

Mechanical Property and Skeletal Silicate Structure of Periodic Porous Silica Films

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1. Introduction

Silica films with nanometer sized pores (porous silica films) have extensively been studied as a candidate for low dielectric constant (low- k) materials. Control of skeletal silicate structures is as important as control of pore structures for development of low- k porous silica film with high mechanical strength. In the present study we examined the dependencies of mechanical properties of silicate structure on their chemical bonding features measured by Fourier transform infrared (FTIR) ellipsometry. Then the mechanical properties of porous silica films are discussed in terms of the effects of skeletal silicate and pore structures.

2. Experimental

Porous silica films were prepared by a surfactant-templated spin-coating sol-gel method on a crystalline silicon substrate under the conditions explained in detail in Ref. [1]. Non-porous spin-on sol-gel silica films were also prepared in the same conditions except for the absence of the template. Film thicknesses were around 300 nm. FTIR ellipsometric parameters and reflectance were measured by using a spectrometer (SOPRA Model GES5-IR). The mechanical properties of the films were measured by nanoindenter (MTS Model XP) with a Berkovitch pyramid indentation tip. Elastic modulus (E) and hardness (H) of each film were determined by averaging the results of ten indents at the indentation depth range of 10 – 30 nm. The Poisson's ratio of the low- k films was assumed to be constant at 0.18 for the analysis.

3. Results and Discussion

Figure 1(a) shows FTIR ellipsometric parameters of a porous silica film. In the infrared region, differently from the visible region, clear interference fringes were not observed, while a peak was observed at around 1200 cm^{-1} . The complex optical constant ($n + ik$) of the porous silica film was then calculated from Fig. 1(a) by using an optical model of a single porous silica layer on Si substrate with known optical parameters [2]. Film thickness was assumed to be identical to the value obtained from the ultraviolet-visible spectroscopic ellipsometry analysis. The result is shown in Fig. 1(b). The spectral structures in between 1000 and 1500 cm^{-1} are assigned as the asymmetric stretching (AS) vibration mode of Si-O-Si bonds. Both the peak position and intensity are different from those of thermal oxides.

Using the obtained optical constants, the complex dielectric function ε ($\varepsilon = \varepsilon_1 + i\varepsilon_2$) was calculated. The peak

positions in the imaginary part of ε , $\text{Im}(\varepsilon)$, correspond to the transverse optical (TO) modes, while peaks in the energy-loss function, $-\text{Im}(1/\varepsilon)$, correspond to the longitudinal optical (LO) modes [3]. In the transverse vibration, the atomic displacements are perpendicular to the direction of periodicity of the elastic wave, whereas in the longitudinal vibrations the displacements are parallel to the wave vector. Figure 2 shows the spectra of $\text{Im}(\varepsilon)$ and $-\text{Im}(1/\varepsilon)$ of porous silica films, which were calculated from the optical constants as in Fig. 1(b). The properties of the samples A – D are summarized in Table I. The profiles of LO and TO modes for asymmetric stretching of Si-O-Si bridges are dependent on preparation conditions and / or post preparation treatments. In $\text{Im}(\varepsilon)$, the peak is observed near 1070 cm^{-1} and, the shoulder peak is observed near 1180 cm^{-1} . In $-\text{Im}(1/\varepsilon)$, the peaks are observed near 1130 and 1230 cm^{-1} . Kirk [4] has proposed that the AS motion gives rise to an in-phase (AS_1) and out-of-phase (AS_2) modes. The AS_1 mode is optically active, while AS_2 is originally inactive optically. However, AS_2 becomes active once the disorder-induced coupling with the strong AS_2 mode occurs. The LO - TO pair for the AS_1 mode was measured at 1070 - 1230 cm^{-1} , while the LO - TO pair for the AS_2 mode was found inverted at 1130 - 1180 cm^{-1} . The LO - TO splitting for AS_1 mode in Fig. 2 is sample dependent. It is known that stronger silica network corresponds to higher AS_1 - LO frequency [5].

The generally accepted structural model for amorphous silica is one in which near perfect SiO_4 tetrahedral units are connected together at bridging oxygen into a continuous random network [3-5]. The mechanical strength of silica depends on the random network structure. The E of a thermal oxide films are about 75 GPa, and change with their chemical structures. Figure 3 shows the measured E as function of the peak position of AS_1 - LO mode of a series of nonporous spin-on sol-gel silica films. Isochronal annealings for 5 hours of the films were carried out in air at temperatures of 673, 723, 773, 873, 973, and 1073 K, and FTIR and nanoindentation measurements were carried out after each annealing step to obtain the data points of type 1 in Fig. 3. With the increase of the annealing temperature, the AS_1 - LO mode shifted from 1208 to 1252 cm^{-1} , and at the same time, the E value increased. The correlation between the AS_1 - LO peak position and E was confirmed by varying the preparation conditions and post preparation treatments of silica films (the types 2 and 3). The observed correlation in Fig. 3 clearly shows that the mechanical strength depends on the silicate network structure. It seems that the change of the

E below 1223 cm^{-1} is more difficult to detect, since the change of the network structure of the silica is smaller than the experimental uncertainty of nanoindentation measurements on the films as thin as 300 nm . The inset of Fig. 3 shows E of the porous low- k films plotted against the AS_1 -LO peak position. Because E of porous silica films depends on both the skeletal network and pore structures, the correlation between the E and the AS_1 -LO peak position for the porous films is unclear presumably due to the effect of nanopore structures. The E measurements are known to be significantly influenced by the mechanical properties of an underlying material especially for such soft and thin material as porous low- k films. Hence, the E vs. AS_1 -LO peak relationship is not very clear yet, but E measurement with SAW will give information on such films. It is likely that the AS_1 -LO peak position nevertheless gives information on the mechanical strength of skeletal silicate of porous films.

4. Conclusions

In order to characterize network structure in periodic porous low- k and non-porous silica films, we determined their optical constants spectra in infrared region by using FTIR ellipsometry for the first time. It is found that E of sol-gel silica films have a correlation with the AS_1 -LO peak position. By using these results, one can quantitatively investigate not only the overall E of porous silica films by nanoindentation, but also the effect of skeletal silicate structure on E by FTIR, which will help developing porous low- k films with higher E .

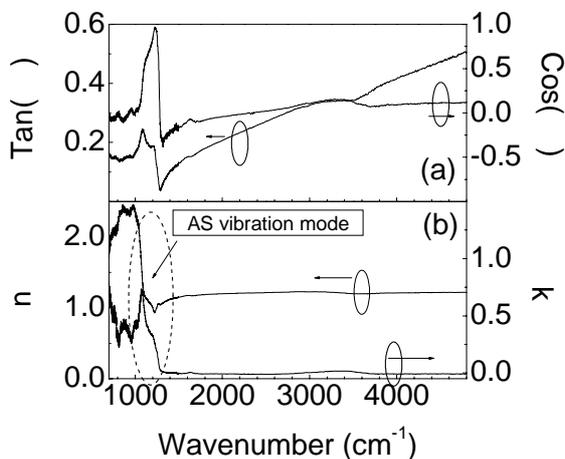


Fig. 1 The value of (a) $\tan(\Psi)$ and $\cos(\Delta)$, and (b) n and k versus wavenumber for porous silica film.

Table I Properties of the porous silica films

Sample	E (GPa)	H (GPa)	Dielectric constant
A	1.3	0.09	2.1
B	3.6	0.36	2.5
C	4.4	0.41	2.6
D	5.2	0.44	2.1

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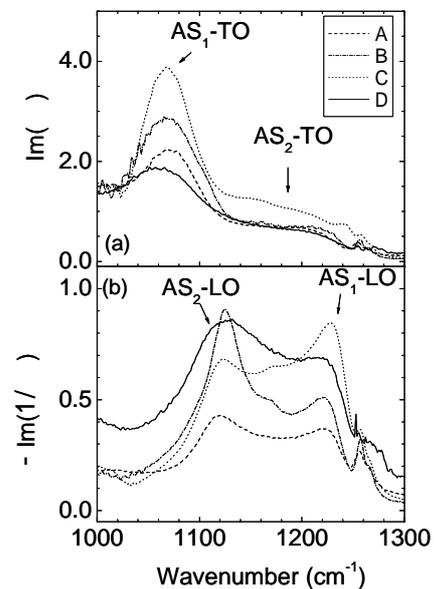


Fig. 2 The value of (a) $\text{Im}(\epsilon)$ and (b) $-\text{Im}(1/\epsilon)$ versus wavenumber for porous silica films.

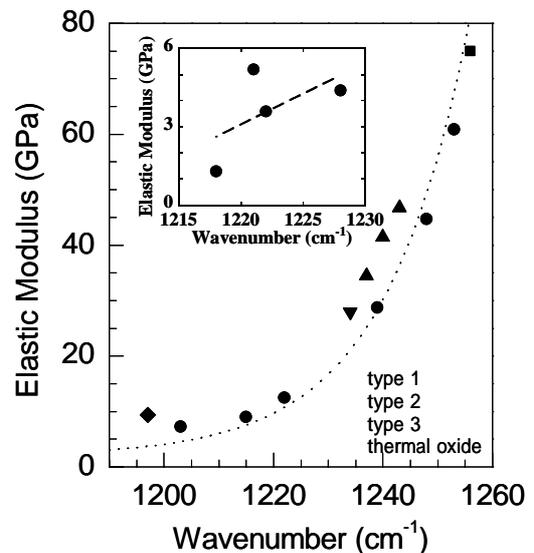


Fig. 3 AS_1 -LO peak position dependence of elastic modulus. The dotted line is guide to eyes.