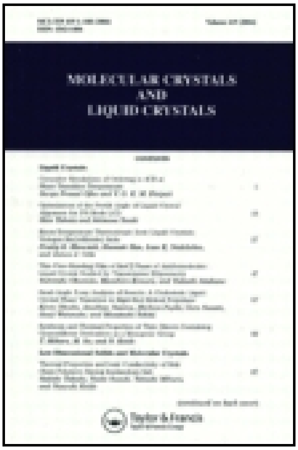

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Epitaxial Growth Mechanism of Titanyl–Phthalocyanine on Solid Substrates

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Thin films of titanyl–phthalocyanine (TiO–Pc) are fabricating on the (001) planes of alkali halides (NaCl, KCl and KBr), muscovite (mica) and the surface of indium–tin oxide (ITO) on glass plate by organic molecular beam deposition (OMBD) technique. They consist of needle and plate crystals depending on the kind of substrates and deposition conditions. The dependence of crystallite sizes and distances between adjacent fine crystallites on the temperatures of K–cell and substrates is evaluated by transmission electron microscopic observation to confirm the activation energies for crystal growth and surface diffusion.

Keywords: titanil–phthalocyanin, epitaxial growth, growth mechanism

INTRODUCTION

It has been arousing a great interest in titanyl phthalocyanine (TiO–Pc) as organic photo conductor. Recently sophisticated method, organic molecular beam deposition (OMBD), has been employed to fabricate organic molecular thin films having molecular orientation controlled structure [1]. To understand the physical and electrical properties of the organic molecular thin films, it is necessary to fabricate films with controlled structure and well-characterized defects. However there are fewer works in the crystal growth field of these thin films.

We have already investigated the formation mechanism of thin films from the thermodynamic point of view for several materials; long chain compound (Calcium stearate) [2], charge transfer complex (TTF–TCNQ) [3], organic dye (Alq_3 and TPD) [4–6] also C_{60} [7, 8]. The nucleation and crystal growth depend on the interaction between molecules, and between molecules and the substrate surface. It is expected that phthalocyanine as a planar molecule should be affected to the molecular orientation with respect to the substrate surface [9]. We will describe the formation mechanism of nucleation and surface diffusion of TiO–Pc molecular crystal on alkali halides, muscovite and indium–tin oxide (ITO) substrate.

MATERIALS AND METHODS

The TiO–Pc powder was put into the K–cell at pressure of 1 x 10^{-7} Torr. The K–cell was heated in the temperature of 620 K. The substrates used were air–cleaved along the (001) surfaces of NaCl, KCl and KBr, muscovite (001) surface and ITO film on glass plate. Prior to deposition, the substrates are backed at 473K for 1 hour under vacuum. Powder samples are sublimated from the precise by temperature–controlled Knudsen cell at a pressure of 10^{-7} Torr and deposited onto the substrates kept between 300 – 620 K for 600 sec. The thin films deposited on alkali halides and muscovite were reinforced by vacuum–deposited carbon film and observed by transmission electron microscope (TEM), Zeiss CEM–902 and scanning electron microscope (SEM), TOPCON DS–720. Thin films on the ITO substrate were observed by an atomic force microscope (AFM), Digital Instruments Nanoscope III.

RESULTS AND DISCUSSION

Figure 1 is transmission electron micrographs and electron diffraction (ED) patterns of thin films of TiO–Pc formed on the (001) surfaces of NaCl (a), KCl (b), KBr (c) and muscovite (d), respectively. The deposition conditions have been as follows: the temperature of K–cell (T_f) and substrat (T_S), and the deposition time were 627 K, 573 K and 600 sec., respectively. The crystallite size, shape and distance between adjacent crystallites are strongly affected the kinds of substrates and the deposition conditions. The TEM observation indicated that the crystal shapes like sheet and needle correspond to the different orientation with respect to the substrate surface. Figure 2 show AFM images of TiO-Pc formed on ITO surface. The TiO–Pc crystallites on ITO surface are planar and oriented along one direction. This direction is parallel to a scratch that might be introduced in polishing process.

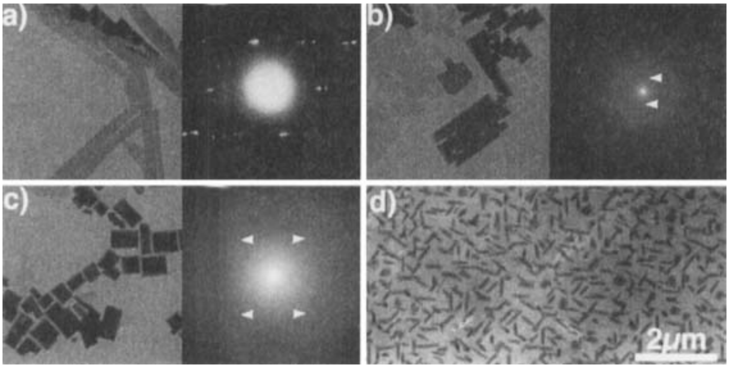

FIGURE 1 TEM images and ED patterns of TiO–Pc films formed on NaCl (a), KCl (b), KBr (c) and muscovite (d).

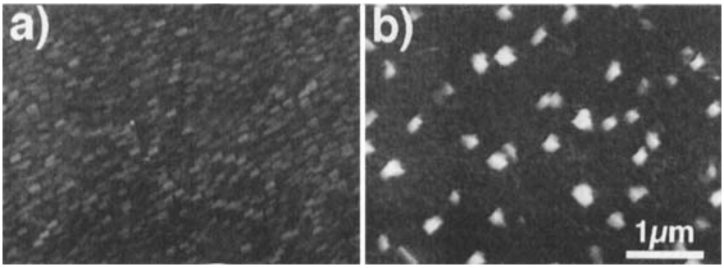

FIGURE 2 AFM images of TiO-Pc formed on ITO surface. The temperatures of substrates are 420K and 520K, respectively.

The temperature dependence of the crystallite density and the crystallite size on the surface give the quantitative value for the activation energy for crystal growth (ΔE_{growth}) and surface diffusion (ΔE_{diff}) of TiO–Pc molecule on various surfaces. The TiO–Pc was deposited at definite condition, so that the crystallite size and the deposition time give the crystal growth velocity (v_{growth}). The normalized crystallites distance might correspond to the diffusion velocity of molecules (v_{diff}). The dependents of v_{growth} and v_{diff} on the inverse of T_S

leads the activation energy for crystal growth (ΔE_{growth}) and surface diffusion (ΔE_{diff}) of molecules as follows:

$$\nu = A \exp(-\Delta E / RT_S),$$

where A is a pre–exponential factor and R is a gas constant. From the experimental data, ΔE_{growth} and ΔE_{diff} for alkali halides, muscovite and ITO are listed in Table 1. With TiO–Pc films on NaCl and muscovite, ΔE_{growth} are smaller than those on KCl and KBr. It proves that the needle crystals appear on those substrates kept above 473 K. It is considered that the one directional ITO surface scratches become nucleation site and set a limit to molecule surface diffusion. Therefore, ITO has relatively large ΔE_{diff} value.

TABLE1 Activation energies for crystal growth (ΔE_{growth}) and surface diffusion (ΔE_{diff}) for TiO–Pc on the substrates of alkali halides, muscovite and ITO.

	NaCl	KCl	KBr	Muscovite	ITO
ΔE_{growth} (kJ/mol)	12. 1	14. 8	16. 4	6. 47	13. 8
ΔE_{diff} (kJ/mol)	15. 2	7. 04	16. 3	5. 05	20. 2

In conclusion it has, for the first time, qualitatively discussed the relationship between the nucleation, surface diffusion and crystal growth and the deposition conditions concerning with phthalocyanine as a planar molecule. And it results that the molecular orientation of planar molecule during surface diffusion and crystal growth would affect the growth mechanism.

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