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Effect of moisture adsorption on the properties of porous-silica ultralow-k films

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Abstract

The effect of adsorbed moisture on the dielectric constant of porous silica was investigated for various TMCTS (tetramethyl-cyclo-tetrasiloxane) vapor-annealing treatment conditions, which change the hydrophobicity of the film. The treatment causes the TMCTS molecules to polymerize on the pore wall surfaces with the coverage controlled by the treatment time and temperature. The amount of adsorbed moisture was estimated from thermal desorption measurements. The results of infrared absorption spectra indicate that the pore wall surfaces without TMCTS coverage react with moisture to form Si–OH bonds. Thus, it is possible to reduce the concentration of Si–OH bond by increasing the TMCTS coverage, thereby preventing the dielectric constant increase.
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1. Introduction

Porous silica is one of the candidates for ultra-low-k interlayer dielectric films of ULSI Cu interconnects because the dielectric constant can be adjusted by changing the pore size distribution as well as the porosity. For practical use, the degradation in mechanical strength and the reduction of hydrophobicity due to the introduction of pores into the silica film remain big concerns. We have developed the tetramethyl-cyclo-tetrasiloxane (TMCTS) vapor annealing treatment to solve these problems [1].

TMCTS is a precursor of low-k CVD film growth. It consists of a ring of four Si–O bonds terminated with –CH_3 or –H. A Si–O–Si network forms on inner surfaces of pore walls during thermal annealing, thus improving the thermal and mechanical stability [2,3]. The TMCTS treatment strengthens the mechanical properties of porous silica film leaving the dielectric constant almost intact [4].

Since a porous material has a larger surface area than a non-porous one, it contains a greater number of hydrophilic Si–OH bonds. The TMCTS treatment is an effective way to provide hydrophobicity because it converts Si–OH to Si–OCH_3 by covering the pore wall surface with its polymer, which prevents the adsorption of moisture. However, for practical use, we need to find out how the TMCTS coverage depends on the treatment conditions. For this purpose the amount of moisture that adsorbs on a silica surface is considered to be a good measure of the TMCTS coverage.

In this study, the effect of adsorbed moisture on the dielectric constant of porous silica was investigated for various TMCTS vapor-annealing treatment conditions, which change the hydrophobicity of the silica film. During annealing, TMCTS is polymerized and covers the pore wall surface with the coverage depending on the treatment time and temperature. The amount of adsorbed moisture was

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estimated from thermal desorption spectroscopy (TDS) measurements The FT-IR spectrum yielded information on the chemical bonds related to the adsorbed moisture. This information is helpful in identifying the main components influencing the dielectric constant and in determining the chemical state of the surface.

2. Experiments

Porous silica films were formed by a sol–gel method based on the self-organization of surfactant templates [5]. The precursor solution consisted of a mixture of tetraethoxysilane (TEOS) as a silica oligomer, ethanol as a solvent, HNO_3 as a catalyst, water, and a surfactant template. This solution was spin-coated on a Si substrate and calcined at 400 °C in air to remove the surfactant template and induce the formation of pores in the silica film. Annealing of the film in TMCTS vapor was performed with nitrogen as the carrier gas at temperatures ranging from 325 °C to 425 °C and treatment time from 15 min to 90 min. The resulting films were about 150 nm thick.

The TDS spectra were taken at temperatures from 80 °C to 1000 °C with a heating rate of 0.5 °C/s. The FT-IR absorption spectra were obtained in an N_2 atmosphere and the absorption bands were decomposed into several Gaussian bands for the analysis of moisture components. The dielectric constant was measured by C–V analysis using Hg probe. The amount of re-adsorbed moisture was almost saturated after 3 h for samples in atmosphere. Afterwards moisture was desorbed by increasing the sample temperature up to 1000 °C. The dielectric constant measurements and FT-IR measurement were carried out after one or two days, and TDS measurement was carried out one week after film formation and TMCTS treatment. Thus, the measured values in this study are surely affected by the saturated moisture.

3. Results and discussion

3.1. Moisture adsorbed to porous silica

Fig. 1 shows a TDS spectrum of the moisture (mass number = 18) that desorbed from porous silica annealed at 400 °C for 15 min in TMCTS vapor. There are two peaks, one near 400 °C and the other near 690 °C. The lower-temperature peak seems to correspond to the moisture that adsorbed on the pore wall surface. Since the film was formed at 400 °C, the integrated intensity of the 400 °C peak corresponds to the amount of moisture adsorbed after film preparation and hence is related to the hydrophilic surface area that remains uncovered with TMCTS.

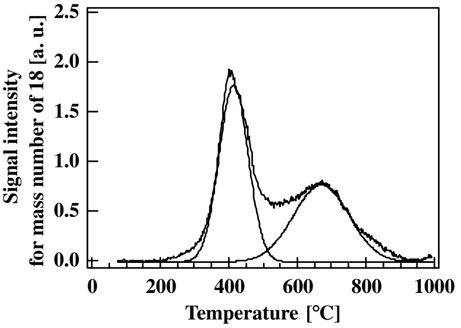

Fig. 1. TDS spectrum of moisture from porous silica subjected to TMCTS treatment at 400 °C for 15 min.

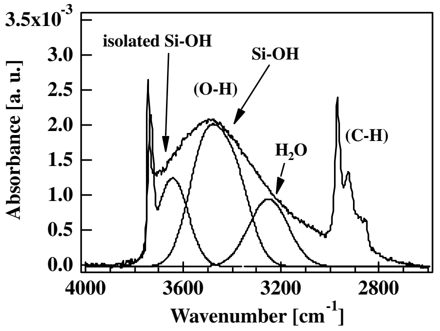

Fig. 2. FT-IR spectrum related to O–H stretching bonds of porous silica subjected to TMCTS treatment at 400 °C for 15 min.

Fig. 2 shows an FT-IR absorption spectrum for porous silica subjected to TMCTS treatment at 400 °C for 15 min. There is a broad absorption band related to O–H stretching bonds between the wave numbers 3000 and 3800 cm^{-1}. As shown in the figure, it can be decomposed into the three contributions: Si–OH with an H bond due to chemically absorbed H_2O, isolated Si–OH (without an accompanying H bond), and H_2O [6–9].

3.2. Dependence of amount of adsorbed moisture on TMCTS treatment conditions

Fig. 3a and b shows the surface coverage of moisture (mass number = 18) that adsorbed on pore wall surfaces and the dielectric constant of the film as a function of TMCTS treatment time and temperature, respectively. Since the surface coverage was constant below the treatment temperature of 350 °C (Fig. 3b), the value is assigned to unity, by which other values are normalized.

The water surface coverage decreases as the treatment time increases up to 90 min (Fig. 3a) and the dielectric constant does as well. Thus, the TMCTS treatment seems to restore the dielectric constant to the value for a film, which has little moisture uptake.

On the other hand, the water surface coverage remains constant as the treatment temperature increases from 325 °C up to around 350 °C or 375 °C and then begins to drop (Fig. 3b). In contrast, the dielectric constant exhibits no such plateau at low temperatures and decreases continuously as the temperature increases.

These results indicate that the increase in the dielectric constant does not correspond directly to the total amount of adsorbed moisture, but rather to certain components.

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