Characterization of porosity and dielectric constant of fluorocarbon porous films synthesized by using plasma-enhanced chemical vapor deposition and solvent process

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Fluorocarbon films obtained in plasma-enhanced chemical vapor deposition with a C_4F_8 compound were composed of a carbon cross-linked network and unlinked species encapsulated in the network [J. Appl. Phys. **89**, 893 (2001)]. The unlinked species were effectively removed from the films. Then, the network probably containing the pore of the species was extracted on wafers when the films were dipped into tetrahydrofran (THF) solvent. The fact implied that fluorocarbon porous films with a low-dielectric constant might be formed by using dry and wet processes. In the present study, x-ray analyses showed that the THF-treated films actually became porous in the dipping process. The dielectric constant of the THF-treated films was consistently low (<1.9) and reduced by 10% from that of as-deposited films. The fluorocarbon network as a porous medium may be applied to interlayer dielectrics for ultralarge-scale integrated circuits. © *2003 American Institute of Physics.*
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Low-permittivity intermetal dielectrics are investigated for the purpose of reducing the resistance–capacitance time delay, which is getting more conspicuous due to shrinkage of the spacing between metal lines in high-density multilayer integrated circuits. Porous film is one of promising materials with a low-dielectric constant (k).[1,2] Recently, attention has been focused upon organosilicate porous films.[3] The porous films are obtained by the process involving spin coating a mixture of the matrix material (e.g., silsequioxanes) and the surfactant called ''porogen,'' which was removed by thermal curing up to 400 °C and formed a mesoscopic pore in the films. Although the thermal process will not be disadvantageous in microelectronics fabrication, we demonstrate the synthesis of a porous film under room-temperature conditions.

In the previous work, we have investigated the structure of films prepared in fluorocarbon plasmas.[4] The films were composed of carbon cross-linked network and unlinked species encapsulated in the network. The unlinked species were easily removed from the films when the films were dipped into tetrahydrofuran (THF) solvent, since the species corresponded to the soluble components in the THF solution. The fluorocarbon network remained after the THF treatment seemed to be porous. In the present study, in order to examine the possibility of the application of THF-treated films to a low-k material, the film structure is precisely investigated in x-ray analyses and the dielectric constant of the film is measured.

Films were deposited on (111) n^+-type Si substrates by plasma-enhanced chemical vapor deposition (PECVD) with the parallel-plate reactor whose setup is described in Ref. 5. Octafluorocyclobutane was used as a monomer compound. The gas flow rate was 3.4 sccm. For the plasma generation, a radio frequency power supply at 13.56 MHz was connected to the lower electrode via a matching network. The power density was varied between 0.079 and 0.71 W/cm^2 (corresponding to the total powers, 5 and 45 W, respectively). The grounded electrode was set 3 cm above the powered electrode. The gas pressure in the reactor was maintained at 23 or 250 mTorr. Then the substrates were exposed to the plasma for 30 min on the lower electrode. Deposited films were dipped into THF for 3 min at a room temperature. When other solvents such as ethanol and acetone were tested, the solubility of fluorocarbon films was lower than that in case of THF. Therefore, THF was employed in this treatment. The dielectric constant of the films was determined by measuring the capacitance of a metal–insulator–semiconductor (MIS) structure consisting of an Al electrode, fluorocarbon film, and n^+ Si at a frequency of 1 MHz. X-ray reflection measurements for the film structure analysis, especially for detecting a pore in the film, were carried out using a Rigaku x-ray diffractometer and a rotating anode x-ray generator of Cu $K\alpha_1$ radiation (wavelength $=0.154$ nm) operated at 30 kV and 200 mA. Optical methods, e.g., ellipsometry, can analyze the film characteristic of porosity. However, the reflection method using an x ray with a wavelength shorter than visible light should be more effective for the THF-treated films, since a pore in the film seems to be formed by the soluble components whose geometrical sizes are esti-

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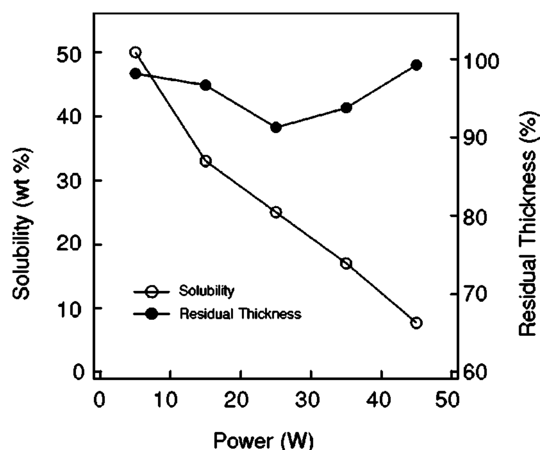

FIG. 1. Solubility and residual thickness of the films prepared at 23 mTorr in the THF treatment as a function of the rf power in the PECVD process.

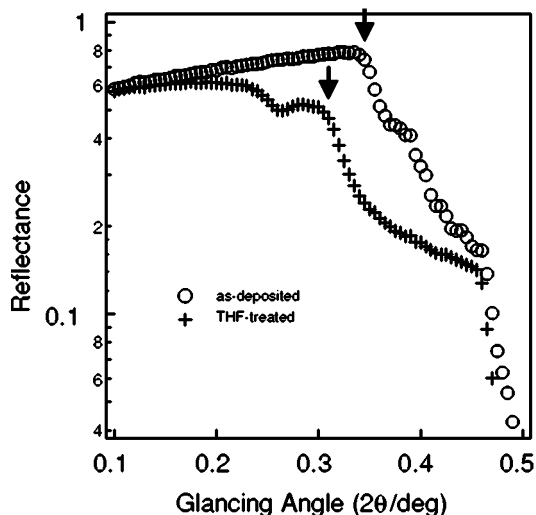

FIG. 2. Reflectance of the x-ray radiation as a function of the glancing angle onto the as-deposited film prepared at 250 mTorr and the THF-treated one. The arrows point to the critical angles of total reflection.

mated to be on the order of nanometer from their molecular weights.[4] The refractive index of a film to the x ray (n) is represented by[6]

$$n = 1 - \delta - i\beta, \tag{1}$$

where

$$\delta = \frac{r_c}{2\pi} N_A \lambda^2 \rho \frac{\Sigma_j x_j z_j}{\Sigma_j x_j M_j}, \quad \text{and} \quad \beta = \frac{\lambda}{4\pi}\mu_\ell . \tag{2}$$

Here, r_c, N_A, λ, ρ, x_j, z_j, M_j, and μ_ℓ are the classical electron radius (2.818×10^{-15}m), Avogadro's constant, x-ray wavelength, atomic density in the film, composition ratio of the jth element, atomic number, atomic weight, and absorption coefficient, respectively. In x-ray reflection on the film surface, the difference of n from unity, δ, is proportional to the atomic density ($\delta \propto \rho$), and critical angle of total reflection, θ_c, is given by $\sqrt{2\delta}$.[6] Therefore, one can compare the films in relative difference of the atomic density by measuring the critical angle. Surface morphology of the films was observed with an atomic force microscope (AFM).

Several film samples were prepared on the powered electrode by changing the rf power from 5 to 45 W at the constant pressure of 23 mTorr. First, we measured the solubility of the films in the THF-treatment, which is defined as the ratio of the weight of a film lost in the treatment to the total weight of the film. The solubility decreased with decreasing rf power as shown in Fig. 1. Here, it should be noted that the absolute values of the self-bias voltage of the powered electrode were measured to increase linearly from 4 to 27 V with increasing the rf power from 5 to 45 W. These results indicate that the cross-linking reactions within the deposited films are enhanced by increasing energy and flux of ion bombardment onto the surface of the growing films, in which the kinetic energy deposited by the ion bombardment can contribute to the polymer network formation.

Second, the residual thickness of the films after the THF treatment was measured as a function of the rf power (plotted together in Fig. 1). Although the solubility of the films prepared at the power less than 30 W was higher than 20%, the thickness loss of the films was less than 10%. This presumably indicated that the films became porous in structure after the THF treatment. Furthermore, the critical angle of total reflection in case of the THF treated film prepared at 250 mTorr was smaller than that in case of the as-deposited one, which actually proved that the THF treatment made the films porous (Fig. 2). Here, the data of the film prepared at 250 mTorr are shown in Fig. 2, since there was the marked difference in the critical angle between the as-deposited and the THF-treated films which was derived from the higher solubility of the film than that of the film treated at 23 mTorr. The tendency in the change of the critical angle before and after the THF treatment did not essentially depend on the pressure for the PECVD process. The components dissolved by THF were verified to be fluorocarbon molecules with the molecular weight less than 2000.[4] Hence, the pore size was estimated to be a few subnanometers.[4,7]

In the x-ray analyses, we calculated the x-ray reflectance of a two-layer film. The calculation was based on the formulas reported in Refs. 8 and 9. The curve fitting to the experimental data of the THF-treated film gave a good approximation of the two-layer model as the structure of the film (Fig. 3). The model showed that the porous layer 97 nm in thick-

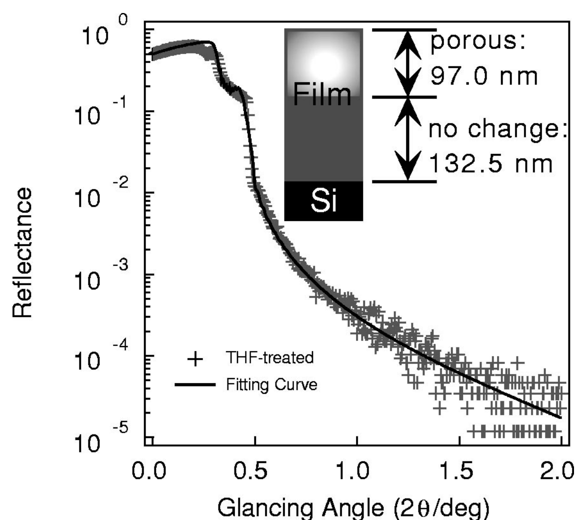

FIG. 3. X-ray reflectance of the THF-treated film. Crosses and solid line indicate the experimental data and the fitted curve, respectively. In the graph, the schematic shows the two-layer model assumed in the calculation.

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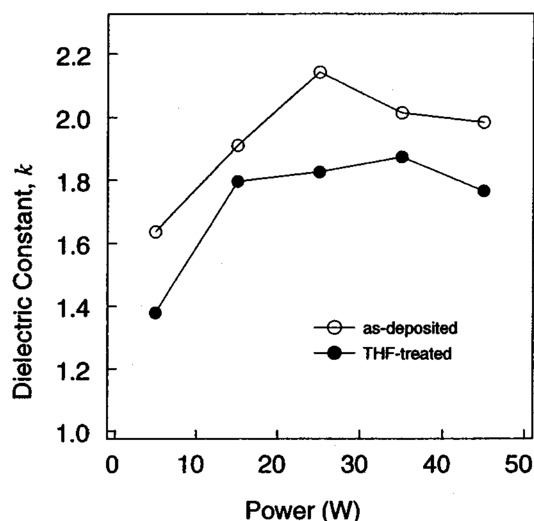

FIG. 4. Dielectric constant of the as-deposited and the THF-treated films shown as a function of the rf power in the PECVD process.

ness with the surface roughness of 5.85 nm (root-mean square), whose atomic density was 23% less than that of the non-THF-treated film, stacked on the as-deposited film of 132.5 nm. Strictly speaking, the atomic density may have changed gradually from the surface to the bulk of the film, and the boundary between two layers should have been ambiguous, since the penetration amount of the solvent depends on depth in the film. Furthermore, the depth of the boundary between the layers, which corresponds to the penetration depth of the solvent, depended on time spent for the THF treatment. However, the mean value of atomic density over the penetration layer was not changed by the time. According to AFM observation, the surface roughness was enhanced by the THF treatment. On the rough surface, the peak-to-valley height was lower than 38 nm. The height was much lower than the thickness of the porous layer estimated in the x-ray analyses. Therefore, the porous structure certainly indicated not the surface roughness but the porous structure formed by the THF treatment.

Figure 4 shows the dielectric constant of the as-deposited films and that of the THF-treated ones. After the THF treatment, the dielectric constants were consistently lower than 1.9 and reduced at least 10% compared to those of the as-deposited films. When films thinner than 100 nm having only a porous layer were formed, dielectric constants of the films were 20% lower than those of the as-deposited films. The decrease of the constant can be easily predicted from the Clausius–Mossotti formula, which implied that fluorine-rich species removed from the films[4] did not considerably affect dielectric properties. No chemical reaction is expected to occur between the deposited fluorocarbon films without radical sites and the THF solvent, since the chemical composition of the polymerized fluorocarbon films is similar to poly-tetrafluoroethylene being known as a chemically stable substance to the solvent. The reduction of the dielectric constant was owed not to chemical reactions on the films but to a decrease of atomic density of the films by the dissolution of the noncross-linked molecules to form the porous structure.

To summarize, the pore formation using the THF dipping process was demonstrated for films deposited in C_4F_8 plasmas. The dielectric constant of the THF-treated films was reduced by 10% from that of as-deposited films. The fluorocarbon porous films may be useful as one of the candidates of the low-k materials for application to ultralarge-scale integrated circuits (ULSI). The films, however, cannot be directly applied to the present processes for ULSI fabrications, due to the properties of the film which are poor in thermal stability, hardness, and so on. Therefore, further investigation and innovative ideas will be necessary to improve the film properties to be acceptable in future ULSI processes. On the other hand, the dipping process combined with chemical vapor deposition is practical for forming the porous media with a nanometer-scale pore, which can be applied to other industrial materials, e.g., optical films, as well as the ULSI dielectrics.

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