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In Situ Characterization of Morphology of Organic Thin Films by Total Reflection X-Ray Analysis

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IN SITU CHARACTERIZATION OF MORPHOLOGY OF ORGANIC THIN FILMS BY TOTAL REFLECTION X-RAY ANALYSIS.

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Abstract *In situ* characterization of the morphology of organic thin films was newly attempted by using total reflection X-ray analysis (TRXA). Due to cover a substrate with organic molecules during deposition, the intensity of total reflection fluorescence X-rays from a substrate surface decreases. It is expected that the decrement depends on the morphology of thin films. Fullerene (C60) thin films on the silver (Ag) substrates were formed at the substrate temperatures of 17, 50 and 100°C. From a result of *in situ* observation for the fluorescence X-rays of Ag substrates by TRXA, the intensity steeply decreased at 17°C and was saturated at 50 and 100°C. It was confirmed that the decay curve indicates the ratio of the coverage of C60 and the growth mode of island or layer-by-layer.

1. INTRODUCTION

Currently, organic ultrathin films epitaxially grown on metals and semiconductors are noted because of the potential for novel photonic devices. By using an organic molecular beam deposition (OMBD) which is one of physical vapor deposition methods in an ultrahigh vacuum (UHV), high crystalline ultrathin films of organic functional molecules such as metal-phthlocyanines, perylene dye, fullerene have been prepared.[1-5] Then, it is important to confirm the growth mechanism such as the crystal structure and morphology of thin films. Therefore, the *in situ* observation methods for organic ultrathin films have been newly developed.

Conventionally, *in situ* observation for the morphology of semiconductor and metal thin films was performed by using Auger electron spectroscopy (AES), reflection high energy electron diffraction (RHEED) and total reflection angle X-ray spectroscopy (TRAXS).[6] However, a number of organic molecules should be considerably damaged by electron beams used as a probe.

A new system of total reflection X-ray analysis (TRXA) combined with OMBD

(TRXA-OMBD) was developed for *in situ* observation of organic ultrathin films.[7] The crystal structures and composition of organic ultrathin films are effectively examined to detect the diffracted and fluorescence X-rays from thin films and substrates. It is known the 1/e depth of penetration into a substrate is a few nanometers under the condition of total reflection.[8] Thus, due to cover a substrate with organic molecules during deposition as shown in figure 1, the intensity of X-rays from the substrates decreases. It is expected that the decrement depends on the ratio of the coverage and the morphology of thin films by the analogy with AES.

In this study, fullerene (C60) thin films with the growth mode of layer-by-layer or island were prepared and it was attempted to examin the morphology by *in situ* TRXA.

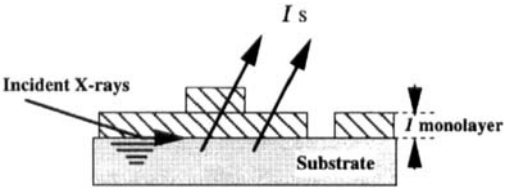

FIGURE 1. A schematic illustration of the principle for the estimation of morphology by TRXA.

2. EXPERIMENTS

Fullerenes (C60, 98%) were supplied from Term USA Co., Ltd. Also, the substrates were prepared by an evaporation of silver (Ag, 99.99%) at a film thickness of 8 nm on optically-flat silicon substrates. The evaporation was performed at the deposition rate of 1 nm/sec and the substrate temperature of 17 °C, respectively. All *in situ* experiments were performed in an UHV chamber (base pressure < 5 $\times 10^{-9}$ Torr) equipped with TRXA system. The details are described elsewhere.[7] The incident X-rays are set up at a glancing angle of 0.10° and the fluorescence X-rays of Ag were detected at a fixed angle of 2θ=6 ° The organic molecular beams were precisely controlled by a Knudsen cell (K-cell). During deposition, the film thickness was monitored by a quartz oscillator beside a substrate. OMBD was performed by the following conditions: the pressure of 2×10^{-8} Torr and deposition rate of 0.025 nm/sec. The X-ray observation was performed till the film thickness was up to 15 nm at the substrate temperatures of 17, 50 and 100 °C. After *in situ* experiments, the morphology of thin films was observed by atomic force microscopy (AFM, SEIKO, SPI-3700).

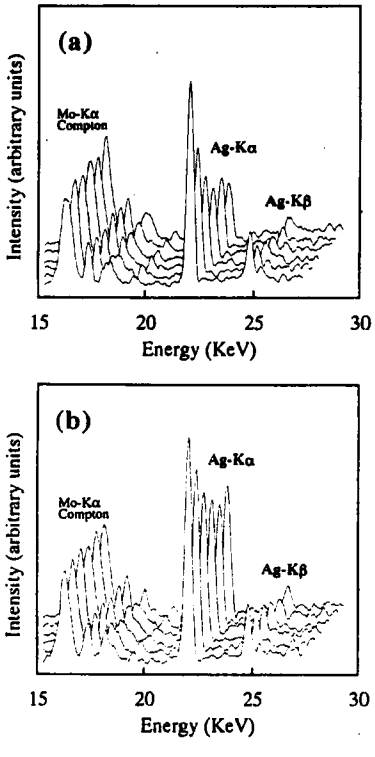

FIGURE 2. TRXA spectra of C60 ultrathin films on Ag substrates at the substrate temperatures of (a) 17 and (b) 100°C during deposition.

3. RESULTS AND DISCUSSION

Figure 2 shows the spectra of C60 ultrathin films on Ag at the substrate temperatures of 17 and 100°C during deposition. The fluorescence X-ray peaks of the Ag-Kα (22.1keV) and Kβ (24.9 keV) emitted from the Ag substrate are seen in these spectra. The intensity of the Ag-Kα decreases as the C60 molecules adsorb. Further, the decay curves of the normalized intensities are different at the substrate temperatures, as shown in Fig. 3. Although the fluorescence intensity at 17°C steeply decreases, that at 50 and 100°C are immediately saturated. It is thought that the difference of curves results from the ratio of the coverage and the morphology of C60. Then, after the deposition at the thickness of 15 nm, the C60 ultrathin films were observed by AFM in the air, as shown in Fig.4. Although the flat crystals at 17°C formed all over, bulky islands grew and a part of substrate was exposed at 50 and 100°C. Thus, it was confirmed that the early saturation of decay curve indicated the island growth.

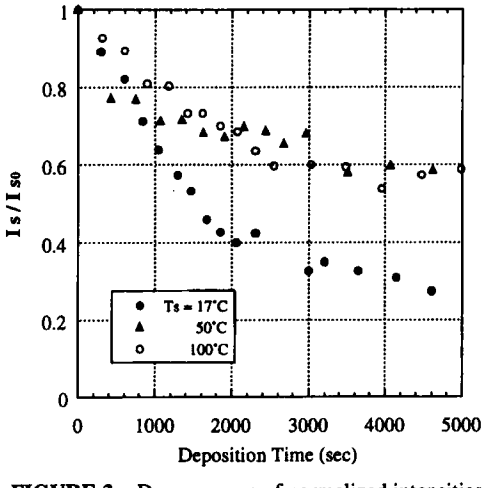

FIGURE 3. Decay curves of normalized intensities of Ag-Ka as a function of the deposition time and the dependence of the substrate temperature.

Figure 5 shows the normalized intensities of Ag-Kα as a deposition of C60 at the first process. The turning point in the decay curve at 17°C is observed near a thickness of a monolayer (0.815

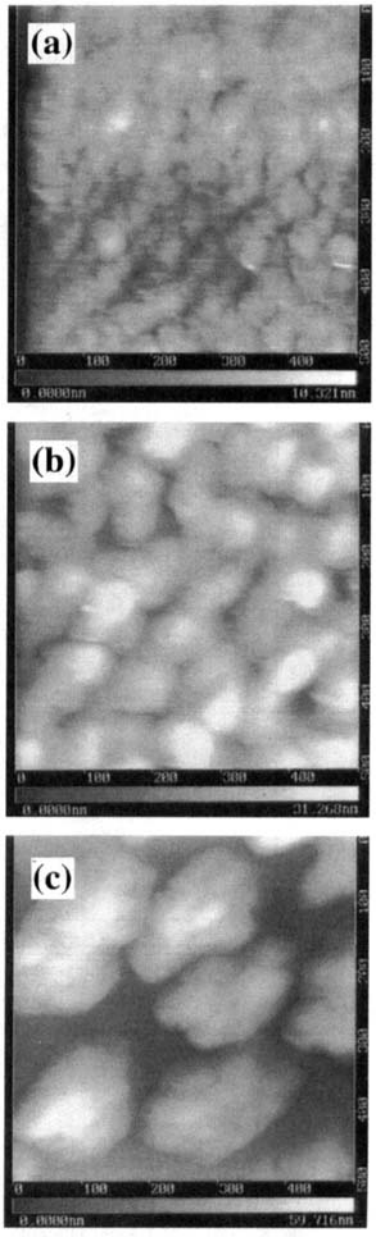

FIGURE 4. AFM images of C60 ultrathin films at the thickness of 15 nm, and the substrate temperatures of (a) 17, (b) 50 and (c) 100°C.

nm). However, there is no turning point at 50°C. Figure 6 shows the AFM images of C60 ultrathin films at the thickness of 3 nm. The substrate surface at 17°C was already covered by C60 crystals all over. By the analogy with AES, it is anticipated that the first turning point of decay curve indicates the overall formation of a monolayer by the growth mode of layer-by-layer. Thus, it is thought that a monolayer of C60 molecules on Ag at 17°C was formed overall and the slight deviation of the turning point was caused by the imperfect layer-by-layer growth.

In this study, it was preliminarily shown that *in situ* TRXA was effective to estimate the morphology of organic thin films as same as a conventional AES

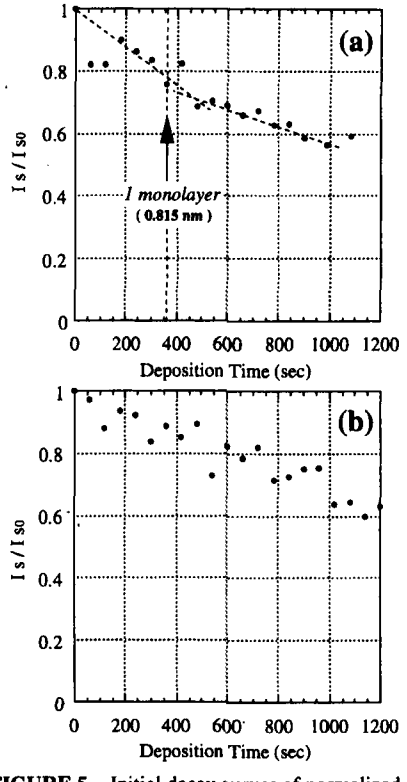

FIGURE 5. Initial decay curves of normalized intensities of Ag-Ka at the substrate temperature of (a) 17 and (b) 50°C.

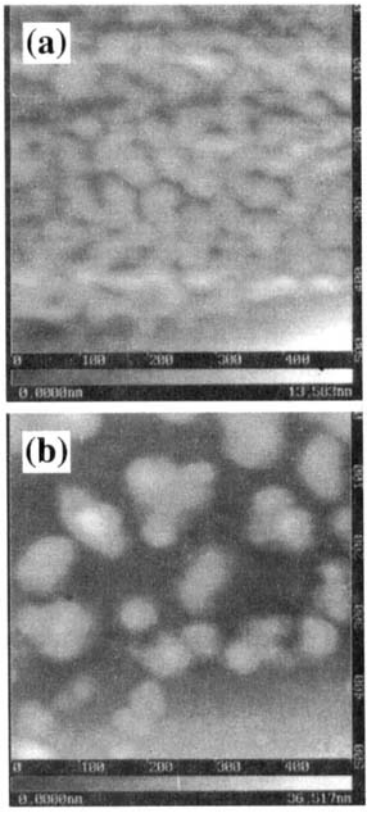

FIGURE 6. AFM images of C60 ultrathin films at the thickness of 3 nm, and the substrate temperatures of (a) 17 and (b) 50°C.

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