Chemistry Letters 1995

Study of Interfacial Degradation of the Vapor-Deposited Bilayer of Alq3/TPD for Organic Electroluminescent (EL) Devices by Photoluminescence

Eun-Mi Han, Lee-Mi Do, Noritaka Yamamoto, and Masamichi Fujihira*
Department of Biomolecular Engineering, Tokyo Institute of Technology, Nagatsuta, Midori-ku, Yokohama 226

(Received October 25, 1994)

The interfacial change of a vapor-deposited TPD (N, N'-diphenyl - N, N' - bis - (3-methylphenyl) - [1,1'-biphenyl] -4,4'-diamine) and Alq3 (Tris-(8-hydroxyquinoline) aluminum) bilayer film was characterized by photoluminescence (PL) 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 organic electroluminescent (EL) devices (ITO/TPD/Alq3/metal). As the substrate plate, a slide glass was used in this work.

In an Alq3/TPD bilayered structure, two PL bands from Alq3 and TPD were observed and the relative PL intensity of Alq3 to that of TPD was increased with time. The change was accelerated with increasing temperature. In case of a co-deposited single layer of TPD and Alq3, an Alq3 PL band predominated and, in addition, the PL intensity was not changed remarkably with increasing temperature. These results support that the PL change observed for the Alq3/TPD bilayered structure is ascribed to quenching of photo-excited TPD by Alq3 as a result of diffusion of the components.into each other layer.

Electroluminescent (EL) devices based on organic multilayer thin films[1,2] have attracted great attention because of their possible application as large-area light-emitting displays. The organic EL devices have an advantage over inorganic ones in being driven by low dc voltage, highly luminescent, and multicolor emissive by their molecular design. But they are still far from practical use because of the lack of running stability and durability. As the origin of the degradation of such organic EL devices, it is assumed that some of failure is attributed to the degradation of both hole and electron injecting contacts[1] and the deterioration of organic layers[3,4] and metal electrodes themselves.[5] However, the degradation mechanism is not fully understood and there is no report on the interfacial degradation of organic layers in EL devices.

Many researchers took the focus upon further improvement in organic materials with the necessary EL properties in order to overcome these shortcomings and to increase EL efficiency and stability. However, until now TPD (i.e., N,N'-diphenyl-N,N'-bis-(3-methylphenyl)-[1,1'-biphenyl]-4,4'-diamine)[6] has been used most widely as the hole transport layer (HTL) in organic EL devices due to its high carrier mobility and amorphous film-forming ability, although crystallization of the TPD layer under continuous operation or storage was reported.[3,4] As the best emitting layer (EML) for use in organic EL devices, Alq3 (i.e., Tris-(8-hydroxyquinoline) aluminum complex)[7,8], which belongs to a well-known metal chelate and one of the most fluorescent and stable molecules, has been used.

It has previously been suggested that the EL efficiency is controlled by the injection of holes from the HTL into the EML in layered organic EL devices (an indium-tin oxide (ITO)-coated glass/TPD/Alq3/metal).[1] Accordingly, the stability of the organic heterointerface plays a very important role in improving the efficiencies of the organic multilayered EL devices.

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 PL properties of the vapor-deposited Alq3/TPD bilayer on the substrate in the temperature range from room temperature to 80 °C. The PL technique such as fluorescence spectroscopy was utilized as a tool to characterize the interface between the TPD and the Alq3 layer.

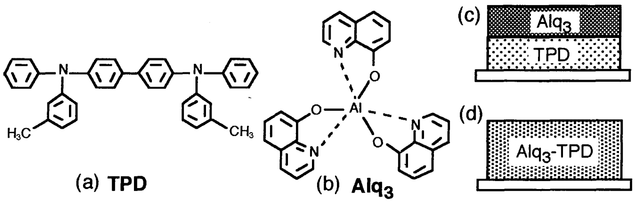

Figure 1. Molecular structures and cross-sectional views of samples studied.

Molecular structures of the organic materials and cross-sectional views of film configuration used in this study are shown in Fig. 1. For the investigation of the interfacial changes in the organic EL devices, we fabricated organic thin films composed of different structures on slide glass plates. One consists of a bilayer of Alq3/TPD film on the substrate (Fig. 1(c)). The other is a single layer of a TPD and Alq3 mixed film which was fabricated by co-deposition using two different sources (Fig. 1(d)). The organic thin films were grown by means of conventional vacuum deposition under a vacuum of about 10^{-6} Torr. Total thicknesses of the films regardless of their structures were about 100 nm and the thicknesses of the TPD and the Alq3 film in the bilayer were about 50 nm, respectively. The storage temperature was changed from room temperature to 80 °C which is above the glass transition temperature (Tg) of TPD. The PL spectra and the PL intensities were measured by a Hitachi 850 fluorescence spectrophotometer with a xenon lamp. All observations were carried out under an ambient atmosphere.

Typical PL spectra of a TPD and an Alq3 single layered film show two sharp PL 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 2 displays the time dependence of PL behavior of an Alq3/TPD bilayer on a glass substrate kept at 60 °C. The spectra were recorded under a UV excitation beam of 355 nm. 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.

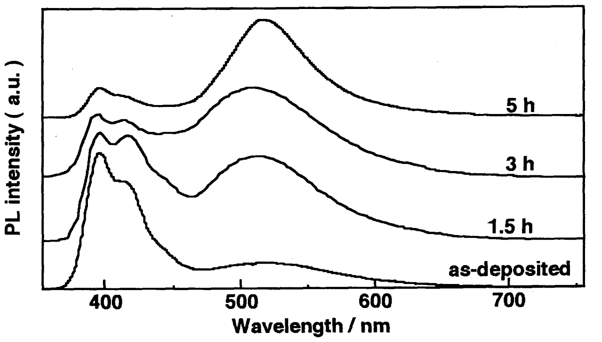

Figure 2. Time dependence of PL spectra in Alq$_3$/TPD bilayer on a glass substrates at 60 °C.

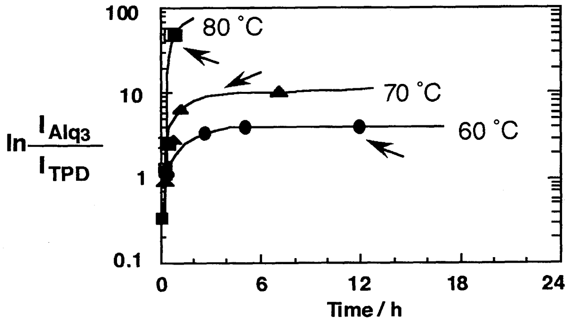

Figure 3. Ratio of PL intensities of TPD and Alq3 in the bilayered structures of Alq3/TPD on a glass substrate as a function of time at 60, 70, and 80 °C.

Figure 3 shows the change in relative PL intensity ratios of Alq3 to TPD with time at 60, 70, and 80 °C. The maximum fluorescence intensities of the TPD and the Alq3 band at around 400 nm and 520 nm were taken as I_{TPD} and I_{Alq3}, respectively. The change with time accelerated with the increasing temperature can be seen in Fig. 3. The arrows in Fig.3 show the times required for crystallization in the single layered TPD film at each temperature. The effect of temperature on the morphology change of the TPD film was studied by atomic force microscopy (AFM). With the increase in temperature, the crystallization of TPD was accelerated and started earlier. As can be seen in Fig. 3, the increasing PL intensity of Alq3 relative to that of TPD was occurred earlier than the crystallization of the single layered TPD film. From this observation, it can be concluded that the change of PL behavior of Alq3/TPD bilayered film was originated from some process occurring prior to the crystallization.

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. If we assume that each of the components of the bilayer diffuses into the other layer, the observed PL change will be rationalized in terms of energy transfer. In addition, the diffusion is generally accelerated by elevated temperature. This interpretation was further 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.

Figure 4 displays the concentration dependence of PL behavior of the co-deposited single layered film of TPD and Alq3. The concentration ratios of Alq3 to TPD in the co-deposited films were 1 : 50, 1 : 10, and 1 : 1 in the spectra in Fig.4(a), (b), and (c), respectively. The spectrum for the as-deposited Alq3/TPD bilayer shown in Fig. 2 was also replotted as Fig. 4(d) for comparison.

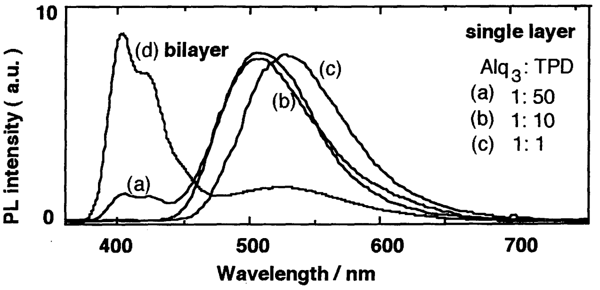

Figure 4. PL spectra of a co-deposited single layer consisting of TPD and Alq$_3$ at various concentration ratios (a~c) and a bilayered Alq$_3$/TPD film (d). ; (a) Alq$_3$:TPD = 1:50, (b) Alq$_3$:TPD = 1:10, (c) Alq$_3$:TPD = 1:1, (d) an Alq$_3$/TPD bilayer.

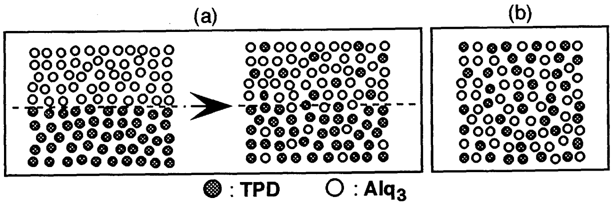

Figure 5. Scheme of (a) diffusion in a bilayered Alq$_3$/TPD and (b) a stable co-deposited single layer of TPD and Alq$_3$.

In case of the co-deposited films, the PL behavior was quite characteristic. There was an undetectable or an extremely weak PL peak for TPD in spite of their larger quantities in the co-deposited films. The behavior was independent of temperature.

From the comparison between the remarkable decrease in the PL intensity of TPD in the bilayered structure with time and temperature and the highly efficient quenching of TPD in the co-deposited film, it can be concluded that the components of the bilayer can diffuse into each other layer (Fig. 5) and that even a small amount of Alq3 diffusing into the TPD layer can quench PL from TPD as well as the major component Alq3 can quench TPD diffusing into the Alq3 layer. The degradation of EL devices in terms of diffusion is now under investigation.

References

1 C. W. Tang and S. A. VanSlyke, *Appl. Phys. Lett.*, **51**, 913 (1987).
2 C. Adachi, S. Tokito, T. Tsutsui, and S. Saito, *Jap. J. Appl. Phys.* **27**, L713 (1988).
3 C. Adachi, T. Tsutsui, and S. Saito, *Appl. Phys. Lett.*, **56**, 799 (1990).
4 E. M. Han, L. M. Do, Y. Niidome, and M. Fujihira, *Chem. Lett.*, 969 (1994).
5 L. M. Do, E. M. Han, Y. Niidome, M. Fujihira, T. Kanno, S. Yoshida, A. Maeda, and A. J. Ikushima, *J. Appl. Phys.*, in press (1994).
6 M. Abkowitz and D. M. Pai, *Philos. Mag. B*, **53**, 193 (1986).
7 D. C. Freeman, JR., and C. E. White, *J. Am. Chem. Soc.* **78**, 2678 (1956).
8 R. Ballardini, G. Varani, M. T. Indelli, and F. Scandola, *Inorg. Chem.*, **25**, 3858 (1986).