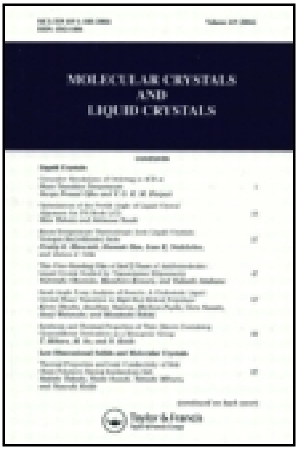

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Epitaxial Growth Behavior of Copper Phthalocyanine Films Under Applied Voltages

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EPITAXIAL GROWTH BEHAVIOR OF COPPER PHTHALOCYANINE FILMS UNDER APPLIED VOLTAGES

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Abstract In order to develop the noble molecular arrangement techniques, we investigated the effects of the electric field on the epitaxial growth process of organic thin films. We deposited interdigitated gold electrodes on KCl substrates, and then grew copper phthalocyanine (CuPc) thin films, with applying the electric voltages during the evaporation process. Using an energy dispersive grazing incidence x-ray diffraction (ED-GIXD) system, we evaluated the in-plane structures of the film samples by detecting the 200 reflection from CuPc crystallites. The CuPc molecules subjected to the electric field were found to orient to the different direction from those of the ordinally epitaxially grown films. These facts suggest that the combination of applying voltage and epitaxial growth provide us a new method to control the molecular orientation in the organic thin films.

INTRODUCTION

Recently, the epitaxial growth of organic crystalline thin films has drawn the interest of many researchers as a new technique for controlling organic materials at a molecular level. In order to realize materials with novel electronic and photonic functions, the orientations of the crystals relative to the substrate lattice structures, and further more the mechanisms of epitaxial growth should be elucidated. Kubono et al.[1] and Yoshida et al.[2] succeeded in orienting polar molecules by applying electric fields during the evaporation process. However, the effects of applying the voltages on the epitaxial growth process have not yet been investigated. In this study, we grew organic thin films, applying voltages during the evaporation process, and obtained notable changes in orientation of the crystals using an energy dispersive-grazing incidence x-ray diffraction (ED-GIXD) system. The results suggest that the combination of applying voltage and epitaxial growth present a new method of controlling the molecular orientation in organic thin films.

EXPERIMENTAL

Copper phthalocyanine (CuPc), which was purified by a sublimation method,[3] was selected as the evaporation sample. Polished faces of KCl (001) were used as substrates. In this experiment, we prepared three film samples, which are called here Sample A, B and C, in order to evaluate the effects of interdigitated electrodes and applying voltages on the epitaxial growth behaviors. Sample A was made by evaporating the CuPc on a bare KCl substrate, which was kept at room temperature under the vacuum condition of 1×10^{-4} pa. The evaporation rate and average thickness were controlled to be about 0.1 nm/s and 100 nm, respectively, using a quartz oscillation monitor.

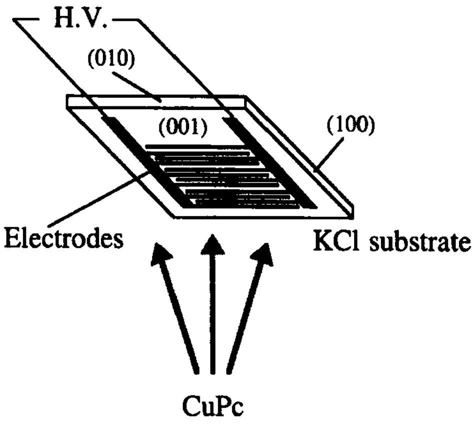

FIGURE 1 Schematic diagram of the evaporation system with equipment for applying voltage.

Sample B and C were prepared by using the KCl substrate with interdigitated electrodes. The interdigitated electrodes were formed by depositing gold onto KCl substrates in such a way that the interelectrodes were parallel to KCl [010]. The interelectrode gap and total length were 100 nm and 320 mm, respectively. Applied voltage were carried out using a Keithley 617 high-impedance electrometer. For the Sample B, the CuPc molecules were evaporated on the substrate without applied a voltage. While for the Sample C, the electric voltage of 100V was applied in the direction of KCl [100] during the CuPc evaporation process, as shown in Fig.1. The electric field between the electrodes was 1MV/m. After the evaporation, the sample was cut to remove the parts to which voltage had not been applied. (i.e., without the interelectrode).

The orientation of the CuPc crystallite was evaluated by the ED-GIXD system, which was developed in our laboratory.[4,5]. The epitaxial growth behavior could be evaluated by measuring the intensity of the diffracted x-rays with rotating azimuthal angle of the sample, ω.[6] The incident white X-rays from a Mo target were operated at 40 kV and 32 mA and the diffracted X-rays were detected by a solid-state detector (SSD). The diffraction condition was $2\theta = 4.6°$, where 2θ is a diffraction angle.

RESULT AND DISCUSSION

The θ-2θ x-ray diffraction profiles for the Sample A, B and C exhibit only 31-3 reflection from the α-CuPc crystal on the KCl surface. The α-CuPc crystal is the most common crystal form obtainable when the sample is evaporated at a substrate temperature near room temperature, and its crystal system is monoclinic with C2/c: a = 25.92 Å, b = 3.790 Å, c = 23.92 Å, $\beta = 90.4°$.[7] Since the angle between the substrate and a-axis of the crystal is calculated as 15° from these data, we controlled the detector position of the ED-GIXD system in order to detect 200 reflection, and measured the x-ray diffraction profiles with varying ω. Figure 2 shows a representative ED-GIXD profile from the CuPc film obtained at $\omega = 28°$, where ω is defined as the angle between the KCl [100] direction and a scattering vector. As shown in this x-ray profile, Cu Kα fluorescent x-rays from Cu atoms in the CuPc molecules and 200 reflection were detected from the CuPc film, in addition to the characteristic x-rays of the Mo element used as the x-ray target.

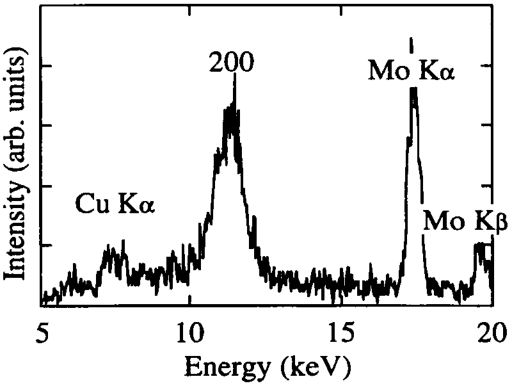

FIGURE 2. Typical x-ray diffraction and fluorescence profiles for CuPc film by ED-GIXD system.

To obtain detailed information on epitaxial growth, the intensity of the 200 reflection was measured as a function of ω. Figures 3 (A), (B) and (C) show the angular variations of the 200 reflection intensities for sample A, B and C. It is clear that the shapes of these profiles are different. The profile in Fig. 3 (A) exhibits two sharp peaks at 28° and 62°, indicating that the angle between the projection of the reciprocal a* axis of the α-CuPc crystal and nearest KCl major axes, [100] and [010], is 28°. This experimental result agrees well with that reported by Ashida[8] and indicates that the CuPc crystallites formed by ordinary epitaxial growth on a polished KCl (001) surface as well as cleaved one.

From Fig. 3 (B), it is known that the peaks observed at 28° and 62° are broadened due to the interdigitated electrodes although the peak positions are unchanged. We confirmed that CuPc

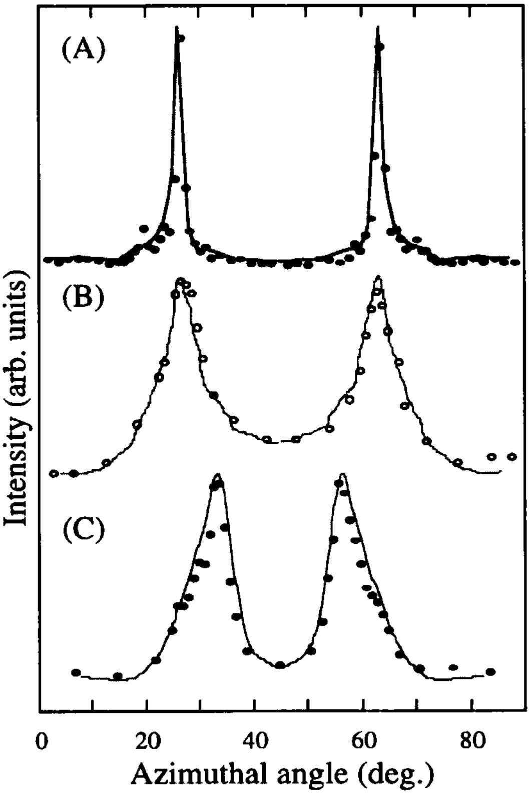

FIGURE 3. Angular variations of the 200 reflection intensities observed for the Sample A, B and C

molecules formed on Au are amorphous by x-ray diffraction method. Therefore, there existed the polycrystal phase on electrodes and epitaxially grown crystalline phase on KCl in Sample B. These two phases were presumed to be interfered at the boundary between Au and KCl surfaces and to be formed intermediate phase. Since this intermediate phase involved the CuPc crystallites oriented to some degree, the broadening of the peaks from the Sample B was considered to be occurred.

The angular variation in Fig.3 (C) has two peaks at 35° and 55° differently from Fig. 3 (B), revealing that the angle between the projection of the reciprocal a* axis of the α-CuPc crystal and the nearest KCl major axis changed from 28° to 35° due to the effects of electric fields and/or currents. Interestingly, the symmetry of the CuPc crystal orientation for the sample with applied voltages is 4-fold, similar to that without applied voltages, although the electric fields are parallel to KCl [100] direction. This experimental result implies that there is no relationship between the orientational change and the direction of electric field and that the changes in orientations induced by voltages do not simply due to the force produced by the electric field and the permittivity anisotropy of CuPc molecules, in contrast to the orientational changes of liquid crystals.

In summary, we evaporated CuPc molecules onto the KCl (001) plane under an applied voltage and observed the orientations of CuPc crystals using an ED-GIXD system. The CuPc molecules subjected to an applied voltage were found to orient in different directions from those of the ordinary epitaxially grown films without applied voltage. The origin of this orientational change induced by applying voltage is as yet unclear. Nevertheless, these results suggest that the combination of applied voltage and epitaxial growth can be constitutes us a new method of controlling the molecular orientation in organic thin films.

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