Comparison of water sorbability of various dielectric films by thermal desorption spectroscopy

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Over the past several years, a great deal of effort has gone into the development of new ultralow-k dielectric materials. Porous silica and organic polymer seem to be promising candidates. However, several reliability issues must be resolved before they can be used confidently in mass production. The problem of water adsorption is particularly troubling as it can lead to device degradation and process incompatibility. In this study, the amount of water that adsorbs to SiLK* resin (*Trademark of The Dow Chemical Company) and to porous silica film was measured and compared to values for thermally grown SiO_2 and TEOS films.

Experiments: SiLK film was spin-coated on a Si wafer covered with SiO_2, and cured at 450°C for 5 min. on a hot plate. Porous silica film was synthesized by the surfactant template method (Courtesy of Dr. Susa of Hitachi Chemical), spin-coated on a Si wafer, and baked at 400°C for 6 min. Thermally grown SiO_2 and plasma CVD TEOS films were formed by conventional methods. For thermal desorption spectroscopy (here after TDS), a WA1000S (Denshi-Kagaku, Japan) was used, and the measurement chamber was evacuated with a turbomolecular pump down to $5x10^{-8}$ Pa. The samples were cut into 8-mm-square specimens and weighed on a microbalance (Mettler Toledo AB204S, Switzerland). Then, the surface area was calculated from the known density and thickness of the Si substrate. Spectra were taken at temperatures from 100 to 450°C for SiLK and porous silica, and from 100 to 800°C for thermally grown SiO_2 and TEOS, considering the thermal stability of each material. The speed of water uptake by SiLK was estimated from successive TDS measurements on the same sample. Namely, after TDS measurement, the sample specimen was stored in clean room ambient, and after a certain time another TDS measurement was done on the same sample.

Results and Discussion: The TDS spectra obtained are shown in Fig. 1, where the amount of desorbed water in units of 10^{16} H_2O molecules/cm^2 is plotted against temperature. The cumulative amount of H_2O desorbed from each sample at temperatures from 150 to 450°C was calculated using the supplied software. The values are 1.1, 19, 6.5 and 0.8 x 10^{16} H_2O/cm^2 for SiLK, porous silica, TEOS and thermally grown SiO_2, respectively. The amount of H_2O that desorbed from SiLK is very small, and is very close to that for thermally grown SiO_2. Six times more H_2O desorbed from TEOS than from SiLK, and 17 times more desorbed form porous silica. It is well known that SiO_2 has a strong affinity to H_2O. However, to understand such a marked difference, another factor besides the chemistry must be considered, and that could be the porous structure. That is, the SiLK used here does not have a porous structure, while the porous silica was intended to have pores in it. Among the types of SiO_2, thermally grown SiO_2 contains less H_2O than either TEOS or porous silica, which were made at lower temperatures. Figure 2 shows the speed of water uptake by SiLK stored in a clean room, desorbed amount of water vs. storage time. Though TDS measurements were carried out at random order, namely the number at each plot denotes the date of TDS measurement, the desorbed amount shows typical saturation curve depending on time. This means the SiLK was not changed by TDS measurements, and water adsorption-desorption cycle is occurred reversibly. The amount of water adsorbed increased for 300 hours. This slow change is one property of an organic polymer, and it is important to take such properties into account in process design.

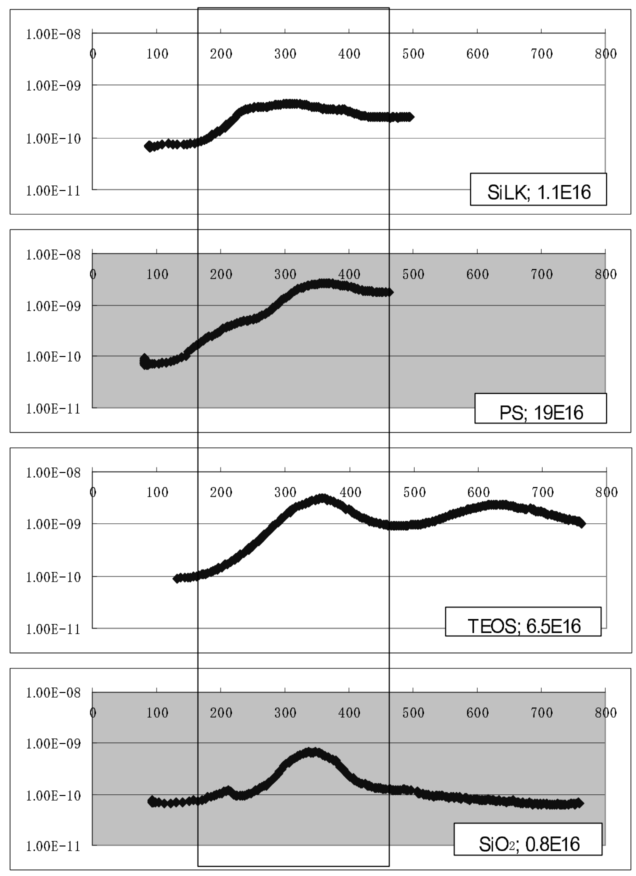

Fig. 1. DTS spectra for various dielectric films

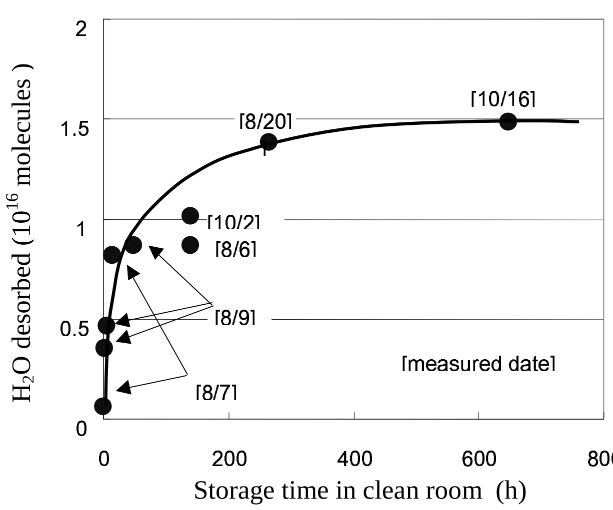

Fig. 2. Speed of water uptake by SiLK resin

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