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Vacuum-deposited Thin Films of (μ-Oxo)bis[(phthalocyaninato) aluminium(III)]($(AlPc)_2O$)

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Thin films of μ-oxo dimer, $(AlPc)_2O$, deposited on KCl and NaCl in vacuum show epitaxy. The high-resolution image, electron and X-ray diffraction patterns indicate that the structure of $(AlPc)_2O$ thin film is the triclinic form reported by Wynne. The crystal grow making their molecular planes parallel to the substrate surface. The crystal orientations on KCl and NaCl are same and the angle between the a'-axis of the film and the $\langle 100 \rangle$ of KCl is about 26°.

Keywords: $(AlPc)_2O$; epitaxial thin film; vacuum-deposition; crystal structure; high-resolution imaging

INTRODUCTION

Since chloro(phthalocyaninato)aluminium has been reported on its higher photocurrent generation, a series of phthalocyanine complexes containing an aluminium atom has been studied on their photoconductivities.[1] One of such complexes, $(AlPc)_2O$, possesses an oxygen atom connecting two central metals in two phthalocyanate ligands. The phthalocyanine complexes like this are called μ-oxo phthalocyanine dimers. Recently Yamasaki *et al.* have reported that

$(AlPc)_2O$ and (μ-oxo)bis[(phthalocyaninato)gallium] ($(GaPc)_2O$) exhibit many polymorphs and some of them are useful as photoconductive materials.[2] $(AlPc)_2O$ is interesting as having the high photoconductivity and the view point of crystal growth on a substrate. Usually phthalocyanine molecules have plane or shuttlecock molecular shapes, which leads to the growth mode for crystals to have molecular planes parallel to the substrate surface. However, when phthalocyanines have different shape like dithallium phthalocyanine, in which thallium atoms are extruded to the both sides of the phthalocyaninato ligand, it is not always true that the plane of phthalocyanate ligand becomes parallel to the substrate surface.[3] In this study we examined the growth mode of a thick disk-like molecule of $(AlPc)_2O$ on substrates.

EXPERIMENTAL

$(AlPc)_2O$ thin films were prepared on the freshly cleaved (001) surface of KCl and NaCl single crystals by vacuum-deposition. During the preparation of thin films, the pressure of a vacuum chamber and the temperature of the substrates were kept at 1×10^{-4} Pa and 170–215 °C, respectively. Structures of the deposited films were examined mainly by electron diffraction using a transmission electron microscope. In addition, the thin film was measured by X-ray diffraction after removed from substrate and fixed on a glass plate. Morphological observation of the films was carried out with an atomic force microscope (AFM).

RESULTS AND DISCUSSION

The electron diffraction diagram show almost a square pattern whose unit is $a'^* = 1/1.25$ nm^{-1} and $b'^* = 1/1.26$ nm^{-1} and the angle between them is about 90° (Figure 1(a)). X-ray diffraction revealed a period of 0.386 nm (= c') in the direction perpendicular to the film plane (Figure 1(b)). Only a peak at 0.386 nm was observed but any other reflection did not appear. However, this spacing was

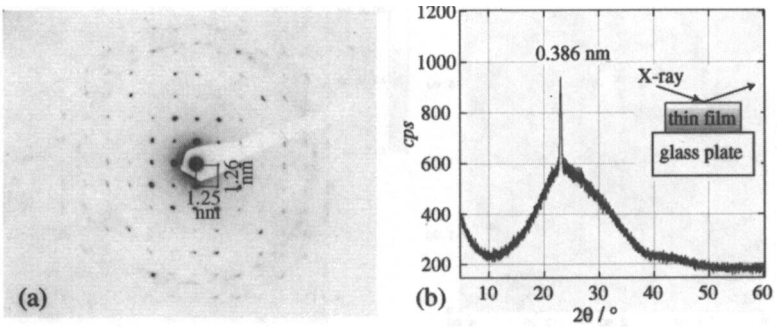

FIGURE 1 (a) A selected-area electron diffraction pattern where the incident electrons are transmitted perpendicularly to the film surface and (b) X-ray diffraction pattern of $(AlPc)_2O$ thin film deposited originally on KCl.

assigned here to (200) reflection. Though the morphologies were varied depending on the preparation conditions and substrates almost flat plate-like crystals were often obtained (Figure 2(a)). Such flat crystalline surfaces have not been observed in other phthalocyanine derivatives so far and such flatness is expected to be useful to fabricate 3D organic multi layers. Fourleaf clover-like images were obtained with a high-resolution electron microscope (Figure 2(b)), which were interpreted as molecular images of $(AlPc)_2O$. Wynne has analyzed the crystal structure of $(AlPc)_2O$, and reported the following cell parameters; *triclinic*, $P\bar{1}$, $a = 0.7694(2)$ nm, $b = 1.2520(3)$ nm, $c = 1.2705(3)$ nm, $\alpha = 91.03(2)°$, $\beta = 94.54(2)°$, $\gamma = 90.37(2)°$.[4] This lattice almost agrees with the present result, so that the incident electron beam direction at the observation of the image is nearly parallel to the a-axis. Accordingly, $(AlPc)_2O$ molecular columns can be seen in the high resolution image as a superimposed illustration in Figure 2(b). These results support that the thin film has the same structure as the triclinic form at least as a major constituent. The electron diffraction and the high resolution image clearly indicate that the dimer molecules in the crystal make its flat planes of phthalocyaninato ligands parallel to the substrate surface as found in other cases of plane or shuttlecock-type phthalocyanines.

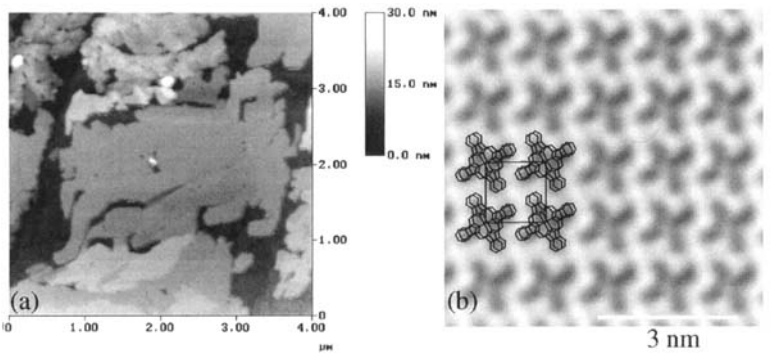

FIGURE 2 (a) AFM image revealing the morphology and (b) a high-resolution electron micrograph of $(AlPc)_2O$ thin film deposited on KCl.

Such the posture of molecules at the first layer on the substrate is considered to be most favourable for 2D crystalline film film to be stabilized with minimum energy in the whole system.

In order to determine the in-plane orientation of the films, electron diffraction patterns were observed from a large specimen area. The electron diffraction diagram showed that 100 spots direction makes the angle of $\sim 26°$ with the $\langle 100 \rangle$ axis of KCl. The orientation for NaCl substrate was the same as for KCl. Because we have no exact answer to explain such orientation, further studies are needed. It would originate from a formation of a pseudomorphic thin layer at the interface between the film and KCl or a particular interaction between the molecule and the surface ions of the substrate, such as electrostatic interaction.

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