Correlation between Potential Barrier and FTIR Spectra in SiOC Film with the C-O Bond of sp³ Structure

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Recently, the semiconducting conjugated organic materials have been studied because of their many applications such as displays, smart cards or microelectroniscs. The field effect mobility of OTFTs (organic thin film transistors) depends on the chemical properties of the surface on gate insulator.[1-3] Therefore, the improvements of the mobility in pentacene-channel organic thin film transistors (OTFTs) were achieved by either treating the gate insulator surface or by using different insulator materials.[4-6] Pentacene has been researched as active materials for organic-TFTs, but inorganic gate insulator has generally been used as a gate insulator. So it is necessary to change organic type materials for the gate insulator. For a high mobility of pentacene-channel OTFTs, it is essential for the gate insulator to have a low-dielectric (low-k) constant without leakage current. The carbon doped silicon oxide film is known as the candidate of next generation's insulator, and estimated as an insulator to fit for organic flexible devices. The carbon doped silicon oxide film possessed various properties from organic to inorganic types by the chemical shifts using FTIR spectra.[7-9] The analysis of FTIR spectra provides an information about the chemical shift to define the bonding structure of the carbon centered system such as the carbon doped silicon oxide film, a-C:F film[10-12] and a-C:H film. In the case of the carbon based system, the carbon doped silicon oxide film involves the chemical shift according to the electron density around C=O bond. The decreasing of electron density near the C=O bond trends the sp² carbon-structure in a final film with a red shift because of the elongation effect of bonding length between atoms. On the other hand, the blue shift originates from the C-H bond condensation owing to the electron-rich group of hydrophobic properties, thus making the sp³ carbon-structure due to the steric hindrance effect. The structure of SiOC films is closely connected with the electrical and mechanical properties, which leads to improve electronic applications.[13,14]

This work reported the reason of the reduction of the leakage current in SiOC film, and the structures by FTIR spectra. The variation of current due to the various flow rate ratios was transformed to the potential barrier and the peak indexing from the data of FTIR spectra was performed and analyzed.

Organometallic Carbon Reaction

In a carbon center system, the conjugated C=C or C=O double bond due to weak alkyl group easily undergoes uncleophilic attack by a metal atom with rich electron, and the results are confirmed by the CH₃-M(Si, p, S) bond. The nucleation induces the effect of a weak boundary layer at the film's surface, and then the bonding structure of the films becomes the sp³ carbon of C-O single bond. There are C=O and C=O bonds as well-defined organic functional group in synthetic organic chemistry. In these organic reactions, there are organometallic carbon and organic carbon reactions. The organometallic carbon reaction induces an ionic bond with ionic polarity, but the organic carbon reaction is a neutral reaction without polarization. The C-O single bond is weaker than the C=O double bond and then the length of C-O single bond becomes long. Therefore, the final film of the sp³ carbon structure displays the chemical shift in FTIR spectra. This work researched the correlation between the organometallic carbon reaction and the chemical shift in SiOC film deposited by PECVD.

Experimental Details

The SiOC films were obtained using the mixed gases of oxygen and bistrimethylsilylmethane(BTMSM) by plasma enhanced chemical vapor deposition. The precursor of BTMSM was purchased from the Applied Materials Corporation. The deposition condition was the substrate temperature at 100 °C for 10 s. The BTMSM was vaporized and carried by argon gas at 35 °C from a thermostatic bubbler. The films were prepared by various flow rate ratios of O₂/BTMSM > 1.0 maintaining the total flow of 120 sccm. The base pressure was 3 Torr and the rf power was 450 W in each experiment. The chemical properties were analyzed from Fourier Transform Infrared Spectrometer (FTIR, Galaxy 7020A). The FTIR spectra of samples were deconvoluted. The current-voltage characteristics were measured on the sample of the MIS (Al/SiOC film/Si) structure using a HP 4155A semiconductor parameter analyzer at 1 MHz.

Result and Discussion

Figure 1(a) shows the leakage currents of SiOC films on the various flow rate ratios. The leakage currents increase for the most SiOC films. However the samples fabricated with the flow rate of O₂/BTMSM = 1.07 and 0.9 abruptly decrease the

(a)

(b)
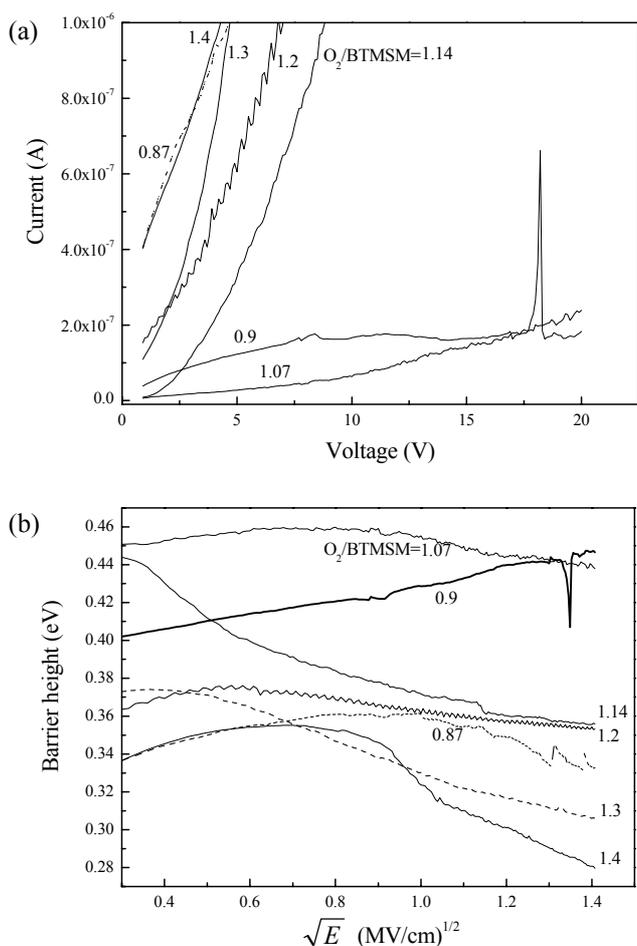
Figure 1. (a) Leakage currents of SiOC films with various flow rate ratios, (b) Potential barrier.

leakage currents. The electric properties of the samples with the flow rate of $O_2/BTMSM = 1.07$ is better than others.

Figure 1(b) is the potential barrier of samples due to the Poole-Frenkel mechanism.

The leakage current density obtained from the Fig. 1(a) is supported by Poole-Frenkel conduction as explained the following Equation

$$J \propto E \exp(-q\Phi_B/kT)\exp[(q/kT)(qE/\pi\varepsilon_0\varepsilon_r)^{1/2}] \qquad (1)$$

where Φ_B, T, q, E, k, ε_0 and ε_γ are the barrier height at the injected electrode, absolute temperature, the electric charge, the electric field strength in the insulator, the Boltzmann's constant, the dielectric constant of free space, and the relative dielectric constant at high frequency, respectively. In the case of low voltage, Φ_B is replaced Φ_{PF} owing to Poole-Frenkel effect depending on the potential barrier height. Reduction of the leakage current is due to the rising of the potential barrier and the potential barriers of the samples with the flow rate of $O_2/BTMSM = 1.07$ and 0.9 are higher than other samples. To investigate the correlation with the bonding structure, samples are analyzed by the FTIR spectra.

Figure 2 shows the FTIR spectra in the full range from 600 cm^{-1} to 4000 cm^{-1} of the SiOC film while increasing the oxygen flow rate ratio. It shows the CH peak near 3000 cm^{-1}, the
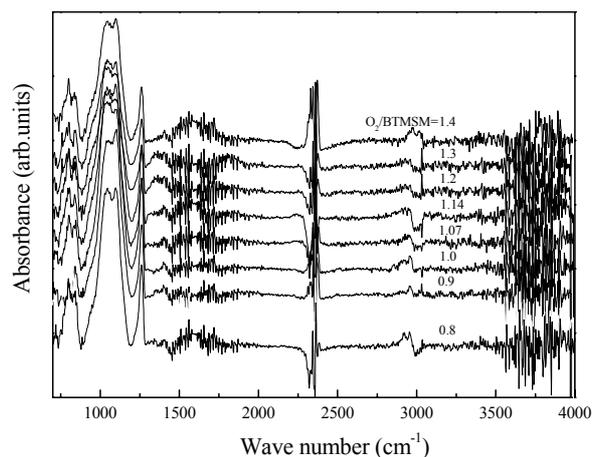
Figure 2. FTIR spectra in the full range from 600 cm^{-1} to 4000 cm^{-1} of the carbon doped silicon oxide film.

conjugated C=O bond of 1500~1750 cm^{-1}, the C=C bond of 1400~1500 cm^{-1}, Si-CH₃ peak near 1260 cm^{-1}, and Si-O-C band of 870~1350 cm^{-1}.

Figure 3(a) shows the Si-O-C related bond of 730~900 cm^{-1}. At the peak of 800 cm^{-1}, most films display one peak, however, the SiOC film with $O_2/BTMSM = 1.07$ divides into two peaks near 800 cm^{-1} in spite of a few differences in the flow rate. Moreover, the SiOC films without the film of $O_2/BTMSM = 1.07$ have two peaks in the position of 838 cm^{-1} and that of $O_2/BTMSM = 1.07$ has only one peak. The SiOC film of $O_2/BTMSM = 0.9$ also displays two peaks in the range of 790~810 cm^{-1} and one peak near in the range of 840 cm^{-1} as shown in Fig. 3(b). Because the C=C bond as organic carbon is attacked by the Si with electron rich group, and becomes the C-O bond as organometallic carbon of sp³ structure. In this study, the organometallic carbon bond shows two peak in the range of 790~810 cm^{-1}. The range of 735~760 cm^{-1} or 735~775 cm^{-1} is the out of plane of C-H deformation mode. The range of 790~810 cm^{-1} is related with the C=C double bond, and the range of 825~850 cm^{-1} is Si-H vibration mode. The band over 880 cm^{-1} is the out of plane of C-H deformation mode.[10,12,14] The C=C bond is basic functional group in the reaction of organic compound, and there are two kinds of reactions depending on the concentration of the nucleophilic, such as the C=O bond of sp² and C-O bond of sp³ structure. The SiOC films of $O_2/BTMSM = 1.07$ and $O_2/BTMSM = 0.9$ have the C-O bond of sp³ structure which is the amorphous structure with high degree, hence decreasing the leakage current as previous figure 1(a). The C=O groups are attacked by the Si atom with much electrons and become the C-O bond of sp³ structure as electron deficient group. Therefore, the C-O bond occurs the split to the two peaks in the range of 790~810 cm^{-1} in FTIR spectra. It is the results as the chemical reaction about the M-OH def vibration mode of 730~880 cm^{-1}. The M-OH mode is the reaction between OH bond and a metal atom with electrons, and makes the Si-O-C bond including the C=O bond of sp² or C-O bond of sp³ structure according to the concentration of electrons. The chemical reaction with the M-OH deformation vibration mode widely spreads from 730 to 880 cm^{-1} and finally makes the Si-O-C main bond. Concerning

(a)

(b)
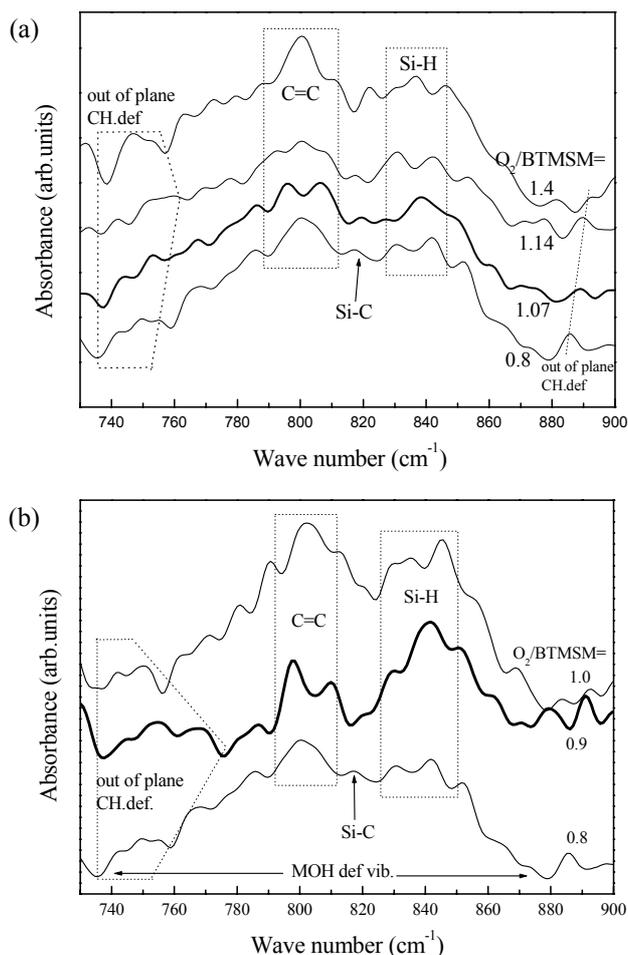
Figure 3. Chemical shift in the range of 730~900 cm^{-1}, (a) SiOC film with O$_2$/BTMSM = 1.07, (b) SiOC film with O$_2$/BTMSM = 0.9.

Si-H bond of 825~850 cm^{-1}, as observed in FTIR measurements, Si-H bond has strong one peak at the films of O$_2$/BTMSM = 1.07 and 0.9 of C-O sp^3 structure. This would suggest that the Si atom attracts the electrons of C=O bond group and recombines in the plasma gas phase.

Figure 4(a) displays the chemical shift of the Si-O-C main band of 870~1200 cm^{-1}, which consists of two peaks, the C-O and Si-O bonds. The films in the range of 0.8 ≤ O$_2$/BTMSM ≤ 1.0 display the high intensity of the right side, but the other films of the range of 1.0 < O$_2$/BTMSM show the high intensity of the left side, respectively. To investigate the elements of the main band of 870~1200 cm^{-1}, the main bonds are deconvoluted.[7]

Figure 4(b) shows the deconvoluted FTIR spectra of the Si-O-C main band of 870~1200 cm^{-1}. The first bond is the Si-O-C cage link, the second bond is the Si-O-C cross link, and the third bond is the Si-O-Si cross link. The Si-O-C cage link and cross link are the carbon related bonds. Especially, the samples of O$_2$/BTMSM = 0.9 and 1.0 show the increasing of the third bond of the Si-O-Si cross link, because of the increasing oxygen flow rate ratio. The cage link and the Si-O-C cross-link decreases due to the weakening effect of porosity. On the other hand, the samples of O$_2$/BTMSM ≥ 1.07 decrease the Si-O-Si cross link bond in spite of the increasing oxygen flow rate.

Figure 5(a) shows the relative bond content, respectively.

(a)

(b)
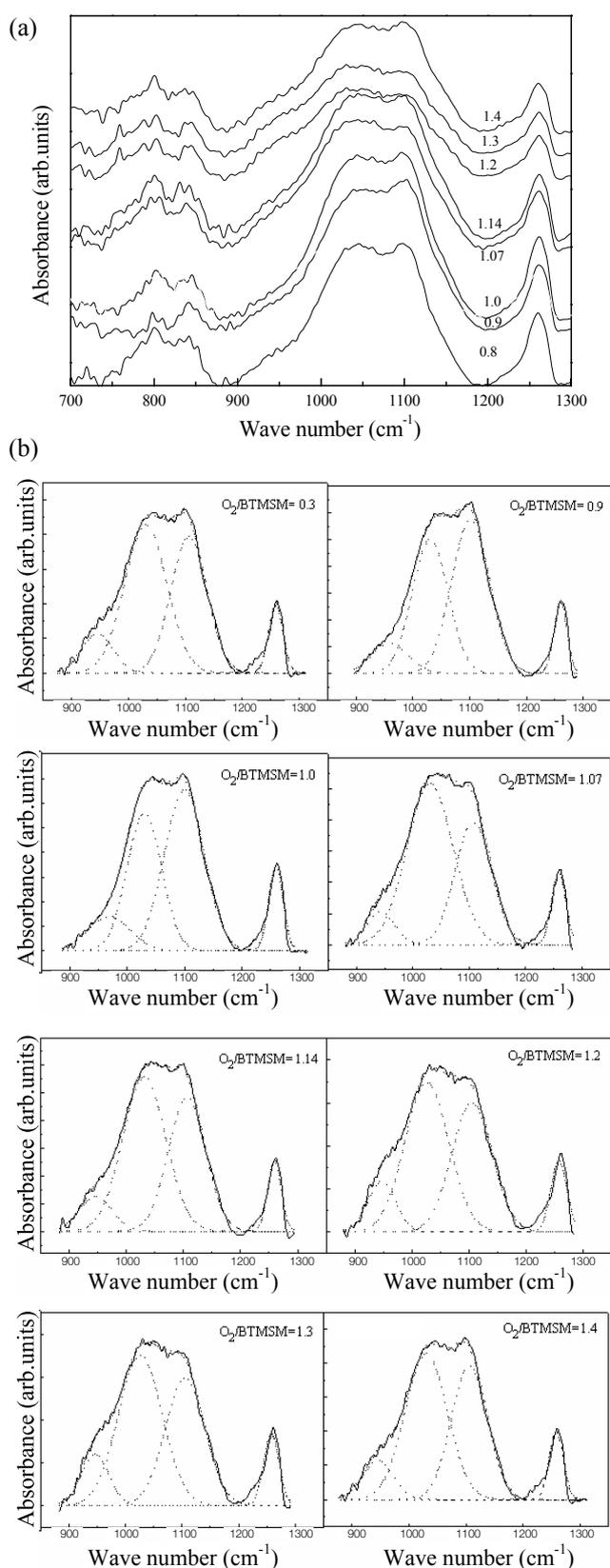
Figure 4. (a) Main band with two peaks in the range of 870~1200 cm^{-1}. (b) Deconvoluted FTIR spectra of 870~1200 cm^{-1}.

The variation between the Si-O-C and Si-O-Si cross-link bond shows a marked distinction in the samples between O$_2$/BTMSM = 1.0 and O$_2$/BTMSM = 1.07 flow rate ratio.

(a)

(b)
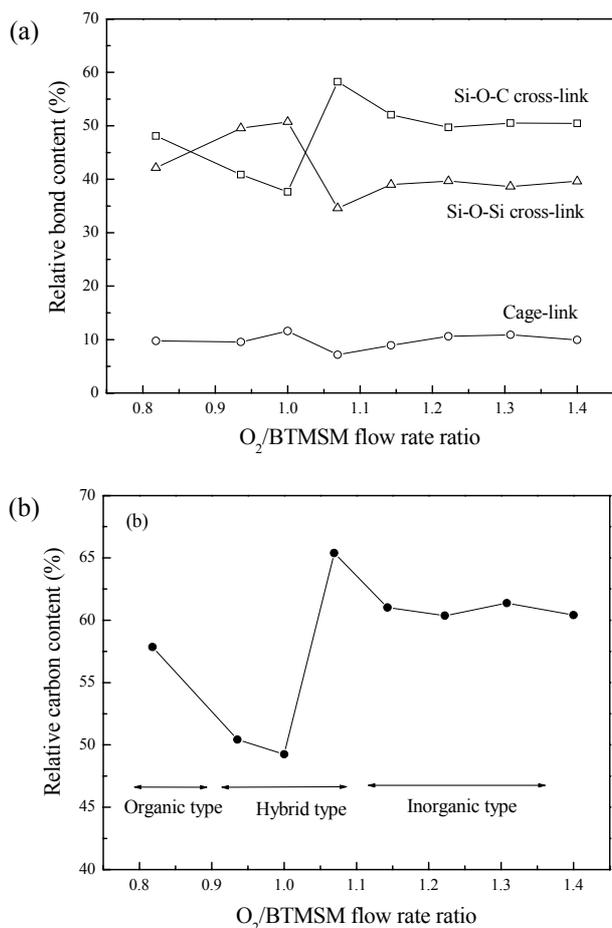
Figure 5. (a) Content of cage link, Si-O-C link and Si-O-Si link, (b) Relative carbon content.

Figure 5(b) shows the relative carbon content of the SiOC film. The relative carbon content is calculated from

$$\frac{(Si-O-C)+(Si-CH_3)}{(Si-O-C)+(Si-O-Si)+(Si-CH_3)} \times 100. \quad (2)$$

The relative carbon content is the largest at the SiOC film of O_2/BTMSM = 1.07, which is the C-O sp^3 structure as shown in Fig. 3(a). The carbon content increases relatively in spite of the increasing of oxygen flow rate. The relative carbon content displays the abrupt variation according to the increasing the flow rate ratio. The difference is related with the variation of bonding structures due to the organometallic carbon reaction. The SiOC film of $0.9 \le O_2$/BTMSM ≤ 1.07 shows the hybrid type with non-polarity by the nucleophilic reaction between the organic and inorganic types with polarization.

Therefore, the SiOC film is divided into three types such as the organic type with the flow rate ratio of O_2/BTMSM < 0.9, hybrid type of $0.9 \le O_2$/BTMSM ≤ 1.07 and inorganic type of O_2/BTMSM > 1.07. The reason of chemical shift at the main bond is important issue in SiOC film, and it is confirmed that

the C-O sp^3 structure generated by the nucleophilic chemical reaction increases the relative carbon content, and decreases the leakage current. It is induced that the SiOC film of C-O sp^3 structure has more performance as low-k materials for inter layer dielectric (ILD) materials.

Conclusion

The SiOC films were obtained by mixing the gases of oxygen and bistrimethylsilylmethane through chemical vapor deposition. The reaction of the M-OH deformation vibration mode of 730~880 cm^{-1} made the Si-O-C main bond, which has the C-O sp^3 or C=O sp^2 structure. The C=O bond of sp^2 structure had the one peak, but the C-O bond of sp^3 structure had two peaks in the range of 790~810 cm^{-1}. In the organic chemistry, the organometallic carbon bond as sp^3 structure is one of important factors and in this study, the organometallic carbon bond shows two peak in the range of 790~810 cm^{-1}. The C-O bond of sp^3 structure generated by the Si atom attack became an amorphous structure due to the electron deficient group. The SiOC film of O_2/BTMSM = 1.07 and 0.9 with the C-O sp^3 structure decreased the leakage current hens increasing the potential barrier. The relative carbon content of SiOC film was researched by the deconvolution of the main bonds. The SiOC film of O_2/BTMSM = 1.07 increased dramatically the relative carbon content in spite of the increasing oxygen flow rate ratio. The C-O sp^3 bond as ionic bond makes the hybrid type as non polarization between organic and inorganic types in SiOC film. Therefore, the hybrid type SiOC film is more amorphous film than any other types, and becomes ideal low-dielectric materials.

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