Characteristic of Organic Thin Film Depending on Carbon Content by Fourier Transform Infrared Spectra and X-ray Diffraction Pattern

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Recently, organic semiconductors have attracted considerable attention to flexible electric application using low-dielectric (low-k) materials or organic thin film transistor. Conjugate polymers derive their semiconduction properties by having delocalized π-electron bonding along the polymer chain. The π and π^* orbitals form delocalized valence and conduction wave functions, which support mobile charge carriers.[1-3] One of the next candidates as low-k materials is SiOC film, which posses a lower dielectric constant due to the presence of lighter C and H atoms, as opposed to Si and O atoms.[4] Pentacene material as an organic conductor has been widely used in organic thin film transistors (OTFTs). However, in comparison with inorganic semiconductors, the electric properties of organic semiconductors are relatively little known. Especially, pentacene growth depends absolutely on the surface's properties on gate insulator due to the organic reaction.[5-7] Therefore, it is important to understand the underlying organic molecular reaction between inter-layers.[8-10] The mobility of pentacene increases dramatically on the hybrid type insulators, which is required an ionic bonding during the reaction. Because it's macrostructure becomes stable and the high degree of the amorphous structure. Finally the dielectric constant increases at the hybrid type sample and the leakage current also decreases.[11,12]

To make the SiO_2 film with hybrid properties, the samples were soaked in dilute *n*-Octadecyltrichlorosilane (OTS) solution to treat the surface. The ratio of the mixed solution of chloroform ($CHCl_3$) and hexane was 300:700, and OTS was injected using a micropipet. The OTS solution was made from OTS:chloroform:hexane = x:300:700 (x = 1-5). It was prepared a dilute OTS solution of 0.1-0.5%. OTS ($CH_3(Cl_2)_{17}SiCl_3$) has an organic composition with many alkyl groups, therefore, the film treated using 0.1% OTS has more hybrid properties than that treated using 0.5% OTS. The SiO_2/Si wafers were soaked in the prepared solution for 30 min. Then the surface was cleaned for 5 s in a mixed solution of chloroform and hexane with the ratio of 300:700 and annealed in a vacuum chamber at 150 °C for 1 h.

Figure 1(a) shows the FTIR spectra in the full range from 600 to 4000 cm^{-1} of the OTS-treated SiO_2 film with various OTS-treatment contents from 0.1 to 0.6%. Generally, an organic compound has its CH peak near 2900 cm^{-1}, but these samples do not have the CH peak near 2900 cm^{-1}. Therefore, OTS-treated SiO_2 films are hybrid-type materials,

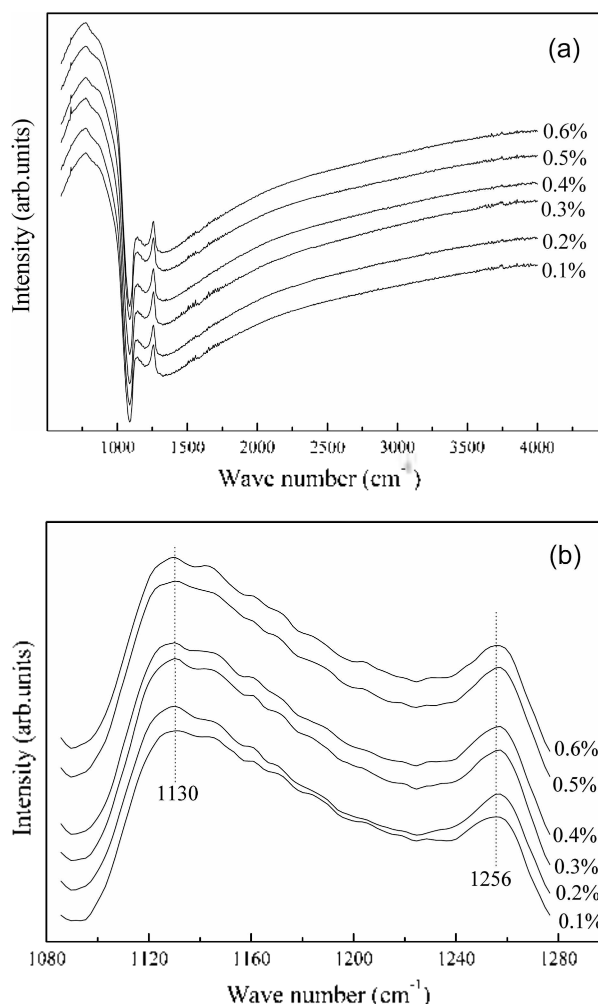

Figure 1. FTIR spectra of OTS treated SiO_2 film according to the increase of OTS treated content. (a) FTIR spectra in the full range from 600 to 4000 cm^{-1}. (b) FTIR spectra in the narrow range from 1110 to 1280 cm^{-1}.

such as SiOC films. The peak below 1100 cm^{-1} is a CH-related bond, and the broad band from 1090 to 1280 cm^{-1} is for the mixed bond attributed to the nucleophilic substitution reaction between SiO_2 film and dilute OTS solution.[4] Figure 1(b) is the FTIR spectra of samples in the narrow range from 1110 to 1280 cm^{-1}. The peak at 1130 cm^{-1} is for a C-O related bond, and the peak at 1256 cm^{-1} is related to a $Si\text{-}CH_3$ bond. Therefore, the broad band from 1090 to 1280

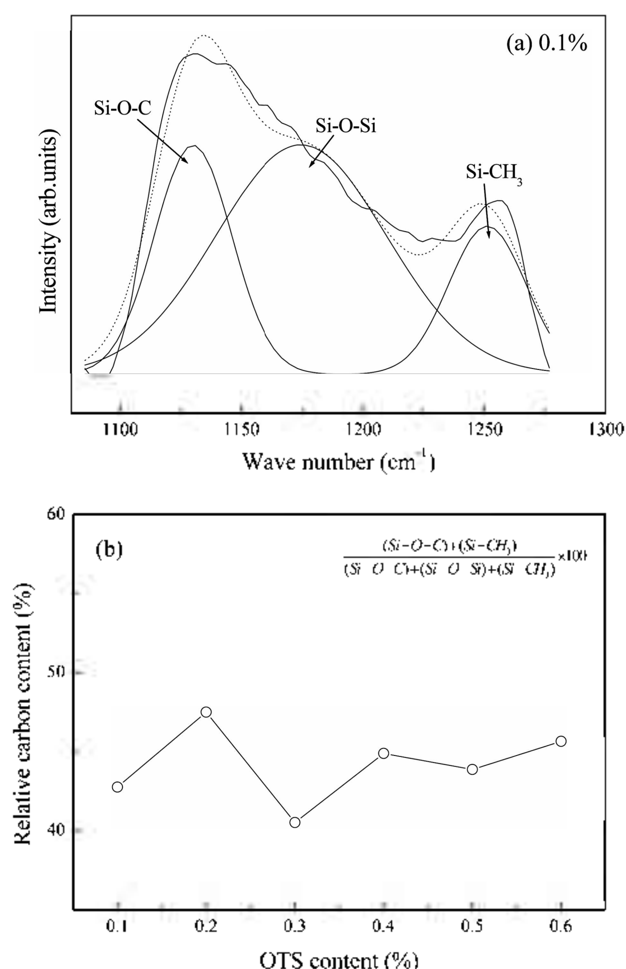

Figure 2. (a) Deconvoluted spectra for various OTS treated SiO_2 film as shown in Fig. 1. (b). Relative carbon content.

cm^{-1} is united the bond peak at 1130 cm^{-1} to the bond peak at 1256 cm^{-1}.

To research the relative bond contents, it was deconvoluted FTIR spectrum in the range from 1090 to 1280 cm^{-1} by using a Gaussian peak fitting as shown in Figure 2(a). The deconvoluted spectrum consists of the first mode of the Si-O-C bond, the second mode of the Si-O-Si bond, and the third mode of the $Si-CH_3$ bond. These bonds have different area or intensity according to the concentration of OTS mixed solution. The first mode of the Si-O-C bond is a result of the nucleophilic reaction between OTS mixed solution and SiO_2 film. The second mode is induced in order that the high electronegative oxygen atom of SiO_2 film reacts with OTS compound. The third mode of the $Si-CH_3$ bond is a vibration mode of the terminal Si atom of the OTS compound. Finally, when the bond peak at 1130 cm^{-1} and the bond peak at 1256 cm^{-1} are combined, the bond structure of the final material shows a broad band from 1090 cm^{-1} to 1280 cm^{-1}.

Table 1 shows the relative carbon content for OTS-treated SiO_2 film with increasing OTS content.

The relative carbon content is calculated from

$$\frac{(Si-O-C)+(Si-CH_3)}{(Si-O-C)+(Si-O-Si)+(Si-CH_3)}\times 100 \quad (1)$$

The relative carbon content obtained from eq. (1) is also the lowest for the 0.3%-OTS-treated sample as shown in Figure 2(b).

Figure 3 shows the chemical shifts that depend on the peak position of the main Si-O-Si bond. The chemical shift originates from the effect of elongation or condensation of CH bonds due to the neighboring highly electronegative atom. The redshift is caused by the elongation of CH bonds by the electron-withdrawing group, but the blue shift causes the condensation of CH bonds owing to the electron-releasing group with abundant electrons.[2] The final materials

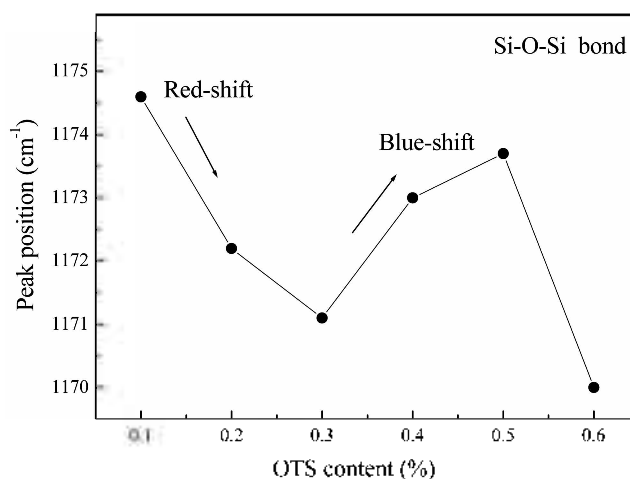

Figure 3. Chemical shift by the peak position of Si-O-Si bond.

Table 1. Relative carbon content for OTS-treated SiO_2 film with increasing OTS content

OTS-treatment content (%)		0.1	0.2	0.3	0.4	0.5	0.6
Si-O-C	area	5.7304	5.9501	5.4822	5.9258	6.175	5.5662
	content (%)	25.97	30.66	23.84	27.47	27.69	25.71
Si-O-Si	area	12.628	10.189	13.674	11.888	12.514	11.767
	peak position (cm^{-1})	1174.6	1172.2	1171.1	1173.0	1173.7	1170.0
	content (%)	57.22	52.51	59.46	55.1	56.12	54.34
$Si-CH_3$	area	3.7109	3.2664	3.8402	3.7601	3.6108	4.3209
	content (%)	16.81	16.83	16.7	17.43	16.19	19.95
Relative carbon content (%)		47.278	47.49	40.55	44.9	43.88	45.66

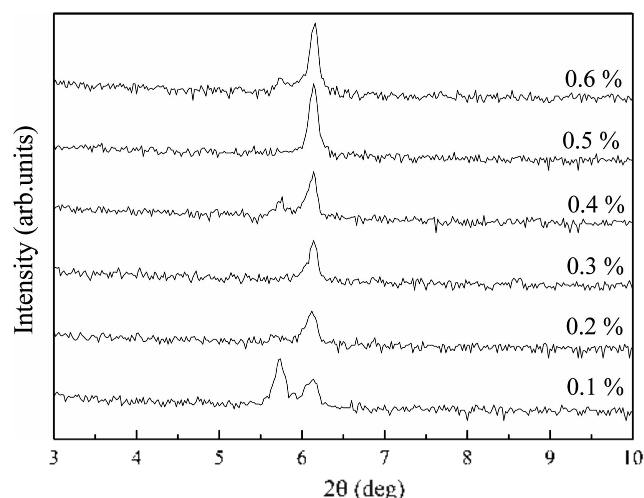

Figure 4. XRD patterns of samples with the increase of OTS-treated content.

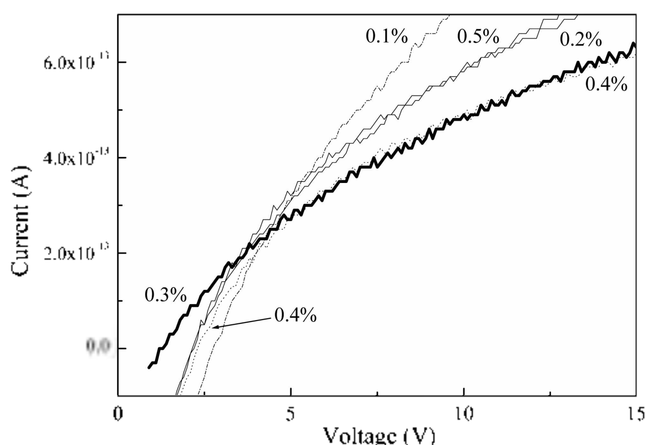

Figure 5. Surface leakage current of samples with the increase of OTS-treated content.

have a difference in surface energy depending on the chemical shift. The surface energy is related to the flatness of the film, and the surface energy decreases due to the effect of CH bond elongation. Consequently, a sample exhibiting redshift with low surface energy has good flatness, which is an important factor in thin films. The electrophysical properties of the redshift and the blueshift are also completely different as previous mentioned. From these results, it is confirmed that the 0.1-0.3%-OTS-treated samples showed red shift and the 0.3%-OTS-treated sample had the greatest redshift. The sample with increasing OTS-treatment content governed the blueshift.

Figure 4 shows the XRD patterns of the samples with increasing OTS-treatment content. The (001) peak near 6° is related to the Si atom, and that of the 0.3%-OTS-treated sample is narrow and low. However, other samples show high-intensity peaks or two peaks, which mean the high crystallization or mixed bonding structure.

Figure 5 shows the surface leakage current of samples with the increase of OTS treated content. The 0.3%-OTS-treated sample has lower leakage current than that of any other samples. The voltage shift at zero current is also lower that any other samples. The above findings lead to conclude that the 0.3%-OTS-treated sample has an amorphous structure, which is required as the low-k materials. The low-k materials such as SiOC film have an amorphous structure and decrease the dielectric constant due to the low polarization.[11]

In conclusion, OTS-treated SiO_2 film was similar to hybrid type SiOC film, which consists of Si, O and C atoms. The Fourier transform infrared spectra of the range from 1110 to 1280 cm^{-1} in the OTS-treated SiO_2 film consisted of Si-O-C, Si-O-Si, and Si-CH_3 bonds. The OTS-treated SiO_2 film was involved in the chemical shifts of blue and red shifts, which was defined from the peak position of Si-O-Si bond. The sample of the dominant redshift showed the least amount of carbon content, which means the turn point of the variation of bonding structures.

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