

The structural origin of determining the coefficient of thermal expansion for porous silica low-k films

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1. Introduction

Adhesion failure, cracking and other forms of device failures are often induced by mechanical stresses. The knowledge of the coefficient of thermal expansion (CTE) enables the evaluation of thermally-induced film stresses in devices with layers of different thermal expansions. While porous silica films have been studied extensively as a potential candidate for interlayer dielectrics in Cu / low-k interconnects in ultralarge scale integrated circuits, the reported values of CTE of porous silica films vary over a wide range from 12 ± 2 to 60 ± 20 ppm K⁻¹ [1,2]. It is the purpose of this work to reveal the structural origin which determines CTE of silica films.

2. Experimental

Porous silica films containing alkyl (C_xH_y) groups were prepared by sol-gel spin-coating (SOD) as well as by plasma-chemical-vapor deposition (CVD) techniques from alkoxysilane or organo-silane precursors [3, 4]. Films without mesopores (non-porous films) were also prepared for comparison, from the same precursors without introducing the porogens. Post-preparation ultraviolet (UV) treatment and isochronal thermal annealing were carried out to obtain series of silica films with different skeletal structures.

In-situ spectroscopic ellipsometry (in-situ SE) in a flow cell of moisture-free air (Fig. 1) was carried out to measure temperature-dependent thickness change of the silica films, from which CTE was calculated [5]. Transmission Fourier-transform-infrared (FTIR) spectroscopy was employed to observe the chemical bonding features in the films.

3. Results and Discussions

Dependencies of CTE on the UV-treatment time (t_{UV}) and annealing temperature (T_{ann}) are shown in Figs. 2 and 3, respectively, where porous and nonporous SOD silica ($k > 2.1$) and CVD SiOC films are compared. These results indicate that CTE decreases with t_{UV} as well as with T_{ann} , suggesting that network formation in skeletal silica is promoted by the UV irradiation or by thermal annealing. Also, it is likely that the rigidity of silica skeletal structure is enhanced, resulting in the decrease of CTE. Figure 4 shows the FTIR spectra from the same sets of samples annealed at various temperatures. The Si-O-Si stretching mode vibration

appears at 1000 – 1100 nm range of the absorbance spectrum. All of the 4 series of the films exhibit increase of the Si-O-Si peak intensity with T_{ann} , while the peak wavenumber remains unchanged. To evaluate the increase of silica skeletal network density with T_{ann} , the film thickness and porosity were taken into account to obtain the silica-skeletal absorption coefficient spectra $\alpha_{sk}(\nu)$, where ν is the wavenumber. CTE was plotted against integrated $\alpha_{sk}(\nu)$ over the wavenumber range around the Si-O-Si peak or $\sigma_{sk}(\text{Si-O-Si})$ as shown in Fig. 5. In Fig. 5, all the data points from the 4 different series of samples appear almost on the single universal curve. Namely, CTE of porous silica film is correlated with $\sigma_{sk}(\text{Si-O-Si})$, or the network Si-O-Si density. On the other hands, plots of CTE against C-H and Si-(CH₃)_x stretching modes at 2970 and 1260-1270 cm⁻¹ are shown in Figs. 6 and 7, respectively. In these figures, data points are scattered unlike those in Fig. 5.

Microscopic origin of CTE of porous silica films is Si-O-Si network deformation by thermo-elastic stress. The value of $\sigma_{sk}(\text{Si-O-Si})$ is associated with the average coordination number of SiO₄ tetrahedron network in amorphous silica structure, which is related to network rigidity R_n through the constraint-counting model of Philips [6] and Thrope [7]. Since the network deformation or CTE is inversely proportional to R_n , the excellent correlation of CTE with $\sigma_{sk}(\text{Si-O-Si})$ was obtained as is seen in Fig. 5. Namely, CTE is predominantly determined by the skeletal silica network density $\sigma_{sk}(\text{Si-O-Si})$ irrespective of the sample preparation conditions (CVD or SOD) and of porosity (porous or nonporous). In order to verify this idea further, an additional experiment was performed to compare CTE of a series of SOD porous silica films prepared by varying porogen concentration premixed into a silica precursor. The results shown in Fig. 8 demonstrate that only a weak correlation between CTE and porosity is seen in the higher porosity region for the low-k films.

4. Summary

CTEs of porous and nonporous silica films with different skeletal structures were measured and compared with chemical bonding features characterized by FTIR. It was found for the first time that CTE of silica film was determined by skeletal Si-O-Si density rather than by C-H,

Si-(CH₃)₃ bond densities or by porosity. The results were explained by the rigidity of silica network structure.

Acknowledgements

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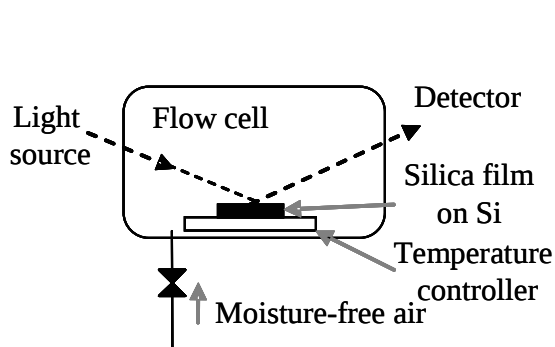


Fig. 1 Schematic diagram of experimental setup for in-situ spectroscopic ellipsometry.

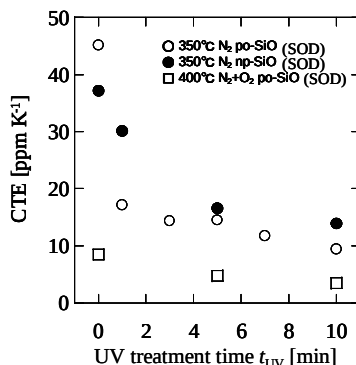


Fig. 2 UV-treatment time dependence of CTE of porous (po) and nonporous (np) silica films prepared at different curing temperatures.

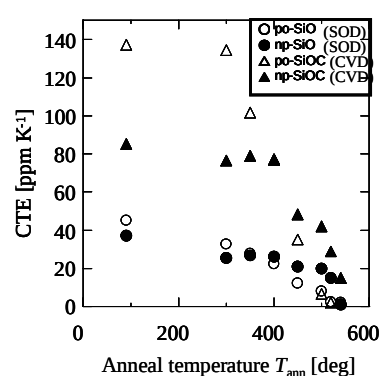


Fig. 3 Annealing time T_{ann} dependence of CTE of silica films.

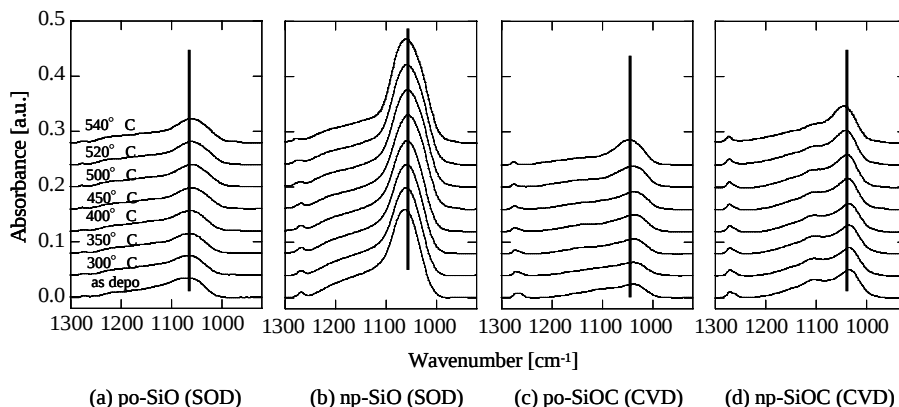


Fig. 4 Mid-infrared FTIR spectra of different silica films annealed at the various temperatures indicated in the figure.

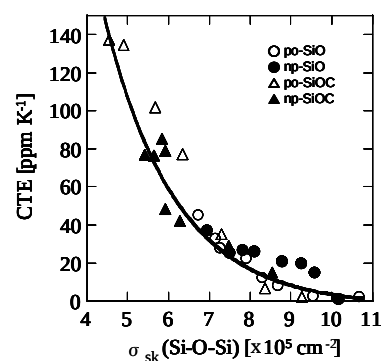


Fig. 5 CTE plotted against integrated intensity of Si-O-Si peak, σ_{sk} (Si-O-Si)

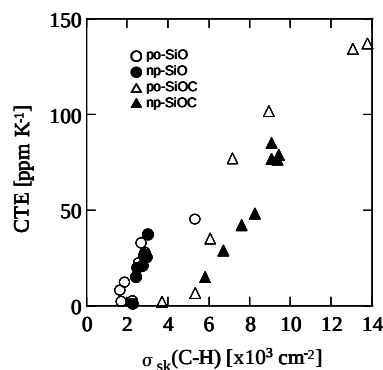


Fig. 6 CTE plotted against integrated intensity of C-H peak, σ_{sk} (C-H).

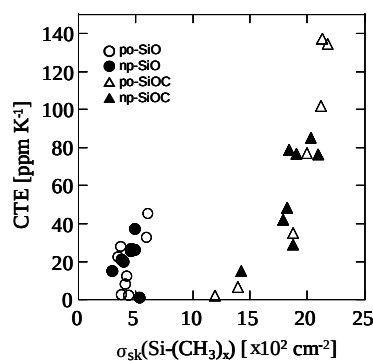


Fig. 7 CTE plotted against integrated intensity of Si-(CH₃)_x peak, σ_{sk} (Si-(CH₃)_x).

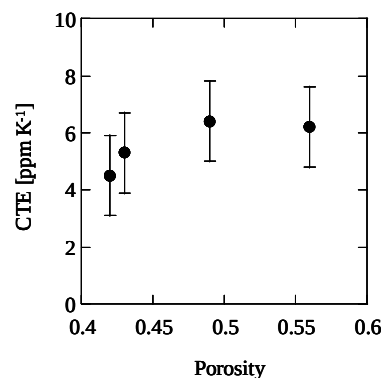


Fig. 8 CTE plotted against porosity for SOD porous silica films.