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Effect of the perfluoroalkyl groups on the preparation of carbon-based transparent and conductive thin films from silylated graphite oxides

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ABSTRACT

Carbon-based transparent thin films were prepared from the pyrolysis of silylated graphite oxide containing perfluoroalkyl groups. The saturated amount of *n*-hexadecylamine molecules which accommodated between the layers of silylated graphite oxide containing larger pefluoroalkyl groups was smaller than that observed for silylated graphite oxide without perfluoroalkyl groups. The resulting intercalation compounds were dispersed in a chloroform/cyclohexane solution and precursor thin films were obtained by a cast method. The sheet resistance of the obtained carbon-based films was about 5 times smaller than that of the films prepared from silylated graphite oxide prepared with the analogous hydrocarbon substituents. The spectroscopic measurements indicated that the number of defects within the carbon layers was larger, however, that of carbon atoms participating π-conjugating system was larger. This probably ascribed to the active fluorine species formed as the result of thermal decomposition of perfluoroalkyl groups. The latter was responsible for the lower sheet resistance of carbon-based thin films.

1. Introduction

Recently, graphite oxide (GO) is attracting much attention for the precursor of carbon-based transparent and conducting thin films from. Graphite oxide can be easily exfoliated to individual layers in an aqueous solution and restacking of them provides thin films. Chemical or thermal reduction of the resulting thin films can provide transparent and conducting thin films and many reports on it have been provided together with those on the electrical properties of reduced graphite oxide thin films [1–12]. In our previous paper, we have shown that carbon-based thin films, which adhere well to the glass substrates were obtained. This was probably because the residual silica originated from the silyalting reagents attached to the layers of graphite oxide worked as a "glue". We have also shown that carbon films with lower sheet resistance were obtained if we use appropriate starting materials [13]. However, the sheet resistance of the carbon films was not satisfactorily low, probably because the complete reduction of graphite oxide is difficult even at high temperatures [12].

On the other hand, recently, CF_3– or –CF_2– groups have been used as fluorine sources for the fluorination of inorganic substances. In case of sol–gel method, pyrolysis of the metal trifluoroacetic acid can give corresponding metal fluorides [14,15]. Perovskite-related metal oxides such as $SrTiO_4$, Ca_2CuO_3, $SrFeO_{3-\delta}$ and $RLaNb_2O_7$ were partially fluorinated by heating them with polytetrafluoroethylene or polyvinylidene fluoride [16–18]. These studies indicate that some active fluorine containing species are generated during the heating of the precursor materials. Therefore, if we introduce perfluoroalkyl groups into the silylated graphite oxide, it is expected that active fluorine species are also formed during heating and they modify the properties of the resulting carbon-based thin films. It is also expected that the introduction of larger perfluoroalkyl groups with lower surface energy can change the intercalation behaviour of alkylamines and exfoliation behaviour of the resulting materials Therefore, in this study, the effect of the perfluoroalkyl groups on the preparation of carbon-based transparent and conductive thin films from silylated graphite oxides was investigated.

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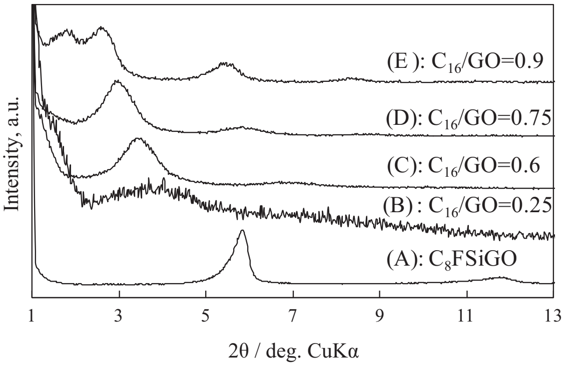

Fig. 1. X-ray diffraction patterns of (A): pristine C_8FSiGO and *n*-hexadecylamine-intercalated C_8FSiGO samples with various *n*-hexadecylamine/GO ratios of (B): 0.25, (C): 0.6, (D): 0.75 and (E): 0.9.

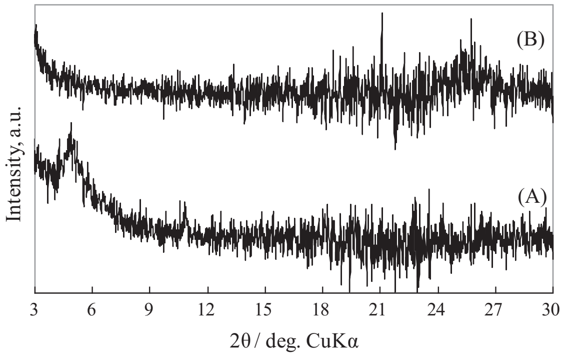

Fig. 3. X-ray diffraction patterns of the C_8FSiGO thin films (A): before and (B): after heated under vacuum at 500 °C.

2. Results and discussion

2.1. Intercalation of n-hexadecylamine into silylated GO

Fig. 1 shows the X-ray diffraction patterns of C_{16}–C_8FSiGO samples with various C_{16}/GO ratios. As the increase of the amount of added C_{16} molecules, the diffraction peak at $2\theta = 5.88^\circ$ ($d = 1.50$ nm) observed for C_8FSiGO shifted to lower angles and reached 3.08° ($d = 2.86$ nm). When the C_{16}/GO ratio was 0.75, a peak at $2\theta = 1.82^\circ$ due to C_{16} crystal deposited on the surface of the sample was observed. This means that the interlayer spacing of the C_8FSiGO was saturated by C_{16} molecules. This value was much lower than that observed for C_8SiGO samples prepared with the analogous hydrocarbon substituents. Considering the larger volume of CF_3– and –CF_2– groups (21.3×10^{-2} nm^3 and 15.3×10^{-2} nm^3) than those of CH_3– and –CH_2– (1.37×10^{-2} nm^3 and 1.03×10^{-2} nm^3) [19], the diameter of the perfluoroalkyl groups is approximately 20% larger than that of alkyl groups. The alkyl and perfluoroalkyl groups are expected to be attached to the same oxygen atoms, therefore, the space available for the C_{16} molecules would be smaller in silylated GO containing peafluoroalkyl groups. This could be the reason why the amount of C_{16} molecules accommodated between the layers of C_8FSiGO. The interlayer spacing reached the value of 3.27 nm for the sample with C_{16}/GO = 0.9, though it contained excess C_{16} crystals. This value indicates that the intercalated C_{16} molecules take bilayer orientation, which lead to the stable dispersion of silylated GO in chloroform/cyclohexane solution. Fig. 2 shows the AFM image of the C_8FSiGO sample on mica substrate. Most of the particles aggregated, however, the lateral size of each C_8FSiGO particles seemed around 50–150 nm, which well corresponded with those observed for C_8SiGO in our previous study [13]. The height profile showed that the thickness of the C_8FSiGO platelets were 1.5 nm, which was similar to the interlayer spacing of C_8FSiGO. By casting the resulting dispersion, the thin film sample of C_{16}–C_8FSiGO was obtained. Then most of the C_{16} molecules were washed with ethanol and the interlayer spacing decreased to 1.73 nm, which was similar to that of the pristine C_8FSiGO.

2.2. Preparation of carbon thin films

Fig. 3 shows the X-ray diffraction patterns of the carbon thin film obtained by heating the C_8FSiGO thin film under vacuum at 500 °C. The diffraction peak at $2\theta = 5.1^\circ$ ($d = 1.73$ nm) observed for C_8FSiGO thin film shifted to 25.5° ($d = 0.35$ nm) after heating. This indicates the formation of the carbon thin film. Fig. 4 shows the absorption spectra of C_8FSiGO thin film before and after heating. The absorption peaks observed for pristine C_8FSiGO thin film at 300 nm disappeared and that at 223 nm shifted to 268 nm. This peak position was slightly longer wavelength than that observed for C_8SiGO sample. This peak is ascribed to the π–π^* transition and it seems that as the number of carbon atoms participating in the π-conjugate system, in other word, the sp^2 carbon fraction increases it shifts to longer wavelength.

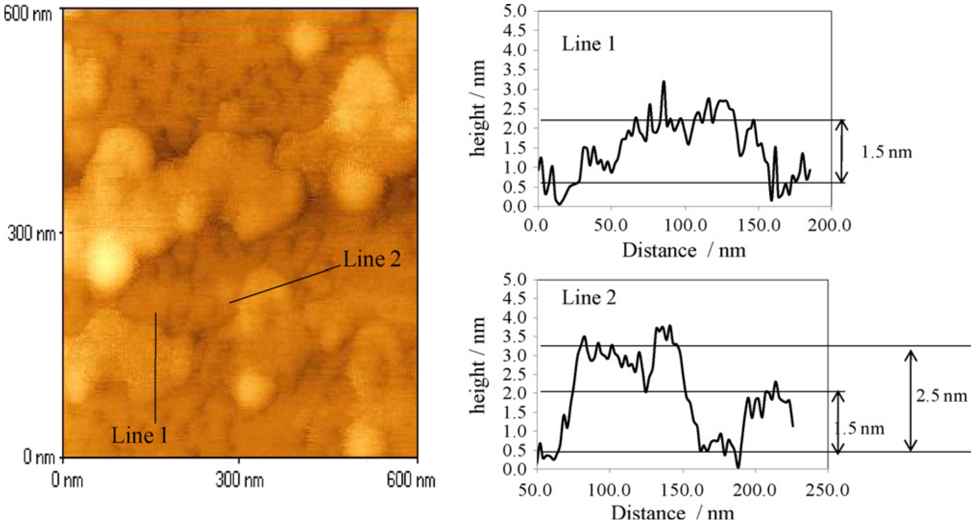

Fig. 2. AFM image and height profiles of C_8FSiGO nanosheets deposited on mica substrate.

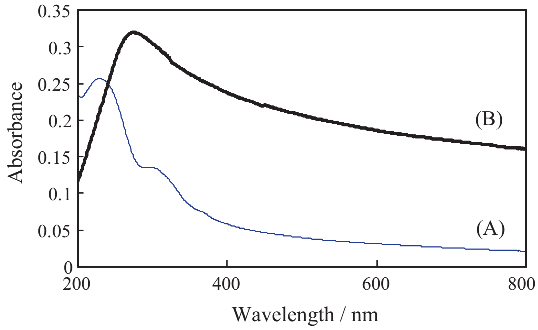

Fig. 4. UV–vis spectra of C_8FSiGO film (A): before and (B): after heated under vacuum at 500 °C.

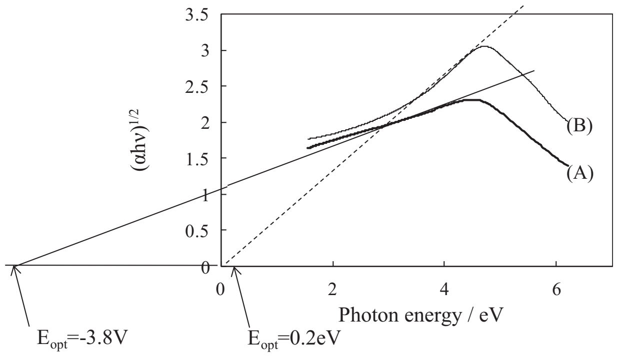

Fig. 6. Tauc's plots of carbon films prepared from C_8FSiGO and C_8SiGO.

2.3. Properties of carbon-based thin films

Fig. 5 shows the relationship between the resistivity of the film prepared from C_8FSiGO and the transparency of it. As was observed for the film prepared from C_8SiGO prepared with the analogous hydrocarbon substituents, it decreased with the decrease in the transmittance of the films and became almost constant values for the thicker films. The sheet resistance of the films prepared form C_8FSiGO was about 5 times lower than those from C_8SiGO and rather similar to those obtained from C_8SiGO at higher temperatures.

Fig. 6 show the Tauc's plot of the carbon film prepared from C_8FSiGO, together with that of the sample from C_8SiGO [20]. While the intercept was 0.2 eV corresponding to the optical band gap for the latter, that of the former was a large negative value of −3.8 e V. As indicated previously, the negative optical band gap is physically meaningless, however, it suggests that a lot of defects are introduced on the carbon layers [21,22].

Fig. 7 shows the XPS spectra of carbon films prepared from C_8FSiGO and C_8SiGO. In C_{1s} region, a large peak at 284.55 eV was observed. When compared with that observed for the carbon obtained from C_8SiGO prepared with the analogous hydrocarbon substituents, the peak position was almost identical, however, the peak was somewhat broader probably because of the higher concentration of defects as suggested by the optical band gap. The percentage of sp^2 carbons estimated from the area of C_{1s} peaks around 284.5 and 286.0 eV was 82 and 83% for carbon from C_8FSiGO and C_8SiGO, respectively. These values were slightly higher than those observed for carbon films from graphite oxide at similar temperatures [12]. The spectra in O_{1s} region were normalized by the area of the peaks in C_{1s} region. The intensity of the peak observed at 532.55 eV for the carbon obtained from C_8FSiGO was considerably lower and the peak at lower binding energy around 530.5 eV was not observed. The normalized peak intensity in the Si_{2p} region was also lower, though the peak position (around 102.9 eV) and the shape for both samples were almost identical. These indicate that the elimination of silicon containing species was enhanced in the film from C_8FSiGO. In F_{1s} region, a very small peak at 687 eV due to "semi-covalent" C–F bonding was observed for carbon film from C_8FSiGO, suggesting a small amount of fluorine atoms was attached to the carbon layers.

The above results strongly indicated that during the heat treatment of C_8FSiGO samples, some active fluorine species are generated as the result of the decomposition of perfluoroalkyl groups. It seems that they accelerate the reduction of graphite oxide to carbon, removing the oxygen or silicon containing species and leads to the increase of carbon atoms participating the π-conjugate system. They also bring about the defects on the carbon layers and some of them are introduced on the carbon layers forming relatively strong C–F bondings. The decrease of sheet resistance could be ascribed to the increased number of carbon atoms participating the π-conjugate system.

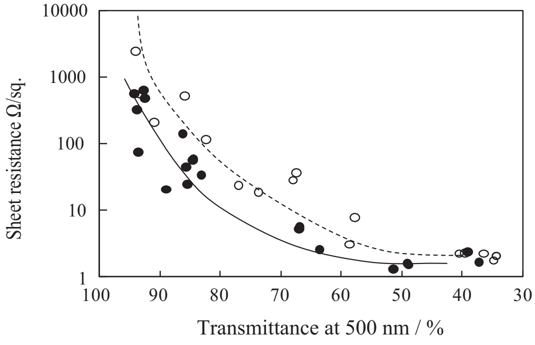

Fig. 5. Variation of the sheet resistance of carbon films prepared from ○: C_8SiGO and ●: C_8FSiGO as a function of their transmittance.

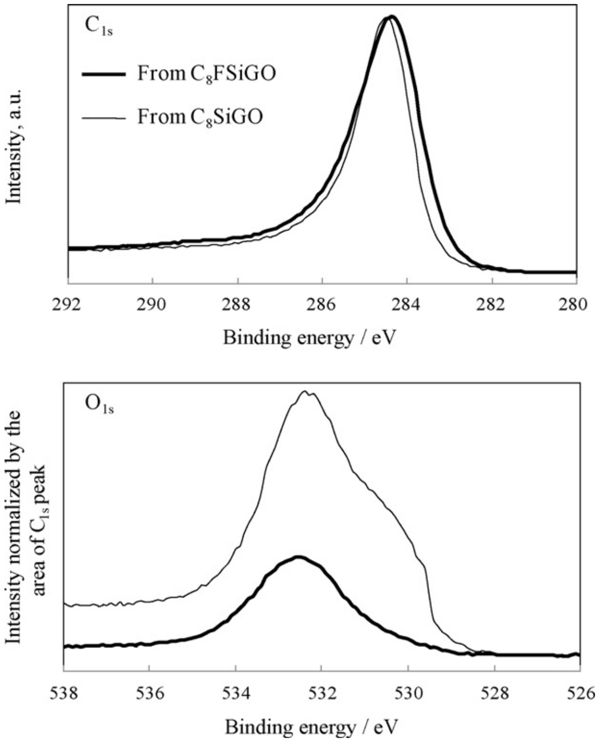

Fig. 7. XPS spectra of carbon films prepared from C_8FSiGO and C_8SiGO in C_{1s} and O_{1s} regions.

3. Conclusions

Carbon thin films with relatively lower sheet resistance were prepared from silylated graphite oxide containing perfluoroalkyl groups. The interlayer space of silylated graphite oxide containing perfluoroalkyl groups was saturated by a smaller amount of *n*-hexadecylamine than that observed for silylated graphite oxide without them. This was because of the larger volume of perfluoroalkyl groups introduced between the layers of graphite oxide. The absorption maximum and optical band gap observed for the carbon thin films obtained from silylated graphite oxide containing perfluoroalkyl groups indicated that they possess more defects, however, the number of carbon atoms participating π-conjugating system was larger. XPS data indicated that fluorine atoms were introduced in the carbon thin films. These suggest that some active fluorine species were generated during the decomposition of perfluoroalkyl groups and they bonded to carbon atoms in the graphite oxide layer and at the same time, etched and/or other elements. The larger number of carbon atoms participating π-conjugating system was responsible for the lower sheet resistance observed for carbon films obtained from the pyrolysis of silylated graphite oxide containing perfluoroalkyl groups.

4. Experimental

GO was prepared by oxidizing natural graphite powder with a particle size of 57–74 μm with $KClO_3$ in fuming nitric acid at 60 °C for 3 h, based on the Brodie's method [23]. This oxidation procedure was repeated for 5 times. The composition of the obtained GO samples determined based on the elemental analysis data of carbon and hydrogen was $C_8O_{5.3}H_{3.2}$.

GO (100 mg) was silylated with 1H,1H,2H,2H-perfluoroctyltrichlorosilane ($C_8F_{13}H_4SiCl_3$, hereafter abbreviated as C_8FSi; 2.0 ml) in the presence of *n*-butylamine ($C_4H_9NH_2$ hereafter abbreviated as C_4; 2.0 ml) under an argon atmosphere for 1 day at 60 °C [24–26]. After centrifugation, the precipitate was washed with acetone several times. The obtained samples were dried at 60 °C under reduced pressure for 12 h. The contents of silylating reagent per GO unit were 0.4, based on the Si content calculated from the weight of residual SiO_2 after thermogravimetric measurement and assuming that the sample contained 0.4 residual C_4 molecules per GO unit. In order to disperse the obtained silylated GO in organic solvents, *n*-hexadecylamine ($C_{16}H_{33}NH_2$ hereafter abbreviated as C_{16}) was intercalated into C_8FSiGO as previously reported [13,26]. Here, intercalation behaviour of C_{16} into C_8FSiGO was also investigated by changing the amount of added C_{16}. In the presence of a small amount of hexane ca 0.5 ml, C_8FSiGO and C_{16} with various weight ratios were well mixed in a pestle until hexane molecules evaporated. The sample with C_{16}/GO ratio of 1 was dispersed in a chloroform/cyclohexane solution (0.05–10 mg/ml, 1:1 by volume) and sonicated, resulting in the light to dark brown homogenous and stable dispersion. The dispersion was cast on a glass or quartz substrate (0.05 ml/cm^2) and the solvent was allowed to evaporate slowly by putting a glass vial of 110 ml on it at room temperature. The resulting thin film was immersed in ethanol for 30 min and C_{16} was removed. Then, it was pyrolyzed under vacuum for 1 h at 500 °C. The temperature increasing rate was 1 °C/min. The thickness of the films estimated from ellipsometry data linearly increased as the increase in the absorbance of them with the same slope as that reported in our previous paper [13]. For comparison, carbon film was also prepared from GO silylated by octyltrichlorosilane [13] in the same manner. The products were analyzed by X-ray diffraction (Rigaku Rint-2100), thermogravimetric measurement (TG; Shimadzu TGA-50), UV–vis (Hitachi U-2010) and X-ray photoelectron spectroscopy (XPS; Shimadzu ESCA-3400). XPS data were recorded for the sample prepared on Pt substrate. The observed binding energies were corrected based on those of $Ag_{3d}^{5/2}$ electrons from the sample holder. TG measurements were performed under air at the temperature increasing rate of 5 °C/min. Electrical conductivity was measured by the potential sweep method using a potentiostat (Hokuto Denko SV-100) at a sweep rate of 1 mV/s between −1 and 1 V. The morphology of the C_8SiGO particles was observed by atomic force microscopy (AFM, Digital Instruments Nanopics1000).

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