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Kiyoshi Yase [a] , Shun-Suke Sumimoto [b] , Hiro Matsuda [a] & Masao Kato [b]

[a] National Institute of Materials and Chemical Research, 1-1 Higashi, Tsukuba, Ibaraki, 305, JAPAN

[b] Faculty of Industrial Science and Technology, Science University of Tokyo, Yamasaki 2641, Noda, Chiba, 278, JAPAN

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FORMATION MECHANISM OF THIN SOLID FILMS OF Alq3 ON SEVERAL SUBSTRATES

KIYOSHI YASE, SHUN-SUKE SUMIMOTO*, HIRO MATSUDA and MASAO KATO*

National Institute of Materials and Chemical Research,
1-1 Higashi, Tsukuba, Ibaraki 305, JAPAN
** Faculty of Industrial Science and Technology,*
Science University of Tokyo, Yamasaki 2641, Noda, Chiba 278, JAPAN

Abstract Functional organic dye, Tris(8-hydroxyquinoline) aluminum complex (Alq3) was deposited onto the surfaces of KBr, ITO and quartz plate. The fundamental parameters in film growth such as nucleation and surface migration of molecules were numerically analyzed to confirm the formation mechanism of thin crystals.

1. INTRODUCTION

It has been interested in organic electroluminescent (EL) diode for new display. Especially Tris(8-hydroxyquinoline) aluminum complex (Alq3) (Fig. 1) is a key component of EL devices with layered structures, in which each layer was amorphous to be prepared by vapor deposition or spin coating[1,2]. To understand the EL property and give it high performance, it should be necessary to take into consideration of and control the formation mechanism of thin films.

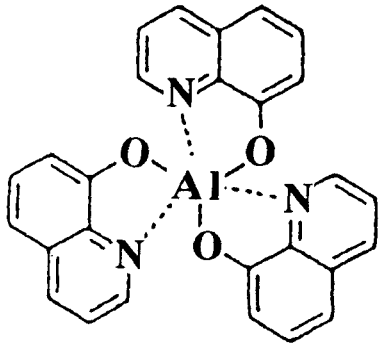

FIGURE 1 Molecular structure of Alq3.

Now we will discuss about formation mechanism of Alq3 films prepared on the surfaces of KBr, ITO and quartz plate.

2. EXPERIMENTALS

Alq3 powder was purchased from Tokyo Kasei Co. and purified by the sublimation in a vacuum. After baked at 300℃ for 1 hr in a pressure less than 1 x 10^{-6} Torr, the substrates of KBr, ITO and quartz plate (fused glass) were maintained at the temperatures between 20 - 150 ℃. The purified specimen was evaporated from K-cell type crucible precisely controlled at 200 and 250 ℃ for 1 to 5 min.

Thin films on the substrates were covered and reinforced by vacuum-deposited carbon film with a thickness of 3 nm. The films were stripped off from the substrate in distilled water or dilute HF aqueous solution. The floating films were transferred onto Cu grids. Film morphology was observed by a transmission electron microscope (Zeiss CEM-902). The size and density of island crystals were quantitatively measured from the TEM images.

3. RESULTS AND DISCUSSIONS

Typical film morphologies on KBr, ITO and quartz plate kept at 100 ℃ are shown in Figs. 2 (a) to (c), respectively. Molecules on KBr grew epitaxially to form slender crystals aligning along the <110> directions on the (001) surface. On the other hand, they formed the hemisphere deposits on ITO and quartz plate. The number of crystals depended on the deposition time (t) and tended to saturate at t ≒ 5 min.

Figures 3 (a) and (b) show the dependence of the number and size of island crystals on the substrate temperature (Ts), respectively. With rising Ts, the number of crystals decreased. At Ts = 120 ℃ for KBr and at Ts= 150 ℃ for ITO and quartz plate, only few molecules could be adsorbed on the substrate. When the temperature of furnace (Tf) was 200 ℃ and the amount of molecules per unit time reached at the substrate surface should be 10^2 times less than that at Tf = 250 ℃[3], the critical temperature of substrate decreased less than those. The adsorption energy of molecules on the substrate could be roughly estimated as RT, in which R is a gas constant (8.314 kJ/mol K) and T is the critical temperature of substrate (K). So the energy should be 3.27 to 3.52 kJ/mol on these substrates. It was rather

smaller than the enthalpy of fusion for Alq3, 138 kJ/mol, which was obtained from differential scanning calorimetry (DSC) measurement.

Although the island crystals grew on KBr in increasing *Ts*, their size did not remarkably increase on ITO and quartz plate. It means that the nucleation and surface migration of molecules on KBr and ITO should be enhanced by the thermal energy supplied from the substrate. If the crystal size were considered as the growth rate from the nuclei of nearly zero nm, the relationship between the rate and the inverse of Ts would lead the activation energy for crystal growth (ΔE_{CG}) as follows:

$$\text{Growth Rate} = A \exp(-\Delta E_{CG}/RT) \qquad \text{Eq.(1)}$$

in which A is a pre-exponential factor.

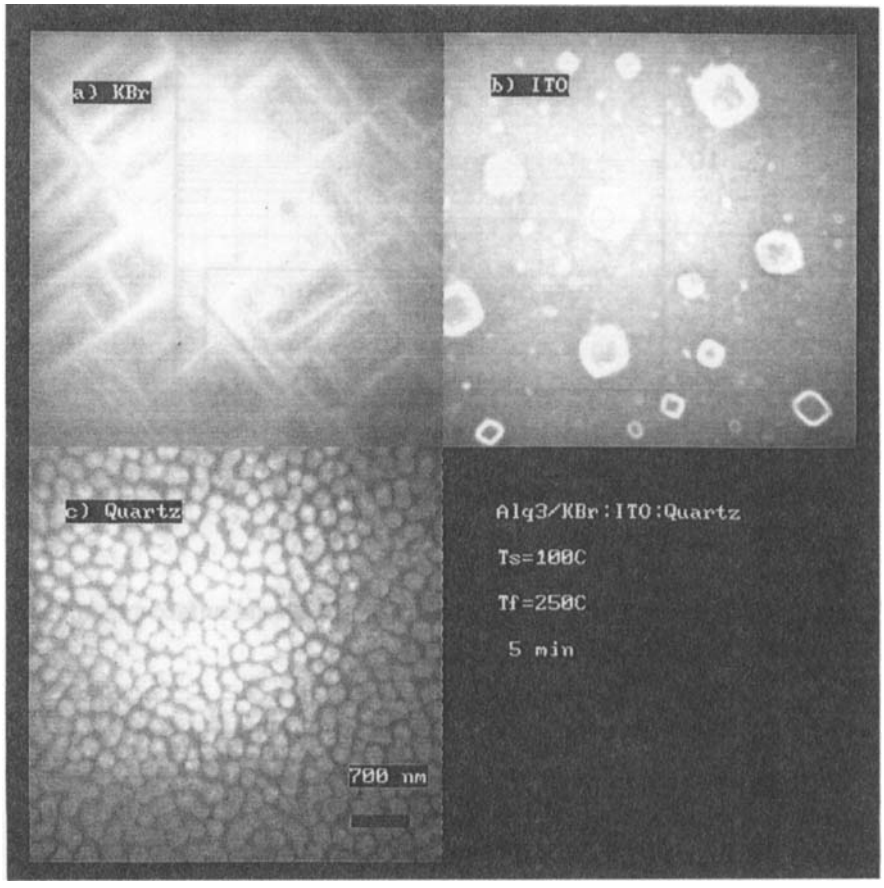

FIGURE 2 Typical electron micrographs of thin films of Alq3 formed on KBr (a), ITO (b) and quartz plate (c) kept at 100 °C.

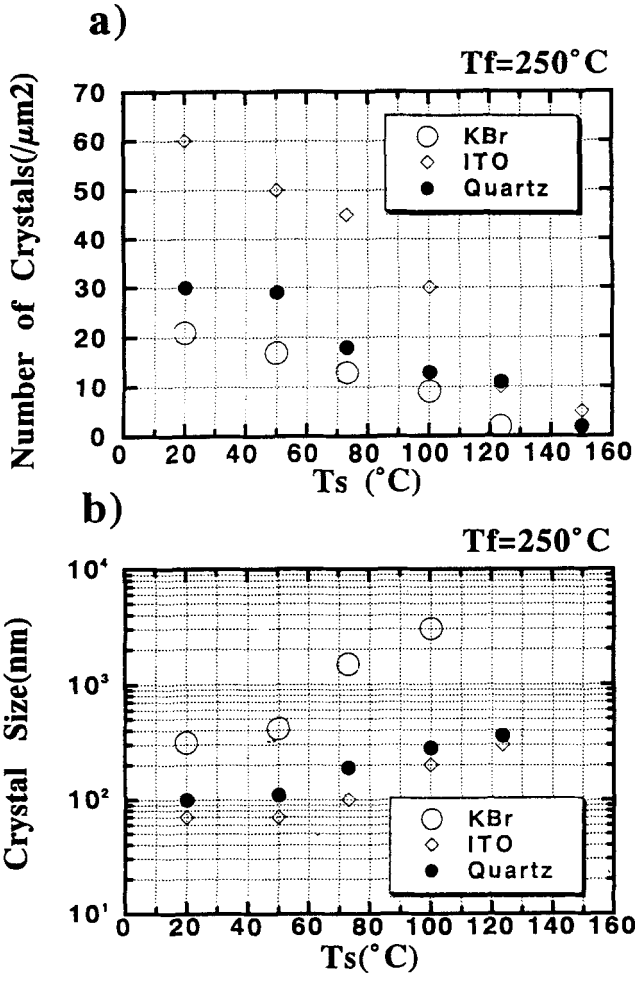

FIGURE 3 Dependence of the number of crystals per unit area ($/\mu m^2$) (a) and the crystal size (nm) (b) on the substrate temperature (*Ts:* °C).

TABLE 1 Thermodynamic parameters for crystal growth and surface migration of Alq3 molecules on KBr, ITO and quartz plate.

Substrate	KBr	ITO	Quartz Plate
ΔE			
Crystal Growth (ΔE_{CG})	26.9	14.3	12.9 kJ/mol
Surface Diffusion (ΔE_D)	9.46	9.64	9.10 kJ/mol

Table 1 exhibits these values, which were less than the enthalpy of fusion and decreased single crystal, polycrystal and amorphous in order as the physical properties of substrate. Especially smaller values on ITO and quartz plate compared with that on KBr represents that although molecules could be adsorbed at everywhere they reached, they would be re-evaporated from the surface at higher *Ts*.

The number of crystals per unit area (n: /μm^2) can relate with the following parameters: the inverse of n corresponds to the area occupied by one crystal, in which molecules around the crystal gather to form larger island crystal, and the square-root inverse of n is the diffusion length of molecules on the substrate surface. In the last one second before finishing the evaporation, deposited molecules migrate on the surface and might be absorbed into the stable crystal. Figure 4 shows the dependence of $1/\sqrt{n}$ on the inverse of Ts. From the slopes in Fig. 4 the activation energies for surface diffusion (ΔE_D) were estimated 9.46 kJ/mol on KBr, 9.64 kJ/mol on ITO and 9.10 kJ/mol on quartz plate, as listed in Table 1. They are same order as ΔE_{CG} and by three times than the adsorption energies of molecules on these substrates.

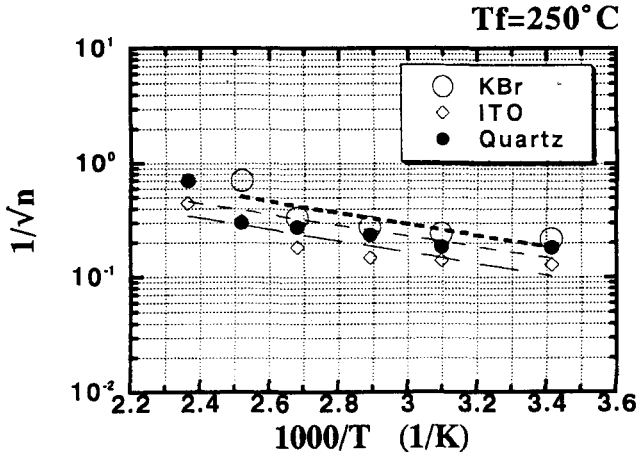

FIGURE 4 Dependence of the square-root inverse of number of crystals per unit area ($1/\sqrt{n}$) on the inverse of the substrate temperature ($1/Ts$).

One of authors have investigated the growth mechanism of long chain molecules such as calcium stearate ($CH_3(CH_2)_{16}$ COO)$_2$Ca) on KCl, mica and amorphous carbon film[4]. The activation energies for crystal growth and surface diffusion on KCl were 87 and 44 kJ/mol, respectively, while the enthalpy of fusion for thin film was 164 kJ/mol. These difference would be led from both the molecular shape and the interaction between molecules.

4. CONCLUSION

It has been, for the first time, found the quantitative values for crystal growth and surface migration of functional dye. Alq3 grew epitaxially on KBr and the activation energies for crystal growth and surface diffusion are half of the enthalpy of fusion. On the other hand, it form hemisphere islands on ITO and quartz plate. Thin film on the substrate surface without any structure has small dependence on the deposition conditions such as the temperature of substrate and furnace.

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