

Paper

Surface Micro-XAFS and Its Application to Real-time Observation of Organic Thin Films

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X-ray absorption fine structure (XAFS) is a powerful tool to investigate electronic structures, valence states and molecular orientations at solid surfaces. In order to observe nano-scaled dynamic phenomena at solid surfaces, we have developed a micro-XAFS system using a photoelectron emission microscopy (PEEM) excited by synchrotron radiation in soft X-ray region. Here we explain the performance of our system concentrating on the recent development of quick measurements, and demonstrated that a PEEM image can be taken in a short time down to 10 msec. As an application of the system, we present the results for the real-time mapping of molecular orientations at nanometer scale for organic thin films. We demonstrated that the orientations of organic molecules in a microscopic region change during surface diffusion.

1. Introduction

Various types of scanning microscopies using focused electron, ion and photon beams have been recently developed [1]. Among them, a photoelectron emission microscopy (PEEM) has excellent characteristics because the microscopic images depending on chemical states can be observed at nanometer spatial resolution [2,3]. However, the measuring time with scanning-type PEEM using micro-focused photon beam has limitations, because the photon beam must be scanned in the region where the image is taken. For the observation of organic and biological samples, another problem is the degradation of the sample due to the irradiation of highly intense photon beams.

In order to observe images for organic and biological samples, a quick measurement without radiation damage is indispensable. For this purpose, another type of a PEEM, so-called imaging-type, is suitable [4-7]. In this type, the photon beam is irradiated on the surface, and total photoelectrons emitted from the microscopic area are expanded by electrostatic lenses. When energy-tunable synchrotron radiation is used as an excitation source in imaging-type PEEM, we can measure the X-ray absorption fine structures (XAFSs) at microscopic regions in a short time [8,9]. Here this technique is called as

“micro-XAFS”. In the previous paper, we have reported our micro-XAFS system using soft X-rays from synchrotron light source [10-13]. The advantage in our system is that the soft X-ray around a few keV is used as an excitation source. Photons in soft X-ray region is fairly effective to excite third row elements like silicon due to the high edge jumps at the *K*-edges, so we can observe clear PEEM images and XAFS spectra [13]. With this method, we have reported the results for the observations of valence-state mapping for silicon compounds [10,11,13] and molecular orientation mapping for organic silicon thin films [12] at nanometer scale.

In the present paper, we show the results for real-time observations of organic thin films, focusing on the nano-scaled mapping of electronic structures and molecular orientations.

2. Experimental

The experiments were performed at the BL-27A station of the Photon Factory, KEK. The PEEM used was Elmitec Co. Model PEEMSPECTOR. The total photoelectrons emitted from the surface were expanded and focused on the YAG screen. The image on the screen was taken in a CCD camera. The time resolution of the PEEM, regulated by that of the CCD camera, was 10 msec. The PEEM was

horizontally located and the incidence angle of the X-rays was 30 degree from the surface. The take-off direction of photoelectrons was surface normal. For annealing experiments, the sample surface was heated by YAG laser through optical fiber. The irradiation of YAG laser does not induce the emission of photoelectrons, so we can observe PEEM images during heating. In order to focus the X-ray beam on the spot where the PEEM image is taken, half poly-capillary lens [14] was equipped in front of the sample. The details of this system are described in reference 15.

For the demonstration of the measuring time of PEEM, we used patterned sample made of gold and silicon. The periodicity of silicon and gold patterns was 25 μm (16 μm Si, 9 μm Au). For organic samples, silicon phthalocyanine dichloride (SiPcCl_2) and poly-dimethylsilane (PDMS) were deposited on metal surfaces as micro-patterns using a mask. The periodicity of the patterns was 12.5 μm .

3. Results and discussion

Fig. 1 shows the PEEM images for the Au-Si micro-pattern. The image (a) was taken by mercury lamp ($h\nu=4.9$ eV), so the brightness of this image represents the work function of each spot. The images (b)-(e) were taken by 3000 eV photons. It is noted that the brightness of each domain in the PEEM image is proportional to the amount of X-ray absorption in the position, because the intensity of the total photoelectrons is approximately proportional to the X-ray absorption in the surface layer. Thus the bright and dark areas correspond to gold and silicon,

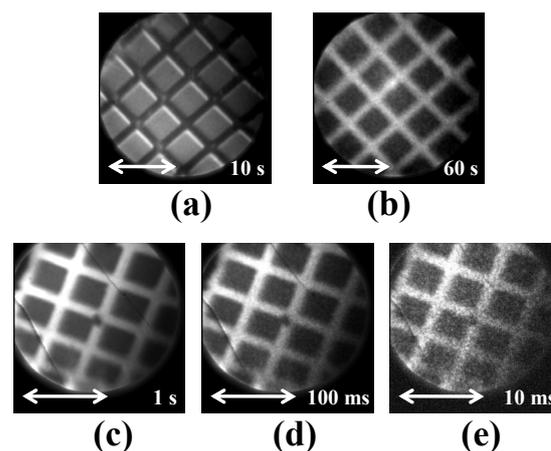


Fig. 1. PEEM images for the micro-patterned sample made of gold and silicon. The periodicity of the mesh pattern is 25 μm (16 μm Si, 9 μm Au). The scale bar shown in each image as an arrow is 50 μm . The image (a) was taken by mercury lamp ($h\nu=4.9$ eV). The images (b)-(e) were taken by synchrotron radiation at 3000 eV. The bright and dark areas of the images (b)-(e) correspond to gold and silicon, respectively. The image (b) was taken without poly-capillary lens, and the images (c), (d) and (e) were taken by collimated beam using poly-capillary lens. The measuring time is shown in each image.

respectively. The image (e) was taken for 10 ms with poly-capillary lens. Although noises increase in image (e) compared with those measured for longer time, a clear micro-pattern is still observed. When the photon energy is scanned around the absorption edges and brightness is plotted, we can obtain micro-XAFS spectra in all domains. For this sample, about half minute is enough to obtain the micro-XAFS. The thicknesses of the gold and silicon layers are fairly larger than the escape depth of

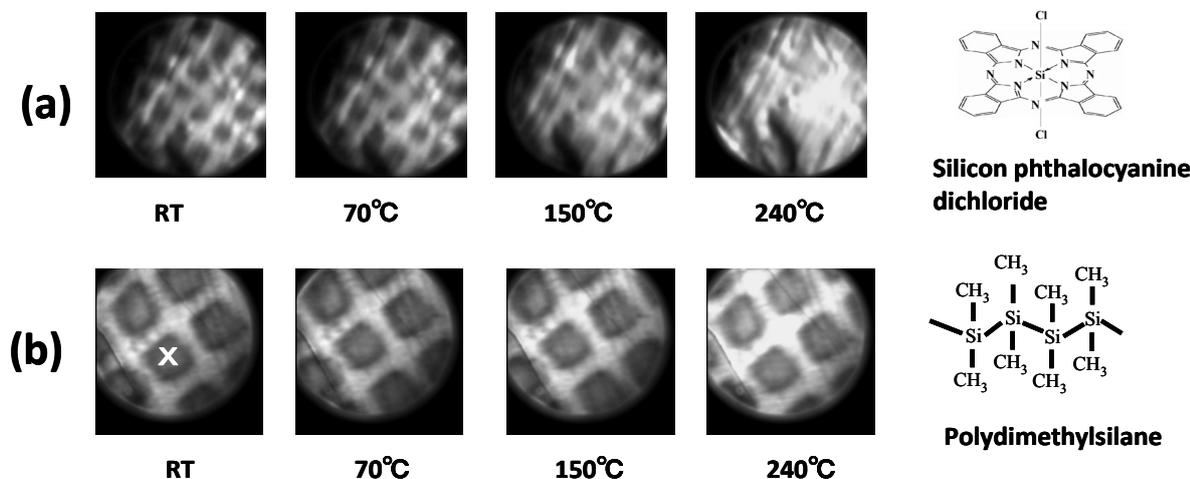


Fig. 2. PEEM images for micro-patterned organic thin films at various temperatures. The measuring time of the images was 1 sec. The field of view is 100 μm . The samples are thin films of (a) silicon phthalocyanine dichloride [12], and (b) polydimethylsilane. The samples were heated at 20°C/min by YAG laser, and the images were observed at real time.

photoelectrons, so the sample is considered to be bulk material. So it is concluded that the minimum measuring time for bulk sample is 10 ms for taking a PEEM image, and about half minute for taking micro-XAFS spectra.

Next, we applied the method to the observations of organic thin films. With the recent rapid development of organic devices such as organic LEDs, FETs and solar cells, it has become quite important to observe nano-scaled images for organic thin films. Many kinds of microscopies provide useful information such as surface morphology and elemental mapping at nanometer scale [1]. However as described in the introduction part, the organic samples are easily damaged by the irradiation of intense micro-focused beams. In the present system, we succeeded in observing nano-scaled images for organic thin films at real time.

The examples are shown in Fig. 2. The measuring time of the images was 1 sec, which was reduced to a one-100th for those taken without poly-capillary lens. For silicon phthalocyanine film shown in (a), the molecules diffuse at high temperature, and the surface become almost homogeneous at 240 °C [12]. This phenomenon is simply understood by the fact that the molecules in the film are bound through weak van-der-Waals force. On the other

hand, the polymers (PDMS) scarcely diffuse, and the patterns are still clearly observed at 240 °C as shown in (b).

The brightness of each spot in the PEEM image is proportional to the amount of X-ray absorption in the spot. So if we scan the X-ray energy, the XAFS spectra in all domains can be obtained. As an example, the brightness of the spot marked "X" in Fig. 2 (b) is plotted as a function of X-ray energy, which is displayed in (a) and (b) of Fig.3. The total measuring time for each plot was in the order of a few minutes, so we did not observe any damages of the molecules due to the X-ray irradiation. Recently, our group found that the PDMS molecules stand up or lie flat depending on the substrate [16]. Solid lines in (c) and (d) of Fig. 3 show the XAFS spectra taken with total electron yield for standing-up and flat-lying PDMS films, respectively, at 30 degree incidence [16]. The brightness plot for room temperature sample (Fig. 3 (a)) is similar to the XAFS spectrum for the standing-up layer (Fig. 3 (c)). On the other hand, the shape of the plot for 240 °C drastically changes, and it becomes rather similar to the XAFS spectrum for flat-lying layer (Fig. 3 (d)). The results suggest that the backbone of the polymer changes from perpendicular to parallel orientations without diffusion. The

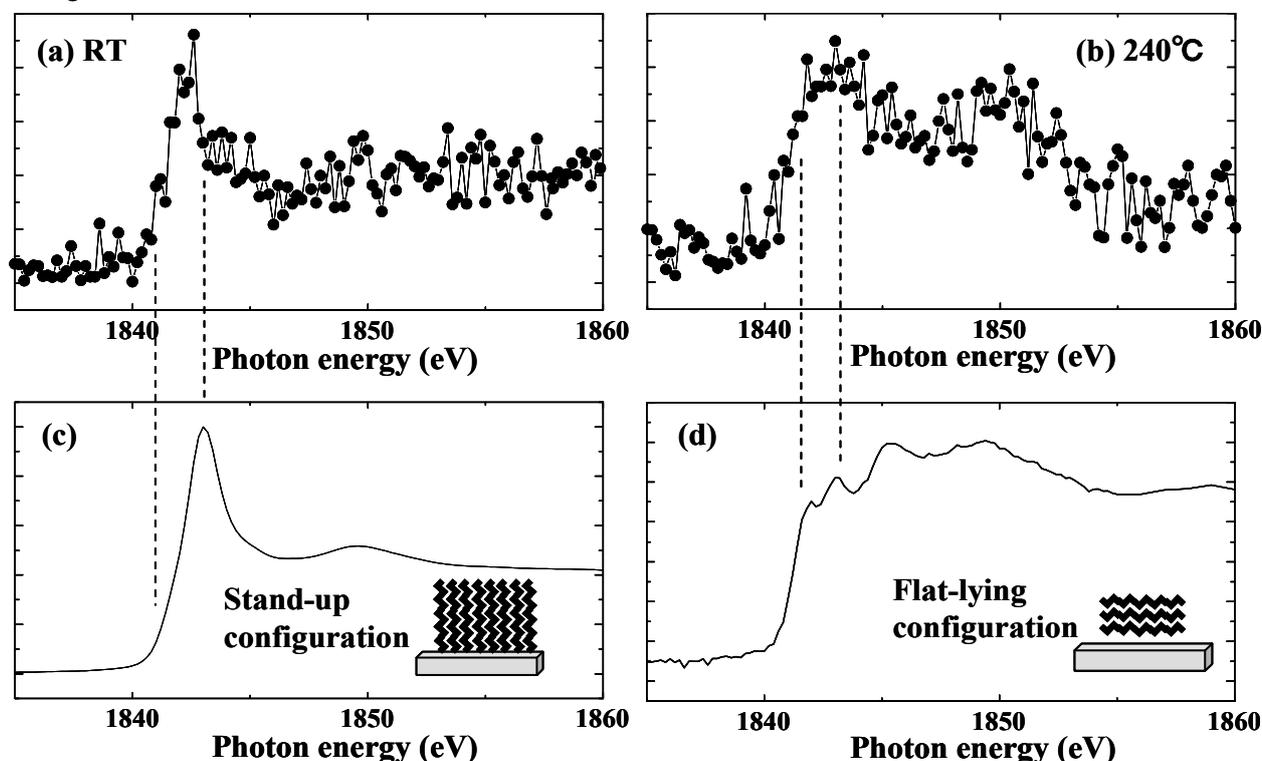


Fig. 3. (a) Brightness of the spot "X" in the PEEM image of Fig. 2 (b) for polydimethylsilane thin film as a function of X-ray energy at room temperature. (b) Same as (a) but at 240 °C. The XAFS spectra at 30 degree incidence for stand-up and flat-lying layers are shown in (c) and (d), respectively.

results are fairly different from those previously observed for thin films of phthalocyanines [12]. For phthalocyanine thin films, the molecules diffusing to fresh metal surface change their orientations from flat-lying to stand-up conformation but the molecules remaining at the original position keep the flat-lying orientation [12]. We consider that the different behavior of the nano-scaled orientations between thin films of SuPcCl_2 (van-der-Waals solid) and PDMS (polymer) is due to the difference in the strengths of the molecule-molecule and molecule-surface interactions. Further experiments are in progress to confirm this speculation.

In conclusion, we have observed microscopic images for organic thin films at real time, and found the orientation changes at nano-scaled domains during diffusion. The present method shed light on the real-time observation of electronic structures and molecular orientations in microscopic domains for thin films of organic molecules with anisotropic shape.

4. Acknowledgement

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