IOPscience iopscience.iop.org

Home Search Collections Journals About Contact us My IOPscience

Effectiveness of NH_3 Plasma Treatment in Preventing Wet Stripper Damage to Low-*K* Hydrogen Silsesquioxane (HSQ)

This content has been downloaded from IOPscience. Please scroll down to see the full text.

2001 Jpn. J. Appl. Phys. 40 L1311

(http://iopscience.iop.org/1347-4065/40/12A/L1311)

View the table of contents for this issue, or go to the journal homepage for more

Download details:

IP Address: 140.113.38.11
This content was downloaded on 28/04/2014 at 05:29

Please note that terms and conditions apply.

Jpn. J. Appl. Phys. Vol. 40 (2001) pp. L 1311–L 1313
Part 2, No. 12A, 1 December 2001
©2001 The Japan Society of Applied Physics

Effectiveness of NH_3 Plasma Treatment in Preventing Wet Stripper Damage to Low-*K* Hydrogen Silsesquioxane (HSQ)

Ting-Chang CHANG[1,3], Yi-Shien MOR[2], Po-Tsun LIU[3], Tsung-Ming TSAI[2], Chi-Wen CHEN[2], Yu-Jen MEI[4] and Simon-M. SZE[2,3]

[1]*Department of Physics, National Sun Yat-Sen University, Kaohsiung, Taiwan, R.O.C.*
[2]*Institute of Electronics, National Chiao Tung University, Hsin-Chu, Taiwan, R.O.C.*
[3]*National Nano Device Laboratory, 1001-1 Ta-Hsueh Rd., Hsin-Chu 300, Taiwan, R.O.C.*
[4]*Department of Electrical Engineering, Ching-Yun Institute of Technology, Jung-Li, Taiwan, R.O.C.*

(Received August 24, 2001; accepted for publication October 12, 2001)

Wet stripper is commonly used to remove photoresist in IC integration processing. However, the high alkalinity of the wet stripper solution often leads to the hydrolysis of hydrogen silsesquioxane (HSQ) film and induces water uptake. As a result, both the leakage current and dielectric constant of HSQ increase. In this study, NH_3 plasma treatment was applied to the HSQ film to form a thin nitrogen-containing layer on the HSQ surface and prevents the hydrolysis of HSQ during photoresist stripping. Dielectric degradation can be prevented by NH_3 plasma treatment.

KEYWORDS: low-*k*, HSQ, wet stripper, hydrolysis, water uptake, NH_3 plasma

As the critical dimension continue to shrinks to 0.25 μm and below, the interconnect delay becomes a limiting factor in the increase of device speed.[1,2] For decreasing the total circuit transmission time (i.e., resistance capacitance (RC) delay), using low-*k* materials as the dielectric film has been proposed.[3–5] One of the most promising low dielectric constant materials is hydrogen silsesquioxane (HSQ).[6,7] However, photoresist stripping which involves O_2 plasma dry ashing and wet stripper solution dipping leads to dielectric degradation in the HSQ film. Moreover, photoresist stripping can not be omitted because it is an indispensable step in integrated circuit fabrication. NH_3 plasma treatment of HSQ has been used for copper interconnection application.[3,8] However, the efficacy of NH_3 plasma treatment of HSQ in preventing wet stripper damage has not been reported extensively. In this study, the impact of wet stripper on HSQ is investigated. In addition, NH_3 plasma treatment is applied to HSQ film in order to prevent dielectric degradation after photoresist stripping.

Unpatterned silicon wafers were coated with a single layer of HSQ film, and baked sequentially on a hot plate at 150°C for 1 min, 200°C for 1 min and 300°C for 1 min. The resulting wafers were then treated by furnace cured at 400°C for 30 min. In this experiment, two types of wafer samples were manufactured. The first type of wafer was the as-cured HSQ film, which was the control sample and was labelled Sample STD. The second type of wafer was HSQ film treated with NH_3 plasma for 3 min, which was labelled Sample NH-3. The NH_3 plasma treatment was carried out in the plasma-enhance chemical vapor deposition (PE-CVD) chamber which was operated at a pressure of 300 mTorr and a radio frequency (rf) power of 200 W. The flow rate was 700 sccm and the temperature of the chamber was kept constant at 300°C. Finally, both types of samples were dipped in wet stripper solution (commercial trademark ACT 935) at 60°C for 10 min, followed by 400°C furnace curing. After completing all of the above steps, aluminum was sputtered onto all samples as the top electrode in order to fabricate the metal-insulator-semiconductor (MIS) capacitors.

In this study, the chemical bonds of the HSQ films were investigated by fourier transform infrared (FTIR) spectroscopy. The thickness of the HSQ films was measured using an N&K analyzer. A Keithley Model 82 CV meter was used to measure the dielectric constants of the HSQ films, and the capacitors were measured at 1 MHZ with an AC bias for high-frequency C–V curves. Finally, an HP4145B semiconductor parameter analyzer was used to measure the leakage current–voltage (I–V) characteristics in order to evaluate the insulation property of the HSQ films.

In the integrated processes, photoresist removal was implemented conventionally by utilizing O_2 plasma ashing and wet stripper solution treatment. We have previously reported the issue of applying O_2 plasma ashing to the HSQ film.[4] In this study, the impact of wet stripper processing on the dielectric properties of the HSQ film is investigated. Figure 1 shows the FTIR spectra of an HSQ film before and after wet stripper treatment. It is found that the Si–OH and H_2O peaks appear after stripper dipping. Furthermore, the intensities of both Si–H and S–O peaks are decreased dramatically.

The reason for the increase of Si–OH bonds is as follows.

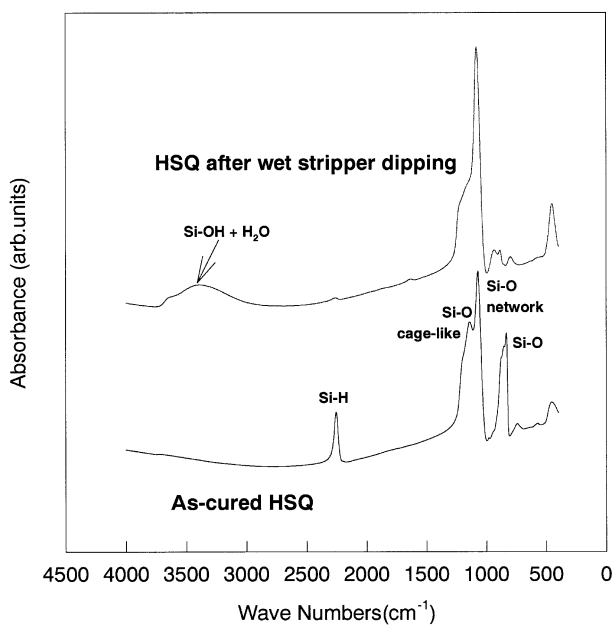


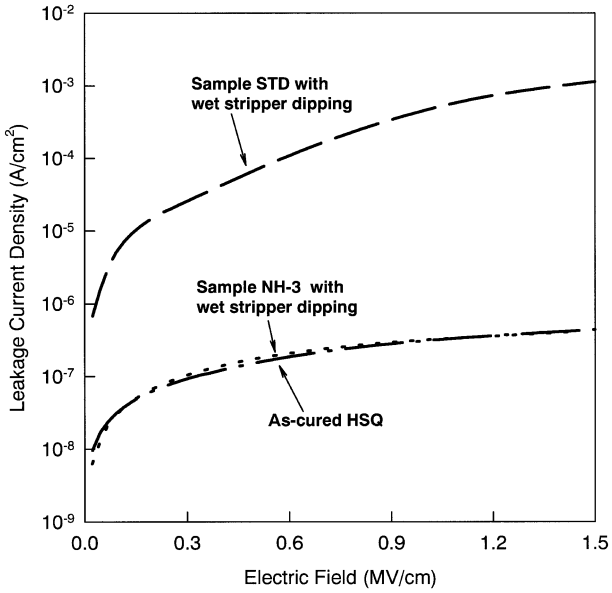
Fig. 1. FTIR spectra of HSQ before and after wet stripper dipping.

The high alkalinity (pH = 12.6) causes film hydrolysis when the HSQ film is dipped into wet stripper. The Si–H bonds in the HSQ film are broken due to the high alkalinity attack. Subsequently, dangling bonds are formed in the HSQ film. The dangling bonds easily react with hydroxide ions (OH^-) in the wet stripper solution and convert themselves into Si–OH bonds.

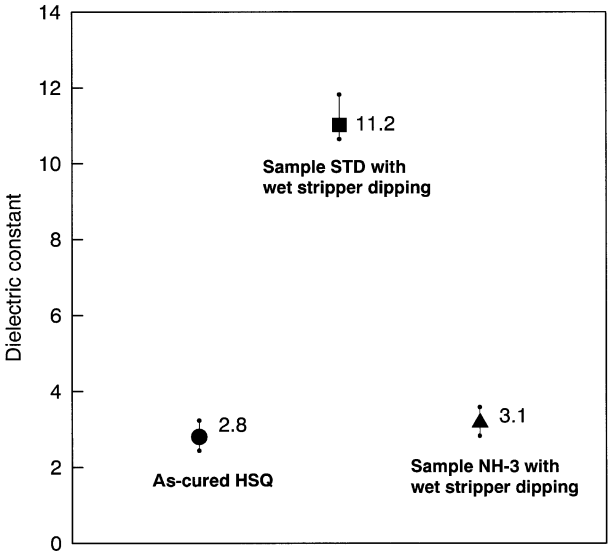
The low-*k* property of HSQ is due to the higher density of Si–H bonds, the minimal formation of Si–OH bonds and the absorption of moisture.[9,10] However, FTIR spectra clearly show that a large amount of Si–H bonds and Si–O bonds decompose. In addition, the Si–OH bonds also increase when HSQ film undergoes wet stripper treatment. For this reason, dielectric loss occurs in the HSQ film after treatment with wet stripper solution.

Figures 2(a) and 2(b) show the dielectric characteristics of Samples STD and NH-3 after undergoing wet stripper treatment. The leakage current and dielectric constant of Sample STD is higher than that of Sample NH-3 after wet stripper treatment. The dielectric degradations are due to the formation of Si–OH bonds in the HSQ. The Si–OH bonds in the HSQ film easily absorb moisture. The polarity of moisture molecules leads to an increase in both leakage current and dielectric constant.[11] However, NH_3-plasma-treated HSQ maintains almost the same dielectric properties as as-cured HSQ even after wet stripper treatment.

The efficacy of NH_3 plasma treatment in preventing wet stripper damage is investigated by FTIR analysis. FTIR spectra of NH_3 plasma-treated HSQ (Sample NH-3) after wet stripper dipping are shown in Fig. 3(a). The intensity of Si–H bonds in Sample NH-3 remains at a high level even after wet

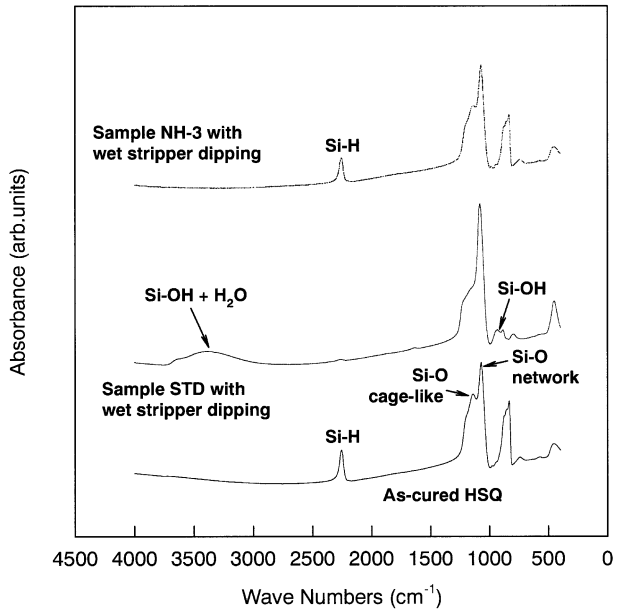


(a)

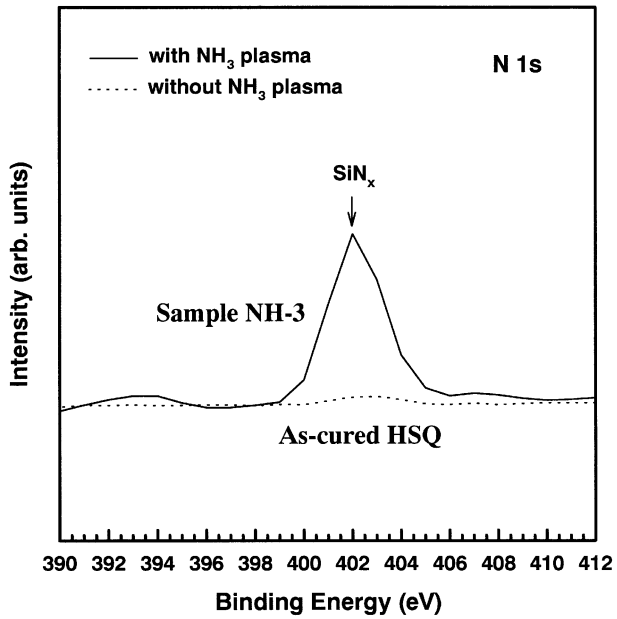


(b)

Fig. 2. (a) Leakage current density and (b) Dielectric constant of Samples STD and NH-3 after wet stripper dipping.



(a)



(b)

Fig. 3. (a) FTIR spectra of Samples STD and NH-3 after wet stripper dipping and (b) XPS spectra of N_{1S} in HSQ with and without NH_3 plasma treatment.

stripper dipping. However, Si–OH bonds and H_2O do not appear in the FTIR spectra. Figure 3(b) shows X-ray photoelectron spectroscopy (XPS) diagrams of NH_3 plasma-treated HSQ film. It is found that a significant signal from nitrogen elements appears at about 402 eV. It is clearly shown that nitrogen atoms are doped in the HSQ film and form a thin nitrogen-containing layer on the NH_3-plasma-treated HSQ surface.

The super wet stripper resistance is due to the existence of a nitrogen-containing layer on the HSQ surface. The thin nitrogen-containing layer is able to not only passivate the HSQ surface but also prevent hydroxide ion (OH^-) attack and moisture uptake during wet stripper solution treatment. Therefore, Si–OH bond formation and moisture uptake are eliminated so that the dielectric constant and leakage current are kept at a low level.

The efficacy of NH_3 plasma treatment on HSQ in preventing wet stripping damage has been investigated in this study. A nitrogen-containing layer is formed on the HSQ surface by NH_3 plasma treatment. The nitrogen-containing layer can protect HSQ from the hydroxide ion (OH^-) attack and Si–OH bond formation. As a result, the nitrogen-containing layer can prevent the wet stripper damage. Consistent with FTIR data, the Si-OH bond signals did not appear even after the NH_3-plasma-treated HSQ film had undergone wet stripper treatment. Therefore, the low-*k* dielectric properties can be maintained. These results indicate that NH_3 plasma treatment is an effective method of protecting HSQ films from chemical wet stripper damage during photoresist stripping processes.

This work was performed at the National Nano Device Laboratory and was supported by the National Science Council of the Republic of China under Contract, Nos. NSC90-2112-M-110-004 and NSC90-2215-E-009-048.

1) *The National Technology Roadmap for Semiconductors* (Semiconductor Industry Association, San Jose, CA, 1997).
2) T. E. Seidel and C. H. Ting: Mater. Res. Soc. Symp. Proc. **381** (1995) 3.
3) P. T. Liu, T. C. Chang, Y. L. Yang, Y. F. Cheng and S. M. Sze: IEEE Trans. Electron Devices **47** (2000) 1733.
4) 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** (1998) 345.
5) P. T. Liu, T. C. Chang, Y. S. Mor and S. M. Sze: Jpn. J. Appl. Phys. **38** (1999) 3482.
6) M. G. Albrecht and C. Blanchette: J. Electrochem. Soc. **145** (1998) 4019.
7) M. J. Loboda, C. M. Grove and R. F. Schneider: J. Electrochem. Soc. **145** (1998) 2861.
8) K. M. Chang, I. C. Deng, S. J. Yeh and Y. P. Tsai: J. Electrochem. Soc. **147** (2000) 1957.
9) T. Gao, A. Witvrouw, B. Coenegrachts, C. Bruynseraede, M. Van Hove and K. Maex: Microelectron. Eng. **50** (2000) 349.
10) H. Meynen, R. Uttecht, T. Gao, M. Van Hove, S. Vanhaelemeersch and K. Maex: *Proc. 3rd Int. Symp. Low & High Dielectric Constant Materials* (Electrochem. Soc., Pennington, 1998) Electrochem. Soc. Proc. Vol. 98-3, p. 29.
11) R. A. Swalin: *Thermodynamics of Solids* (A Wiley-Interscience Publication, New York, 1972) 2nd ed., Chap. 13, p. 302.