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Enhancing the resistance of low-*k* hydrogen silsesquioxane (HSQ) to wet stripper damage

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Abstract

The interaction between low-*k* hydrogen silsesquioxane (HSQ) film and wet stripper was investigated. The wet stripper has been commonly used to remove photoresist in IC integration processing. However, the high content of alkalinity in the stripper solution often leads to the hydrolysis of HSQ film, forming dangling bonds in the HSQ. The dangling bonds in the HSQ film can easily react with hydroxide ion (OH⁻) in wet stripper solution and form Si–OH bonds. The resultant HSQ film will tend to uptake water and consequently increase both the leakage current and dielectric constant. In this study, H₂-plasma pre-treatment was applied to the HSQ film. The hydrogen plasma treatment passivates the HSQ surface and prevent HSQ from water uptake during photoresist stripping. Therefore, dielectric degradation can be avoided with the H₂-plasma pre-treatment. © 2001 Elsevier Science B.V. All rights reserved.

Keywords: HSQ; Hydrogen plasma; Low *k*; Wet stripper; PR removal

1. Introduction

With an increase in device density, the surface of a wafer cannot offer enough area to manufacture interconnect circuits. As a result, multilevel interconnection for high performance ULSIs are developed. For deep sub-micron CMOS technology, the speed of the devices is limited more by interconnect delay (*RC* delay) and less by intrinsic gate delay [1,2]. Therefore, interconnect delay becomes a dominant factor in determining signal propagation speed in ULSIs.

Copper with its relatively low resistivity and interlayer films with lower dielectric constant has been proposed for reducing the *RC* delay. For interlayer formation, many methods have been used for deposition. Spin-on deposition (SOG) is one of the superior methods to form the low-*k* films [3–5]. SOG possesses good plan-

arization and process simplicity in multilevel manufacture. One of the most promising low dielectric materials is hydrogen silsesquioxane (HSQ) [6–8]. This class of inorganic spin-on dielectric potentially combines the desired features of gap filling, planarization and low dielectric constant. The low-*k* properties can be achieved if the density of Si–H bonding is maintained at a high level and if the formation of –OH bonds and absorption or creation of water in the film is minimized [8,9]. However, dielectric loss usually occurs during processing integration. In multilevel manufacturing, photoresist removal is commonly performed with O₂ plasma and wet stripper solution. Many documents have revealed that the integration issues resulted from O₂-plasma dry ashing [7]. However, there are few reports discussing the effects of wet stripping on dielectric properties.

In this study, the effect of wet stripper solution on HSQ is investigated to understand the impact of integration processing on the dielectric film quality. In addition, H₂ plasma treatment is carried out on the HSQ for improving the resistance to stripper solution.

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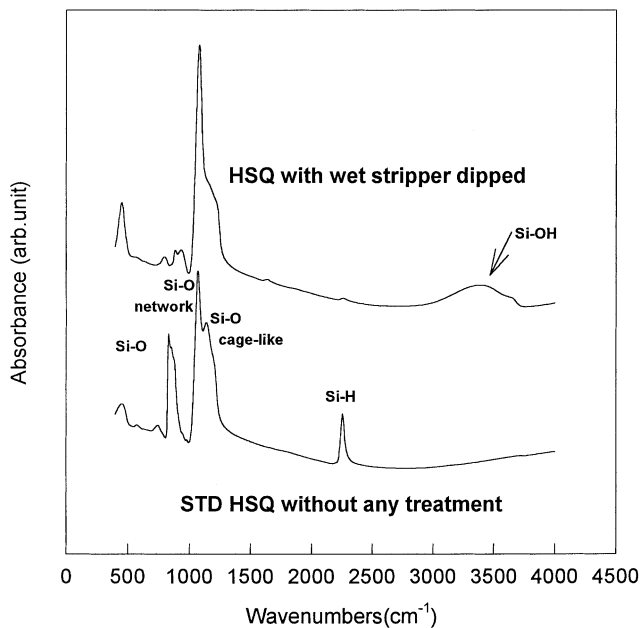


Fig. 1. The FTIR spectra of HSQ before and after wet stripper dipping.

2. Experimental

The unpatterned silicon wafers were coated with a single layer of HSQ film and baked sequentially on the hot plate at 150, 200 and 300°C for 1 min, respectively. The resulting wafers were further processed by furnace curing at 400°C for 30 min. For each condition, shrinkage, refractive index and Fourier-transform infrared absorption spectra (FTIR) were evaluated. In this experiment, two groups of samples were manufactured. The first group of wafers, the control sample, was the as-cured HSQ film. The second group of wafers were HSQ films with H₂ plasma treatment for 3, 6 and 9 min, which were labelled as sample H3, H6 and H9, respectively. Both groups of samples were dipped into wet stripper solution (commercial trade mark is ACT 935) at 60°C for 10 min.

The PE-CVD chamber was used for H₂ plasma treatments. H₂ plasma was operated at a pressure of 300 mtorr, with an rf power of 200 W. The flow rate for each of these hydrogen gases was 300 sccm and the temperature of chamber was kept at 300°C.

For electrical measurements, metal–insulator–semiconductor (MIS) capacitors were fabricated by sputtering aluminum contacts onto as the top electrode. A Keithley Model 82 CV meter was used to measure the dielectric constants of HSQ films. The capacitors were measured at 1 MHz with an AC bias for high frequency C–V curves. Leakage current–voltage (*I*–*V*) characteristics of HSQ were measured by an HP4145B semiconductor parameter analyzer.

3. Results and discussion

In integrated processes, the photoresist removal is implemented conventionally by utilizing O₂ plasma ashing and wet stripper solution treatment. The issue of O₂ plasma ashing to the HSQ film has been previously shown [6]. In this study, the impact of wet stripper processing on the HSQ film is investigated. Fig. 1 shows FTIR spectra of HSQ film before and after dipping in the wet stripper solution. The Si–OH and H–OH peaks appear after stripper dipping. Furthermore, both the intensity of Si–H and S–O peaks are decreased dramatically. There are factors that might cause an increase in the Si–OH bonds. By dipping HSQ films into wet stripper, the high alkaline content may cause the hydrolysis of HSQ films. The Si–H bonds in HSQ films will be broken due to the high alkalinity. Subsequently, the dangling bonds will be present in the HSQ film. The dangling bonds easily react with hydroxide ions (OH[−]) in wet stripper solution and convert themselves into Si–OH bonds. As a result, the HSQ becomes unstable when exposed to wet stripper solution. FTIR spectra clearly shows that a large amount of the Si–O bonds and Si–H bonds in HSQ decompose after wet stripper treatment.

Fig. 2 shows the leakage current density of HSQ before and after wet stripper processing. The leakage current of HSQ film increases after being dipped into the wet stripper solution. In addition, the dielectric constant of HSQ increases significantly, as shown in Fig. 3. These degradations are due to the formation of Si–OH bonds in the HSQ, which is consistent with

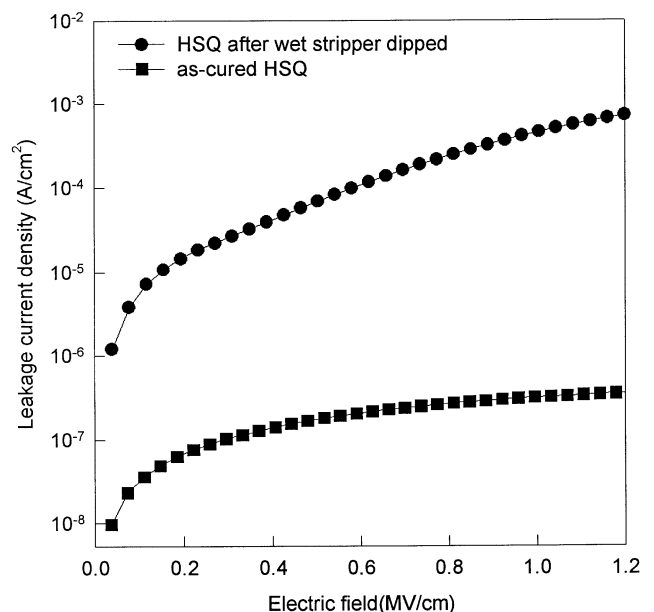


Fig. 2. The leakage current density of HSQ films before and after wet stripper dipping.

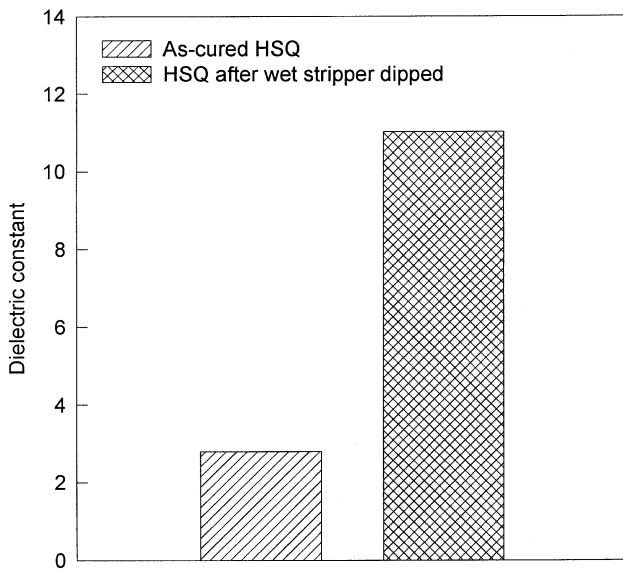


Fig. 3. The dielectric constant of HSQ films before and after wet stripper dipping.

FTIR data. The HSQ film with Si–OH bonds will easily absorb moisture. The polarity of moisture molecules leads to an increase in both leakage current and dielectric constant [10].

The resistance to wet stripper attack was investigated by H₂ plasma treatment. FTIR spectra of the H₂ plasma-treated HSQ films (samples H3, H6 and H9) after wet stripper dipping are shown in Fig. 4. In comparing with as-cured HSQ film, no significant change is observed in

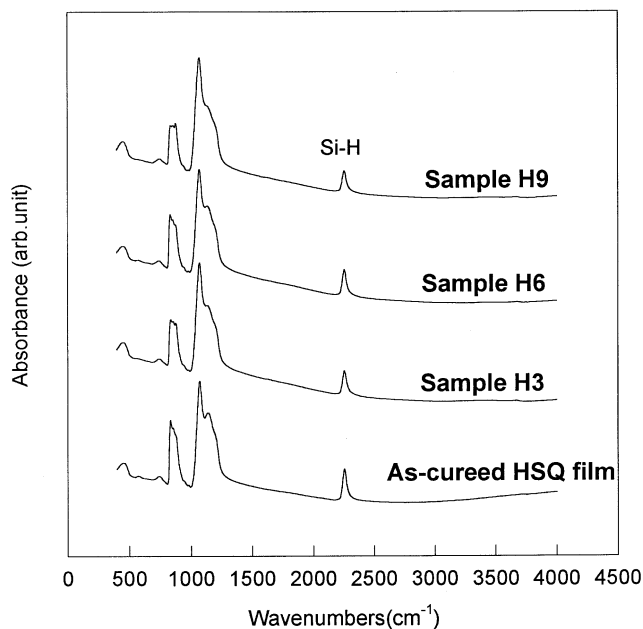


Fig. 4. The FTIR spectra of samples H3, H6 and H9 after wet stripper treatment.

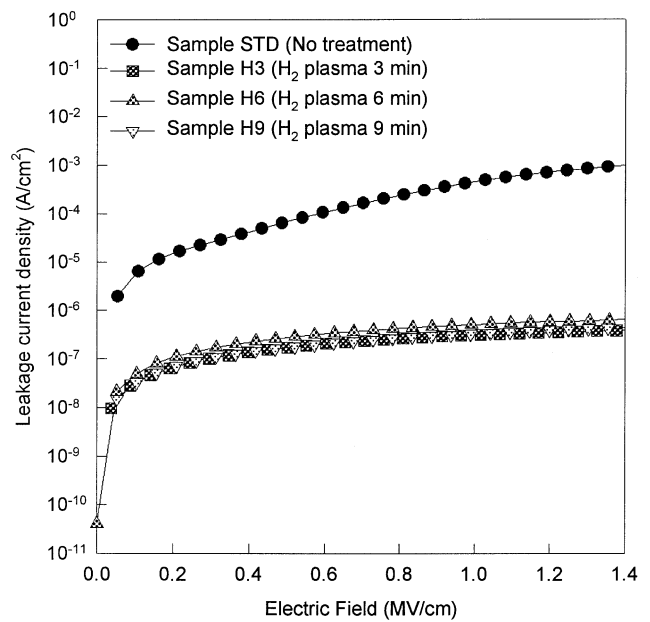


Fig. 5. The leakage current density of sample STD, 3H, H6 and H9 after wet stripper treatment.

the H₂ plasma-treated HSQ films. The Si–H bonds in the samples H3, H6 and H9 still maintain a high level even after dipping in the wet stripper solution. Meanwhile, Si–OH bonds and H–OH bonds do not appear in the FTIR.

Figs. 5 and 6 show the leakage current and dielectric constant of samples H3, H6 and H9 after stripper

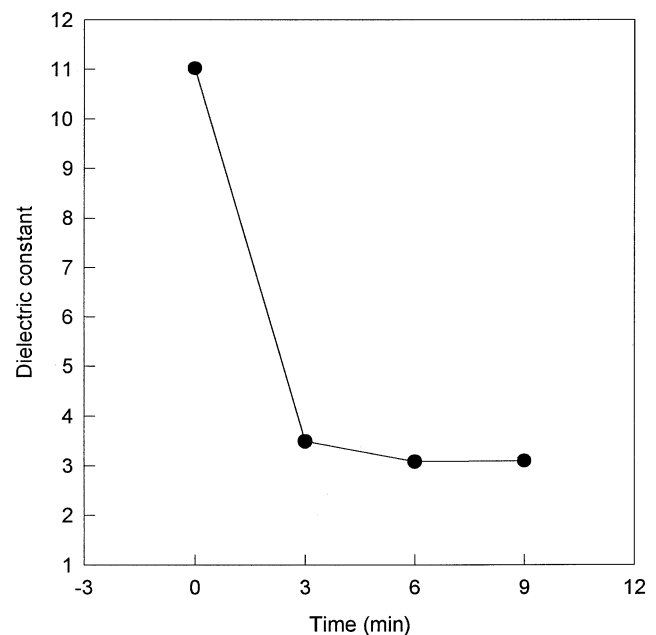


Fig. 6. The dielectric constant of sample STD, H3, H6 and H9 after wet stripper treatment.

dipping, respectively. The leakage current of HSQ films decreases when H₂ plasma treatment time is >3 min. In addition, the dielectric constant of H₂ plasma treated HSQ maintains a stable value, even if HSQ is dipping into the stripper solution. The operational temperature for the H₂ plasma treatment is 300°C, which is less than the curing temperature of 400°C. As a result, we conclude that the dominant effect on leakage reduction of the HSQ is hydrogen plasma treatment. The temperature factor is not as important as the hydrogen plasma treatment. The effect of hydrogen in stabilizing the HSQ is proposed as follows.

In this work, hydrogen plasma treatment provides active hydrogen radical to passivate the porous HSQ. The porous structure of HSQ results in a low dielectric constant. However, in the case of depositing HSQ without a capping oxide layer, the exposed surface area is very large. If the HSQ is not passivated, most of those dangling bonds will remain exposed. Dangling bonds can then react easily with the hydroxide ion (OH⁻) in wet stripper solution and form Si–OH bonds. Sequentially, the Si–OH bond will lead to moisture uptake so that both the dielectric constant and leakage current will increase. The H₂ plasma treatment provides hydrogen to passivate the HSQ and reduce the dangling bond content in HSQ. Therefore, the dielectric properties of H₂ plasma-treated HSQ film are superior than that of untreated-HSQ film. Electrical characteristics are also consistent with our model.

4. Conclusions

In this study, the effects of H₂ plasma pre-treatment on HSQ films have been investigated. The quality of low dielectric constant HSQ films is significantly improved by hydrogen plasma pre-treatment. The H₂ plasma treatment passivates the porous HSQ with additional hydrogen radicals and protects dielectric proper-

ties from wet stripper damage. Consistent with our inference, the signal of Si–OH bounds have not appeared in the FTIR spectra when HSQ film was pre-treated using hydrogen plasma. This indicates that hydrogen plasma treatment is an effective method against the damage of chemical wet stripper solution during photoresist stripping.

Acknowledgements

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