The effects of surface-plasma treatment of thin-film hydrogen silesquioxane low *k* dielectric

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Hydrogen silesquioxane (HSQ) is a low dielectric constant material and a potential substitute for conventional silicon dioxide insulator in ULSI system. In this study, the effect of plasma treatment on HSQ films is investigated. The bond structure changes of HSQ after curing, plasma treatment, and water absorption were observed with Fourier transform infrared spectroscopy. Densification of the film occurs after curing, the higher the curing temperature, the lower the dielectric constant and refractive index of the film. Both H_2- and O_2-plasma treatments are employed in this study. The H_2-plasma bombardment enhances the formation of the network structure but raises the moisture absorption of HSQ films. It is found that films subjected to both H_2- and O_2-plasma treatments have lower dielectric constant than those subjected to O_2 treatment alone. Possible mechanisms for the effects of plasma treatments are explored. The residual stress of HSQ film is also studied.
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1. Introduction

As the circuit feature size shrinks below sub-quarter micrometer, the increase of RC propagation delay due to interconnections becomes dominant [1]. Therefore, lower dielectric constant ($k < 3$) materials and lower-resistivity metals instead of silicon dioxide and aluminum have been intensively proposed to achieve high-performance interconnection with smaller RC delay.

The further requirements for the new interlayer dielectric materials are high quality and reliability, low stress, simplicity of process, and ease of integration. Hydrogen silesquioxane (HSQ) is one of the promising candidates with a highly porous three-dimensional network structure. The general formula for HSQ is $(HSiO_{1.5})_{2n}$ where $n = 3–8$ [2]. HSQ has many advantages such as low dielectric constant (about 2.7), its carbon-free nature, non-etchback processing, excellent gap-filling, good planarization, and low moisture uptake. However, HSQ also has many integration issues such as Si–H bonds thermal dissociation, oxidation, plasma damage, etc. [3]. It was reported that with appropriate plasma treatments the thermal stability of HSQ could be enhanced [4]. Nevertheless, the plasma treatment may damage the surface and/or change the surface chemistry of HSQ [5, 6], and the reliability of the low-*k* dielectric HSQ may degrade.

In this study, HSQ thin films are subjected to H_2- and/or O_2-plasma treatments, and the impacts of these processes on the dielectric films including: bond structure, surface roughness, water absorbance, and dielectric constant, are investigated.

2. Experimental procedures

Four-inch p-type, (1 0 0)-oriented Si wafers with a nominal resistivity of 10Ω cm were employed as substrate. The Si wafers were cleaned with the standard RCA cleaning process. HSQ was prepared by spin coating Dow-Corning Flowable Oxide (FOx®-15) on the wafer. The spin cycle was carried out at 500 r.p.m. for 5 s and the final ramp cycle was 2500 r.p.m. for 25 s. The wafers were baked on three different hot plates sequentially at 150 °C, 200 °C, and 300 °C for 1 min each. A curing process was performed in a N_2 furnace at 350–500 °C for 1 h. The thickness of the cured layer is about 450 nm. H_2 and O_2 plasma treatment was followed at 250 °C with 100 and 300 W power, respectively, by PECVD. The time of plasma treatment varied from 0 to 10 min. After plasma treatment, some samples were immersed in DI water for 10–30 h to observe the moisture absorbency of HSQ with different plasma-treatment time.

Samples for electrical measurement had a Pt/HSQ/Pt/ TaN/Si MIM structure patterned by a shadow mask process. The capacitance of the MIM structure was measured and the dielectric constant of the film calculated.

The imizidation and chemical-bond structure of HSQ films were investigated by an FT-IR spectrometer (QS300 FT-IR System, Bio-Rad Laboratory, Inc., USA). The range is from 400 to 4000 cm^{-1}. The thickness and refractive index of HSQ films were measured by an n&k analyzer (Nano Spec/AFT Models 210UV) and a cross-sectional view was obtained using a field emission scanning electron microscope (FESEM, S-

4000, Hitachi, Japan). An atomic force microscope (AFM, DI5000, Digital Instrument) was employed to measure the surface morphology and roughness of the films. The residual stress of HSQ films was measured with a film-stress measurement system (Tencor FLX-2320, KLA-TENCOR Cor., CA., USA). The FLX-2320 determines stress by measuring the curvature change pre- and post-deposition of the film. The difference in curvature is used to calculate stress with Stoney's equation, which relates the biaxial modulus of the substrate, thickness of the film and substrate, and the radius of curvature of pre- and post-process samples.

3. Results and discussion

The three-dimensional porous network structure of HSQ is obtained through curing. A typical structure of HSQ is an Si–O cage containing Si–H bonds. Upon curing, some of the Si–H bonds dissociate and the cage is rearranged into a network structure as shown schematically in Fig. 1 [7]. Fig. 2(a) shows the Fourier transform infrared (FTIR) spectra before and after a series of baking and curing steps. The spectra exhibit a Si–H peak at $2252\,cm^{-1}$, a Si–O cage-like peak at $1130\,cm^{-1}$, a Si–O stretch network peak at $1070\,cm^{-1}$, and a Si–O bend cage-like peak at $864\,cm^{-1}$ [7]. The Si–H bond $(2252\,cm^{-1})$ absorbance decreases as the curing temperature increases. The Si–O cage-like bond $(1130\,cm^{-1})$ and the Si–O bend bond $(864\,cm^{-1})$ break to form a Si–O network-like bond $(1070\,cm^{-1})$. As shown in Fig. 2(b), the peak ratios of $1070\,cm^{-1}/1130\,cm^{-1}$, $1070\,cm^{-1}/864\,cm^{-1}$, and $2252\,cm^{-1}/1070\,cm^{-1}$ are almost constant when specimens are baked at temperatures $\leq 300\,°C$, while abrupt changes in peak ratios are observed after curing at $400\,°C$. This suggests that the

Figure 2 (a) FTIR spectra of HSQ before and after a series of baking and curing steps, (b) absorbance peak ratio as a function of baking or curing temperature. Data in the brackets are the relative ratio based on the as-spun sample.

structure of HSQ changes from a cage-like structure to a network structure after it was cured at $400\,°C$ for 1 h.

Fig. 3 shows the thickness and refractive index of HSQ as a function of curing temperature. The thickness of cured samples decreases with increasing curing temperature, which means a denser structure is obtained after curing at higher temperature. The thickness of the $500\,°C$-cured sample is about 9.5% less than that of the $350\,°C$-cured one. The refractive index of HSQ film is 1.38 for the $350\,°C$-cured one and then increases to 1.41 with curing at $500\,°C$. Fig. 4 is the FTIR spectra of PECVD TEOS SiO_2. The major difference between the spectra of TEOS SiO_2 and HSQ is the presence of the Si–H bond in HSQ.

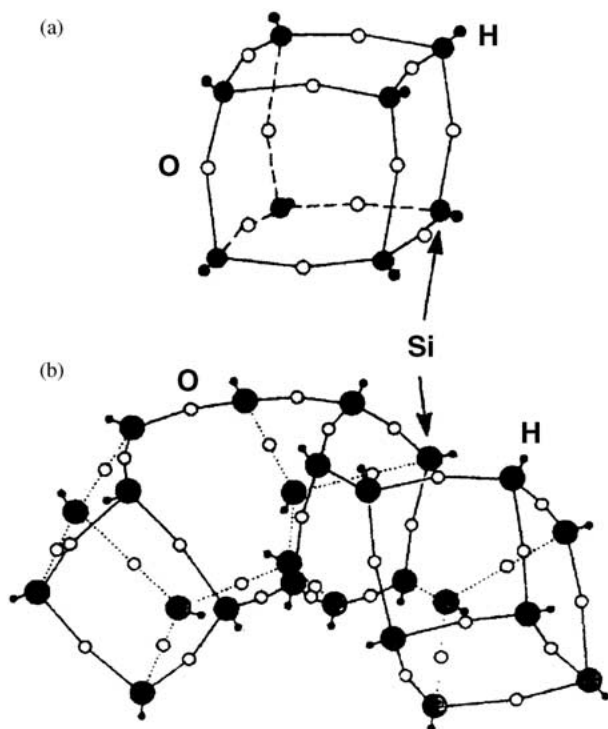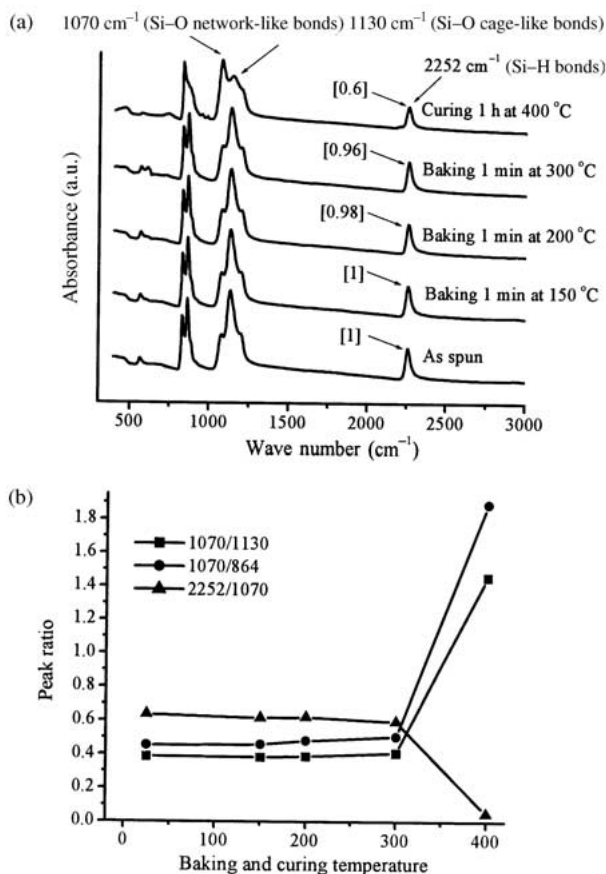*Figure 1* Schematic diagram of the molecular structure of HSQ (a) Si–O cage containing Si–H bonds and (b) network structure [7].
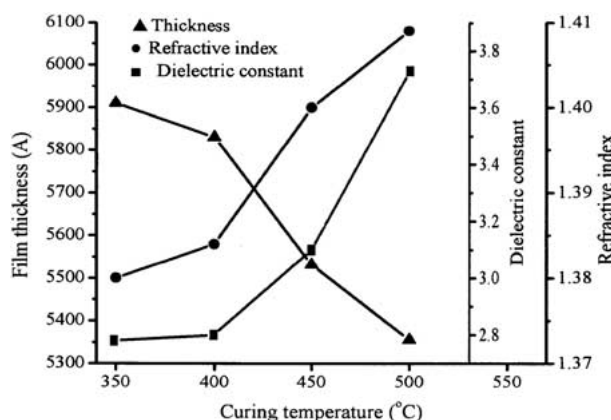

Figure 3 Thickness, dielectric constant, and refractive index of HSQ with different curing temperature.
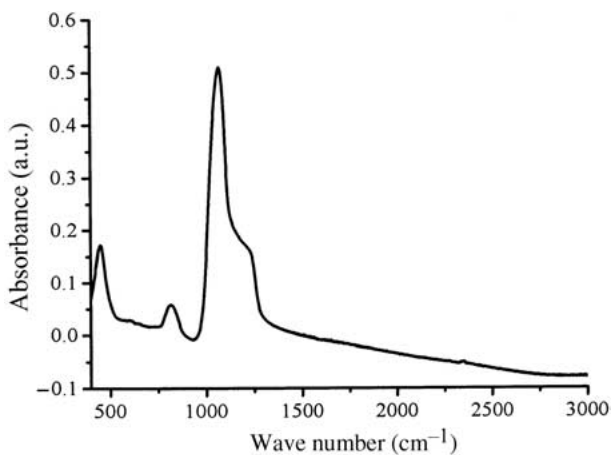
Figure 4 FTIR spectra of PECVD TEOS SiO$_2$.

Figure 5 FTIR spectra of HSQ after H$_2$-plasma treatment at 250 °C for various times.
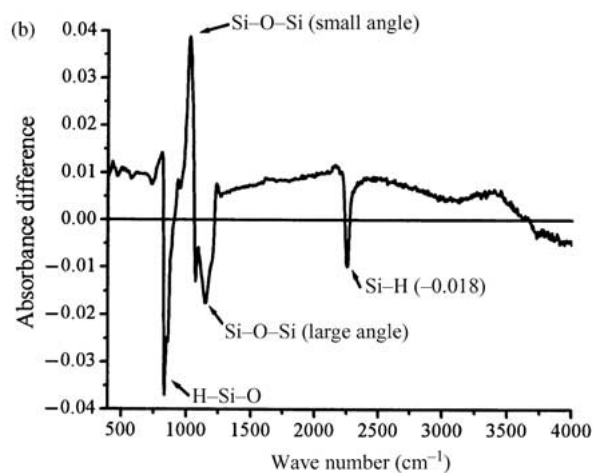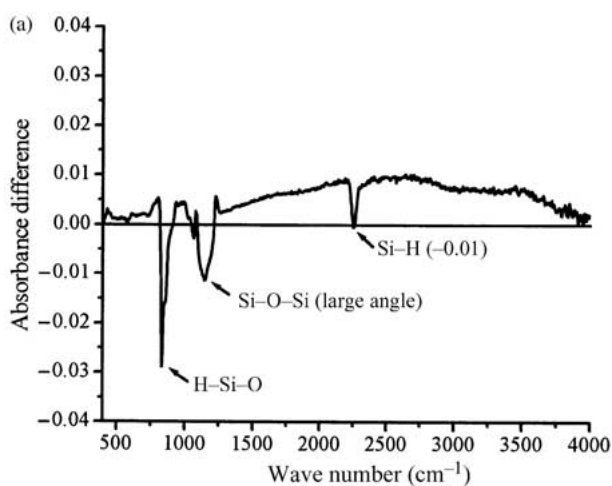

Figure 6 Difference in FTIR absorbance between H$_2$-plasma-treated HSQ and the as-spun HSQ. (a) 5-min plasma treatment and (b) 10-min plasma treatment.
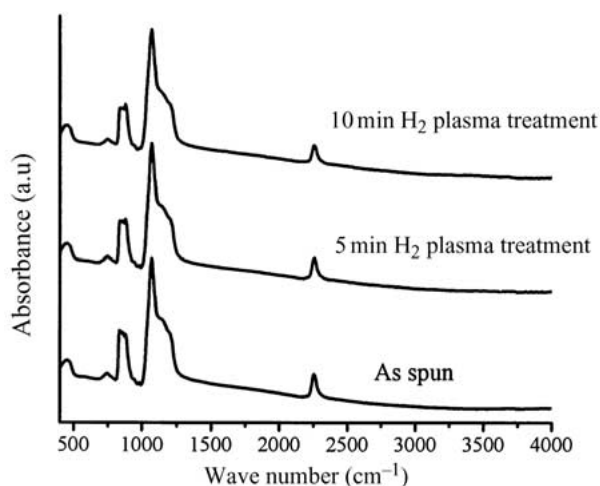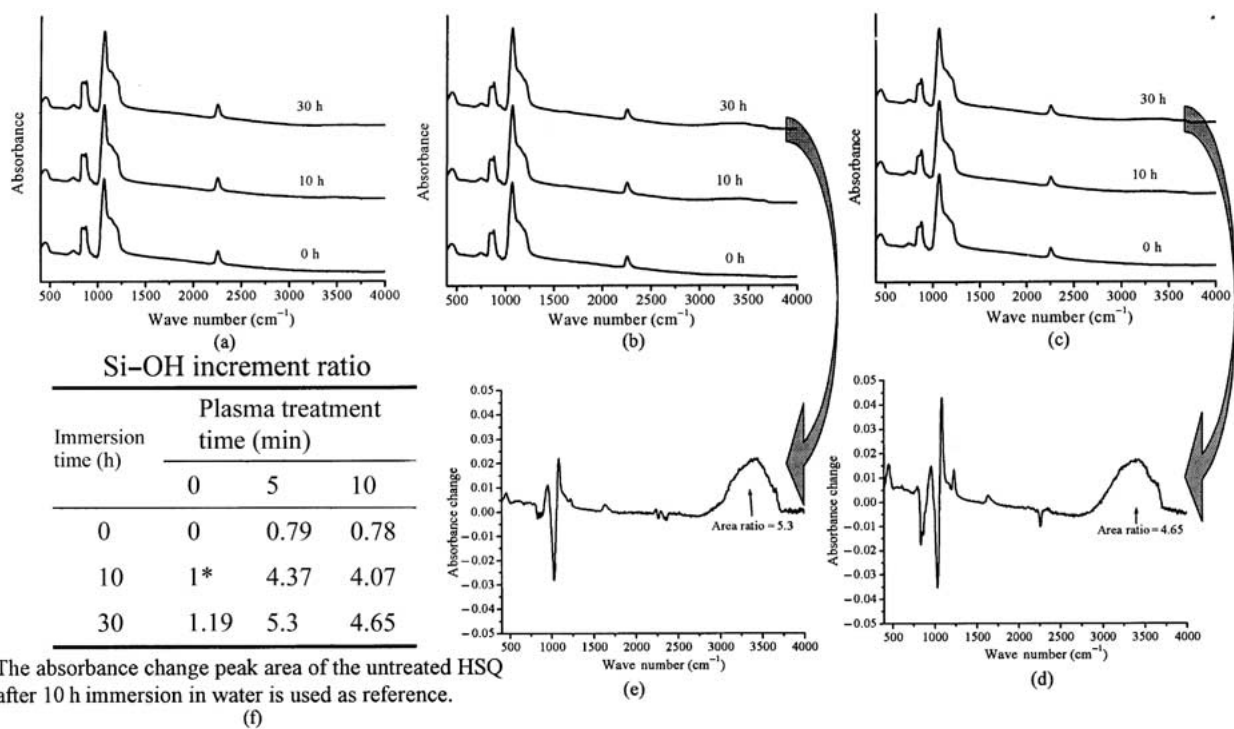

Si–OH increment ratio

Immersion time (h)	Plasma treatment time (min)		
	0	5	10
0	0	0.79	0.78
10	1*	4.37	4.07
30	1.19	5.3	4.65

*The absorbance change peak area of the untreated HSQ after 10 h immersion in water is used as reference.

(f)

Figure 7 FTIR spectra of (a) 0-min; (b) 5-min; and (c) 10-min-H$_2$-plasma treated HSQ immersed in water for various times. FTIR absorbance change of (d) 10-min- and (e) 5 min-H$_2$-plasma-treated HSQ after 30 h immersion in water. (f) FTIR absorbance change peak area ratio for the Si–OH bond.
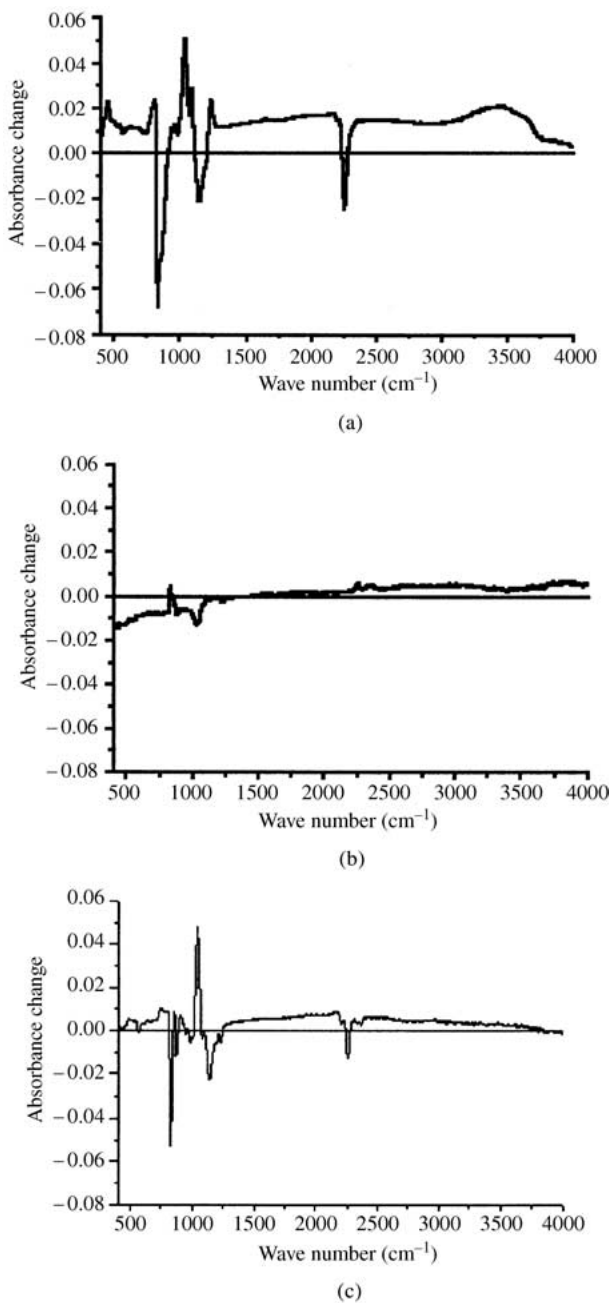
Figure 8 Change in FTIR absorbance after HSQ films subjected to various plasma treatments. (a) 10-min O_2 plasma; (b) 5-min H_2 plasma followed by 10-min O_2 plasma; and (c) 10-min H_2 plasma followed by 10-min O_2 plasma.

Fig. 5 is the FTIR spectra of HSQ after H_2-plasma treatment at 250 °C for various times. Fig. 6 is the difference in FTIR absorbance between H_2-plasma-treated HSQ and the as-spun HSQ), (i.e., the absorbance peak of plasma-treated HSQ minus that of as-spun HSQ), the decrease of Si–H and Si–O cage-like bond absorbance as well as the increase of the Si–O network-like bond absorbance suggest that H_2-plasma bombardment breaks the Si–H and Si–O cage-like bonds and enhances the transformation of HSQ from a cage-like structure to a network structure.

Fig. 7(a)–(c) are the FTIR spectra of HSQ immersed in water for various times as a function of H_2-plasma-treated time. Fig. 7(d) and (e) give the absorbance change after 30 h immersion in water as compared to the un-immersed one of Fig. 7(c) and (b), respectively (i.e.,

spectra of 30-h immersion minus spectra of 0-h immersion). Fig. 7(f) gives the summary of the increase of Si–OH ($3600 \, \text{cm}^{-1}$) bonds in terms of the absorbance change peak area ratio. More Si–OH bonds are formed after H_2-plasma treatment, this suggests that H_2-plasma treatment raises the moisture absorption of HSQ films.

Liu *et al.* [4], on the basis of leakage current of HSQ films, proposed that the Si–H bonds passivated the surface of HSQ and prevented the dangling bonds on the HSQ surface from reacting with moisture to form Si–OH bonds. They also proposed that the H_2-plasma treatment provided hydrogen to passivate the surface and reduced the dangling-bond content in HSQ. However, on the basis of the FTIR spectra shown in Fig. 6, H_2-plasma decreases the content of Si–H bonds. Moreover, the results of the moisture-absorption experiments, exhibited in Fig. 7, indicate an increase of Si–OH bonds after H_2-plasma treatment. Hense, the role of hydrogen in the plasma treatment of HSQ is very complicated and subjected to further investigation.

The surface roughness of HSQ films increases from 0.748 nm for the untreated film to 0.965 and 1.204 nm for films subjected to H_2-plasma treatment for 5 and 10 min, respectively.

The effect of O_2 plasma treatment on HSQ was also investigated. Fig. 8(a) is the difference in FTIR spectra (absorbance change) between 10-min O_2-plasma-treated HSQ and the as-spun HSQ. An increase of the Si–OH bond and a decrease of Si–H bond are obvious, which suggest the conversion of the Si–H bonds into Si–OH bonds when O_2-plasma is applied to HSQ. However, for HSQ films pretreated with H_2-plasma before applying O_2-plasma, the changes in Si–OH and Si–H bonds are not as apparent, as exhibited in Fig. 8(b) and (c).

The dielectric constant and residual stress of HSQ films subjected to various plasma treatments are summarized in Table I. The dielectric constant of HSQ increases from 2.64 of the as-cured sample to 3.7 of the 10-min O_2-plasma-treated one. Exposure to the O_2-plasma causes Si–H bonds to break as indicated in Fig. 8(a). The breaking of Si–H bonds leads to the formation of dangling bonds that absorb water rapidly when the HSQ is exposed to air after the O_2-plasma treatment. Hence, an increase in the dielectric constant is observed. However, for HSQ films pretreated with H_2-plasma before applying O_2-plasma, the dielectric constant decreases as the H_2-pretreatment time increases. They are 3.3 for 5-min pretreatment and 2.7 for 10-min pretreatment

The chamber temperature was kept at 250 °C during plasma treatment. Hence, besides bond breakage, annealing and bond rearrangement occur simultaneously, which lead to the densification of the film, especially at the film surface. This may explain the decrease of the Si–OH absorbance change peak area ratio as H_2-treatment time increases from 5 min to 10 min (Fig. 7(f)), the little change in Si–OH and Si–H bonds for H_2 pretreated HSQ (Fig. 8(b) and (c)), and the decrease of dielectric constant with the increase of H_2-pretreatment time (Table I). The annealing and bond-rearrangement process reduce the dangling bond content and result in a denser film surface, which prevents further absorption of moisture as suggested by the data shown in Figs. 7 and 8 and Table I.

T A B L E I Dielectric constant k and residual stress σ of HSQ films subjected to various plasma treatments at 250 °C

Treatment conditions	0 min (as-cured)	10 min O$_2$	5 min H$_2$ followed by 10 min O$_2$	10 min H$_2$ followed by 10 min O$_2$
k	2.64	3.7	3.3	2.7
σ (MPa)	120	131	157	170

The as-cured HSQ film has a residual tensile stress of ~ 120 MPa. The stress increases with the amount of plasma treatment as given in Table I. As discussed before, plasma treatment induces a denser surface (i.e., film shrinks more) and, consequently, results in a higher residual tensile stress.

4. Conclusions

Fourier transform infrared spectroscopy was employed to monitor the chemical change of HSQ thin films as a function of baking temperature, curing temperature, and plasma treatment. On the basis of the FTIR spectra, the structure of HSQ changes from a cage-like structure to a network structure after curing at 400 °C for 1 h. Densification of HSQ films occurs after curing. With the increase of curing temperature, the film thickness decreases and the dielectric constant as well as the refractive index of HSQ films increases. The effect of plasma treatment on HSQ is multiple. The plasma bombardment breaks the Si–H and Si–O cage-like bonds and enhances the transformation of HSQ to a network structure. However, the breaking of Si–H bonds also leads to the formation of dangling bonds that absorb water easily and results in an increase of film dielectric constant. Nevertheless, the simultaneous annealing and bond rearrangement during plasma bombardment provide a denser film surface that prevents further degradation of HSQ films when more plasma is applied. As a result of film densification, the residual tensile stress of HSQ film increases with the increase of plasma treatment.

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