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Real-time observations on surface diffusion of phthalocyanine thin films by photoelectron emission microscopy

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Introduction

Organic thin films have recently attracted much attention as new functional devices replacing silicon-based materials. One of the essential problems in organic thin films is fast surface diffusion in comparison with inorganic films, because organic molecules are stacked on solid surface mainly through van-der-Waals forces. Thus, the real-time observation on surface diffusion at nanometer scale is indispensable to explore new functional organic devices. However, microscopic methods using focused electron beams cannot be applied to the observation on organic systems due to high radiation damage by electron irradiation. Here we present the results for the real-time observations on surface diffusion of phthalocyanine molecules deposited on gold surface by means of photoelectron emission microscopy (PEEM) excited by soft X-rays.

Experimental

The experiments were performed at the BL-27A station. The micro-patterned mask of 12.5 μm periodicity was put on gold surface. Silicon phthalocyanine dichloride (SiPcCl$_2$) molecules were deposited on the gold using Knudsen-cell evaporator. In the separate experiments, it was elucidated that the SiPcCl$_2$ molecules nearly lie down on gold surface [1]. After the deposition, the mask was removed. Sample surface was illuminated by synchrotron soft X-rays around the Si *K*-edge. The total photoelectrons emitted from the microscopic area were observed by PEEM (Elmitech. Co. PEEMSPECTOR). A mercury lamp ($h\nu$=4.9) was also used as an UV excitation source. The lateral spacial resolution of the PEEM was about 40 nm. The sample surface was heated by YAG laser from the outside of the vacuum chamber through optical fiber.

Results and discussion

Figure 1 shows the PEEM images of micro-patterned SiPcCl$_2$ films deposited on gold surface. At room temperature, periodic bright-and-dark patterns are clearly seen by X-ray (a) and UV (c) excitations. For Si *K*-edge excitation, it is assumed that the dark areas correspond to the regions where SiPcCl$_2$ molecules are deposited, while bright areas are attributed to the gold surface. In order to confirm this assignment, the brightnesses of the dark and bright areas are plotted as a function of the photon energy. The results are displayed in fig. 2(b). In comparison with the X-ray absorption spectrum measured by total electron yield (shown in fig.2 (a)), it is certified that the dark areas are composed of the deposited SiPcCl$_2$ molecules. When we annealed the sample, the lateral diffusion of the deposited layer is observed (fig.1 (c)-(h)). Surface diffusion begins at 240ºC, and the micro-patterns observed by UV excitation are almost disappeared at 380ºC. From these images, we succeeded in observing in-situ the surface diffusion monitoring the chemical states at each domain in the image.

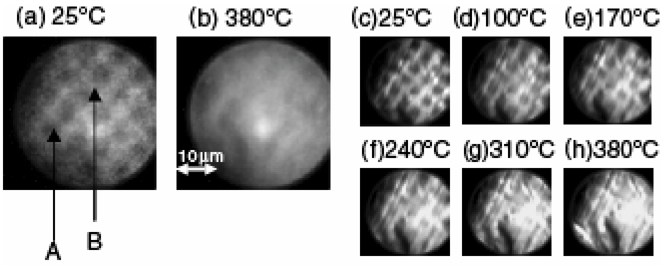

Fig.1 PEEM images of SiPcCl$_2$ micro-pattern deposited on gold surface. Field of view is 50 μm. Images (a) and (b) were taken by 1847 eV photons corresponding to the resonance excitation from Si 1s to σ*. Images (c) -(h) were taken by mercury lamp ($h\nu$=4.9 eV). The annealing temperature is indicated in the upper side of each image.

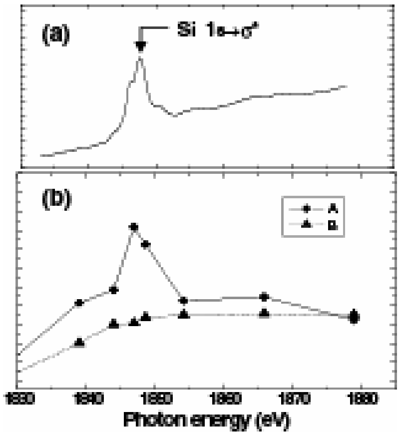

Fig.2 (a) X-ray absorption spectrum of SiPcCl$_2$ deposited on gold. (b) Brightness of the spots A and B in fig.1(a) as a function of the photon energy.

Reference

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