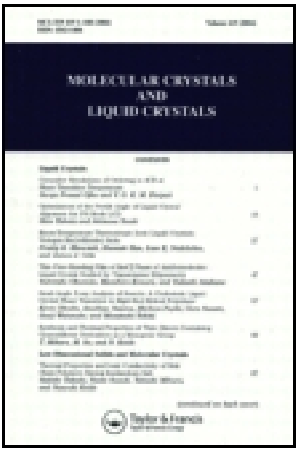

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STUDY OF INTERFACIAL DEGRADATION AND MORPHOLOGICAL CHANGE OF THE VAPOR-DEPOSITED BILAYER OF ALQ3 / TPD FOR ORGANIC ELECTROLUMINESCENT DEVICES BY AFM AND PL TECHNIQUE

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Abstract The morphological change of vapor-deposited films of TPD (N, N'-diphenyl-N, N'-bis-(3-methylphenyl)-[1,1'-biphenyl]-4,4'-diamine) and Alq3 (Tris-(8-hydroxyquinoline) aluminum) and the interfacial degradation of Alq3/TPD bilayer were characterized by atomic force microscopy (AFM) and fluorescence spectroscopy, respectively, in the temperature range from room temperature to 80 °C under an ambient atmosphere. The TPD and the Alq3 film are widely used as a hole transport and an emitter layer, respectively, in an organic electroluminescent device (an indium tin oxide (ITO) coated glass/TPD/Alq3/metal). As the substrate plate, an ITO coated glass or a slide glass was used in this work.

The relative photoluminescence (PL) intensities of Alq3 to that of TPD in an Alq3/TPD and a TPD/Alq3 bilayer were increased with time. The changes were accelerated with increasing temperature and ascribed to quenching of photo-excited TPD by Alq3 diffusing into the TPD layer.

INTRODUCTION

Electroluminescent (EL) devices based on organic multilayered thin films structure have attracted great attention because of their possible application as large-area light-emitting displays. Tang and VanSlyke[1] demonstrated that the use of a diamine derivative, i.e., N,N'-diphenyl-N,N'-bis-(3-methylphenyl)-[1,1'-biphenyl]-4,4'-diamine (TPD)[2], as a hole transport layer (HTL) for hole injection from an anode into the emitting layer (EML), i.e., tris-(8-hydroxyquinoline) aluminum complex (Alq3)[3,4] significantly improves the efficiency of the EL cell (an indium tin oxide (ITO) coated glass/TPD/Alq3/metal). Accordingly, the stability of the organic heterointerface plays a very important role in improving the efficiencies of the organic multilayered EL devices. However, there is no report on the interfacial degradation of organic layers in EL devices and thus degradation mechanism of the EL devices is not fully understood.

Crystallization of the vapor-deposited TPD film was reported.[5] However, until now TPD has been used most widely as the HTL in organic EL devices due to its high carrier mobility and its amorphous film-forming ability.

In this work, in order to propose the mechanism of interfacial degradation in the EL devices consisting of a TPD and an Alq3 layer, we studied the temperature dependence of the morphology and the photoluminescence (PL) property of the vapor-deposited Alq3/TPD or TPD/Alq3 bilayer as well as the sigle layer of TPD or Alq3 on the substrate in the temperature range from room temperature to 80 °C under an ambient atmosphere. The morphological change was directly observed by atomic force microscopy (AFM). The PL technique such as fluorescence spectroscopy, was utilized as complementary tool to characterize the interface between the TPD and the Alq3 layer.

EXPERIMENTAL

Molecular structures of the organic materials used in this study were shown in Fig. 1.

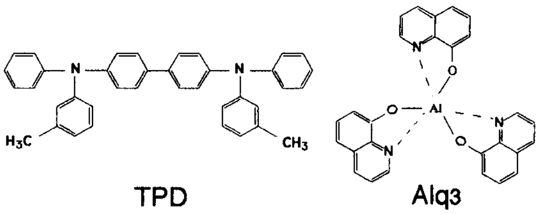

FIGURE 1 Molecular structures of TPD and Alq3.

We fabricated organic thin films composed of different structures on an ITO coated glass or a slide glass plate by means of conventional vacuum deposition under a vacuum of about 10^{-6} Torr. One is a single layer of a TPD or an Alq3 film on the substrate. The other is comprised of a bilayer of an Alq3/TPD or a TPD/Alq3 structure. The thickness of each layer was about 50 nm. The measurements of AFM were carried out with a SEIKO SPA-300 unit controlled with a SPI-3700 controller. Olympus microfabricated triangular Si_3N_4 cantilevers of 100 μm-long with a normal spring constant of 0.09 Nm^{-1} were used. The PL spectra and the PL intensities were measured by a Hitachi 850 fluorescence spectrophotometer with a xenon lamp. The storage temperature of the sample was set in the range from room temperature to 80 °C which is above the glass transition temperature of TPD. All observations were carried out under an ambient atmosphere.

RESULTS AND DISCUSSION

MORPHOLOGY OBSERVATION OF VAPOR-DEPOSITED FILMS BY AFM

We observed the morphological changes of the vapor-deposited TPD or Alq3 single layer film and the bilayered Alq3/TPD film by AFM. A series of AFM images in Fig. 2 illustrate the time dependence of morphology of the vapor-deposited TPD film on the slide glass substrate under an ambient atmosphere at room temperature. They show the change in AFM topographic images (upper) and their cross-sections (lower) of the film with time, from immediately after the deposition to the beginning of the crystallization. All AFM images are the size of 20 x 20 μm^2. White areas correspond to higher parts in the AFM topographic images (upper). An as-deposited TPD film (Fig. 2(a)) exhibited an entirely amorphous and flat surface with average roughness, Ra, of ca. 0.6 nm and its morphology changed gradually even in room temperature. The roughness increased appreciably after 5 ~ 8 h from the deposition (Fig. 2(b)). As time went by, two different

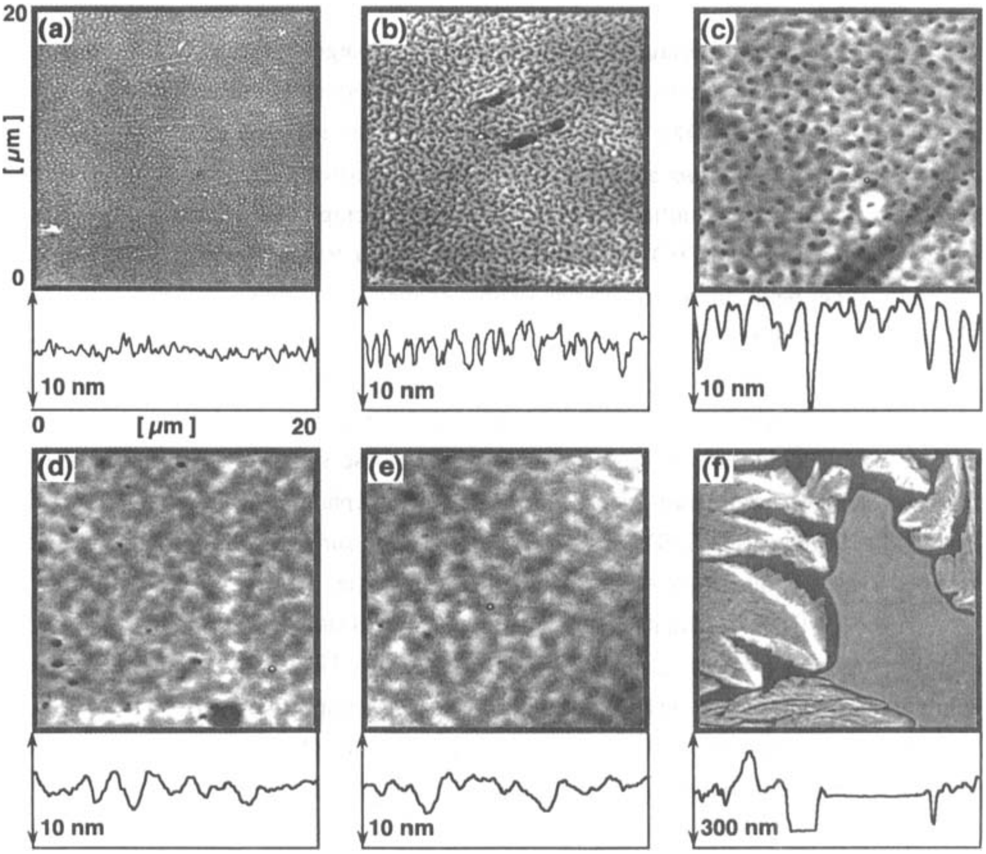

FIGURE 2 AFM images (upper) and cross sections (lower) of the surface change of a TPD film with time under an ambient atmosphere at room temperature.; (a) as-deposited, (b) 5 h, (c) 1 d, (d) 3 d, (e) 7 d (amorphous region of (f)), (f) 7 d. The scan range is 20 x 20 μm^2.

parts appeared in the film. One is deep parts and the other is thick parts as can be seen in a cross section of Fig. 2(c). About a week later, however, the AFM image of the TPD film became distinctive due to partial crystallization as can be seen in Fig. 2(f). Figure 2(e) corresponds the amorphous part in Fig. 2(f) after a week when the crystallization began. There was no remarkable difference between the AFM image of Fig. 2(e) and that of 3 days later (Fig. 2(d)). Along with the crystallization of the TPD film, it is clearly seen from the cross section (lower) of Fig. 2(f) that valleys were also created between crystals. The valley formation was necessary, because the heights of the crystals were higher than that of the as-deposited TPD film. From the cross section of Fig. 2(f), we found that the depth of lowest valleys from the plateau of the amorphous film is nearly equal to the thickness of the as-deposited TPD film itself. It indicates that the bare substrate surface was revealed by the crystallization, which was confirmed by friction force microscopy measurement.[5]

The effect of temperature on the morphology change of the TPD film was also studied by AFM. The crystals of TPD were partially observed within about 12 h at 60 °C and within about 3 h at 80 °C, respectively. With the increase in temperature, the crystallization of TPD was accelerated and started earlier. The most of increasing roughness before the crystallization (Fig. 2(c)) was accomplished within a day at room temperature. In case of a TPD film annealed under higher temperatures at 60, 70, and 80 °C, on the other hand, there was no remarkable change in roughness as long as the TPD film was not crystallized.

Morphology of an overlying Alq3 layer of an as-deposited Alq3/TPD bilayered structure was observed as well as that of an as-deposited Alq3 single layer. Although morphology of these surfaces was more difficult to be observed by AFM because the Alq3 film was scratched more easily by the AFM tip, the morphology was flat and similar to that of the as-deposited TPD (Fig. 2(a)). The small surface roughness can be also ascribed to amorphous nature of the as-deposited Alq3 layer.

Although the Alq3 film itself shows extreme thermal stability for a long term even at a high temperature of 80 °C, morphology of the Alq3/TPD bilayer studied by AFM exhibited the change from the flat to a rough surface within approximately 10 h at 60 °C, 1 h at 70 °C, and 10 min at 80 °C, respectively. The morphological change appeared remarkably and the difference in heights increased with time and temperature.

STUDY OF INTERFACIAL REGION BETWEEN TPD AND ALQ3 LAYERS BY PL TECHNIQUE

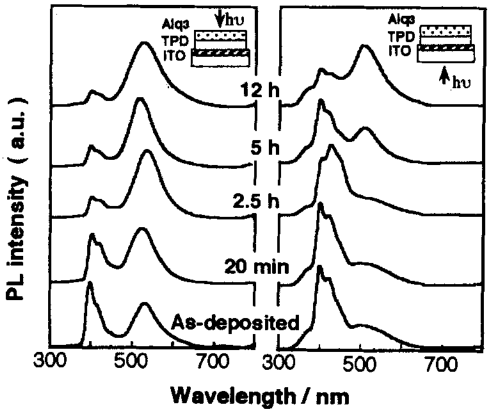

FIGURE 3 Time dependence of PL spectra in the Alq3/TPD bilayer on ITO substrates at 60°C. (a) and (b) represent the direction of incident light from the overlaying Alq3 layer and the ITO substrate, respectively.

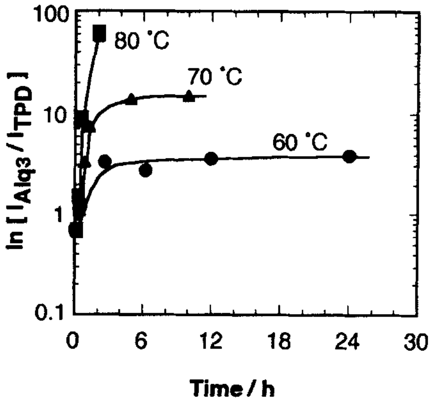

FIGURE 4 Change in relative PL intensity ratios of Alq3 to TPD in the Alq3/TPD bilayer as a function of time at 60, 70 and 80 °C.

Typical PL spectra of a TPD and an Alq3 single layered film show two sharp peaks at 400 and 420 nm for TPD and a broad PL band around 520 nm for Alq3, respectively. For the single layer of TPD or Alq3, no change in the PL intensity was observed with time even at 80 °C.

For the bilayer structures, however, the PL intensities of the constituents were changed with time. Figure 3 displays the time dependence of PL behavior of an Alq3/TPD bilayer on an ITO coated glass substrate kept at 60 °C. The spectra (a) and (b) were recorded under two different illumination modes of a UV excitation beam of 355 nm: for spectra (a) the excitation beam was illuminated from the overlaying Alq3 side, while for spectra (b) from the ITO substrate side, as shown in the insets of Fig. 3. The PL band for Alq3 observed around 520 nm increased with time at the expense of the peak intensity for TPD at 400 and 420 nm independently of the illumination modes. The relative PL intensity of the Alq3 to that of TPD in the spectra, however, was higher in the spectra (a) than that of spectra (b). The difference is ascribed by the filtering effect depending upon the illumination modes.

The change in relative PL intensity ratios of Alq3 to TPD with time at 60, 70 and 80 °C is shown in Fig. 4. The maximum fluorescence intensities of the TPD and the Alq3 bands at around 400 nm and 520 nm were taken as I_{TPD} and I_{Alq3}, respectively. The change with time was accelerated with the increase in temperature. The similar behavior was observed also for a TPD/Alq3 bilayer on an ITO coated glass substrate.

Next, we have to argue the reason why the relative PL intensities were changed with time and why the change was accelerated with the increase in temperature in the bilayer films. The morphological change observed by AFM described above may be one of and possible candidates for the interpretation. But if the crystallization proceeds in the TPD layer and consequently the contact between the TPD and Alq3 layers become worse, we will expect the decrease in the efficiency of energy transfer from excited TPD to Alq3 at the interface between two layers. However, the observation described above was against this expectation. If we assume diffusion of Alq3 into the TPD layer, the observed change in PL spectra will be rationalized in terms of energy transfer from photoexcited TPD to Alq3 diffusing into the TPD layer. The diffusion can be accelerated in general by elevated temperature. This interpretation was confirmed by the fact that efficient energy transfer was observed in a mixed film of Alq3 and TPD which was formed by co-vapor deposition of Alq3 and TPD.[6]

CONCLUSIONS

In order to propose the mechanism of interfacial degradation in the EL devices utilizing a TPD and an Alq3 layer, the temperature and time dependence of morphology and interfacial properties in the vapor-deposited Alq3/TPD bilayer on substrate was studied by AFM and PL technique such as fluorescence spectroscopy.

The experimental results are summarized as follows. The crystallization of TPD film was observed about a week later and accelerated and started earlier with the increase in temperature. PL technique was utilized as a tool for investigation of interfacial change in the Alq3/TPD bilayers. From acceleration of the increase of relative PL intensity of Alq3 to that of TPD in the bilayered structure of Alq3/TPD or TPD/Alq3 with time by increasing temperature, it is concluded that Alq3 acted as a quencher to the photoexcited TPD by mixing of TPD and Alq3 near the interface by diffusion.

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