Infrared Complex Dielectric Function Analysis for Chemical Bonding Structure of Porous Silica Low Dielectric Constant Films

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1. Introduction

Fourier transform infrared (FTIR) spectroscopy has been a powerful technique to reveal the chemical bonding features of ultra low dielectric constant (ultralow-*k*) films [1]. The conventional analysis procedure of FTIR spectra based on the Lambert-Beer's law, $A \equiv \log_{10} (I_0/I_d)$, where I_0 and I_d are the incident and transmitted light intensities, is, in principle, valid only in the limit of weak-absorption regime. In strong absorption regime, such as for the Si-O-Si stretching bond of silica-based ultralow-*k* films, the experimental data must be analyzed in terms of complex dielectric function. In this paper, we report the results from complex dielectric function analyses of FTIR spectra to evaluate the chemical bonding structures in ultralow-*k* porous silica films.

2. Experimental

Porous silica films were prepared by spin-coating of a precursor solution of acidic silica sol with nonionic surfactant HO $(C_2H_4O)_{13}$ $(C_3H_7O)_{20}$ $(C_2H_4O)_{13}$ H. The films were annealed at three different temperatures of 623, 673, and 698 K. Then, they were exposed to organosiloxane vapor at the same temperature to provide hydrophobicity. Details of the film preparation condition were reported earlier [2].

An FTIR spectrometer was used to record infrared transmittance spectra, and the ratio of the transmitted infrared intensities with $(I_{F/Si})$ and without (I_{Si}) porous silica film on Si substrate was calculated, to get rid of the effects of

 $\begin{array}{c} 1.00 \\ 0.95 \\ I_{F/Si} \\ 0.90 \\ I_{Si} \\ 0.90 \\ 600 \\ 800 \\ 1000 \\ 1200 \\ 1400 \\ Wavenumber (cm⁻¹) \end{array}$

Fig. 1 Experimental (open symbol) and simulated (solid line) FTIR transmittance spectra of porous silica film.

absorption by impurities such as interstitial oxygen and / or other elements in the Si substrate. Thus obtained transmit tance spectra were fitted by regression analysis to a simple optical model considering multiple reflection of single-layer porous silica film on the Si substrate. Mid-infrared dielectric constant in the wavenumber range of 600-1500 cm⁻¹ of the film was modeled by a linear combination of up to 20 Lorenz oscillators. The film thickness and refractive index were obtained from the analysis of ellipsometry spectra in a UV-visible range. Dielectric constant *k* was evaluated by a capacitance-voltage characteristics measurement by using a mercury-probe system.

3. Results and Discussion

Figure 1 shows an example of measured (open symbols) and simulated (solid line) FTIR transmittance spectra, in which a good agreement is seen. The obtained infrared complex dielectric function (solid lines) of porous silica film, by the regression analysis to get the simulated curve in Fig. 1, is shown in Fig. 2. The dielectric function obtained by using the conventional Lambert-Beer's law (dotted lines) is also shown in Fig. 2. Imaginary part of dielectric function, Im (ϵ), which was obtained by the Lambert-Beer's law exhibited lower value than that obtained by the regression analysis. Furthermore, information of the real part of dielectric function Re(ϵ) associated with the



Fig. 2 Real and imaginary parts of mid-infrared complex dielectric function of porous silica ultralow-*k* film. Solid and dotted curve are spectra by the regression analysis and Lambert- Beer's law, respectively.

absorption peak is completely missing in the Lambert-Beer's analysis.

Figure 3 shows infrared dielectric functions obtained by the analysis of the experimental data of four different porous silica films (Sample I - IV). The spectral structure in between 1000-1250 cm⁻¹ is assigned to asymmetric stretching vibration mode of Si-O-Si, which depends on chemical bonding features of porous silica films [3], while the peak at 1270 cm⁻¹ corresponds to bending motion of Si-CH₃ bonds [1]. The peaks below 1000 cm⁻¹ are attributed to a combination of H-Si-O and Si-CH₃ vibrations, and Si-O-Si bending [1]. Re(ε) at the highest end of the wavenumber ε_{∞} is dominated by the contribution of electronic polarization, while Re(ε) at the lowest end of the wavenumber ε_0 carries contributions not only from the electronic polarization but also from the ionic polarization associated with the midinfrared absorption bands analyzed in the present study.

The inset of Fig.3 shows dependence of Young's elastic modulus *E* on dielectric constant *k* for samples I – IV. We have shown that *k* and *E* of porous silica films depend on the bonding feature of skeletal silica, porosity, pore shape, and pore arrangement [3-5]. The *k* value is sensitive also to moisture uptake. Figure 4 shows the differences $k - \varepsilon_0$ and $\varepsilon_0 - \varepsilon_\infty$, respectively, of samples I – IV. The observed varia-



Fig. 3 The complex dielectric constant spectra of sample I, II, III, and IV. The inset shows Young's elastic modulus E plotted against dielectric constant k.



Fig. 4 The differences in k and ε_0 , ε_0 and ε_{∞} , respectively, for sample I, II, III, and IV.

tion in $k - \varepsilon_0$ among the samples I – IV is interpreted as the consequence of variation in the orientational polarization. k of the sample II is lower than that of the sample IV, while E is comparable, which could correspond to the differences in $k - \varepsilon_0$ between these films. The increase of $k - \varepsilon_0$ could be due to moisture uptake, or the adsorbed water molecule on the internal surface of the pores. On the other hand, the observed variation in $\varepsilon_0 - \varepsilon_\infty$ among the samples I – IV is interpreted as the consequence of variation in the ionic polarization, or the cross-linking density of skeletal Si-O-Si network which is correlated with the mechanical strength of skeletal silica [3]. E of sample III is higher than that of sample IV, while k remains almost the same. The differences in $\varepsilon_0 - \varepsilon_\infty$ between those samples might explain the difference in E between those films.

4. Conclusions

The complex dielectric functions of porous silica ultralow-k films were determined by a regression analysis of multiple-Lorenz-oscillator dispersion model from FTIR transmission spectra. The infrared complex dielectric function analysis of the chemical bonding structure of porous silica ultralow-k films enabled us to distinguish the contributions of electric, ionic, and orientational polarization, respectively, in those films, which correlated with the changes in k and E.

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