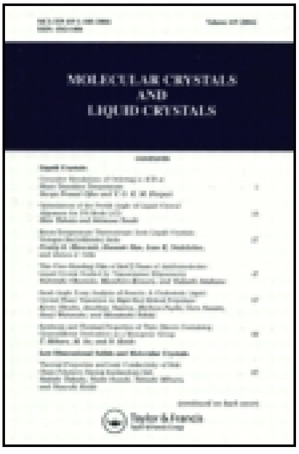

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Anisotropic Photoluminescence from Alq3 and TPD Films on Solid Substrates

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ANISOTROPIC PHOTOLUMINESCENCE FROM Alq3 AND TPD FILMS ON SOLID SUBSTRATES

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Abstract To fabricate "polarized" electroluminescence (EL) devices as a next generation, the growth mechanism of dye materials on several substrates, KBr, KCl, indium tin oxide (ITO) and quartz plate (fusued silica glass) was characterized by TEM and SEM to control the molecular orientations in films. The qualitative analysis of photoluminescence (PL) from Tris(8-hydroxyqunoline) aluminum (Alq3) films epitaxially grown on KCl was done to confirm successively the anisotropic emission.

1.INTRODUCTION

It has been attended to organic electroluminescent (EL) devices or light emitting diodes (LED) to be employed not only as a back light of liquid crystal display but also as future devices for optical communication. The key materials for organic EL devices are Tris(8-hydroxyqunoline) aluminum (Alq3) and triphenyl-diamine (TPD) [1,2]. The molecular structures and device setup are shown in Fig. 1.

There are few works concerning of aggregation mechanism of such compounds on an indium-tin oxide (ITO) [3-7], because most of devices were fabricated as an amorphous state. Although thin films on ITO were amorphous just after prepared, it was found that they tended to coagulate each other to change to crystals. Such phenomena should led to break the device properties.

As for the back light of liquid crystal display, if the polarized illumination had been achieved, it should be neglected the polarized filter, which decreases the brightness by a half of intensity from the back light. Moreover, the principle of "luminescence" and the function of EL from organic dyes or their assemblies should be led from the consideration about polarized photoluminescence. Recently it has been reported that the devices consisting of elongated polymer film with dyes or surface rubbed dye film were emitted the polarized EL [8,9].

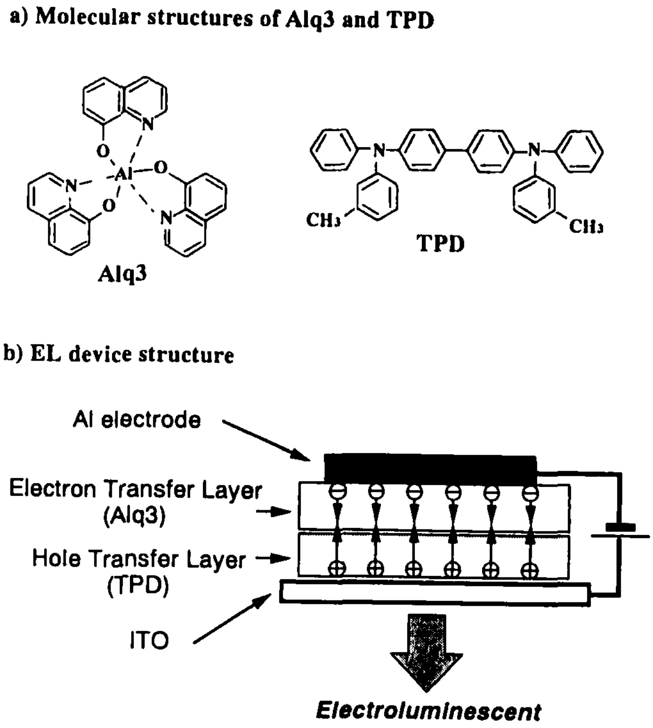

Fig. 1 Molecular structures of Alq3 and TPD (a) and a layer structure for EL device (b).

We have investigated thin film formation mechanism of Alq3 and TPD on several crystal surfaces [3,4]. In these studies we have evaluated the growth rate of molecular crystals and the surface diffusion length of molecules on several kinds of substrates; KBr, ITO, quartz plate (fused silica plate) and slide glass plate. Vacuum-deposited films were characterized by using transmission electron microscope (TEM) and scanning electron microscope (SEM) to measure the size and density of small crystals depending both on the temperatures of furnace and substrate, and on the deposition time. It was found that they tended to grow epitaxially on the crystal surface like alkali halide to align the molecules along the array of anions or cations on the substrate surface.

This work will present the growth mechanism of the molecular assemblies of Alq3 and TPD on ITO and the anisotropic photoluminescence in Alq3 film having controlled molecular orientation.

2. EXPERIMENTALS

Alq3 and TPD powders were set in a quartz tubes coiled by W wire. The tube has a diameter of 10 mm and a length of 80 mm. The directionally controlled molecular beam could be obtained so that the tube is considered as a Knudsen-cell (K-cell). The substrates used here were air-cleaved (001) planes of KCl and KBr, indium tin oxide (ITO), quartz (fused silica glass) and slide glass plate. After being preheated at 300 °C in a pressure of 10^{-7} Torr (10^{-4} Pa), the substrates were maintained at 20, 50, 74, 100 and 120 °C. Powder sample was sublimed from K-cell kept at 200 or 250 °C for 5 - 60 min. Fine Cu-Constantan thermocouple with a diameter of 50 μm was inserted into the K-cell and directly measured the sample temperature during deposition. In this experiment the temperatures of K-cell (T_f) and substrate (T_s) were precisely controlled within ± 2 °C.

Thin films formed on the substrates were covered by either plasma polymerized carbon or osmium in D.C. glow discharge by using NL-OP80-NS, Nippon Laser and Electric Laboratory [10]. The plasma polymerized films were a mixture of methane (CH_4) and ethylene (C_2H_4) gases, and osmium tetraoxide (OsO_4), respectively. The carbon-coated films were stripped from the substrate on the water surface to be picked up by copper grids. The plasma polymerized osmium film was conductive so that it could be observed the surface morphology of films by SEM. TEM and SEM used here were Zeiss CEM-902 and TOPCON DS-720, respectively.

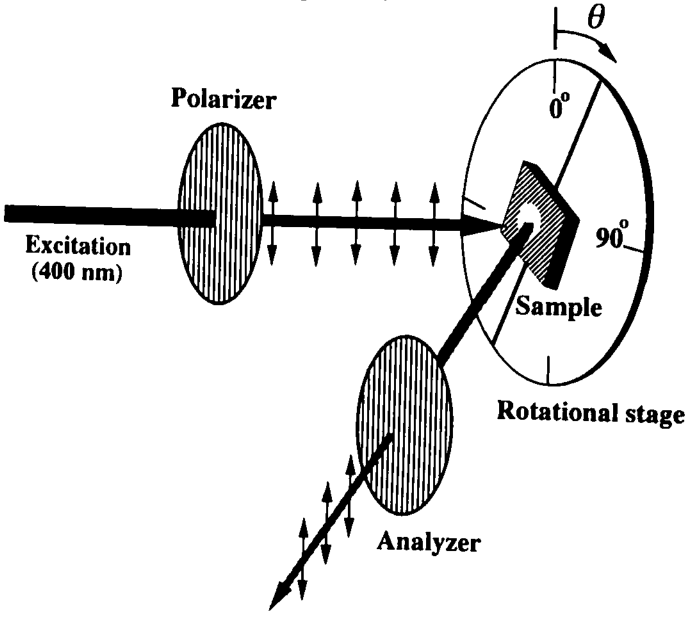

Figure 2 Geometrical setup of photoluminescence measurement from Alq3 films formed on solid substrates.

Thick films formed on quartz were characterized by RIGAKU RAD-C powder diffractometer system at room temperature.

Anisotropic optical properties were measured by JASCO FP-777 Spectrometer. The emission by using polarized excitation illumination with wavelengths of 400 nm for Alq3 and 375 nm for TPD was characterized by the detector after passing through the parallel polarizer to the incident light. The dependence of the photoluminescence on the rotation angle of sample with respect to one of the epitaxial directions of thin films. The geometrical setup of the measurement is illustrated in Fig. 2. The polarized excitation light was illuminated the sample with an angle of 90° and the emission was detected at an angle of 45° with respect to the sample surface. The angular dependence of PL on the sample rotation was characterized.

3. RESULTS AND DISCUSSION

Typical film morphologies of Alq3 and TPD formed on KCl are shown in Figs. 3(a) and (b), respectively. Alq3 films formed on KCl and KBr represented needle crystals along the <110> directions of the substrate surface to grow epitaxially, as shown in Fig. 3(a). Films of Alq3 on ITO and quartz, and TPD on these substrates, however, tended to form molecular aggregates with hemisphere shape, as shown in Fig. 3(b). These sizes of aggregates and distances between adjacent islands depended on the deposition condition. With increas-ing T_S and decreasing T_f, the aggre-gate size tended to increase and the density per unit area tended to de-crease [3,4].

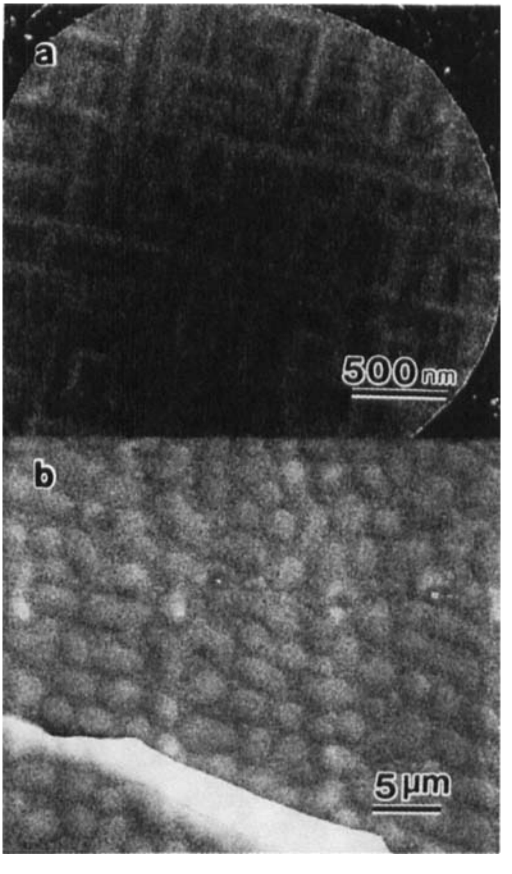

Figure 3 TEM image of Alq3 film (a) and SEM image of TPD film (b) formed on KCl substrate.

No electron diffraction spots from all of those films could be observed so that they should have less crystallinity. Since thick samples on Alq3 and TPD on ITO and quartz had also no characteristic X-ray diffraction peaks, they should be macroscopically amorphous.

Thin films of Alq3 and TPD with a thickness of 20 nm formed on KCl substrates were characterized about the anisotropic optical features. Only the anisotropic PL for Alq3 films could be observed, as shown in Fig. 4. Although very weak PL anisotropy in TPD films on KCl could be detected, it is caused from the less ordering of molecular alignment in the film. Surely it might be proved that anisotropic molecular arrangement should exhibit the anisotropic optical features. Unless no certification in crystal structure and molecular arrangement in thinand film has been done, dye molecules should arrange along the <110> axes of the (001) surface. The relationship between molecular orientation and the surface structure should be anisotropic so that these anisotropic molecular arrangement should be due to such anisotropic optical properties. Whether the surface modification of ITO substrate or single crystalline conductive films as a substrate would promise the polarized emission in organic EL devices.

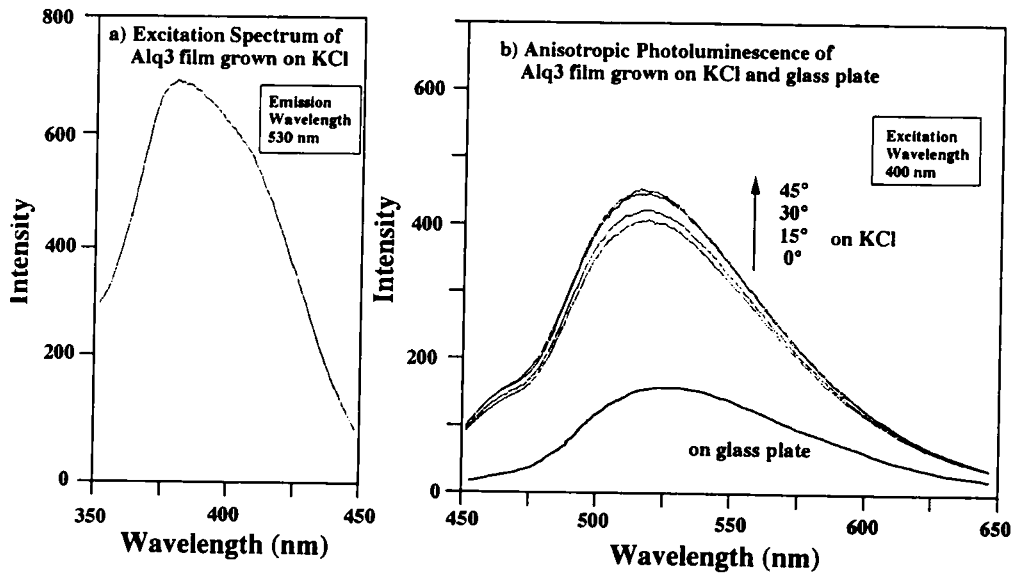

Figure 4 Excitation spectrum of Alq3 film formed on KCl with a emission wavelength of 530 nm (a) and photoluminescence (PL) of it excited at 400 nm (b). The PL spectrum from the film on glass plate was inserted in the figure.

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