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TEMPERATURE CHANGE IN STRUCTURE OF BILAYERS OF ALQ/TPD-DOPED POLYCARBONATE FILMS FOR ORGANIC ELECTROLUMINESCENT DEVICES

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Abstract The change of surface and interface in bilayers of Alq (Tris-(8-hydroxyquinoline) aluminum) / TPD (N,N'-diphenyl-N,N'-bis-(3-methylphenyl)-(1,1'-biphenyl)-4,4'-diamine)-doped polycarbonate (PC) films for organic electroluminescent devices was characterized by atomic force microscopy (AFM), SEM, and fluorescence microscopy, in the temperature range from R.T. to 250 °C under the air. As single layer films, the dip-coated TPD-doped PC film on indium-tin oxide (ITO)-coated glass and the vapor-deposited Alq films on various substrates showed good thermal stability compared with the vapor-deposited TPD film itself. However, in the bilayered structure of Alq / TPD-doped PC films, the Alq film as the overlaying layer was deteriorated readily, which was accelerated with increasing temperature and TPD concentration in the TPD-doped PC film.

INTRODUCTION

Electro-conductive organic dyes have been studied extensively, especially in the field of organic photoconductor (OPC). Recently, great progress in organic electroluminescent (EL)[1,2] device was made by fabricating multilayered EL cells with these dyes. However, the EL cells consisting of these dyes still have serious problem due to short lifetimes. The degradation of the cell was mainly originated from the lack of stability of organic films. Until now TPD (N,N'-diphenyl-N,N'-bis-(3-methylphenyl)-(1,1'-biphenyl)-4,4'-diamine)[3] as a hole transport layer (HTL) and Alq (Tris-(8-hydroxy quinoline) aluminum complex)[4,5] as an electron transport and emitter layer (EML) have been most widely used in organic EL devices due to their amorphous film-forming ability. There are very few reports for the stability of metal oxinates in solution[4] and no report on the stability of Alq in solid states like a thin film. We have previously reported that the inter-diffusion of the components in the vapor-deposited bilayer of Alq / TPD occurred in

their interfacial region with time and increasing temperature.[6~8] The diffusion started earlier than crystallization of the TPD film.[7,9] In addition, it was also found that the crystallization of Alq in the interface of the bilayer or in the co-deposited single layer proceeded before the crystallization of TPD.[10]

In this study, first, the thermal stability of vapor-deposited Alq thin films and their dependence on various substrates will be described. In addition, the enhanced thermal stability of the HTL by TPD-doping in inert polymer will be demonstrated. The concept of molecularly doped polymers (MDP's) has found important application in transporting charges in OPC and organic EL devices[11], because the materials allow measurements of charge transport in broader ranges of electric field, temperature, and concentration than those in any other transport materials studied so far.

A second focus is the effect of molecular diffusion in the interfacial region between Alq and TPD-doped polymer film on crystallization.

EXPERIMENTAL

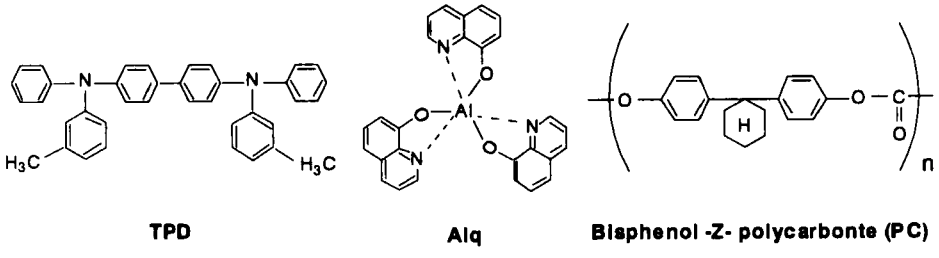

FIGURE 1. Molecular structures of TPD, Alq, and PC used in this study.

Molecular structures of TPD, Alq, and bisphenol Z polycarbonate (PC) ($\bar{M}v$ = 50,200) used in this study are shown in Fig. 1. PC is optically and electronically inert, and has a good film forming property with a high glass transition temperature (Tg) of 180 °C.

The three different doping-TPD concentrations of the solid solution, i.e., 30, 50, and 70 wt.%, were examined. The thickness of the TPD-doped PC films was determined to be about 50 nm with a Taylor-Hobson profile meter. A dichloroethane solution containing proper amounts of TPD and PC filtered with 2 μm-diameter pores was dip- or spin-coated onto a cleaned optical glass slide or an indium-tin oxide (ITO)-coated glass substrate. After sufficient evaporation of solvent under vacuum for several hours, Alq films were vapor-deposited on the TPD-doped PC films on ITO substrates under a

vacuum of about 3 x 10^{-6} Torr. The Alq thin films were also deposited directly on various substrates, such as glass, ITO, quartz, and oxidized silicon wafer (100) plates which were kept at R.T. during the deposition. The deposition rate of Alq was about 2 ~ 3 Å·s^{-1} and the thickness of films was about 50 nm.

The storage condition of the films was in the temperature range from R.T. to 250 °C under the air.

Characterization of surfaces of the organic films was carried out by atomic force microscopy (AFM), SEM, and fluorescence microscopy. The measurements of AFM of the films 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. Because the Alq film was scratched easily by an AFM tip under contact mode AFM, Olympus microfabricated cantilevers with a resonance frequency of 142 kHz and a normal spring constant of 15 Nm^{-1} were used to characterize the surfaces of the Alq thin films by non-contact mode AFM. All observations were carried out under an ambient atmosphere.

Differential scanning calorimetry (DSC) measurements were also made on some of the thick samples fabricated on slide glass by spin coating with concentrated solutions.

RESULTS AND DISCUSSION

Observation of Vapor-Deposited Alq Thin Films by Fluorescence Microscopy and Non-Contact Mode AFM

The photoluminescence (PL) emission from Alq film is yellowish-green around 520 nm under UV excitation of 355 nm. From fluorescence microscopic observation under UV excitation of 365 nm, it was found that the vapor-deposited single layered film of Alq is not crystallized even for more than a few years under an ambient atmosphere.

Figure 2 shows the change in PL images of the Alq films on various substrates kept at 100 °C for 2 days (upper images) and at 250 °C for 20 minutes (lower images). As the substrates, ITO-coated glass(a, b), optical slide glass(c, d), quartz(e, f), and oxidized silicon wafer(g, h) were used. At 100 °C, the Alq film underwent some changes. However, it was very difficult to observe crystallization except the film on quartz in which partial crystallization was observed. The films emitted fluorescence evenly on the other substrates. At the higher temperature of 250 °C, crystals of Alq were observed readily within 20 minutes except the film on the ITO-coated substrate of Fig. 2(b). The shape of crystals strongly depended on the kinds of the substrates. The crystals emitted more strongly than the uncrystallized parts.

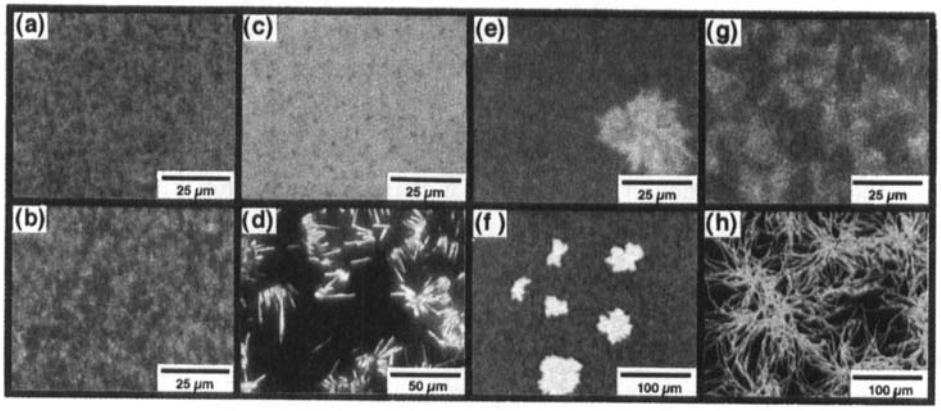

FIGURE 2 PL images of vapor-deposited Alq thin films on various substrates kept at 100°C for 2 days (upper images) and at 250 °C for 20 min (lower images), respectively. Substrates: (a), (b), ITO-coated glass; (c), (d), optical glass; (e), (f), quartz; (g), (h), oxidized silicon wafer. See Color Plate V.

Non-contact AFM images (upper) and their cross-sections (lower) of a vapor-deposited Alq film on ITO-coated glass are shown in Fig. 3. Figures 3(a) and 3(b) correspond to the as-deposited film and the annealed one at 100 °C for 10 hours, respectively. The size of the AFM images is 10 x 10 μm^2. The brighter areas correspond to the higher parts in the AFM topographic images. The as-deposited film exhibited an entirely flat surface with almost the same roughness as the ITO substrate surface. At 100 °C, however, the morphological change appeared and the roughness was more than 3 times that of the as-deposited one, as can be seen in Fig. 3(b).

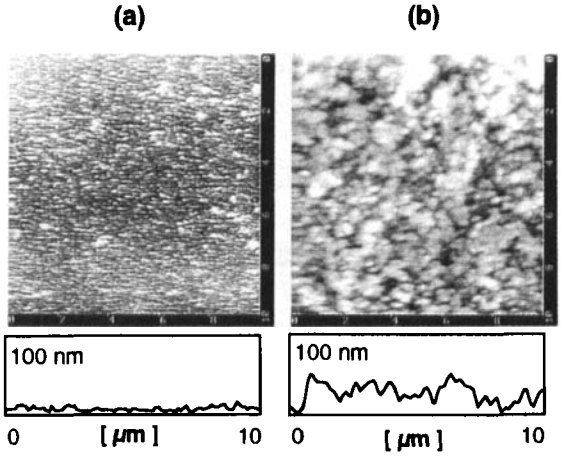

FIGURE 3 AFM images (upper) and cross sections (lower) of the surfaces of an Alq film deposited on an ITO-coated glass plate. (a) As-deposited, (b) after 10 h at 100 °C under the air.

It was extremely difficult to observe partially crystallized Alq films because the films were scratched easily by the AFM tip even in the non-contact mode AFM. Figure

4 shows the 15th scanned AFM image of a crystallized part of the partially crystallized Alq film on a quartz plate kept at 100 °C for 4 days. The first scanned topographic AFM image was not clear because the surface of Alq crystals was covered with soft materials, which could be scratched easily. It was possible to observe the crystals of Alq by scratching technique with AFM tip. After the 15th scan, the needle-type crystals of Alq appeared clearly on the topographic AFM image as shown in Fig. 4.

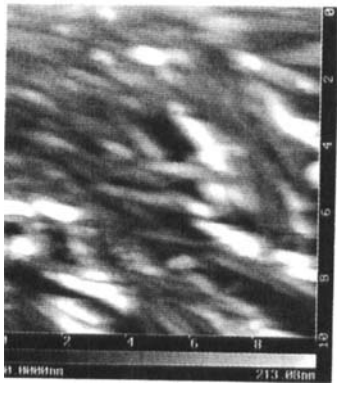

FIGURE 4 The 15th scanned non-contact AFM image of a partially crystallized Alq film on a quartz plate kept at 100 °C for 4 days. The scan area is 10 x 10 μm^2.

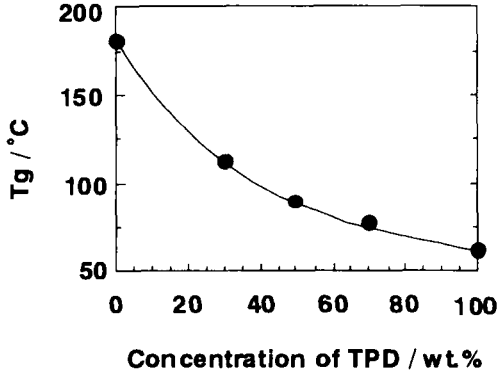

FIGURE 5 Glass transition temperatures (Tg) as a fuction of TPD doping level in PC binder.

Observation of Bilayers of Alq/TPD-doped PC Films by SEM, AFM, and Fluorescence Microscopy

Figure 5 shows the dependence of Tg on TPD concentration in TPD-doped PC thick films prepared by spin coating. The dispersed TPD molecule is compatible with the binders in the full doping range. The plot shows typical behavior of Tg depression with increasing TPD concentration, i.e., with increasing the content of PC, Tg increased.

From observation of AFM and fluorescence microscopy (365 nm excitation), it was found that the surfaces of TPD-doped (30, 50, 70 wt. %) PC films maintained the same AFM and PL images as the as-prepared one even at 100 °C for 3 days, as can be expected from the DSC result of enhanced thermal property. Figures 6(a) and 6(b) show topographic AFM images of partially crystallized TPD film stored for a week at R.T.[7,9] and a heat-treated TPD (70 wt. %)-doped PC film at 80 °C for 18 hours, respectively. Contrary to the unstable TPD pure film, there was almost no difference in flat surface

between the as-prepared TPD-doped PC and the annealed one. At 120 °C, however, the TPD crystals partially appeared on the TPD doped film surface.

From the results of a previous study[10], it was shown that the stable Alq film was deteriorated by molecular diffusion in the interfacial region. If we use the thermally stabilized TPD-doped PC film as an underlying layer, it is expected that the stability of the overlaying Alq film will be also increased.

Figure 7 displays the PL images of bilayered Alq / TPD-doped PC films with the three different concentrations of TPD dip-coated on ITO substrates. The samples were kept at 80 °C for 18 hours. The dopant contents of TPD were 70 % (a), 50 % (b), and 30 % (c). In spite of the enhanced stability of TPD-doped PC films, the PL images were

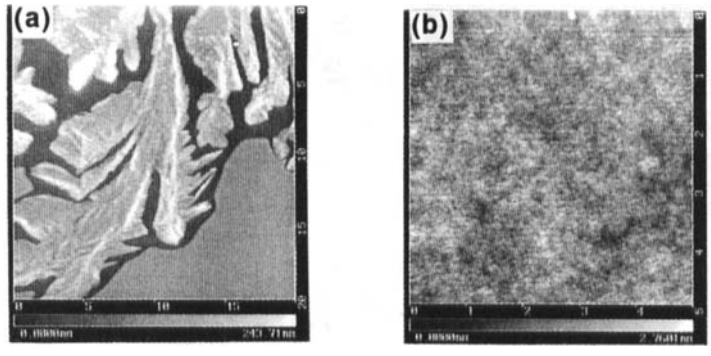

FIGURE 6 Topographical AFM images of (a) the partial crystallized TPD (20 x 20 μm^2) stored at R.T. for a week and (b) the heat-treated TPD (70 wt.%)-doped PC film (5 x 5 μm^2) at 80 °C for 18 h.

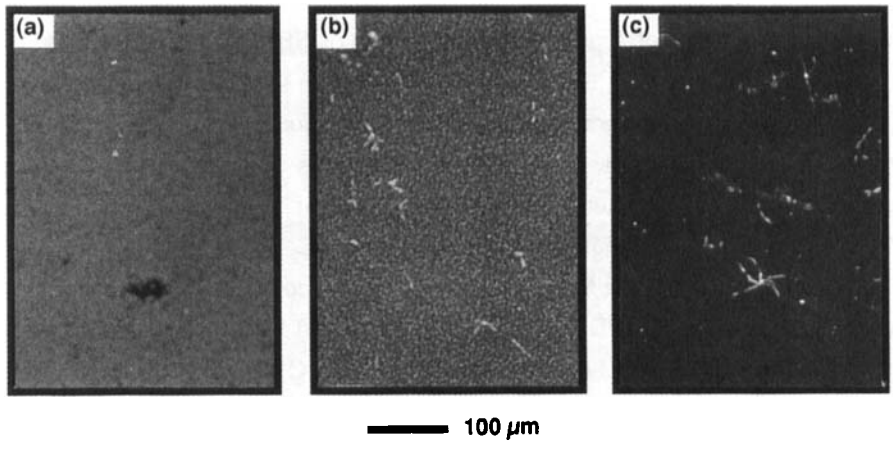

FIGURE 7 PL images of the bilayers of Alq/TPD-doped PC films with different doping concentrations on ITO substrates kept at 80 °C for 18 h. TPD contents (wt.%) : (a) 70 %, (b) 50 %, (c) 30 %. See Color Plate VI.

quite characteristic as follows. With increasing TPD concentration, the numbers of the bright yellowish-green spots or clusters observed in the PL images increased. The film with lower concentration of TPD showed that appearance of the bright yellowish-green spots was retarded relatively.

The distribution of the bright yellowish-green spots in the PL images can be related to the state of TPD dispersion in PC. If TPD is phase separated in the MDP system, distribution of the spots will be inhomogeneous. However, the spots are seen all over the place in the same density. Therefore, it is considered that TPD molecules were uniformly dispersed in the matrix polymer without phase separation between TPD and PC. In addition, the retardation observed in the lower concentration of TPD can be related to the higher Tg and thus the higher thermal stability of the MDP. In other words, the interfacial stability was increased in the bilayer system with the MDP in comparison with that with the TPD underlying layer. But, the lower hole transport is expected in the MDP and thus we can not predict only from these results which system is preferable in terms of the total stability in the EL cell.

Figure 8 shows SEM micrographs of the surfaces of (a) an annealed single layer of Alq and (b, c) overlaying Alq films deposited on 70 wt.% TPD-doped PC films as bilayers, on ITO substrates. The Alq film itself on ITO substrate was extremely stable (Fig. 8(a)) after 18 hr at 80 °C, while the one deposited on the TPD-doped PC films was crystallized in the same condition (Fig. 8(b)). Figure 8(c) displays the SEM image of the

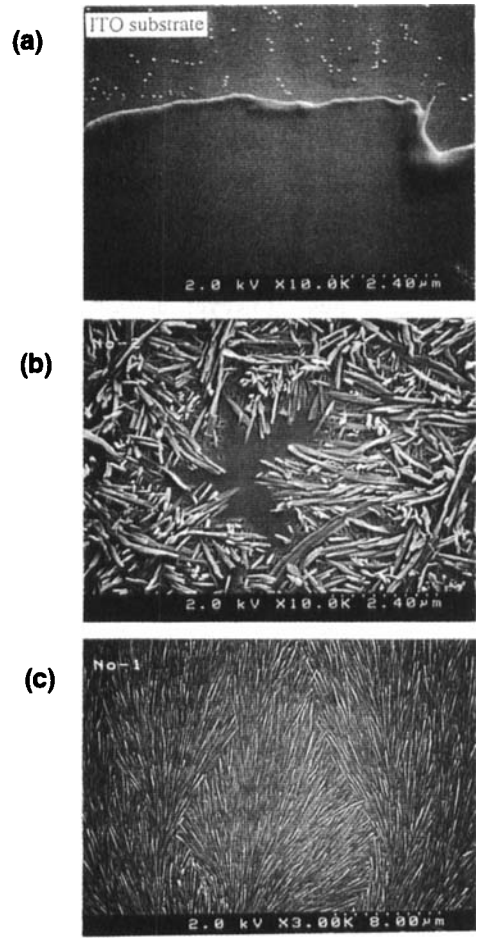

FIGURE 8 SEM micrographs of (a) the stable Alq film, (b) the bilayers of Alq/TPD (70 wt.%)-doped PC films on ITO substrate kept at 80 °C for 18 h, and (c) that kept at 100 °C for 18 h.

bilayer kept at 100 °C for 18 hours. With increasing temperature, the crystallization was accelerated and needle-type crystals on the Alq film surface grew and well oriented to one direction, as shown in Fig. 8(c).

Assignment of the crystal phase to Alq was based upon the similarity of the shape of the needle-type crystals observed here to those observed in the single component films shown in AFM image of Fig. 4.

CONCLUSIONS

The crystallization of vapor-deposited Alq films on various substrates and on TPD-doped PC films was characterized by AFM, SEM, and fluorescence microscopy in the temperature range from R.T. to 250 °C.

The vapor-deposited Alq film as a single layer showed high thermal stability on various substrates. However, in the bilayered structure of Alq / TPD-doped PC, the Alq film as the overlaying layer was crystallized. The crystallization of Alq was accelerated with increasing temperature and TPD concentration in the MDP systems. The latter effect can be related to the interaction of Alq with TPD in the TPD-doped PC film.

It was found that compatibility between the binder polymer and TPD affected the interfacial stability between the EML and the HTL in multilayered organic EL devices consisting of MDP.

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