Effect of oxygen plasma exposure of porous spin-on-glass films

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Hydrogen-methyl-siloxane-based porous spin-on-glass films were exposed to an oxidative plasma. The plasma exposure resulted in the loss of hydrophobic groups such as Si–H and Si–CH_3. The formation of silanole groups, the decrease in film thickness, and moisture uptake were also observed. When the substrate was biased during exposure, these tendencies were found to be suppressed. © *2000 American Vacuum Society.* [S0734-211X(00)03603-9]

I. INTRODUCTION

The application of low-dielectric-constant (so-called low-κ) materials to interlayer/intermetal dielectrics in Si integrated circuits is now of considerable concern for realizing high-speed electrical interconnections. Various low-κ materials, such as hydrogensilsesquioxane[1,2] and methylsilsesquioxane spin-on-glasses (SOG),[2,3] fluorine doped silicon oxide,[4,5] and fluorinated amorphous carbon,[6–8] have been proposed, and their application to multilevel interconnections were reported.[8,9] The use of porous materials as an intermetal dielectric was recently proposed to hear the ultimate dielectric constant of unity.[10,11] Silicate-based porous materials are very attractive because of their potential compatibility with conventional Si technology.

Manufacturing of Si integrated circuits involves many process steps that use plasmas, from dry etching, to chemical vapor deposition to plasma cleaning. Plasma tolerance under oxidative chemistry is one of crucial SOG properties from an integration point of view,[12,13] because oxidative plasma is widely used in production, e.g., for resist removal and for postdry etch cleaning. The oxidation of xerogel-based porous films in an oxygen plasma afterglow was recently studied, and it was demonstrated that spontaneous shrinkage occurs upon the removal of the surface organic groups that sustain the silica backbone.[14] In this article, we report the plasma oxidation behavior of hydrogen-methyl-siloxane-based porous low-κ SOG films.

II. EXPERIMENT

Hydrogen-methyl-siloxane-based porous SOGs,[15] synthesized from silicon alkoxide, silica sol, and pyloric composite polymer, were formed on Si wafers. The composite polymer dissipates during the final cure (450 °C for 30 min in nitrogen), leaving small pores. The dielectric constants of the pristine films used in this work were 1.9–2.4, and the thickness of the films was about 5000 Å. The open porosity (Π) and average pore diameter (d_p) were determined in another series of experiments with Barrett–Joyner–Halenda porosimetry using liquid nitrogen. The values were $\Pi\sim60\%$ and $d_p\sim8$ nm for a film with dielectric constant (κ) of 1.9, and $\Pi\sim50\%$ and $d_p\sim6$ nm for a film with $\kappa=2.4$.[15] Plasma exposures were carried out in an inductively coupled, high-density rf plasma processor that had a loadlock system. The base pressure of the chamber was $\sim5\times10^{-6}$ Pa. Semiconductor-grade oxygen gas was purified by an active-type purifier and was used as a plasma source gas. The substrate holder was located downstream of the plasma source, and a different rf generator was connected to the holder to apply bias. The volumetric power density of the plasma source was about 0.05 W/cm^3, and the area power density of the bias rf was 0.16 W/cm^2. The substrate holder temperature was 30–35 °C. The SOG films were characterized with Fourier transformation infrared (FTIR) spectroscopy, x-ray photoelectron spectroscopy (XPS), and ellipsometry. Dielectric constants were measured at 100 kHz with a Hg probe.

III. RESULTS AND DISCUSSION

A. Loss of hydrophobic groups

Figure 1 shows the FTIR spectra of SOG films, the initial dielectric constant (κ_{init}) of which is 2.4. The C–H stretching (2956 cm^{-1}), Si–H stretching (2250 cm^{-1}), and Si–CH_3 bending (1276 cm^{-1}) peaks are clearly seen in the spectrum of the pristine film. The main peak at 1054 cm^{-1} and a shoulder peak at 1140 cm^{-1} correspond to Si–O–Si bridging and a cage-like network, respectively. Very clear after observation of O_2 plasma exposure (3 min) is the appearance of a broad OH (stretching) band at around 3300 cm^{-1}. This is safely attributed to adsorbed water[16] and also to hydrogen-bonded silanole.[17] A peak at about 3650 cm^{-1} is attributed to perturbed silanole.[18] The peak intensities of the C–H, Si–H, Si–CH_3, and Si–O shoulder peaks are decreased after the plasma exposure. Figure 2(a) shows the change in peak intensities with O_2 plasma exposure time for films with $\kappa_{init}=2.4$. The intensities of Si–CH_3, Si–H, and C–H decrease with exposure time, and the area intensity of the OH band increases simultaneously. The same tendency is observed for the films with $\kappa_{init}=1.9$ [Fig. 3(a)].

When the substrate was rf biased during the O_2 plasma exposure, less of an intensity increase of OH and less of an

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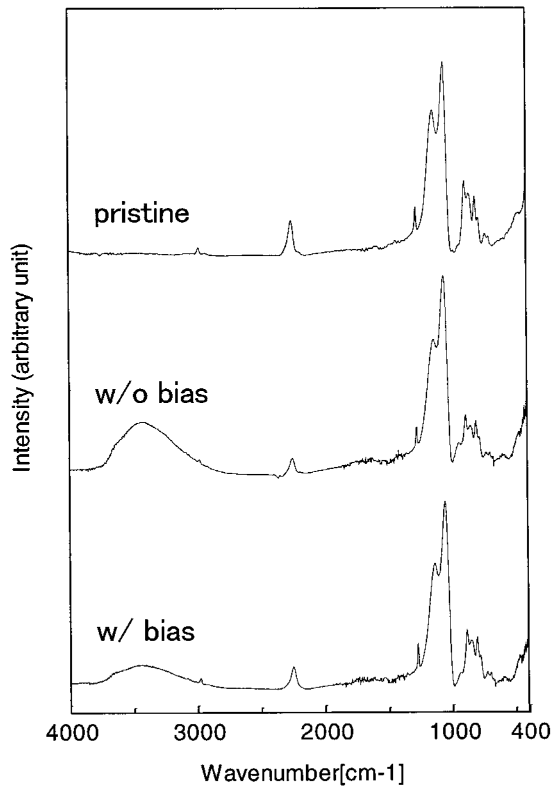

FIG. 1. FTIR spectra of porous SOG films.

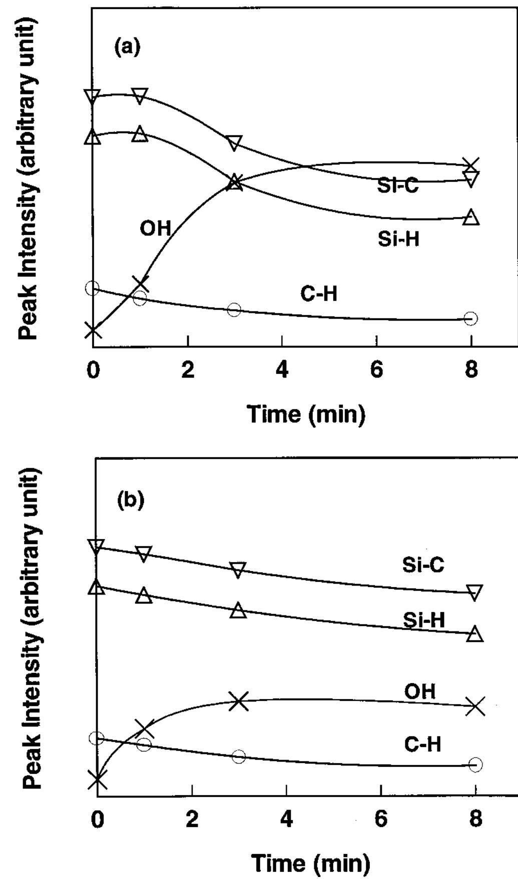

FIG. 2. Change in FTIR peak intensities with O_2 plasma exposure time for SOG films with an initial dielectric constant of ~2.4. (a) Without bias; (b) with bias.

intensity decrease of the functional groups were observed [Figs. 1, 2(b), and 3(b)] for both types of SOG, $\kappa_{\mathrm{init}}=1.9$ or 2.4.

Figure 4(a) shows the results of XPS depth profiling for a film with $\kappa_{\mathrm{init}}=2.4$ treated without bias for 8 min. A slight lack of carbon is seen in the surface region. On the other hand the film treated with bias shows less of a decrease in the surface carbon content [Fig. 4(b)]. No significant amount of carbon is observed anywhere in the thickness for films with $\kappa_{\mathrm{init}}=1.9$ after the same plasma exposure (data not shown). These XPS results agree well with the FTIR data.

B. Film thickness change

Figure 5 shows the change in film thickness with O_2 plasma exposure time. The SOG films show a larger thickness decrease than the thermally grown SiO_2 (th-SiO_2). It is also said that films with a larger porosity ($\kappa_{\mathrm{init}}=1.9$) show a larger decrease in thickness. In this case of the th-SiO_2, the decrease in thickness is significant only when the substrate was biased, obviously because of sputtering. For the SOG films, a larger decrease in thickness is seen when the substrate is biased. This is consistent with the results of the th-SiO_2, however, a significant loss in thickness is seen even when the substrate bias is not used.

In order to have insight into the thickness change caused by the plasma exposure, the film refractive indices are plotted against the film thicknesses according to the Lorentz–Lorenz relationship. The Lorentz–Lorenz equation that describes the relationship between refractive index, N, and refraction, R, is[19]

$$\frac{N^2-1}{N^2+2}=\frac{R_M\rho}{M}\equiv R, \tag{1}$$

where R_M is the molar refraction, M is the molar weight, and ρ is the mass density. R represents the electronic dipole moment per unit volume, or the number density of the dipoles, in the film. If the film shrinks without changing the mass or R_M, R varies proportionally according to the reciprocal film thickness (RFT). That is, the R-RFT plot follows a line that crosses the origin of the graph and the initial R-RFT point.

Figure 6 shows Lorentz–Lorenz plots for the porous SOG ($\kappa_{\mathrm{init}}=1.9$ and 2.4) and th-SiO_2 films exposed to the O_2 plasma. The dashed lines are the ones expected from Eq. (1). Three types of experimental trajectories can be seen. The first type is that the R-RFT points obey the Lorentz–Lorenz equation. This is the case for the porous SOG films treated without substrate bias (symbol ○). In the second case, the thickness decreases without changing R. This is seen for the th-SiO_2 film treated with substrate bias (♦). This indicates that the film is sputtered away by oxygen ion bombardment and that this effect does not cause a significant change in the dielectric (optical) film properties. The third type is seen for the porous SOG films treated with substrate bias (●). The

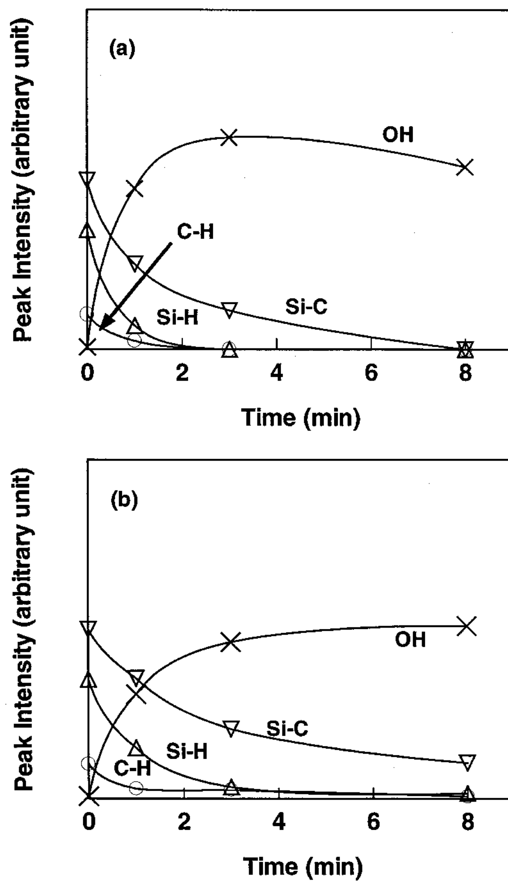

FIG. 3. Change in FTIR peak intensities with O_2 plasma exposure time for SOG films with an initial dielectric constant of ~1.9. (a) Without bias; (b) with bias.

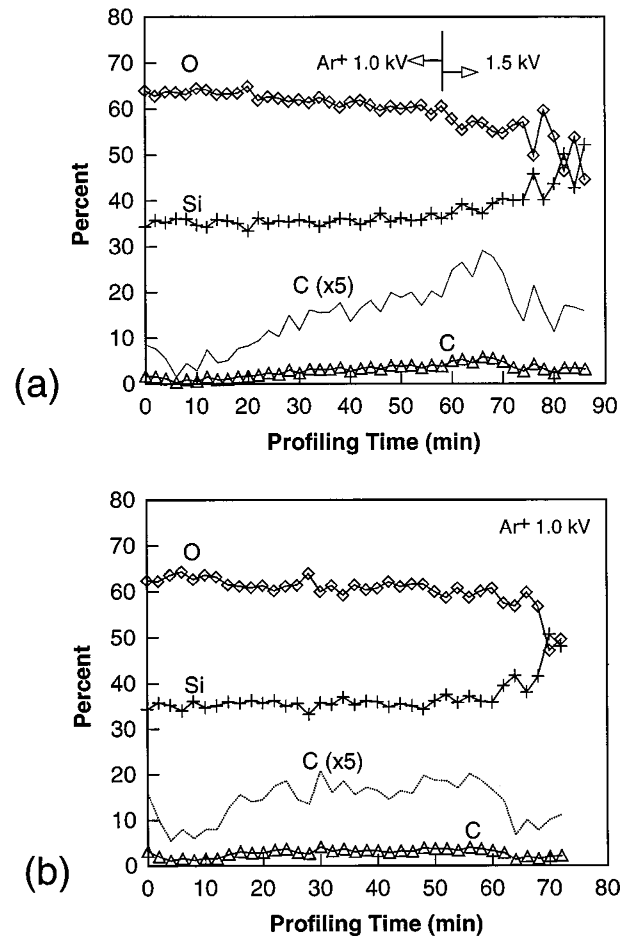

FIG. 4. XPS depth profiles of SOG films with an initial dielectric constant of ~2.4 exposed to O_2 plasma (a) with and (b) without rf bias.

film thickness decreases over time but the increase in R is less than what is expected from the change in RFT. This suggests that shrinkage and sputtering, e.g., chemical and physical processes, occur concurrently. A relatively small increase in R suggests that less shrinkage has occurred in the film and that the decrease in thickness is mainly due to sputtering.

It is interesting that the degree of shrinkage and oxidation is diminished when the substrate is biased. Possible mechanisms for this are described below.

C. Oxidation and shrinkage

Pristine porous SOG films are hydrophobic as seen from the FTIR spectrum in Fig. 1. Hydrophobic groups such as Si–H and Si–CH_3 are removed by plasma oxidation, accompanied by a simultaneous increase of the OH content in the films (Figs. 2 and 3). It is well known that small silica capillaries with surface silanole groups shrink spontaneously.[20] This shrinkage is mainly due to chemical interaction between silanole groups and partly due to surface energy minimization. Likewise, our SOG films can shrink if the surface of open porosity is hydrated by the plasma oxidation.

When the substrate is not biased during the plasma exposure, the main oxidative agent is thought to be atomic oxygen that diffuses from the plasma toward the film. On the other hand, when the substrate is biased, the film is bombarded with energetic ions. Put simply severe oxidation can be expected to occur in the film, because more oxidative species are incident on the film. However, our observation shows that the films were oxidized less when the substrate was biased (Figs. 1–4).

One possible reason that can account for this discrepancy is surface densification. That is, a dense oxide layer can form in the surface region by the incidence of the energetic oxidative species. This oxide layer blocks further penetration of the gaseous oxidative species into the film so that oxidation does not proceed significantly deep inside the film. Because of the competition between the formation and sputtering of the dense layer, the thickness of this layer is speculated as being small.

Another possible reason is that the formation and annihilation of the silanole groups proceed competitively. Reactive sites are generated by the oxidation of the hydrophobic groups and/or by the physical removal with the incident energetic ions. Silanole groups are then formed by the addition reactions of H or OH to the reactive sites. However, these reactive sites and silanole groups can also be physically removed, or sputtered away, by the incident ions. As a result, the net amount of oxidation is decreased.

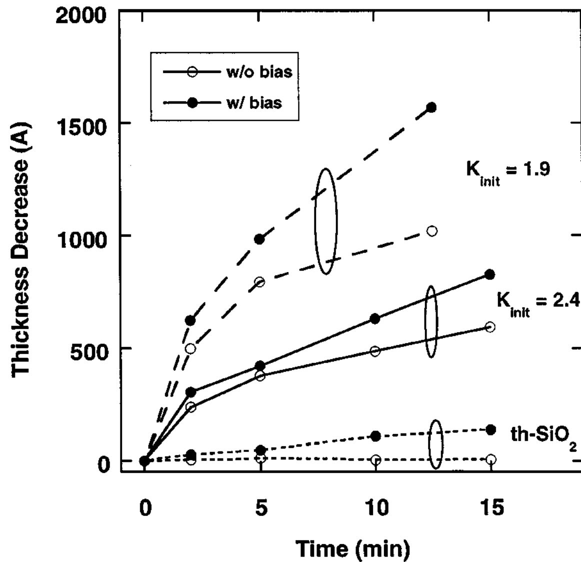

FIG. 5. Change in film thickness with O_2 plasma exposure time.

Either mechanism assumes competition between the formation and removal of the oxidization products, which can explain our finding that substrate biasing is effective in diminishing the loss in thickness and intake of water.

D. Dielectric properties

So far, we have discussed the film dielectric properties from the point of view of the refractive index. In a general form of Eq. (1) dielectric constant ϵ and molar polarization P_M are used instead of N^2 and R_M (the Clausius–Mossotti equation).[19] P_M involves electronic, ionic, and dipole polarization components. The N and ϵ values of porous films can be calculated as functions of the apparent porosity, assuming that the films consist of dense SiO_2 and void. The $N-\epsilon$ relationship obtained with this model is shown as a solid curve in Fig. 7, where the measured N (ellipsometric) and ϵ (100 kHz) values of a th-SiO_2 are used as a reference. Fairly good agreement with the model is seen for pristine porous SOG films (□).

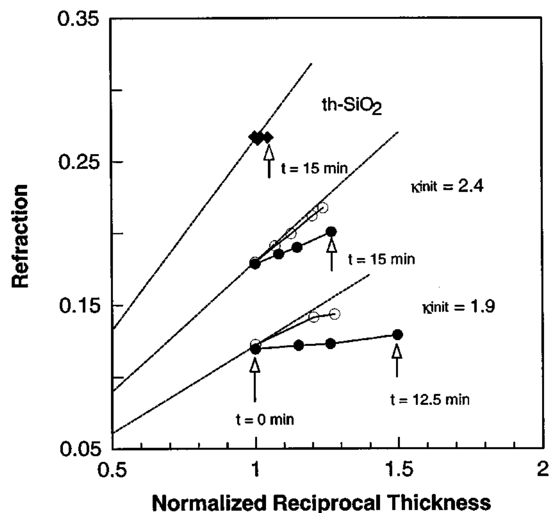

FIG. 6. Lorentz–Lorenz plot of SOG films exposed to O_2 plasma with (●) and without (○) rf bias.

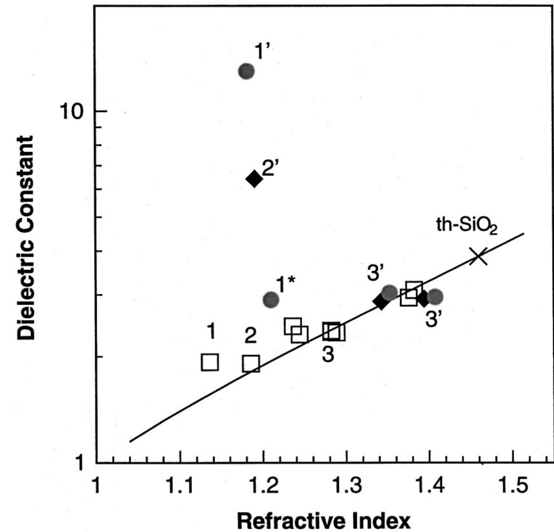

FIG. 7. Relationship between the refractive index and the dielectric constant (at 100 kHz). The solid curve is calculated from a dielectric model, assuming that the film consists of dense SiO_2 [thermally grown SiO_2 (×)] and void. For additional information, see the text.

The N and ϵ values after O_2 plasma exposure are plotted by symbols (◆ and ●) for biased and nonbiased experiments, respectively. The specimens labeled 1 and 2 ($\kappa_{\text{init}} \sim 1.9$) show a very significant increase in ϵ after exposure (1′ and 2′), e.g., significant deviation from the model, obviously due to water adsorption. The adsorbed water can be released by baking, as has been reported for ordinal SOGs.[12,21] In fact, specimen 1′ showed a much smaller κ value after baking at 200 °C for about 5 min (1*). Presumably, most of the moisture is weakly bounded to the surface and in the film. On the other hand, for the specimen group labeled 3 ($\kappa_{\text{init}} \sim 2.4$), the N and ϵ values after the O_2 plasma treatment (labeled 3′) do not show much deviation from the theoretical curve. That is, seemingly, the increase of N and ϵ is caused only by the decrease of the porosity and the effect of water uptake on ϵ is not catastrophically large. Quantitative study of the origins of the polarization will be done in the future.

IV. CONCLUSIONS

We studied plasma oxidation of hydrogen-methyl-siloxane-based porous SOG films. The FTIR analyses show that the intensities of hydrophobic groups such as Si–H and Si–CH_3 decrease with plasma exposure time. An increase in the OH intensity and decrease in the film thickness were also observed. From the ellipsometric analyses, it is proposed that the loss of hydrophobic groups causes spontaneous film shrinkage. When the substrate was biased during O_2 plasma exposure, less film oxidation, shrinkage and moisture uptake were observed. The mechanism that causes the suppressed oxidation was discussed from the point of view of competition between oxidation and sputtering.

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