BL-27A/2008G712

Orientation of silicon phthalocyanine thin films revealed using polarized X-ray absorption spectroscopy

Tetsuhiro Sekiguchi*, Yuji Baba, Iwao Shimoyama, Norie Hirao, Mitsunori Honda, Juzhi Deng
Japan Atomic Energy Agency, Tokai-mura, Naka-gun, Ibaraki 319-1195 Japan

1 Introduction

High degrees of molecular orientation play an important role in the enhancement of the carrier density in organic semiconductors. One of promising methods to control the orientation can be proposed that oriented films be prepared as a result of polymerization of monomers on the atomically flat surface. In the present study, we have prepared reactant films of silicon phtalocyanine dichlorides ($SiPcCl_2$) where Pc refers to phthalocyanine ring, which is an organic semiconductor, on graphite substrates and the product films through hydrolysis and dehydration polymerization by annealing. We have investigated the atomic configuration and orientation of the films using x-ray absorption fine-structures (NEXAFS) spectroscopy and XPS.

2 Experiment

NEXAFS spectra were measured with total electron yields (TEYs), which were recorded by monitoring the sample drain current. Oriented thin films were prepared by the solution process: Saturated $SiPcCl_2$ solutions were prepared by dissolving it into n-hexane (n-C_6H_{14}) solvent; The solutions were dropped on HOPG substrates, which were followed by spinning and annealing at ca. 350 °C. It has been reported that $SiPcCl_2$ in solution turns to $[SiPcO]_n$ polymers by heating owing to hydrolysis (Si-Cl → Si-OH) and dehydration polymerization (Si-OH + HO-Si →Si-O-Si) [1].

3 Results and Discussion

Figure 1-f shows Si 1s NEXAFS spectrum for the thin films produced from $SiPcCl_2$ solution after annealing. It show two marked resonances at 1847.2 eV and ~1852.6 eV; here, the latter is not observed for the reactant $SiPcCl_2$ (Fig. 1-a)[2]. Areas of these resonances depend on incident angles of x-rays, which manifests that the silicon phthalocyanine planes are oriented. To determine the direction of molecular orientation, it is important to know what the resonances originate from. Thus, the spectrum was compared with those for several reference compounds as shown in Fig. 1-b, -c, and -d. It is worthy to note that the resonance at ~1852 eV is observed only for two substances in which the centered metal Si is bonded to oxygen of hydroxy group (Fig.1-c and 1-d). Therefore, the higher energy peak can most probably be assigned to σ*(Si–O) resonance. The lower energy peak at 1847.2 eV of Fig.1-f was assigned to σ*(Si–N) resonance, which is in consistent with the fact that reference compounds all having Si–N bond in Pc ring all represent the lower energy peak as well.

To confirm the mentioned assignments, molecular orbital calculations under Z+1 approximation were performed for $SiPc(OH)_2$ structure (Fig. 1-e). The results reveal that the lower energy feature originates from σ*(Si–N) and the higher one from σ*(Si–O). Moreover, it was found that transition moments for σ*(Si–N) and σ*(Si–O) align horizontal and perpendicular to Pc plane, respectively.

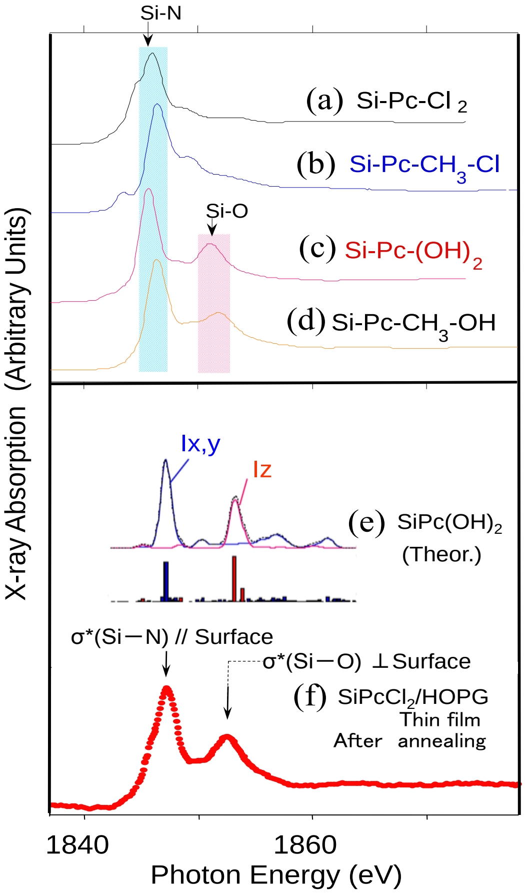

Fig. 1: (a-d) Si 1s NEXAFS for powdered reference compounds. (e)Simulated Si 1s spectra for $SiPc(OH)_2$ structure, which was calculated by the HF method under Z+1 approximation. Blue and red bars denote probabilities of electronic transitions horizontal and perpendicular to Pc plane, respectively. $I_{x,\ y}$ and I_z show their convoluted curves with 1eV width. (f) Si 1s NEXAFS for the thin film prepared from $SiPcCl_2$ solution followed by annealing at ca. 350 °C.

In summary, the two resonances for reaction products were consistently assigned. With the help of the assignment, it was concluded that SiPcO chain is oriented with Si–O axis perpendicular to the graphite surface.

References

[1] C.W. Dirk *et al.*, *J.Am.Chem.Soc* **105**, 1539 (1983).
[2] T. Sekiguchi *et al.*, *Surf. Interface Anal.* **42**, 863 (2010).

* sekiguchi.tetsuhiro@jaea.go.jp