Ceramics-Silikáty 62 (3), 293-297 (2018)
www.ceramics-silikaty.cz doi: 10.13168/cs.2018.0024

THE EFFECT OF CH4 PLASMA TREATMENT ON LOW DIELECTRIC HSQ FILMS

#GUIQIN YIN, QIANGHUA YUAN

Key Laboratory of Atomic and Molecular Physics & Functional Materials of Gansu Province,
College of Physics and Electronic Engineering, Northwest Normal University, Lanzhou 730070, China

#E-mail: yinguiq@126.com

Submitted March 25, 2018; accepted May 22, 2018

Keywords: Ceramics, Thin films, Sol-gel

The commercial hydrogen silsesquioxane (HSQ) is made up from low-density and low dielectric constant (low-k) materials. In this paper, low-k HSQ films are obtained by spin-on deposition (SOD) and then followed by treatment with CH_4 plasma using electron cyclotron resonance (ECR). Fourier-transform infrared spectroscopy (FTIR) is used to identify the network structure and cage-like structure of the Si–O–Si bonds and other bonds. Capacitance-voltage (C–V) measurements are used to determine the dielectric constants. A slow positron beam is conducted in order to investigate the pore connectivity within these films. The results suggest that the dielectric constant of the HSQ films, which were treated with CH_4 plasma, increased a little after annealing. CH_4 plasma treatment can restrain the increase in the dielectric constant of the HSQ films.

INTRODUCTION

Dimensions of devices in ultra-large scale integrated circuits (ULSI) continue to shrink according to the international technology roadmap for semiconductors (ITRS), which will delay the signal propagation speed and increase power consumption. This RC delay can be solved by using high conductivity metals for the interconnects, and by using low-k materials as the dielectric [1-2]. At present, the lower dielectric constant of a film can be obtained by producing pores or reducing the polarity of the chemical bonds. Many studies focused on the characteristics of low dielectric constant materials [3-12]. Different kinds of low dielectric constant materials, such as methylsilsesquioxane (MSQ), HSQ, SiCOH, a porous silica, silica-carbon and fluorinated-carbon, have been investigated in recent years. HSQ has a highly porous and three-dimensional network structure, so HSQ is one of the promising candidates for 32 nm ULSI technology. The lower dielectric constant of the HSQ can be achieved by maximising the density of Si–H bonds and minimising the Si–OH bonds. On the other hand, the HSQ dielectric film was prepared by spin-on deposition that is compatible to different processes employed in ULSI [13]. It is well known that annealing is necessary in ULSI circuits in order to keep the stability and decrease the surface roughness of the devices. However, the dielectric constant commonly increases after annealing because of surface structure changes. Some different plasma treatments were found to be effective in restraining the increase in the dielectric constant after annealing. Plasma treatment can reduce the roughness of the surface and change the structure of the film. The densities of the films can be changed also, which will lead to a change in the k-values [14]. H_2/He reactive plasma clean treatment (RPC) successfully prevented Cu from diffusing into low-k polymer after annealing at 200°C for 1000 h. This method is proven to be effective for characterising and improving pore-sealing and barrier performance for Cu/porous ultra-low-k interconnects [15]. Plasma treatments are identified in order to enhance adhesion without degrading the dielectric constant [16]. CHF_3 plasma treatment on the SiCOH film lead to the reduction of the flat-band voltage V_{FB} shift and leakage current of the Cu/SiCOH/Si film [17]. On the other hand, the porous low-k film is damaged as it induced plasma etching radicals [18]. Air-plasma exposure can increase the defect concentrations by breaking the silicon–hydrogen bonds. Nitrogen-plasma exposure, as well as free-radical exposure, has only a small influence on breaking the bond. Ultraviolet curing can improve the chemical-damage resistance of the dielectric [19].

In the paper, we chose the CH_4 molecule as the plasma due to its tetrahedral structure and its C-H bonds that can help form Si-H bonds in the HSQ films. The characteristics of the HSQ films which were treated by CH_4 plasma and then followed by annealing at different temperatures was investigated. The results suggested that the dielectric constant of the HSQ film treated with CH_4 plasma does not substantially increase after annealing.

EXPERIMENTAL

The P–Si (100) wafers cleaned by standard RCA were spin-coated with HSQ at 2000 rpm for 20 s, and baked sequentially on a hot plate at 400°C for 1 min. The CH_4 plasma treatments were carried out in an ECR-CVD chamber. The CH_4 gas flow rate was 5 SCCM and the substrate temperature was kept at 100°C. The MW (2.45 GHz) power was 300 W, I_1 was 140 A and the I_2 was 110 A. The chamber pressure was maintained at 3 mTorr. These films were annealed in a furnace at 300°C and 400°C respectively for 1.5 h in a nitrogen ambient. The annealing time was 1 min, 2 min, 3 min, 4 min and 5 min, respectively.

The HSQ films' thicknesses were measured by an ET 350 profilometer. The HSQ films' chemical bonds and structures were characterised by a FTIR spectroscopy JASCO 600 Plus with 4 cm^{-1} resolution. The dielectric constant (k) was calculated from the C–V characteristics measured at 1 MHz frequency by an HP4294A. The C–V characteristics were undertaken on a MIS structure fabricated as Aluminium/MSQ/p-Si. Slow positron beams were conducted to investigate the pore connectivity within these films.

RESULTS AND DISCUSSION

The result of FTIR

Figure 1 shows the FTIR spectra of the HSQ films treated with CH_4 plasma without annealing. The peak intensities of the Si–H and Si–O bonds only change a little with different CH_4 plasma treatment times. The results indicate that CH_4 plasma treatments have little influence on the non-annealed HSQ films.

The FTIR spectra of the HSQ films treated with CH_4 plasma and annealed at 300°C for 1.5 h in a nitrogen ambient is shown in Figure 2. According to the spectra, the Si–O stretch cage-like peak (1130 cm^{-1}) decreases and the Si–O stretch network peak (1070 cm^{-1}) increases when the HSQ film was treated with CH_4 plasma for 1 min. However, the peak intensity of the Si–O stretch cage-like bonds increases and the peak intensity of the Si–O stretch network bonds decreases with an increase in the CH_4 plasma treatment times. These indicate that the CH_4 plasma treatments changed the structure of the HSQ films annealed at 300°C.

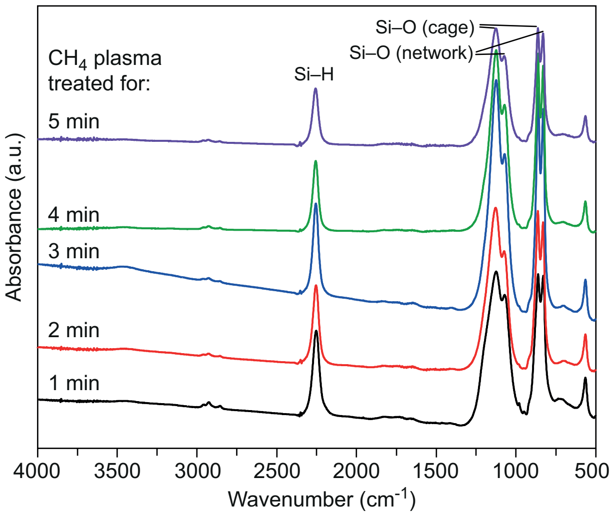

Figure 1. The FTIR spectra of the HSQ films treated with CH_4 plasma without annealing.

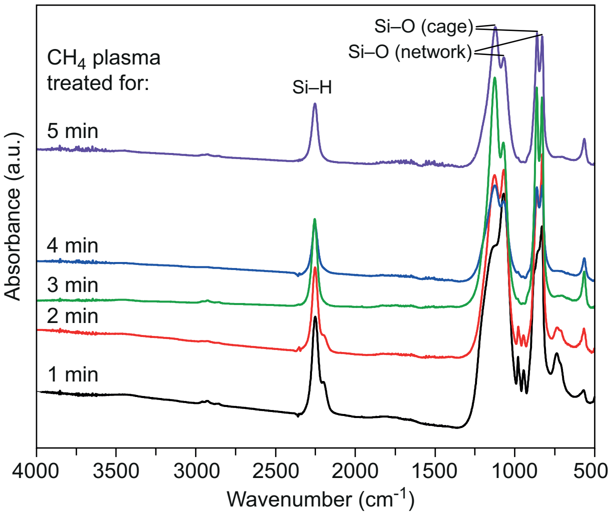

Figure 2. The FTIR spectra of the HSQ films treated with CH_4 plasma and annealed at 300°C for 1.5 h in a nitrogen ambient.

The FTIR spectra of the HSQ films treated with CH_4 plasma and annealed at 400°C for 1.5 h in a nitrogen ambient is shown in Figure 3. The peak intensity of the Si–O stretch cage-like peak (1130 cm^{-1}) decreases and the Si–O stretch network peak (1070 cm^{-1}) increases

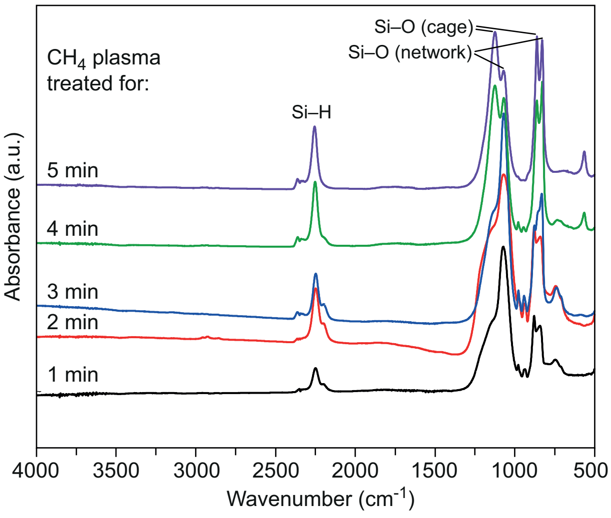

Figure 3. The FTIR spectra of the HSQ films treated with CH_4 plasma and annealed at 400°C for 1.5 h in a nitrogen ambient.

compared with that annealed at 300°C. The peak intensity of the Si–O bonds changes a little with an increase in the CH_4 plasma treatment time, which is similar to that in Figure 2. It can be expressed as follows:

$$\text{H–Si–O} + CH_4 \text{ -> Si–O–Si} + H_2O$$

The Si–O cage-like structure can decrease the density of the films, so it is a benefit to low-k materials. This indicates that CH_4 plasma treatments are a benefit to keep the cage-like structure for the annealed HSQ films.

The result of relative area ratio (%) of the Si–H bonds

The relative area ratio (%) of the Si–H bonds is shown in Figure 4. The relative area of the Si–H bonds firstly increases and then decreases with an increase in the CH_4 plasma treatment time. The relative area of the Si–H bonds increases with an increase in the annealing temperature. With 2 min CH_4 plasma treatments, the relative area of the Si–H bonds increased from 23.06 % (at 300°C) to 39.2 % (at 400°C). The Si–H bonds are hydrophobic, so the HSQ films will be more hydrophobic after the CH_4 plasma treatment. The hydrophobic surface will reduce the moisture uptake.

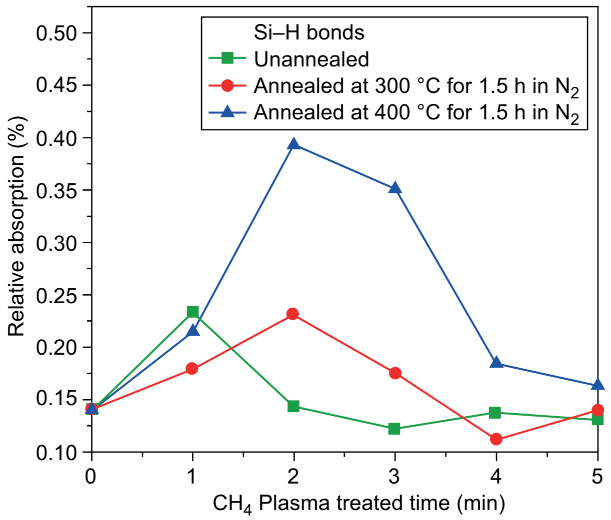

Figure 4. The relative area ratio (%) of the Si–H bonds (peak area/total area of spectrum between 736 and 2393 cm^{-1}) for the results for Figure 1, 2 and 3.

The result of dielectric constants

The dielectric constants of the HSQ films treated with different CH_4 plasma treatment times are shown in Figure 5. The dielectric constant increases with an increase in the CH_4 plasma treatment time for the non-annealed sample. It is 3.02 for the sample that was treated with CH_4 plasma for 3 min. The dielectric constants of the annealed samples are higher than the non-annealed samples. It is 3.12 at 300°C and 3.15 at 400°C, respectively, with CH_4 plasma treatment for 1 min. The dielectric constants of the annealed HSQ films and non-annealed HSQ films all decrease with an increase in the CH_4 plasma treatment time. The increase in the dielectric constant is due to the conversion of the Si–O cage-like structure into the Si–O network in the CH_4 plasma treatment and the annealed samples. The conversion decreases with an increase in the CH_4 plasma treatment time. The Si–O cage-like structure is a benefit to keep the low density of the HSQ films, so the dielectric constant of the annealed samples increased slightly with an increase in the CH_4 plasma treatment time.

The dielectric constants of the annealed HSQ films will increase due to the conversion of the structure. We found that the dielectric constants of the HSQ films, which were treated with CH_4 plasma, increased slightly after annealing, so the CH_4 plasma treatment can keep the low dielectric constant. The properties of the SiOCH films can be significantly enhanced by CH_4 plasma treatment also [20].

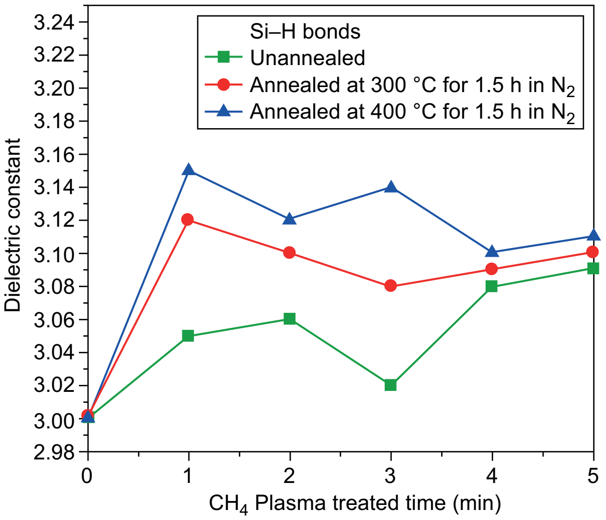

Figure 5. The dielectric constant of the annealed and non-annealed HSQ films with various CH_4 plasma treatments time.

The results of slow positron beam measurements

The results of slow positron beam measurements are shown in Figure 6. The S values are shown as a function of the positron implantation energy. The S data of the sample treated with CH_4 plasma for 3 min and 5 min, and then annealed at 300°C for 1.5 h in a nitrogen ambient, are lower than the others. This means that the implantation depths of these samples are smaller than the others [21]. This suggests that the porous density is smaller than the others as the porous density is proportionate to the implantation depth. As shown in Figure 6, it is similar to the samples treated with the CH_4 plasma for 5 min with and without annealing at 400°C for 1.5 h in a nitrogen ambient. These results show that the porosities of the HSQ films treated with CH_4 plasma changed a little after annealing at 400°C. The low-density materials have low dielectric constants. The dielectric constant of the HSQ films treated with CH_4 plasma increased slightly after being annealed at 400°C. The S data of the sample treated with CH_4 plasma for 5 min and annealed at 300°C for 1.5 h in a nitrogen ambient is lower than that annealed at 400°C. The reason may be that the higher annealing temperature destroys the Si–O bonds and produces porosities. These results suggest that a proper annealing temperature can keep proper porosities.

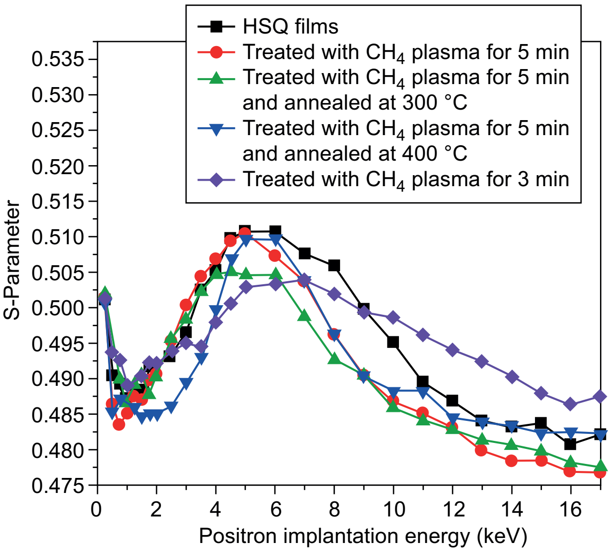

Figure 6. The s-parameter vs. the positron implantation energy (slow positron beam measurements).

CONCLUSIONS

The effect of CH_4 plasma treatment for stabilising low dielectric HSQ films has been investigated. As it is known, annealing is an important step in obtaining ULSI. The structure and the electrical properties, such as the leakage current density and the dielectric constant of the annealed HSQ films are more stable than that of the non-annealed one. In this paper, we concluded that: (1) CH_4 plasma treatment can prevent the structure of the annealed HSQ films from becoming destroyed from the FTIR results. (2) The results of the slow positron beams also suggest that the porosities of the HSQ films treated with CH_4 plasma only changed a little after being annealed. (3) CH_4 plasma treatment can keep the characteristics (low leakage current density and low dielectric constant) of the HSQ films after annealing. Therefore, CH_4 plasma treatment is an effective method to keep the low dielectric constant of the annealed HSQ films.

Acknowledgements

The authors gratefully acknowledge the support provided by the Project of Natural Science Foundation of China (11165012), the Project of Natural Science Foundation of GanSu province (145RJZA159).

REFERENCES

1. Zhao X. Y., Liu H. J. (2010): Review of polymer materials with low dielectric constant. *Polymer International*, *59*(5), 597-606. doi: 10.1002/pi.2809
2. Chen Y. H., Jeng U. S., Leu J. (2011): Effect of curing on the porogen size in the low-k MSQ/SBS hybrid films. *Journal of The Electrochemical Society*, *158*(3), G52-G57. doi: 10.1149/1.3529246
3. Yin G., Yuan Q., Ning Z. (2013): Synthesis and structure characterization of low dielectric constant MSQ films by using octamethyl cyclotetrasiloxane (D4) as a porosity promotion agent. *Vacuum*, *96*, 59-62. doi: 10.1016/j.vacuum.2013.03.007
4. Volksen W., Miller R. D., Dubois G. (2009): Low dielectric constant materials. *Chemical reviews*, *110*(1), 56-110. doi: 10.1021/cr9002819
5. Liu P. T., Chang T. C., Hsu K. C., Tseng T. Y., Chen L. M., Wang C. J., Sze S. M. (2002): Characterization of porous silicate for ultra-low k dielectric application. *Thin solid films*, *414*(1), 1-6. doi: 10.1016/S0040-6090(02)00423-6
6. Wang X., Yuan Q., Zhou Y., Yin G., Dong C. (2014): Deposition of Polymer Thin Film Using an Atmospheric Pressure Micro-Plasma Driven by Dual-Frequency Excitation. *Plasma Science and Technology*, *16(1), 68.* doi: 10.1088/1009-0630/16/1/15
7. Chen Y. H., Tu H. E., Leu J. (2012): Effect of surfactants on the porogen size in the low-k methylsilsesquioxane/polystyrene hybrid films. *Microporous and Mesoporous Materials*, *162*, 181-188. doi: 10.1016/j.micromeso.2012.05.042
8. Maex K., Baklanov M. R., Shamiryan D., Lacopi F., Brongersma S. H., Yanovitskaya Z. S. (2003): Low dielectric constant materials for microelectronics. *Journal of Applied Physics*, *93*(11), 8793-8841. doi: 10.1063/1.1567460
9. Yin G., Yuan Q., Ning Z. (2012): Repairing oxygen plasma-damaged on low dielectric constant MSQ (methylsilsesquioxane) films with anneal. *Journal of electroceramics*, *28*(1), 70-73. doi: 10.1007/s10832-011-9679-y
10. Yin, G., Ning, Z., Yuan, Q., Ye, C., & Xin, Y. (2007). Structure characterization of HSQ films for low dielectrics uses D4 as sacrificial porous materials. *Journal of the American Ceramic Society*, *90*(6), 1943-1945. doi: 10.1111/j.1551-2916.2007.01713.x
11. Yin G. Q., Ning Z. Y., Yuan Q. H. (2007): Structure characterization of HSQ films for low dielectrics using D5 as sacrificial porous materials. *Chinese Physics Letters*, *24*(12), 3532. doi: 10.1088/0256-307X/24/12/066
12. Yuan Q. H., Yin G. Q., Ning Z. Y. (2013): Effect of oxygen plasma on low dielectric constant HSQ (Hydrogensilsesquioxane) films. *Plasma Science and Technology*, *15*(1), 86. doi: 10.1088/1009-0630/15/1/14
13. Seraji S., Wu Y., Forbess M., Limmer S. J., Chou T., Cao G. Z. (2000): Sol-Gel-Derived Mesoporous Silica Films with Low Dielectric Constants. *Advanced Materials*, *12*(22),

1695-1698. doi: 10.1002/1521-4095(200011)12:22<1695::AID-ADMA1695>3.0.CO;2-V

14. Yang P., Lu D., Kumar R., Moser H. O. (2005). Influence of plasma treatment on low-k dielectric films in semiconductor manufacturing. *Nuclear Instruments and Methods in Physics Research Section B: Beam Interactions with Materials and Atoms*, *238*(1-4), 310-313. doi: 10.1016/j.nimb.2005.06.068
15. Chen X. T., Gui D., Mo Z. Q., Du A. Y., Chi D. Z., Wang W. D. et al. (2006): Effect of plasma process on low-k material and barrier layer performance. *Thin solid films*, *504*(1-2), 248-251. doi: 10.1016/j.tsf.2005.09.160
16. Humbert A., Mage L., Goldberg C., Junker K., Proenca L., Lhuillier J. B. (2005): Effect of plasma treatments on ultra low-k material properties. *Microelectronic engineering*, *82*(3-4), 399-404. doi: 10.1016/j.mee.2005.07.022
17. Xing Z. Y., Ye C., Yuan J., Xu Y. J., Ning Z. Y. (2009): Effect of CHF3 Plasma Treatment on the Characteristics of SiCOH Low-k Film. *Plasma Science and Technology*, *11*(6), 674. doi: 10.1088/1009-0630/11/6/08
18. Iba Y., Ozaki S., Sasaki M., Kobayashi Y., Kirimura T., Nakata Y. (2010): Mechanism of porous low-k film damage induced by plasma etching radicals. *Microelectronic Engineering*, *87*(3), 451-456. doi: 10.1016/j.mee.2009.07.027
19. Ren H., Jiang G., Antonelli G. A., Nishi Y., Shohet J. L. (2011): The nature of the defects generated from plasma exposure in pristine and ultraviolet-cured low-k organosilicate glass. *Applied Physics Letters*, *98*(25), 252902. doi: 10.1063/1.3601922
20. Yang C. S., Yu Y. H., Lee H. J., Lee K. M., Choi C. K. (2005): The effect of the CH4 plasma treatment on deposited SiOC (–H) films with low dielectric constant prepared by using TMS/O2 PECVD. *Thin Solid Films*, *475*(1-2), 150-154. doi: 10.1016/j.tsf.2004.07.019
21. Brusa R. S., Spagolla M., Karwasz G. P., Zecca A., Ottaviani G. et al. (2004): Porosity in low dielectric constant SiOCH films depth profiled by positron annihilation spectroscopy. *Journal of applied physics*, *95*(5), 2348-2354. doi: 10.1063/1.1644925