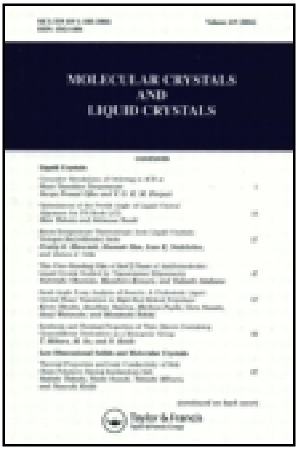

Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals

Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl19

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Version of record first published: 24 Sep 2006

To cite this article: Gernho Back, Takeshi Hanada, Yuji Yoshida, Hiroshi Takiguchi, Koji Abe, Nobutaka Tanigaki & Kiyoshi Yase (1999): Growth Mechanism of Highly Ordered Oriented Films of Copper (II)Phthalocyanine on Solid Substrates, Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals, 327:1, 147-152

To link to this article: http://dx.doi.org/10.1080/10587259908026801

*Mol. Cryst. Liq. Cryst.*, 1999, Vol. 327, pp. 147-152
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# Growth Mechanism of Highly Ordered Oriented Films of Copper(II)Phthalocyanine on Solid Substrates

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*(Received June 30, 1998; In final form July 15, 1998)*

Thin films of functional organic compound, copper phthalocyanine (Cu-Pc), are fabricated on the (001) surfaces of alkali halides (NaCl, KCl and KBr) and tin-doped indium oxide (ITO) by physical vapor deposition (PVD) technique. Dependence of sizes and distances between adjacent crystallites on substrate temperatures is evaluated from morphological observation by scanning electron microscope to determine the activation energies for crystal growth and surface migration of molecules. Increasing substrate temperature, the size and distance corresponding to the growth and diffusion rates, respectively, tend to increase. Particularly in the case of Cu-Pc on alkali halides, plate and tetrahedral crystals having different molecular orientations with respect to the surface appear depending on the kind of substrates and deposition conditions.

*Keywords:* Copper phthalocyanine; physical vapor deposition; crystal growth; organic thin film; organic photoconductor

## INTRODUCTION

It has been aroused an interest in copper phthalocyanine (Cu-Pc) as one of derivatives of the greatest commercial importance in the field of organic photoconductor. Their thin films were prepared by physical vapor deposition (PVD) technique. Recently more sophisticated method, organic molecular beam deposition (OMBD), has been employed to fabricate thin films having molecular orientation controlled structure [1,2]. To understand the physical and electrical properties of thin films, it is necessary to prepare films with controlled structure and well characterized defects and dislocations. Ordered films of metallophthalocyanines has been fabricated from vapor phase onto the cleaved surfaces of muscovite (mica) [3] and potassium chloride (KBr) [4].

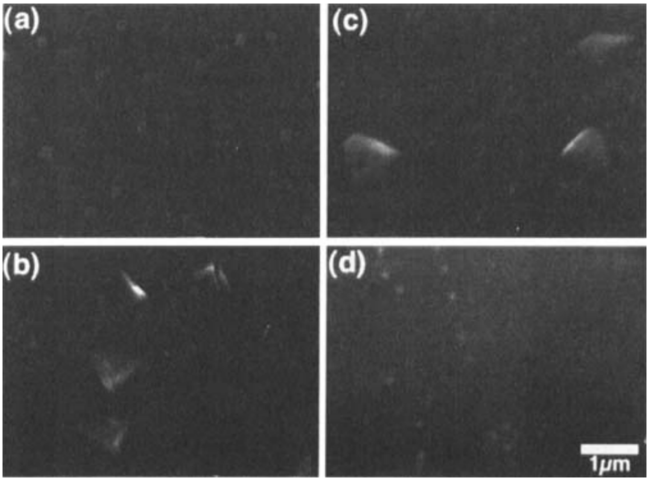
We have already investigated the formation mechanism of thin films from the thermodynamic point of view for several organic materials; long chain compounds (Calcium stearate) [5], charge transfer complex (TTF-TCNQ) [6], organic dyes (Alq3 and TPD) [7,8] as well as fullerene (C60) [2,9,10]. It has been well-known that the molecular structure drastically affects to the growth mechanism on the substrate, especially for epitaxial growth. The nucleation and crystal growth depend on the interaction between molecules, and between molecules and substrate surface. It has been expected that phthalocyanine as a planar molecule should be affected to the molecular orientation on the surface [11]. We will describe the formation mechanism such as nucleation and surface diffusion of Cu-Pc on alkali halides and tin-doped indium oxide (ITO) as substrates.

## EXPERIMENTAL

Cu-Pc ($C_{32}H_{16}N_8Cu$) was purchased from Nacalai Tesque Inc., Kyoto, Japan and employed without any further purification. Powder sample was put into a quartz glass tube wound by tungsten wire with a diameter of 0.7 mm. The furnace was heated in the range of 300 - 500 °C to control the deposition rates between 0.01 and 0.2 nm/s, respectively. The substrates have been air-cleaved along the (001) planes for alkali halides such as NaCl, KCl and KBr, and ITO coated glass with a sheet resistance of ca. 10 - 30 $\Omega/cm^2$. Prior to deposition the substrates were baked out at 200 °C for 1 hour under a pressure of $10^{-6}$ Torr to make the surface clean. Deposition was performed at various substrate temperatures of 50 - 230 °C and for different deposition times of 300 - 600 sec. After deposition, the samples were picked out from vacuum chamber for observation of the surface morphology. The thin films on substrates were reinforced by plasma polymerized osmium tetraoxide ($OsO_4$) film with a thickness of 3 - 5 nm which was prepared in a D.C. glow discharge by using an NL-PF30-N, Nippon Laser and Electric Laboratory, Nagoya, Japan [12]. Then they were observed by a field emission scanning electron microscope (FE-SEM), TOPCON DS-720.

## RESULT AND DISCUSSION

Figure 1 shows scanning electron micrographs of Cu-Pc thin films formed on the (001) surfaces of NaCl (a), KCl (b), KBr (c) and ITO (d), respectively. The deposition conditions were as follows: the temperatures of furnace (Tf) and deposition time were 470 °C and 300 sec, respectively. The substrate temperatures (Ts) were 170 °C, except for KCl (b), which was 150 °C. The size, shape and distance between adjacent crystallites are strongly affected by the kinds of substrate and deposition conditions.



FUGURE 1 SEM images of crystallites of Cu-Pc formed on NaCl (a), KCl (b), KBr (c) and ITO (d).

From the results of FE-SEM observation, most of crystals whose shapes were like tetrahedrons on the substrate surfaces on KCl and KBr. It is good coincidence with Ashida's result [4].

When the Ts was less than 100 °C, no crystallines could be observed and the films were amorphous. Between the substrate temperatures at 100 and 200 °C, planar crystals were formed on NaCl, KBr and triangle ones were on KCl.

The dependence of growth rate ($\upsilon_{growth}$) (nm/sec) and diffusion velocity ($\upsilon_{diff}$) on the inverse of Ts leads the quantitative value for the activation energies for crystal growth ($\Delta E_{growth}$) and surface diffusion ($\Delta E_{diff}$) of molecules as follows:

$$\upsilon = A \exp(-\Delta E / RTs),$$

where A is a pre-exponential factor and R is a gas constant. The grwoth rate and diffusion velocity were estimated from the devision of crystal size into deposition time and the inverse of root square of number of crystallites in unit area ($1/\sqrt{(n)}$), respectively. The dependence of $\upsilon_{growth}$ and $\upsilon_{diff}$ on substrate temperatures for Cu-Pc molecules on various surfaces are shown in Figure 2(a) and 2(b).

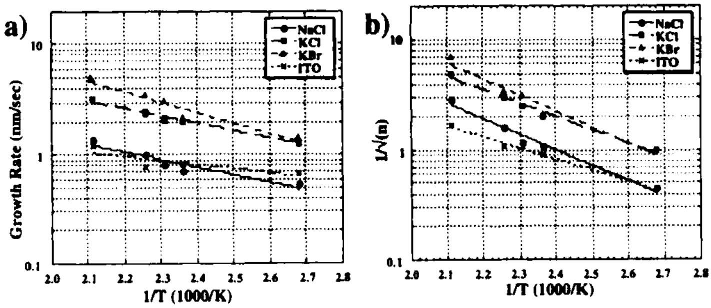


FIGURE 2 Dependence of growth rate (nm/sec) (a) and diffusion velocity (b) on the substrate temperature at Tf = 470 °C.

From the experimental data, $\Delta E_{growth}$ and $\Delta E_{diff}$ for alkali halides and ITO are listed in Table 1.

TABLE 1 Activation energies for crystal growth ($\Delta E_{growth}$) and surface diffusion ($\Delta E_{diff}$) of Cu-Pc molecules on alkali halides and ITO.

| | NaCl | KCl | KBr | ITO |
|---|---|---|---|---|
| $\Delta E_{growth}$ (kJ/mol) | 13.1 | 13.5 | 17.4 | 7.8 |
| $\Delta E_{diff}$ (kJ/mol) | 26.8 | 22.9 | 27.8 | 19.4 |

The activation energies for crystal growth of Cu-Pc on alkali halides are prominently larger than that on ITO. Since the molecules epitaxially grew on alkali halides to arrange with the molecular orientation parallel to the surface, it means that they have strong interaction with substrate surface. While, so small $\Delta E_{growth}$ and $\Delta E_{diff}$ on ITO represent that as the needle crystals were frequently observed on ITO surface, Cu-Pc molecules would migrate and aggregate with the molecular orientation normal to the surface. And molecues on the rough surface of ITO polycrystalline might be restricted the nucleation and diffusion (See Figure 1(d)). The Cu-Pc crystallites on mica surface were needle as same as Ashida's result [4].

In conclusion, it has been, for the first time, quantitatively discussed the relationship between nucleation, namely crystal growth and surface diffusion, and the deposition conditions concerning with copper phthalocyanine. And it resulted that the molecular orientation having planar shape would affect the growth mechanism during surface diffusion and crystal growth.

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