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Preventing dielectric damage of low-k organic siloxane by passivation treatment

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Abstract

An organic SOG, the Hybird-Organic-Siloxane-Polymer (HOSP), has high applicability to ULSI processes, because of the low dielectric constant of about 2.5. However, the HOSP film will be damaged after photoresist removal. The function groups of HOSP will be destroyed by O_2 plasma ashing and chemical wet stripper, which leads to electrical degradation. In order to avoid the issue, H_2 plasma treatment is proposed to prevent HOSP film from photoresisit stripping damage. It is found that leakage current is decreased significantly and the dielectric constant is still maintained at a low k value even after photoresist stripping. Therefore, H_2 plasma treatment is an effective technique to enhance the resistance of HOSP film against photoresist stripping damage. © 2002 Elsevier Science B.V. All rights reserved.

Keywords: HOSP; Photoresist removal; Electrical degradation; Stripping; H_2 plasma

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 due to parasitic resistance and capacitance of the interconnections. In addition, interconnection becomes a bottleneck in improving the chip performance such as the speed and power consumption [1,2].

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Using low dielectric constant (low k) materials as an intermetal dielectric is one of the effective ways to decrease RC delay. Spin-on glass (SOG) with low dielectric constant is the promising intermetal dielectric [3–7]. The requirements of SOG must conform to low cost, good local planarization capability, high performance and process simplicity. However, most of low-k SOG materials cannot meet all the requirements for ULSI application. Therefore, how to improve the quality of SOG will become more important in multilevel interconnection.

An organic SOG, Hybird-Organic-Siloxane-Polymer (HOSP), belongs to SiO_2-base materials, which has high applicability to the ULSI processes because of the low dielectric constant of about 2.5 [8]. The lower dielectric constant of HOSP comparing to conventional siloxane-based SOG is due to the partial presence of $Si–CH_3$, $Si–H$ and $C–H$ bonds instead of $Si–O$ bonds.

Photoresist stripping is an indispensable process in IC integration. The traditional photoresist stripping contains O_2 plasma dry ashing and wet stripper dipping treatment. However the dielectric properties of the HOSP film often degrade after photoresist stripping process [9,10]. For this reason, we investigate the H_2 plasma treatment to improve the quality of HOSP film. In this study, the properties of H_2 plasma-treated HOSP film are evaluated by electrical measurement as well as chemical composition analyses. In addition, the effect of O_2 plasma and wet stripper treatment are investigated to understand the impact of integrated processes on the dielectric film quality.

2. Experimental

The wafers were coated with the HOSP solution at a rotation of 500 rpm for 5 s and the sequential spin was up to 2500 rpm for 20 s. After coating process, the sequential bakes were conducted on the three hot plates at 150 °C, 200 °C, and 350 °C for 1 min, respectively. Finally, the resulting wafers were further processed by furnace curing at 400 °C under nitrogen ambient for 1 h.

Four samples (Samples STD, 3H, 6H and 9H) were manufactured in this experiment. Sample STD was the as-cured HOSP film without plasma treatment for comparison. Sample 3H, Sample 6H and Sample 9H were the as-cured HOSP films with H_2 plasma treatment for 3, 6 and 9 min, respectively. The H_2 plasma treatment was carried out in Plasma Enhanced Chemical Vapor Deposition (PECVD) chamber. The H_2 plasma was operated at a pressure of 300 m-Torr, and a rf power of 200 W. The flow rate was 700 sccm, and the operation temperature was kept at 300 °C. Then all of the samples were exposed to O_2 plasma ashing for 3 min and followed by wet stripper (commercial trade mark is ACT 935) dipping at 60 °C for 10 min. After photoresist stripping, metal-insulation-semiconductor capacitors (MIS) were manufactured by depositing aluminum onto all of the samples as the top-electrode.

In this study, the molecular bonding of the HOSP films was investigated by fourier transform infrared spectroscopy (FTIR). FTIR measurements were performed on the Bio-Red QS300 FTIR and their data were collected in the absorbance mode. The thickness of the HOSP films was measured by a n&k analyzer. The dielectric constant of HOSP films was measured by a Keithley Model 82 CV meter. The capacitance–voltage ($C–V$) characteristic was measured at 1 MHz with an AC bias for high frequency. Finally, the current–voltage ($I–V$) characteristics were also measured using MIS structure to evaluate the insulated property of HOSP film.
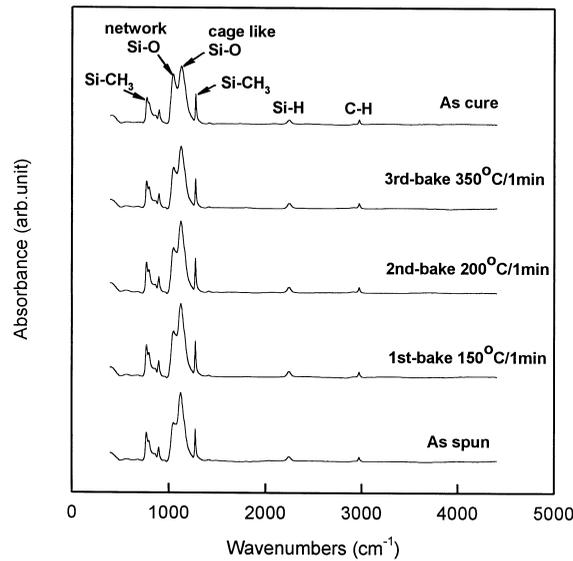
Fig. 1. The FTIR spectra of HOSP films before and after a series of baking and curing steps.

3. Results and discussion

Fig. 1. shows the FTIR spectra of HOSP 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 signal is decreased and Si–O–Si (network) peak intensity is increased. After 400 °C curing, the network structure appeared significantly. It is shown clearly that a large amount of Si–O bonds crosslink into Si–O–Si bonds and form a more rigid network structure.

In the integration processes, photoresist stripping is the indispensable step to remove organic elements. The photoresist removal is implemented conventionally by utilizing O_2 plasma ashing and wet stripper solution treatment. Therefore, the impact of O_2 plasma and chemical wet stripper on the quality of HOSP film must be investigated. Fig. 2 shows the FTIR spectra of the as-cured HOSP film before and after photoresist stripping process. Si–OH and H–OH bonds appear after photoresist stripping. Furthermore, the intensity of Si–H, C–H and Si–CH$_3$ peak signals are also decreased dramatically.

Fig. 3 shows the leakage current density of the HOSP films before and after the photoresist stripping process. The leakage current of HOSP film is increased after photoresist stripping, and furthermore the dielectric constant is also increased after photoresist stripping, as shown in Fig. 4.

No matter electrical measurement or material analysis, these results show that film degradation occurs in the HOSP films after photoresist removal. During O_2 plasma ashing, Si–CH$_3$ bonds and Si–H bonds in HOSP film will be broken by oxygen radicals attack. The broken Si–H, C–H and Si–CH$_3$ bonds will form the dangling bonds, leading to the unstable film. Sequentially, the high-alkalinity content of wet stripper solution (pH = 12.6) lead to a continuous hydrolysis reactions of HOSP films, forming even more dangling bonds. These dangling bonds will react with hydroxide ion (OH$^-$) in wet stripper solution and convert themselves into Si–OH bonds continuously. In
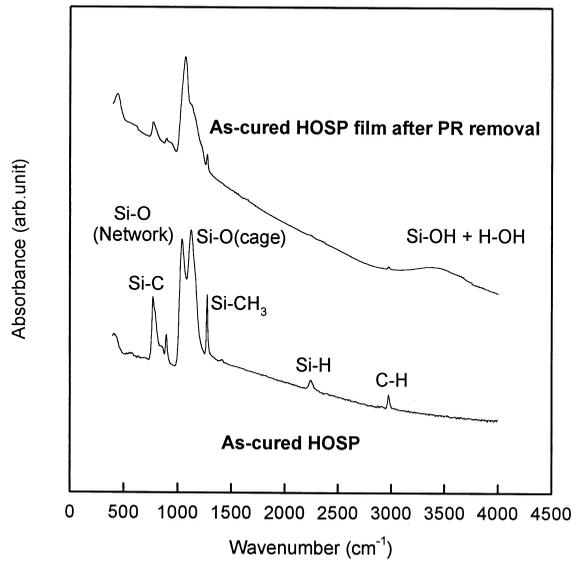
Fig. 2. The FTIR spectra of HOSP films before and after photoresist stripping processes (i.e. O_2 plasma ashing and wet stripper dipping).

addition, the Si–OH bonds in the damaged HOSP films often lead to moisture uptake. Hence the leakage current and the dielectric constant will be increased.

For this reason, H_2 plasma is used to treat HOSP film in order to enhance the resistance against photoresist stripping damage. Fig. 5 shows the leakage currents density of H_2 plasma-treated HOSP films (Samples 3H, 6H and 9H) after photoresist stripping process. The leakage currents of H_2
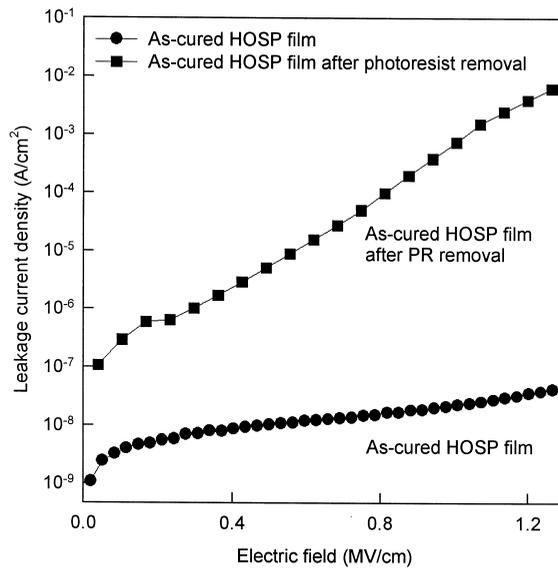
Fig. 3. The leakage current density of HOSP film before and after photoresist stripping processes.
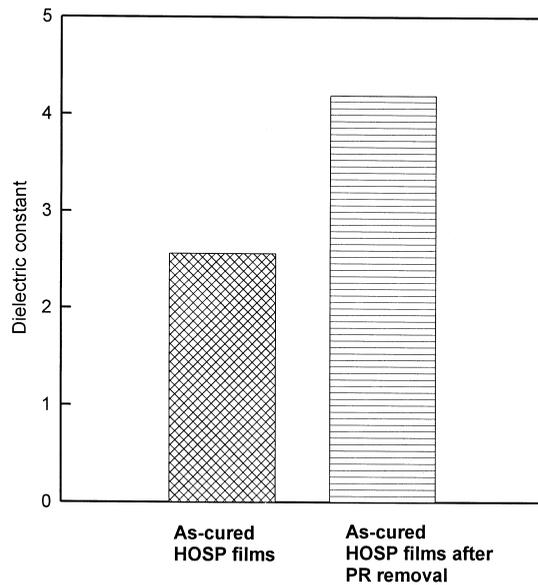
Fig. 4. The dielectric constant of HOSP film before and after photoresist stripping processes.

plasma-treated HOSP films are much lower than that of untreated HOSP film after photoresist stripping. Moreover, the dielectric constants of H_2 plasma-treated HOSP films (Samples 3H, 6H and 9H) can still maintain stable after photoresist stripping, as shown in Fig. 6.

Fig. 7 shows the FTIR spectra of H_2 plasma-treated HOSP films (Samples 3H, 6H and 9H) after being undergone photoresist stripping. All the function group signals of the H_2 plasma-treated HOSP
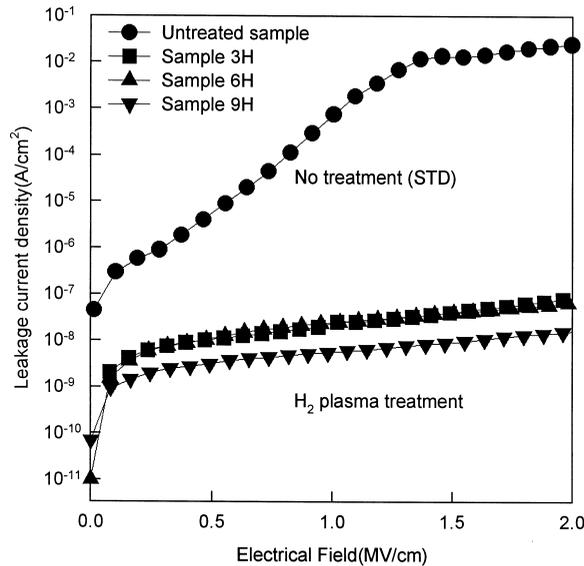
Fig. 5. The leakage current density of Sample STD, Sample 3H, Sample 6H and Sample 9H after photoresist stripping processes.
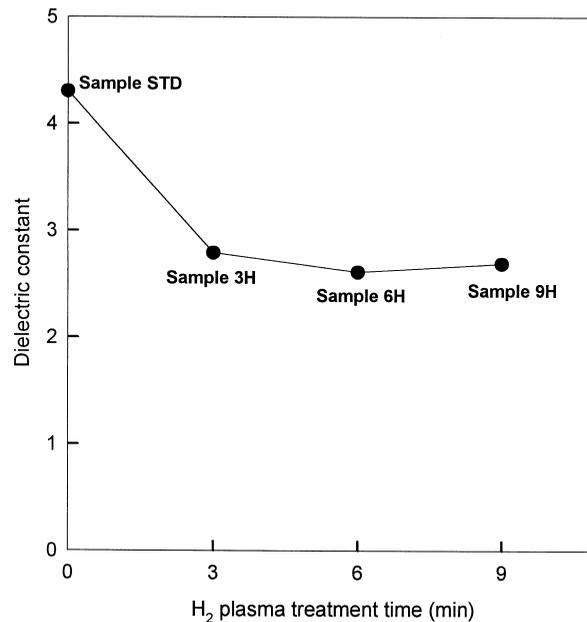
Fig. 6. The dielectric constant of Sample STD, Sample 3H, Sample 6H and Sample 9H after photoresist stripping processes.

films can be observed and the peak intensity is still maintained at a high level even after photoresist stripping. In addition, the peaks of Si–OH bonds and H–OH bonds do not appear in the FTIR spectra.

The dangling bonds in HOSP surface can easily convert to Si–OH bonds, absorbing moisture and lead to the reduction of reliability. The H_2 plasma treatment provides active hydrogen to passivate the
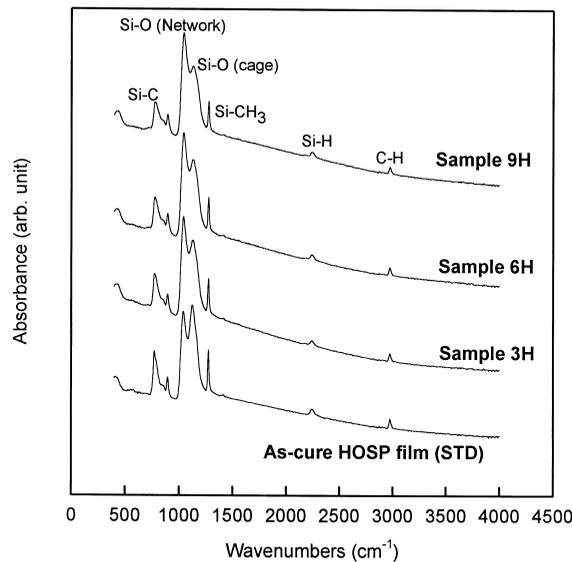
Fig. 7. The FTIR spectra of Sample STD, Sample 3H, Sample 6H and Sample 9H after photoresist stripping processes.

HOSP surface and forms a thin passivation layer. For this reason, the dangling bond content in HOSP film could be decreased by the H_2 plasma treatment. The thin passivation layer on the HOSP surface can enhance the resistibility against moisture uptake. Therefore, the leakage current will decrease and dielectric constant will keep at a low k value when H_2 plasma-treated HOSP films undergoes photoresist stripping process.

4. Conclusions

In this work, H_2 plasma treatment to the HOSP film is investigated during photoresist stripping processes. The H_2 plasma treatment can passivate the HOSP surface with active hydrogen radicals and prevent dielectric loss originating from O_2 plasma and wet stripper processes. Material analyses and electric measurements can confirm our inference. The Si–OH bounds do not appear in the FTIR spectra even after H_2 plasma-treated HOSP film undergoes photoresist stripping. It is also found that the leakage current of H_2 plasma-treated HOSP films is decreased significantly and the dielectric constant are also maintained at a low k value. These results indicate that H_2 plasma treatment is a promising technique to enhance the resistance of HOSP film against photoresist stripping damage.

Acknowledgements

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