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Microstructure Characterization of Skeletal Silica in Porous Low-*k* Films by Infrared Spectroscopic Ellipsometry

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1. Introduction

Porous silica films are thought to be a promising material for low dielectric constant (low-*k*) insulator in future ultra large scale integrated circuits [1]. It is indispensable to develop the characterization methods which monitor the change in skeletal structure of porous low-*k* films with different process conditions. Infrared spectroscopy has been widely used to characterize the structure of amorphous SiO_2 prepared by the sol-gel process [2]. We have investigated the chemical bonding features of porous silica films using the Fourier transform infrared (FTIR) spectroscopy [3]. In this paper, the change in the complex dielectric constant ε of porous silica films in the infrared range is analyzed using Bruggeman effective medium approximation [4]. In addition, chemical bonds in the skeletal silica at the different stages of the film thermal curing are reported.

2. Experimental

Porous silica films were produced by spin-coating of a precursor solution of acidic silica sol with nonionic surfactant such as polyethylene oxide (PEO)-polypropylene oxide (PPO)-PEO triblock copolymer. The films were annealed in air for 3 hour at different temperatures from 100 to 450°C. The film thickness and refractive index were measured by UV-visible spectroscopic ellipsometry. FTIR absorption spectra were measured at an incidence angle of 70°. Differential scanning calorimetry (DSC) was carried out in air at a heating rate of 5°C/min. Young's modulus (*E*) and hardness (*H*) of the films were measured using nanoindentation. Poisson's ratio of porous silica films was assumed to be constant at 0.18 in analyses. FTIR ellipsometric parameters were measured at 69, 72 and 75° of incidence and analyzed using an optical model of a single layer on Si.

3. Results and Discussion

Figure 1 shows the annealing temperature dependence of refractive index at 633 nm and film thickness. The refractive index decreases with annealing up to 250°C, and it is almost constant above 250°C. Figure 2 shows the infrared absorbance of porous silica films annealed at different temperatures. The peak at 2900 cm^{-1} and the broad peak around 3400 cm^{-1} are attributed to the C-H stretching vibrations and O-H stretching vibration, respectively. The C-H absorption decreases with increasing annealing temperature and becomes almost
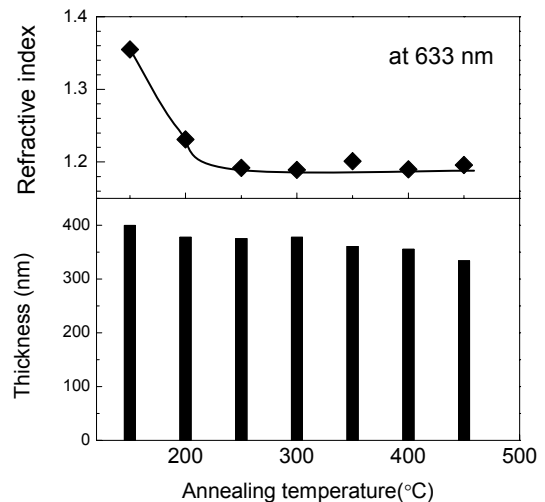

Fig. 1 Refractive index and film thickness of porous silica films plotted against annealing temperature.
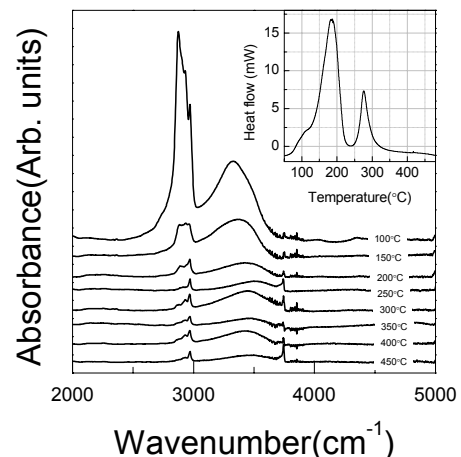

Fig. 2 FTIR absorption spectra of porous silica films as a parameter of annealing temperature. The inset is a DSC curve.

constant above 250°C. The C-H absorption which remains above 250°C is ascribed to C-H bonds in the skeletal silica, which are not dissociated by 450°C annealing. The inset of Fig. 2 shows the DSC spectrum, in which two exothermal peaks at 185 and 275°C are observed. The former is attributed to decomposition of surfactant which corresponds to the refractive index changes (Fig. 1) and the latter is ascribed to hydrolysis of residual alkoxide species and polymerization. Young's modulus *E* and hardness *H* at each annealing tempera-

Table I	Annealing temperature dependence of E and H.						
Temp. (°C)	150	200	250	300	350	400	450
E (GPa)	2.10	2.03	2.51	2.70	2.89	3.63	4.53
H (GPa)	0.18	0.22	0.26	0.25	0.28	0.37	0.48

ture are compared in Table I. By annealing above 250°C, the refractive index (Fig. 1) and C-H and O-H absorption intensities (Fig. 2) remain almost unchanged, while E and H increase.

In order to understand the change in the skeletal silica in porous silica films at different stages of annealing steps, the complex dielectric constant ε was measured in the infrared range as shown in Fig. 3. It is known that the spectral structure in between 1000 and 1400 cm^{-1}, assigned as the asymmetric stretching vibration mode of Si-O-Si bonds, slightly depends on the chemical bonding features of bulk SiO$_2$. On the other hands, the spectra of porous silica films contain the information on both skeletal silica and pore. We extracted only the change in skeletal silica including pore wall surfaces from the structural change of the complex dielectric constant ε (Fig. 3). The peak position in imaginary part of ε, Im(ε), corresponds to the transverse optical (TO) modes, while peaks in the energy-loss function, Im($1/\varepsilon$), correspond to the longitudinal optical (LO) mode. These peak positions correspond to the cross-linking density and mechanical strength [3]. The value of ε of skeletal silica was extracted from the measured ε of porous silica film by using the Bruggeman effective medium approximation in

Fig. 4 Annealing temperature dependences of ω_{TO}, ω_{LO}, and $\omega_{LO}^2/\omega_{TO}^2$.

which the measured porosity was employed. The dotted curves in Fig. 3 show the extracted ε of skeletal silica. In comparison with ε of porous silica, the peak position of TO mode ω_{TO} in extracted ε slightly shifts to the lower wavenumber, while that of LO mode ω_{LO} shifts to the higher wavenumber.

Figure 4 shows the annealing temperature dependences of ω_{TO}, ω_{LO} and $\omega_{LO}^2/\omega_{TO}^2$ of skeletal silica, respectively. The observed small shift of ω_{TO} with annealing below 250°C implies that the average Si-O-Si bond angle slightly increases with the hydrolysis of residual alkoxide species in skeletal silica, while the shift of ω_{TO} above 250°C shows that average the bond angle decreases with the polymerization. Further polymerization causes ω_{LO} shift to the higher wavenumber with the densification of skeletal silica. The increase of $\omega_{LO}^2/\omega_{TO}^2$ above 250°C can be interpreted as the enhancement of cross-linking density of skeletal silica which results in mechanical strength of porous low-k films.

4. Conclusions

We have developed a new characterization technique of skeletal silica in the porous low-k films using FTIR spectroscopic ellipsometry. The structural changes in skeletal silica which correspond to E and H of porous low-k films were detected by the infrared complex dielectric constant for the first time. This novel method enables us to monitor precisely the change in skeletal structures under different process conditions.

References

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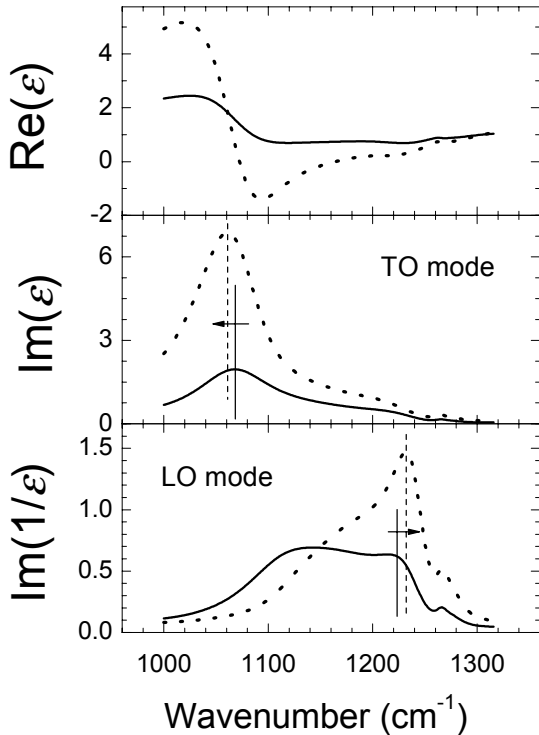[4] D. E. Aspnes, Thin Solids Films **89** (1982) 249.

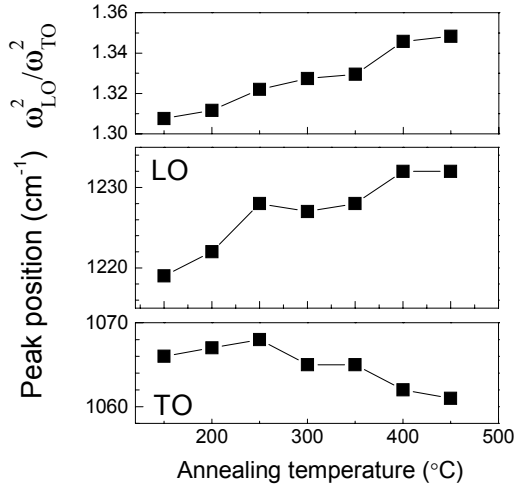Fig. 3 Complex dielectric constant vs. wavenumber. Solid and dotted curves represent the results of porous silica film and skeletal silica, respectively.