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FTIR Characterization of Fluorine Doped Silicon Dioxide Thin Films Deposited by Plasma Enhanced Chemical Vapor Deposition *

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Fluorine doped silicon dioxide (SiOF) thin films have been prepared by plasma enhanced chemical vapor deposition. The Fourier transform infrared spectrometry (FTIR) spectra of SiOF films are deliberated to reveal the structure change of SiO_2 and the mechanism of dielectric constant reduction after doping fluorine. When F is doped in SiO_2 films, the Si-O stretching absorption peak will have a blue-shift due to increase of the partial charge of the O atom. The FTIR spectra indicate that some Si-OH components in the thin film can be removed after doping fluorine. These changes reduce the ionic and orientational polarization, and result in the reduction in dielectric constant of the film. According to Gaussian fitting, it is found that the Si-F_2 bonds will appear in the SiOF film with increase of the fluorine content. The Si-F_2 structures are liable to react with water, and cause the same increase of absorbed moisture in the film.

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Low dielectric constant interlayer dielectrics are increasingly needed in ultra large scale integrated-circuits (ULSI) technology, because multilevel interconnection induces larger wiring capacitance, which affects the operation speed of ULSI devices.[1,2] As promising substitutions for conventional SiO_2 dielectrics ($\varepsilon = 4.1$), the fluorine doped silicon dioxide (SiOF) thin films deposited by plasma enhanced chemical vapor deposition (PECVD) are proposed.[3−5] However, the effect of doped fluorine on the SiOF thin film structure and the reduction mechanism in dielectric constant are not clear yet. In this paper, the SiOF films with low dielectric constant are deposited using PECVD method. Through the Fourier transform infrared spectrometry (FTIR) analysis, the structure changes and the mechanism of decreasing dielectric constant due to F doped in SiO_2 are investigated.

The SiOF films are deposited on silicon wafers using $TEOS/O_2/SiF_4$ mixture in a PECVD system at frequency of 13.56 MHz. The rf power is fixed at 100 W. The substrate temperature is as high as 300°C and the gas flow rate ratio of SiF_4/TEOS is varied from 0 to 3 for depositing SiOF films with the different F content.

The FTIR spectra of SiOF films are determined by NICOLET MEGNA-IR 550-2 analyzer. The dielectric constants of the SiOF films are obtained through capacitance-voltage ($C - V$) measurements of metal-insular-silicon (MIS) at 1 MHz. Films with a target thickness of 100 nm were deposited on low resistance silicon wafers. Then the aluminum films are deposited on the SiOF films as the top electrodes and the back of silicon wafer to assure ohmic contact. The thickness and refractive indices of the films are measured by ellipsometer at a wavelength of 632.8 nm.

One typical FTIR spectrum for SiOF film is shown in Fig. 1. Two absorption peaks corresponding to the Si−O and Si−F bonds are observed at the wave numbers around 1080 and 930 cm^{-1}. The other absorption peaks at 3670, 3300 and 820 cm^{-1} stem from Si−OH stretching mode, H−O−H stretching mode and Si−O bending mode, respectively. Because the Si−F content in the thin film is approximately proportional to the peak area ratio of Si−F stretching mode to that of Si−O stretching mode, the peak area ratio of the Si−F at 930 cm^{-1} to the Si−O at 1080 cm^{-1} has been used for determining the Si−F/Si−O (%) value in the film after baseline correction.

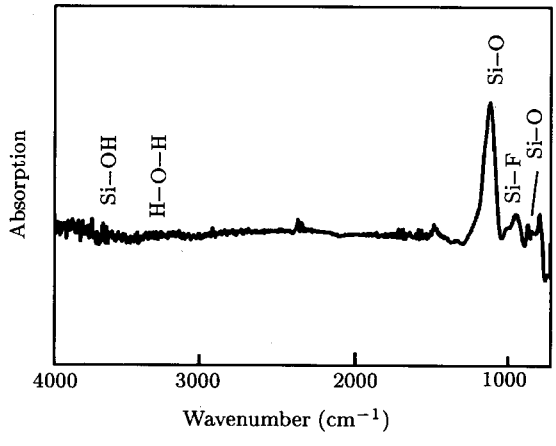

Fig. 1. A typical FTIR spectrum of SiOF film. The Si−O and Si−F bond stretch vibration centers are around 1080 and 930 cm^{-1} and the peaks at 3670, 3300 and 820 cm^{-1} correspond to Si-OH stretch, H−O−H stretch and Si−O bending mode, respectively.

From the FTIR spectra of SiOF films with different F content, we find that the peak position of Si−O

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stretch mode shifts with the F content changing. Figure 2 shows the dependence of Si−O stretching absorption frequency (ν_{Si-O}) and dielectric constants of the SiOF films on the Si−F/Si−O(%) value. With the Si−F/Si−O(%) value increasing, the dielectric constants of SiOF films decrease and the Si−O stretching absorption peak was found to shift to blue. This increase in ν_{Si-O} may be explained by the change of the charge distribution on the Si−O bonds due to the incorporation of the F atoms in the thin film. The distribution of charge on the Si−O bond in the SiOF films can be calculated by the following equations, which are the basic expression of Siegbahn's model,[6]

$$q_i = Q_i \pm \sum_{i \neq j} n I_{ij}, \tag{1}$$

$$I_{ij} = 1 - \exp\left[-\frac{(X_i - X_j)^2}{4}\right], \tag{2}$$

where I is the ionicity of bond, Q the charge number and q the partial charge on atom, X the electronegativity of atom, which should be adjusted with the changing partial charge on atom. Table 1 is the calculated results of partial charge for the films of $Si-O_2$ and SiOF. It can be seen that the partial charge of the O atom in the SiOF film increases, which means that the fluorine atoms incorporated in the films change the charge distribution on the Si−O bonds by dragging electron from O which is negatively charged in the $Si^{\delta+}-O^{\delta-}$ bond. This change will enhance the covalence of the Si−O bonds and therefore result in the increase of ν_{Si-O}. In addition, the relaxation of thin film will also result in the increase of ν_{Si-O}. Lee *et al.* reported that the F dopant in SiO_2 would result in the reduction of film density.[7] In the relaxed film, Si−O−Si bond angle will increase.[8] In consideration of the intensity effect,[9] the hybrid orbital of the Si atom in the SiO bond is composed of more than 2*s* components when the Si−O−Si bond angle increases. Because the 2*s* orbital is spherical symmetry while the 2*p* orbital is spindle-shaped. The increase of 2*s* character in the 2*s* and 2*p* hybridization reduce the bond length of Si−O. Therefore, the Si−O stretching mode absorption peak will have a blue shift. According to the above discussions, the fluorine atoms incorporated in the films will enhance the covalence property and reduce the polarizability of the Si−O bonds, which results in the decrease of electronic polarization in the SiOF film. The dielectric constant will decrease due to the decreasing electronic polarization.

Table 1. Partial charge distribution in Si−O and F−Si−O.

Atom	Electronegativity	Partial Charge in Si−O	Partial Charge in F−Si−O
Si	1.95	0.51	0.59
O	3.65	−0.26	−0.20
F	4.00	——	−0.28

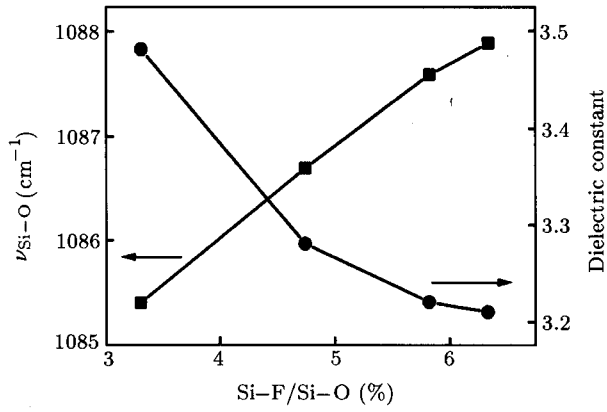

Fig. 2. Dependence of Si−O stretch absorption frequency (ν_{Si-O}) and dielectric constants on the Si−F/Si−O(%) value.

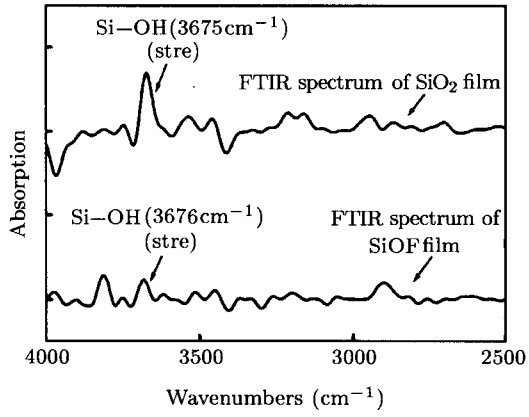

Fig. 3. FTIR spectra of the SiO_2 and SiOF films in the range of 2500 to 4000 cm^{-1}, Si−OH stretching mode absorption peak is near 3670 cm^{-1}.

Figure 3 shows the spectra of the SiOF and SiO_2 films in the region of 2500−4000 cm^{-1}. It is found that the Si−OH stretching mode absorption is weakened in the FTIR spectrums of the SiOF films, which indicates that the fluorine atoms incorporated in the films will reduce the Si−OH contents. It was reported that Si-OH bond in SiO_2 films formed by PECVD TEOS contributes a lot to the dielectric constant because it is strong polarized.[10] So the reduction in dielectric constant maybe partly result from the less content of Si-OH in the thin film due to the doping fluorine.

From the C−V measurements, it is found that the SiOF films have lower dielectric constant with increase of the SiF_4 flow rate. The dielectric constant can be reduced to 3.2 when the flow rate of SiF_4 is as high as 60 sccm. However, some researchers reported that the water resistibility would be seriously degraded in the high fluorine content films.[11,12] In order to seek the relationship between the F content and the water absorption of the film, the Si−F stretching absorption peaks for two SiOF films with different F content are analyzed according to the Gaussian fitting, as shown in Fig. 4. In Fig. 4(a), which corresponds to the SiOF film with 6% Si−F/Si−O, obvious shoulders appear on the solid line of the Si−O stretching

mode absorption peak at 980 cm^{-1}. Figure 4(b) corresponds to the SiOF film with 3% Si–F/Si–O. The dotted lines in Figs. 4(a) and 4(b) are Gaussian deconvolution results of the Si–F stretching mode absorption peaks. In Fig. 4(a), the peaks at 900, 928 and 984 cm^{-1} correspond to the Si–F_2 symmetric stretching mode, Si–F stretching mode and Si–F_2 asymmetric stretching mode, respectively. However, only two components are found in Fig. 4(b), the absorption peak at 932 cm^{-1} is identified as that of Si–F stretching mode. Another absorption peak at 910 cm^{-1} is due to the cooperative vibration mode of the pair of the Si–F bonds via the oxygen structure from the preliminary *ab initio* quantum chemical calculation.[7] Comparing Fig. 4(a) with 4(b), we find that there are Si–F_2 structures in thin films with more F content. These two films are exposed to air for moisture absorption test. After 10 days, the obtained FTIR spectra in the region from 2500 to 4000 cm^{-1} of these two films are shown in Fig. 5. The FTIR spectrum labeled with *a* corresponds to Fig. 4(a), and the other spectrum labeled with *b* corresponds to Fig. 4(b). Obviously, there is a larger absorption peak around 3300 cm^{-1}, which corresponds to H-O-H bond, in the spectrum labeled with *a* as compared with the spectrum labeled with *b*. The reason is that the Si–F_2 structure is not stable and liable to react with moisture. Therefore, the water resistibility of the SiOF film will degenerate if fluorine content in the thin film is high.

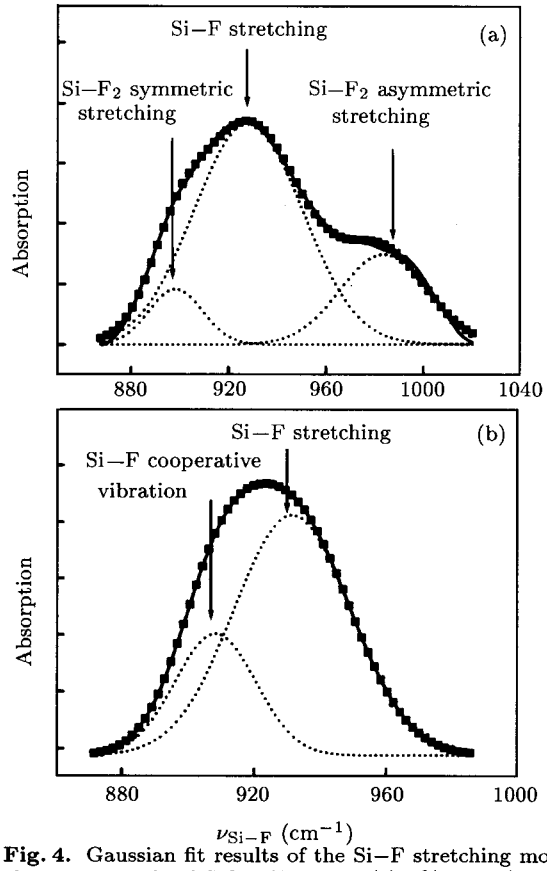

Fig. 4. Gaussian fit results of the Si–F stretching mode absorption peak of SiOF film with (a) 6% Si–F/Si–O. and (b), 3% Si–F/Si–O.

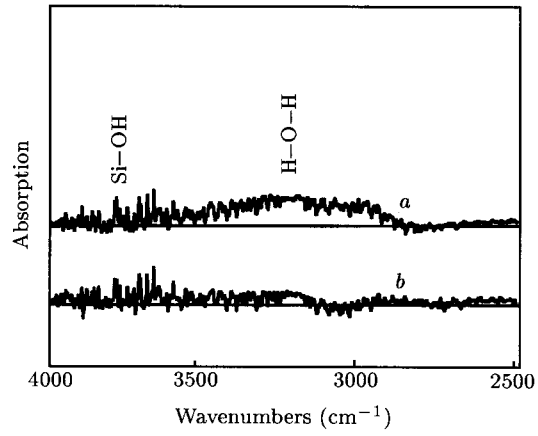

Fig. 5. FTIR spectra of two SiOF thin films in the range of 2500 to 4000 cm^{-1} after the moisture absorption test. (spectrum *a* corresponds to the film with 6% Si–F/Si–O, spectrum *b* corresponds to the film with 3% Si–F/Si–O).

In conclusion, the FTIR spectra of the SiOF films prepared by PECVD are analyzed in detail to reveal the structure change of SiO_2 and the mechanism of dielectric constant reduction after fluorine doping. When F is doped in the SiO_2 films, the Si–O stretch absorption peak will have a blue shift due to the increase of the partial charge of the O atom. The FTIR spectra indicate that some Si–OH components in the thin film can be removed after doping fluorine. These changes reduce the orientational and electronic polarization, and result in a decrease of dielectric constant of the film. According to Gaussian fitting, it is found that the Si–F_2 bonds will appear in the SiOF film with the increasing fluorine content. The Si–F_2 structures are liable to react with water, and cause an increase of absorbed moisture in film.

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