping processes.

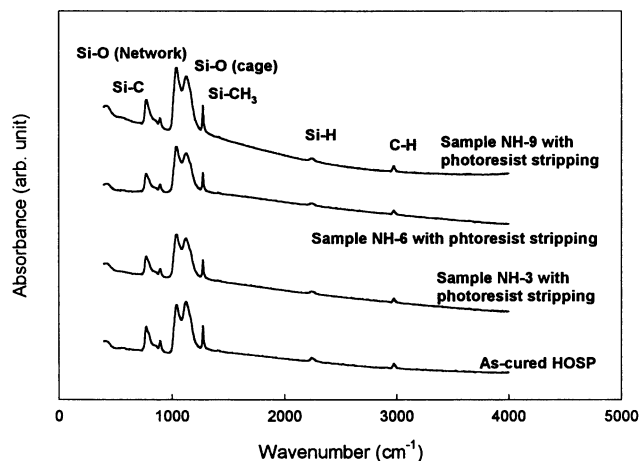


Fig. 5. FTIR spectra of Samples STD, NH-3, NH-6 and NH-9 after photoresist stripping processes.

Fig. 3 shows the leakage current density of the HOSP films before and after photoresist removal. The leakage current increased after photoresist removal. The dielectric constant also increased significantly, as shown in Fig. 4. The dielectric loss is due to the destruction of functional groups in the HOSP films after photoresist removal, as shown in Fig. 2. In order to address these issues, NH₃ plasma treatment was developed to enhance the resistance to photoresist stripping processing.

Fig. 5 show FTIR spectra of NH₃ plasma-treated HOSP films (i.e. samples NH-3, NH-6 and NH-9) after photoresist stripping. It is found that all the intensity of functional groups still remained at a high level. Meanwhile, Si-OH bonds and H-OH bonds did not appear in the FTIR spectra.

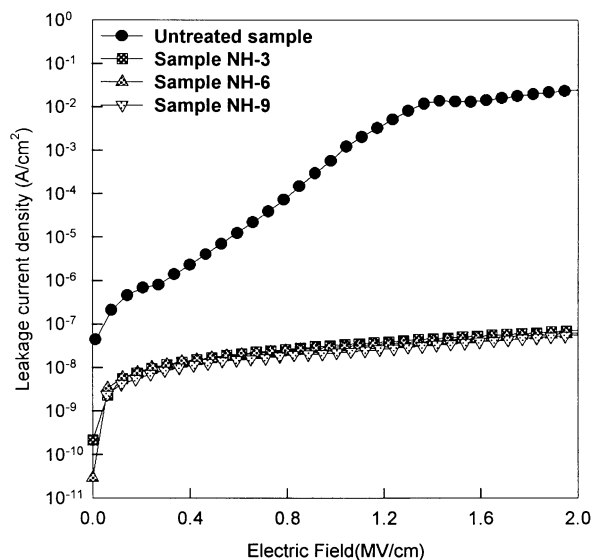


Fig. 6. Leakage current density of Samples STD, NH-3, NH-6 and NH-9 after photoresist stripping processes.

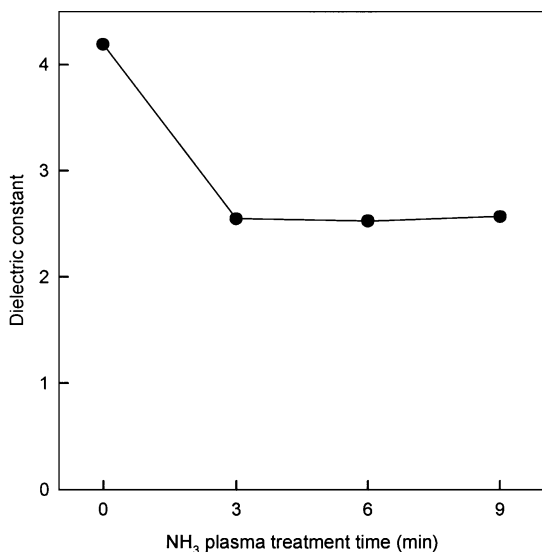


Fig. 7. Dielectric constant of Samples STD, NH-3, NH-6 and NH-9 after photoresist stripping processes.

These leakage currents of NH₃ plasma-treated HOSP films are much lower than that of untreated HOSP films after photoresist removal, as shown in Fig. 6. Moreover, the dielectric constants of NH₃ plasma-treated HOSP films can still maintain a low-*k* value, as shown in Fig. 7.

Fig. 8a,b shows the XPS diagrams of as-cured and NH₃ plasma-treated HOSP films, respectively. In contrast to Fig. 8a, it is found that a significant signal of nitrogen appears at approximately 400 eV in Fig. 8b. This indicates that nitrogen atoms are doped in the HOSP films and form a thin nitrogen-containing layer on the NH₃ plasma-treated HOSP surface.

The thin nitrogen-containing layer generated from NH₃ plasma is thought to be a barrier against photoresist stripping damage. The nitrogen-containing layers passivate dangling bonds on the HOSP surface and prevent moisture uptake. As a result, both the leakage current and dielectric constant of NH₃ plasma-treated HOSP films will maintain low-*k* properties after photoresist stripping.

4. Conclusions

In this study, NH₃-plasma treatment was applied to HOSP films. The NH₃ plasma treatment transforms the HOSP surfaces into a thin nitrogen-containing layer. The nitrogen-containing layer is a good barrier against O₂ plasma and high-alkalinity wet stripper solution attack. Material analyses verified our interpretation. The Si–OH bonds were not observed in the FTIR spectra when NH₃ plasma-treated HOSP films underwent photoresist stripping processes. In addition, electrical measurements also show that the leakage current of NH₃ plasma-treated HOSP films is decreased significantly

and the dielectric constant is maintained at a low-*k* value.

Acknowledgements

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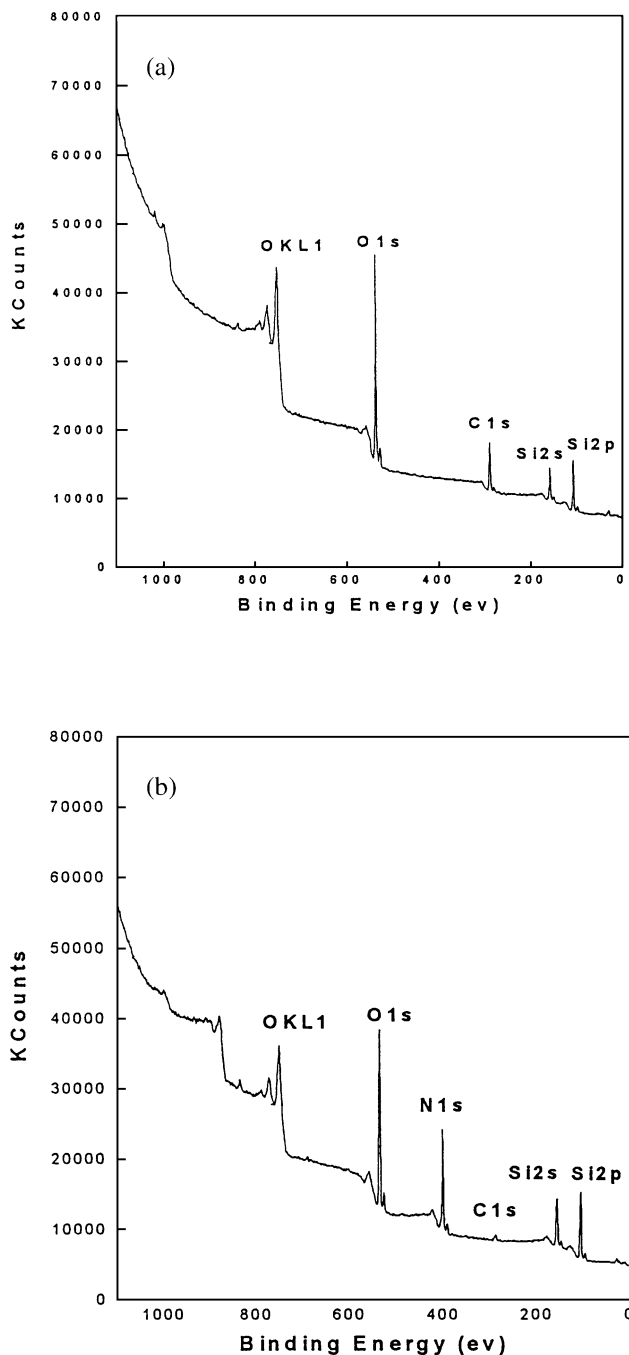


Fig. 8. XPS diagram of as-cured and NH₃ plasma-treated HOSP films.

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