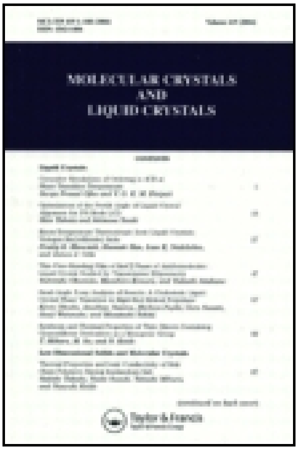

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Interface Structure of Organic Double-Layered Film (VOPC/GeOPC) Studied by Electron Microscopy

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INTERFACE STRUCTURE OF ORGANIC DOUBLE-LAYERED FILM (VOPc/GeOPc) STUDIED BY ELECTRON MICROSCOPY

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Abstract Organic double-layered film composed of vanadyl phthalocyanine (VOPc) and poly-Ge-O-phthalocyanine (GeOPc) was obtained by vapor deposition. Structure of the interface between the layers was investigated by molecular imaging with high resolution electron microscopes and good commensurate structural correlation was observed.

INTRODUCTION

It is indispensable to clarify interface structures of organic double- or multi-layers, in order to understand the mechanism of a heteroepitaxy of organic molecules and also to design functional organic multi-layered films. So far, however, there are a few structural investigations on such organic multi-layers.[1-4] We report here a structural study of a double-layered film composed of VOPc and GeOPc by high resolution electron microscopy (HREM). VOPc is known to exhibit interesting optical properties[5,6] and GeOPc to be conductive when doped with iodine.[7] This double-layered film is considered to be one of model systems combining photoactive and electrically conductive microsystems. They are expected to form a double-layered film in an epitaxial relation, because they individually crystallize on KCl (001) with a very similar crystallographic orientation.

EXPERIMENTAL

VOPc was synthesized and purified according to the Linstead's method[8] and monomeric GeOPc was supplied by Dr.Y.Kuwae, Cannon Inc. A single-layer of VOPc or GeOPc was made by vapor deposition on an air-cleaved (001) surface of KCl preheated for 1 hr. at 400°C before deposition under a vacuum of 10^{-5} Pa. The double-layer was obtained by subsequent deposition of VOPc after the formation of GeOPc on KCl (001) surface. The respective thickness of VOPc and GeOPc forming the double-layered film was controlled to be 5 nm by monitoring with quartz microbalance. The deposition rate was usually 1.0 nm/min and the substrate was kept at 180°C during the deposition. Electron diffraction patterns and molecular images were taken with JEM-1000ARM operated at 800 kV and JEM-200CX operated at 200 kV. Elemental micro-analysis was performed with JEM-2010 equipped with an energy dispersive X-ray analyzer (EDX).

RESULT AND DISCUSSION

Figure 1 shows a selected area electron diffraction (SAED) pattern from a GeOPc film grown epitaxially on KCl, where the incident beam direction is perpendicular to the film surface. This pattern indicates that the c-axis of the tetragonal GeOPc crystal is perpendicular to the film surface and the a-axis aligns along <210> of KCl as reported previously.[9] The unit cell dimensions are a=b=1.372 nm and c=0.68 nm. A corresponding high resolution molecular images are shown in Figure 2 as the c-axis projection, where the tetragonal array of the GeOPc stacking in columns can be clearly observed. The image well corresponds to the computer-simulated images of the molecular stacking in face-to-face but in staggered manner.

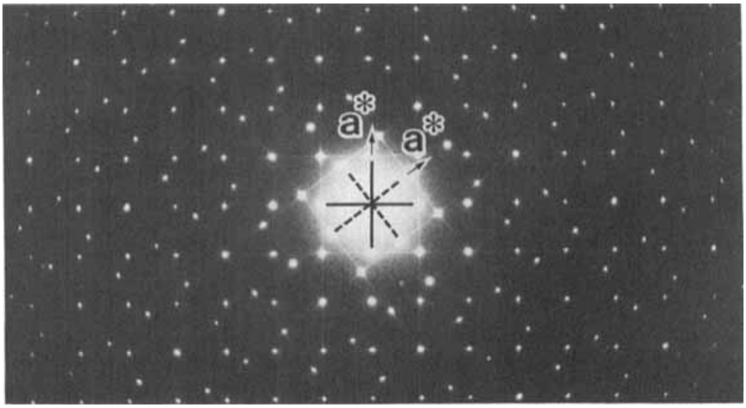

FIGURE 1. SAED of GeOPc showing the c-axis projection.

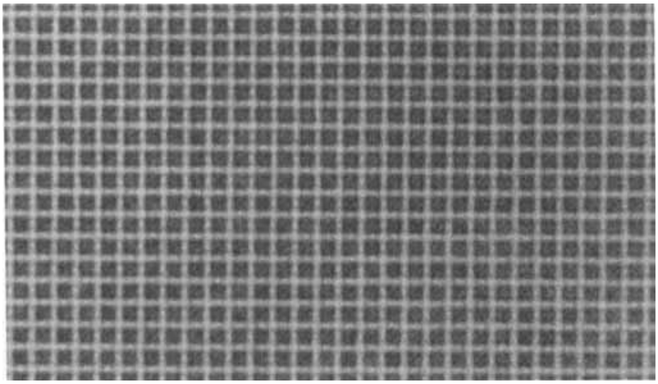

FIGURE 2. High resolution molecular images of GeOPc.

On the other hand, VOPc was reported to crystallize on KCl by molecular beam epitaxy as a tetragonal form having the a-axis of 1.4074 nm.[10,11] In our case, however, VOPc crystallizes in two different crystalline forms, whose lattice dimensions in a basal plane are a=1.352 nm or a'=1.305 nm, respectively (Figure 3). One crystalline form with a=1.352 nm (Type-I) was imaged by HREM in a tetragonal array as shown in Figure 4, while the other crystal with a'=1.305 nm (Type-II) gave only lattice fringes along one direction in HREM, which means that the main axis of this crystal is not perpendicular to the film plane. Therefore, it might have another crystalline form, *e.g.*, triclinic or monoclinic form. In Figure 3, the incident beam direction is perpendicular to the film

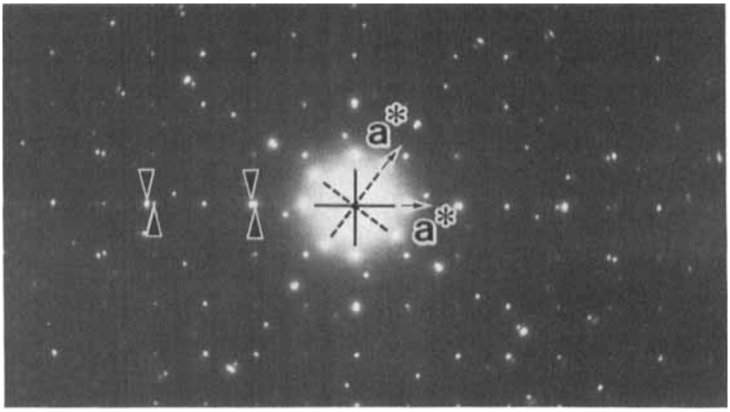

FIGURE 3. SAED of VOPc, where Type-I and -II are observed as shown by the triangles.

plane (along the c-axis of Type-I). The epitaxy of Type-I on KCl is just the same with the case of GeOPc, *i.e.*, the a-axis orients along <210> of KCl. From Figure 4, the molecules of VOPc are considered to stack along the c-axis making the molecular planes perpendicular to the stacking axis (c-axis).

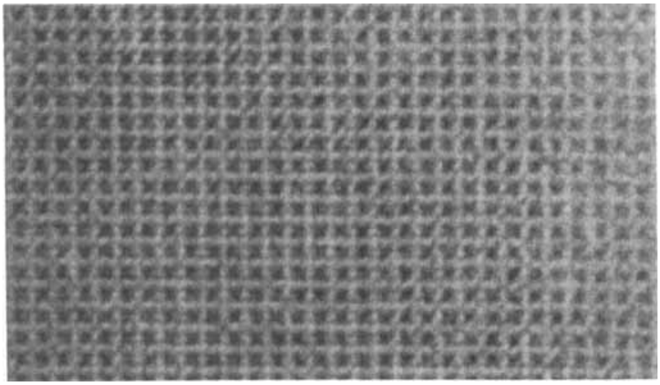

FIGURE 4. High resolution molecular images of VOPc in Type-I.

A SAED pattern from the double-layered film is shown in Figure 5, which displays no distinct difference from the superposition of Figures 1 and 3. In Figure 5, VOPc crystallizes again as Type-I and -II, and GeOPc as the tetragonal form. This SAED could be interpreted simply by overlapping of the diffractions from them. However, the V- and Ge-atoms were simultaneously detected by EDX in many places of the film with a molar ratio of about 50:50, which agrees well with the

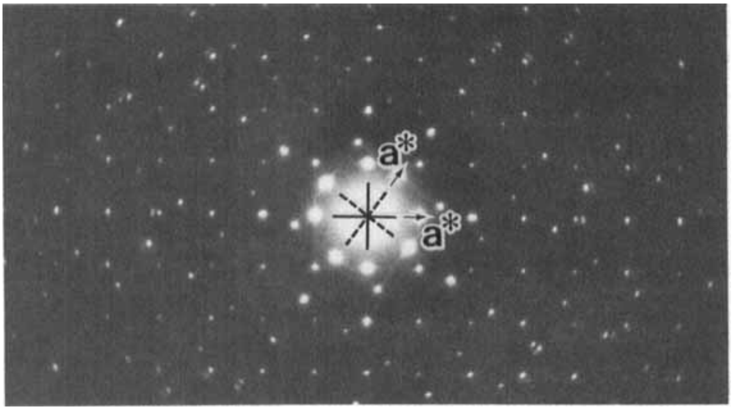

FIGURE 5. SAED pattern of the double-layered film.

ratio expected from the controlled thicknesses during the deposition. EDX analysis was carried out for a domain of 50 nm in diameter, which coincides roughly with a picture size shown in Figure 6.

High resolution images were obtained as a projection perpendicular to the double-layered film surface. The image can be interpreted as an overlap of two individual molecular images of VOPc and GeOPc. The molecular images are observed to align in tetragonal with a basic spacing of about 1.37 nm as shown in Figure 6. The basic periodicity corresponds to the lattice spacing of GeOPc. The image enlarged was from a double-layered region, which can be recognized easily from the image contrast in micrograph. EDX analysis showed the coexistence of V- and Ge-atoms in such tetragonal image area. Therefore, it can be concluded that the VOPc coherently crystallizes overlapping just on the molecules of GeOPc and that a tetragonal crystalline form of VOPc having a larger lattice unit than Type-I is forced to appear. The supposed interface of VOPc/GeOPc is illustrated in Figure 7, as a projection along the a-axes of VOPc and GeOPc.

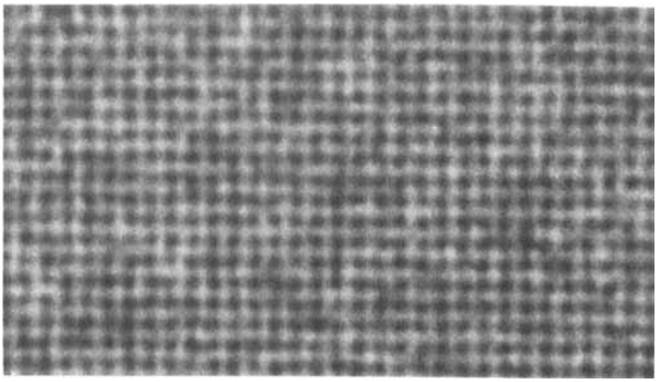

FIGURE 6. High resolution molecular image of double-layered region.

VOPc molecule may possibly be deposited making its protruded oxygen atom upward on GeOPc surface so as to avoid interference with the protruded OH-group on the top layer of GeOPc. On the contrary to this case, Cl-tetraphenylporphinate-Fe (ClTPPFe) crystallized on GeOPc surface shifting its molecular centers with a distance of one-forth of GeOPc lattice along <1 1 0> direction,[4] though ClTPPFe has an protruded chlorine atom and its crystalline form is tetragonal with nearly the same a-axis dimension with that of GeOPc.

HREM can give us information on structural correlation of two crystals at interface, including translational correlation that is hard to be analyzed only by SAED.

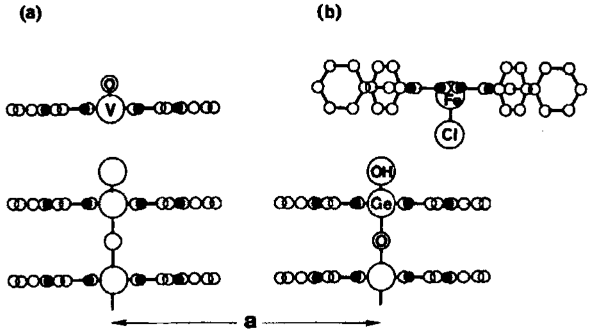

FIGURE 7. Schematic drawing of the see-through interface along the a-axis of GeOPc. a.VOPc/GeOPc, b.ClTPPFe/GeOPc.

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