

## Effect of substrates on the molecular orientation of silicon phthalocyanine dichloride thin films

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### Introduction

Organic semiconductor thin films have been receiving an increasing amount of attention in recent years. Silicon phthalocyanine (SiPc) derivatives, together with some metal phthalocyanines, form electric conducting molecules if the molecules are stacked face-to-face and provide co-axially contiguous pathway for carrier delocalisation. In the present work, we investigated the molecular ordering and orientation of thin films of silicon phthalocyanine dichloride (SiPcCl<sub>2</sub>) deposited on different substrates.

### Experimental

The experiments were performed at the BL-27A station. X-rays from bending magnet were linearly polarized at the horizontal direction. The chemical structure of SiPcCl<sub>2</sub> is shown in figure 1. Three different substrates were used, i.e., highly oriented pyrolytic graphite (HOPG), polycrystalline gold, and indium tin oxide (ITO). The SiPcCl<sub>2</sub> films were deposited on the substrates using Knudsen-cell evaporator. The thickness of the film was 5 molecular layers. Near-edge absorption fine structure (NEXAFS) spectra were taken by total electron yield. For the measurements of the polarization dependences, the sample was rotated around the vertical axis. The surface morphologies of the substrates were observed by atomic force microscopy (AFM).

### Results and discussion

The silicon *K*-edge NEXAFS spectra for SiPcCl<sub>2</sub> films deposited on HOPG at three different incident angles are shown in fig.2. The peaks A and B are attributed to the resonance excitations from the Si 1s to the unoccupied  $\sigma^*$  orbitals localized at the Si-Cl bonds (peak A) and the Si-N bonds (peak B), respectively [1]. The two peaks exhibit an opposite angular dependencies.

Peak intensity  $I$  of the NEXAFS spectra using the synchrotron beam of electric field  $E$  is expressed as,

$$I \propto |E \cdot O|^2 \propto \cos^2 \delta \quad (1)$$

where  $O$  is the direction of the final state orbit and  $\delta$  is the angle between  $E$  and  $O$ . Considering that the orbitals of  $\sigma^*_{\text{Si-N}}$  and  $\sigma^*_{\text{Si-Cl}}$  are distributed in-plane and out-of-plane, respectively, the observed polarization dependence indicates that the molecular planes are parallel to the surface. Quantitative analyses (shown in right part of fig.2) have revealed that the average tilted angle is 2°. This result is deduced from the fact that HOPG has

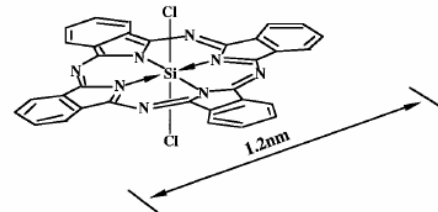


Fig.1 Molecular structure of SiPcCl<sub>2</sub>

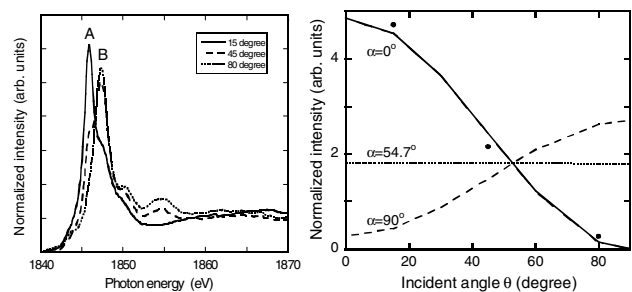


Fig.2 Left: Polarization dependence of NEXAFS spectra for SiPcCl<sub>2</sub> molecules deposited on HOPG substrate. Right: Intensity  $I(\theta)$  of the  $\sigma^*_{\text{Si-Cl}}$  resonance peak in the NEXAFS spectra as a function of the x-ray incidence (polarization) angle  $\theta$ . Best-fit curve is shown as solid line. Also shown are theoretical curves calculated with three different tilted angles, i.e., 0° (chain lines), 54.7° (dotted lines) and 90° (broken lines).

perfect flat surface and its lattice constant of the top surface is 0.25 nm, which is fairly smaller than the molecular size of SiPcCl<sub>2</sub>. On the other hand, it was also found that the average tilted angles of SiPcCl<sub>2</sub> on gold and ITO are 20° and 26°, respectively. The AFM observations on ITO surface revealed that the vertical undulation of the ITO surface is in the order of 10 nm, which is larger than the molecular size of SiPcCl<sub>2</sub>. This means that the SiPcCl<sub>2</sub> molecules lie down along the morphology of the top surface layer of the substrate, and the orientation of the first layer determines that of the multi-layer.

### Reference

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