Synchrotron Radiation Studies of the Orientation of Thin Silicon Phthalocyanine

Dichloride Film on HOPG Substrate

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1. Introduction

Organic semiconductor thin films have attracted increasing attention due to their possible applications in optical and electronic devices [1]. Silicon phthalocyanine derivatives, together with some metal phthalocyanines, represent one of the most promising candidates for such organic thin films in organic electronics because these systems form electronic conducting molecules if the molecules are stacked face-to-face and provide a co-axially contiguous pathway for carrier delocalization [2]. This fact easily makes us infer that the ordering and orientation of such molecules in thin films are crucial for device property [3].

In the present work, therefore, we investigated the electronic structure and orientation nature of silicon phthalocyanine molecular film on highly oriented pyrolitic graphite (HOPG) substrate using Near-edge x-ray absorption fine-structure (NEXAFS) and synchrotron radiation based photoelectron spectroscopy.

2. Experimental

The experiments were performed at the end station of the beam line BL27A of the photon factory in the High Energy Accelerator Research Organization (KEK-PF), Tsukuba, Japan. The Si and Cl NEXAFS spectra were taken by the total electron yields. The thin films were prepared by dropping 1 (or 10) mM- SiPcCl₂/hexane solution on HOPG and heating them at 345 $\,^{\circ}$ C for 5 minutes.

3. Results and discussion

Figure 1 shows the Si K-edge NEXAFS spectra of the powdered $SiPcCl_2$ sample (marked a) before heating and the thin $SiPcCl_2$ sample (marked c) after heating.

It is noteworthy only for the heated samples that a new clear peak is observed at 1852.4 eV (peak B) in addition to a strong feature at 1847.2 eV (peak A), and also that the spectra noticeably depended on polarization angles.

For comparison, NEXAFS spectrum for silicon phthalocyanine hydroxide (SiPcOH) powder sample (marked b) is shown in Fig. 1. We can easily find that the SiPcOH spectrum also shows a peak at 1852.4 eV, agreeing with that of new peak B seen in the heated sample.

In addition to this fact, considering that the films were heated in air, we assume that phthalocyanine molecules were oxidized and Pc-Si-O structure was formed; that is, Si–Cl bond was replaced with Si–O. The breakage of Si–Cl bond was confirmed by XPS measurement.



Fig.1. NEXAFS spectra at the silicon K-edge taken by total electron yield. (a) thin powder SiPcCl₂ before heating. (b) thin powder SiPcOH. (c) polarization dependence for thin SiPcCl₂ on HOPG after heating. \boldsymbol{E} is the electric field vector of synchrotron beam and θ is the incident angle defined by the angle between sample surface and synchrotron beam.

Moreover, we calculated unoccupied molecular orbitals in the core excited states (Equivalent core approximation) for SiPcCl₂ and SiPc(OH)₂ molecules using the molecular orbital method. Based on the calculations, we assign peak A and peak B to in-plane and out-of-plane transitions, respectively. All these pieces of evidence agree with the fact that peak A and peak B in Fig. 1-(c) can be assigned to Si 1s $\rightarrow \sigma^*_{Si-N}$ and $1s \rightarrow \sigma^*_{Si-O}$ transitions, respectively.

For the spectrum of thin film on HOPG (Fig.1 C), two clear peaks are observed at 1847.2 eV and 1852.4 eV, respectively. With the molecular orbital theory, we obtained most stable molecular structure by optimizing potential energy and we get unoccupied molecular orbital in the excited states. From this calculation, we assigned peak A and peak B to Si $1s \rightarrow \sigma^*_{Si-N}$ and $1s \rightarrow \sigma^*_{Si-O}$, respectively. Comparing with the spectrum of Si-Pc-OH powder sample (Fig1. b), we can easily find there is a clear peak at 1852.4 eV too. This spectrum characteristic is in agreement with our conclusion.

The remarkable feature observed in the Peaks A and B is the clear polarization dependence of their intensity. The intensity of the peak A increases with the increase in the incident angles of the synchrotron beam. In contrast, the intensity of the peak B decreases with the increase in the incident angles of the synchrotron beam. The peak intensity I of the NEXAFS spectra using the synchrotron beam of electric field E is expressed as follow [4],

$$I \propto |E \cdot O|^2 \propto \cos^2 \delta \tag{1}$$

Where **O** is the direction of the final state orbital and δ is the angle between *E* and **O**. Thus, the polarization dependences in Fig.1 indicate that the final state orbital represented by the peak A is parallel to the basal plane of graphite sheet, while that represented by the peak B is perpendicular to the basal plane. Considering that the orbitals of $\sigma^*_{\text{Si-N}}$ and $\sigma^*_{\text{Si-O}}$ are distributed in-plane and out-of-plane, the observed polarization dependence indicates that molecular planes tend to be oriented and nearly parallel to the basal plane.

To certify those speculations, we estimate more quantitatively the angles of Si-N and Si-O bonds with respect to the substrate normal axis. Fig. 2 shows the $\sigma^*_{\text{Si-N}}$ and $\sigma^*_{\text{Si-O}}$ resonance intensities as a function of polarization angles, θ . Also shown are the results of curve-fit analysis using a plane-type and vector-type equations [4] written above the relevant plots. The averaged tilted angle of the molecular plane ($\sigma^*_{\text{Si-N}}$) and Si-O bond axis were found to be roughly 42 and 49° to the surface, respectively. The

consistency corroborates also the validity of our resonance assignments.

4. Conclusions

We have investigated the orientation of silicon phthalocyanine dichloride thin films on HOPG using NEXAFS and photoelectron spectroscopy. Heating process was found to cause Si-Cl cleavage and Si-O bond formation. Moreover, the quantitative analysis of the polarization dependence revealed that the Si-N bond is lying down on the surface, while the Si-O bond lies perpendicularly. We conclude that large molecules like [Pc-Si-O]_n chains are grown at high temperature and such molecular chains are oriented perpendicularly on graphite sheet.



Fig.2. Plots of intensities, $I(\theta)$ as a function of x-ray incidence (polarization) angle θ . Also shown are the best-fit curves (solid lines) and hypothetical curves calculated for the best fit angle plus 5 (chain lines) and minus 5 (dotted lines) with respect to the surface normal.

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