

Observation on morphology, electronic structure, and molecular orientation at nanometer scale for phthalocyanine thin films by SR-excited PEEM

Yuji BABA¹, Tetsuhiro SEKIGUCHI¹, Iwao SHIMOYAMA¹, Mitsunori HONDA¹, Norie HIRAO¹, Ayumi NARITA¹ and Juzhi DENG^{1,2}

¹Japan Atomic Energy Agency, Tokai-mura, Naka-gun, Ibaraki-ken 319-1195, Japan

²East China University of Technology, Fuzhou, Jiangxi Province 344000, P.R. China

Introduction

Growth of organic thin films on solid surfaces has attracted significant attention in recent years, on the basis of various potential applications as electronic and optical devices. Thin films of metal phthalocyanine, one of the macrocyclic planar aromatic molecules, have been extensively studied due to their unique semiconducting property and thermal stability. Since the electric and optical properties of thin films fairly depend on the ordering of the layer, it is important to elucidate the molecular orientation as well as morphology and electronic structure at nanometer scale. Here, we present results for the observation on molecular orientations for a micro-pattern of silicon phthalocyanine dichloride (SiPcCl₂) films by photoelectron emission microscopy (PEEM) illuminated by linearly polarized soft X-rays. Changes of molecular orientations upon heating were also observed by the XANES spectrum at each domain in the PEEM image.

Experimental

The experiments were performed at the BL-27A station. SiPcCl₂ molecules were deposited on a clean gold surface using Knudsen-cell evaporator. The micro-pattern was made as follows. First, a mask of 12.5 μm periodicity was put on a gold surface. Then SiPcCl₂ molecules were deposited, and the mask was removed after the deposition.

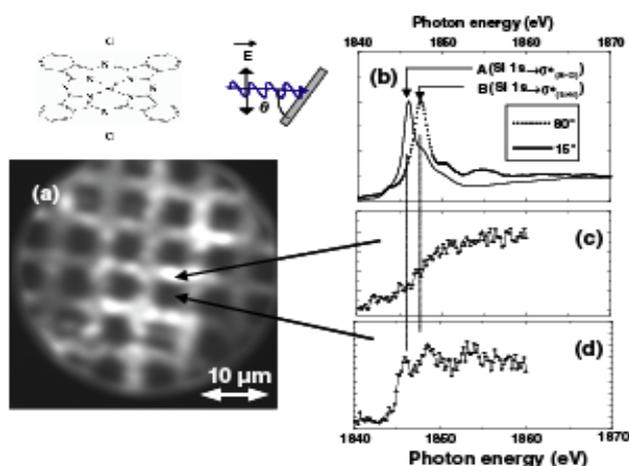


Fig.1 (a) PEEM image excited by 1847 eV photons for SiPcCl₂ micropattern. (b) Incident angle dependence of the XANES spectra for the 5-layered SiPcCl₂ thin film. Photon-energy dependences of the brightnesses of the bright and dark regions in the PEEM image are shown in (c) and (d), respectively.

The incident angle of the X-rays for PEEM measurements was fixed at 30° from the surface. The total photoelectrons emitted from the microscopic area were observed by PEEM (Elmitech. Co. PEEMSPECTOR). The lateral spacial resolution of the PEEM images was about 40 nm. The sample surface was heated by YAG laser from the outside of the vacuum chamber through an optical fiber.

Results and discussion

Fig.1(b) shows the Si K-edge XANES spectra for the SiPcCl₂ film in an average wide area at two different incident angles [1]. The peaks A and B are attributed to the resonance excitations from the Si 1s to the unoccupied σ^* orbitals localized at the Si-Cl bonds (peak A) and the Si-N bonds (peak B), respectively. 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. Fig.1(a) shows the PEEM image excited by 1847 eV photons for SiPcCl₂ micropattern. The dark regions represent deposited layer, and the bright ones originate from bare gold. The photon-energy dependences of the brightnesses of the bright and dark regions in the PEEM image are shown in figs.1 (c) and (d), respectively. The curve shown in (d) represents the XANES spectrum at 30° incidence angle for flat-lying layer. Fig. 2 shows the changes in the PEEM images upon heating. Similarly to the figs.1 (c) and (d), we have plotted the brightnesses of various regions in the PEEM images in order to elucidate the orientation of the SiPcCl₂ molecules. As a result, it was found the the deposited SiPcCl₂ molecules still lies down even after annealed at 240°C. On the other hand, SiPcCl₂ molecules diffused to bare gold surface rather stand up.



Fig. 2 Changes in PEEM images upon annealing.

Reference

[1] J. Deng, Y. Baba, T. Sekiguchi, N. Hirao, M. Honda, J. Phys. Condens. Matt. **19**, 196205-1 (2007).