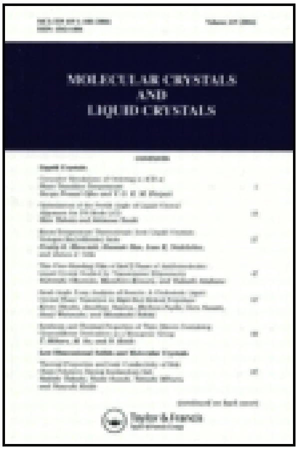

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Thermal Stabilities of Organic Layer in Electroluminescent Devices

Lee-Mi Do [a] , Eun-Mi Han [a] , Noritaka Yamamoto [a] & Masamich Fujihira [a]

[a] Department of Biomolecular Engineering, Tokyo Institute of Technology, 4259 Nagatsuta, Midori-ku, Yokohama, 226, Japan

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THERMAL STABILITIES OF ORGANIC LAYER IN ELECTRO-LUMINESCENT DEVICES

LEE-MI DO, EUN-MI HAN, NORITAKA YAMAMOTO AND MASAMICHI FUJIHIRA
Department of Biomolecular Engineering, Tokyo Institute of Technology,
4259 Nagatsuta, Midori-ku, Yokohama 226, Japan

Abstract The thermal stability of organic EL devices was investigated by using an infrared thermal imaging radiometer, SEM, AFM, and fluorescence spectroscopy. The morphology of the electroluminescent (EL) devices was changed by high current flow which led to the increase in temperature of the devices. The interdiffusion between two organic layers was accelerated with the increase in temperature. The stability of the organic layers was improved by co-deposition of TPD-Alq as the hole transport layer.

INTRODUCTION

The degradation of organic EL devices is currently being studied extensively to understand basic parameters for their practical use. This fundamental information is of considerable interest for the device application. For the past few years, a large number of researches have been made on the organic EL devices, and superior EL characteristics have been successfully demonstrated.[1-3] However, the most serious problem of the organic EL devices is the short operating lifetime due to instability of organic layers. The degradation mechanism in the organic EL devices is not fully understood. Previous studies indicate that degradation is partly due to crystallization and thus deformation of the organic layers during the applied voltage.[4-6] However, to date, there has been no report concerning the thermal stability of the organic layers in detail.

This paper focuses on thermal stability of the organic EL devices. Furthermore, the morphological change in the devices due to high temperature will be also described.

These results provide further understanding of the degradation process caused by Joule heating in the organic EL devices.

EXPERIMENTAL

The EL cell studied consisted of typical two organic layer structure, i.e. ITO / a hole transport layer (HTL) / an emitter layer (EML) / Metal. The HTL used was N,N'-diphenyl-N,N'-bis(3-methylphenyl)-(1,1'-biphenyl)-4,4'-diamine (TPD), the EML was tris(8-hydroxy-quinoline)aluminum (Alq_3), and the metal top electrode was aluminum. The thickness for the organic layers and the Al electrode were about 500 Å, respectively. Top and cross sectional imaging and chemical analysis of the devices were performed by a JEOL JSM-6320F scanning electron microscope (SEM) combined with energy dispersive X-ray spectroscopy (EDS). Observation of the surface morphology was performed by a Seiko SPA-300 AFM unit with a SPI-3700 probe station. Olympus silicon nitride triangle AFM cantilevers with a length of 100 μm and a spring constant of 0.089 Nm^{-1} were used. The PL spectra were recorded by a Hitachi 850 fluorescence spectrometer at a 355 nm excitation wavelength. *In situ* measurements of temperature were carried out with an Inframetrics model 760 infrared thermal imaging radiometer. The annealing temperatures and time were controlled by a Mettler FP900 system. All experiments were performed under ambient conditions.

RESULTS AND DISCUSSION

1. Joule Heat

Figure 1 shows (a) an SEM image and (b) EDS spectra of an organic EL device which was degraded by heat due to applying voltage. From morphologies observed at points 1 and 2 in Fig. 1(a), it is clear that the flat Al electrode surface was partly changed into an undulated one. The morphological change of the device can be due to thermal instability of the organic layers during the applying voltage. In order to confirm the chemical change of composition in the electrode surface, we analyzed the surface with EDS. Figure 1(b) shows the chemical composition of the Al electrode surface at points 1 and 2. The intensity of carbon was not dependent on the position of points. However, the intensity of oxygen in point 1 was smaller than that in point 2, conversely that of Al. It indicates that the Al top electrode in point 1 remained almost unoxidized, while that in point 2 was oxidized. The results were in good agreement with previous Auger analysis results.[5] In

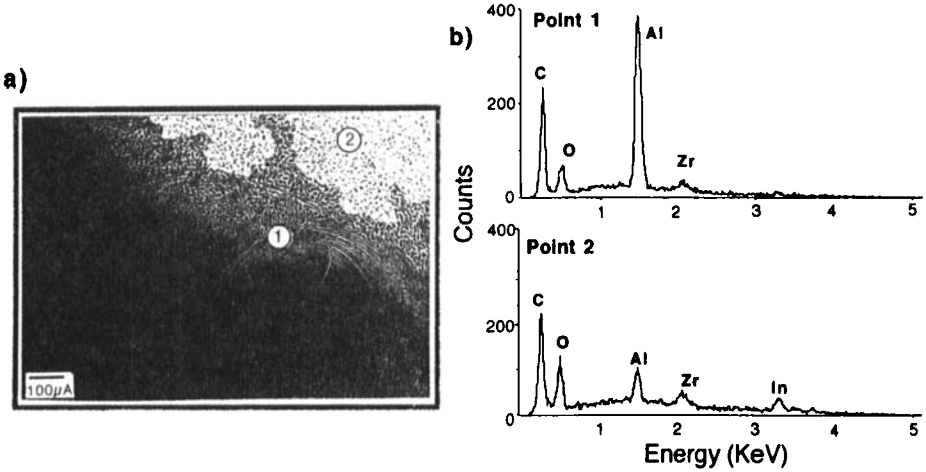

FIGURE 1 (a) An SEM image and (b) EDS spectra of an Al electrode after applying a voltage of 30 V for 10 min. Points 1 (dark gray) and 2 (bright gray) show the normal and the degraded surface with undulating patterns, respectively.

point 2, the peak of In appeared although it was not observed in point 1. This result corresponds to the appearance of the Auger peak of In at earlier stages of Ar ion sputtering for the depth profile due to the destruction or deformation of organic layer by evolved heat.[5]

To confirm the heat evolution in the organic EL devices, temperature of a device was measured *in-situ* with the infrared thermal imaging radiometer during applying voltage. Figure 2 shows (a) a thermal image and (b) a measured temperature vs. current density curve on the same device. As shown in Figure 2(a), the temperature of the device is distributed circularly in such a way as the temperature in the central part was higher than the outer part. The central part corresponds to the center of the intersection of the ITO base and the Al top electrode crossed perpendicularly. The measured temperature increased with the increase in the current density by increasing the applying voltage. When 30 V was applied, the temperature was about 78 °C which was higher than Tg of TPD.

To verify the morphological change in the device due to the Joule heating, we took cross-sectional images by using the SEM. Figure 3 shows a typical cross-sectional image of the device annealed at 90 °C for 10 min. The morphological change of the surface was initiated by the change in the organic layer. Especially, due to the Tg of TPD, which is lower than that of Alq, one can clearly see that the morphological change in the device was originated from the TPD layer at the high temperature.[7] Base on the comparison of the SEM and the PL images (the PL image is not shown here) between positions 1 and 2 in Figure 3, we can conclude that thermal instabilities of TPD layer leads to the change in

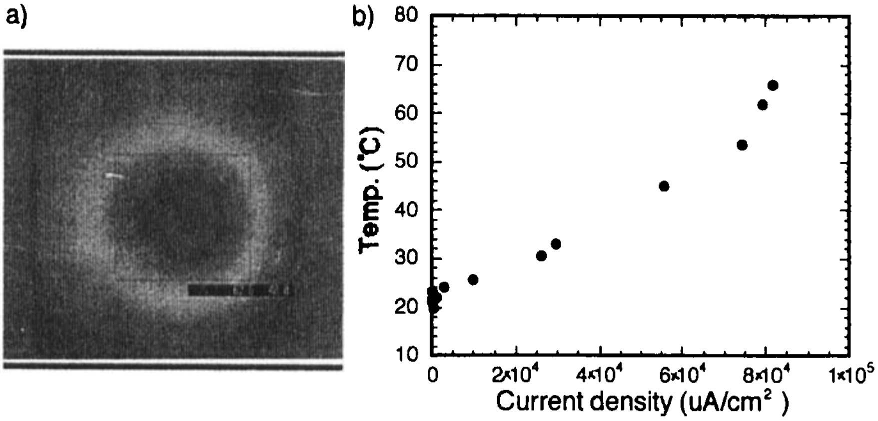

FIGURE 2 (a) A thermal image measured *in-situ* by applying a voltage of 28 V and (b) a temperature - current density curve of an EL device measured by changing the applying voltage.

the morphology of the TPD / Alq bilayer film. In the PL image, the colors of positions 1 and 2 in the cross sectional SEM image were green and yellowish-green, respectively, in the undulating pattern. Especially, elongated strips in the undulate pattern in Figure 1 were also the undulate pattern in Figure 1 were also clearly observed in the PL images as observed previously in the bilayered film without an Al top electrode.[8]

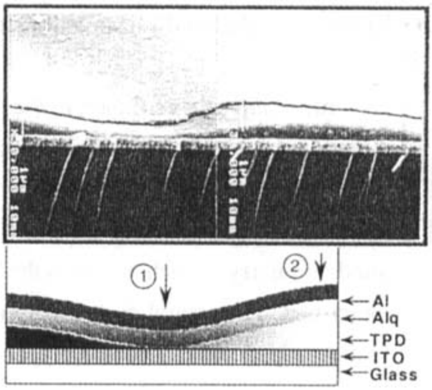

FIGURE 3 (a) A cross-sectional SEM image of an ITO / TPD / Alq / Al device. (b) Schematic representation of the cross section. Positions 1 and 2 correspond to the positions where green and yellowish-green emissions were observe in the PL image, respectively.

2. Photoluminescence Spectra

In general, interdiffusion in the organic layers is accelerated by heating which also leads to the morphological change in the organic bilayer.[8]

To confirm the interdiffusion phenomena in the organic layers in the EL device,

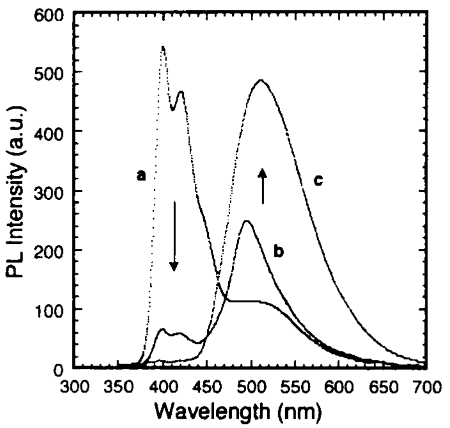

FIGURE 4 The change in the PL spectra for ITO / TPD / Alq / Al devices annealed at different temperatures. a) 60 °C, b) 70 °C, and c) 80 °C. The annealing time was 2 h.

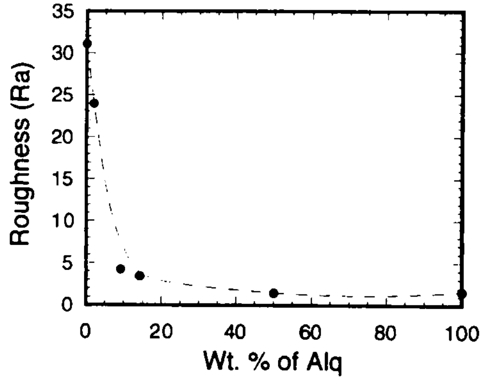

FIGURE 5 The change in roughness of the surface of the organic bilayers deposited on ITO without the Al top electrode, i.e. ITO / a TPD-Alq mixed HTL / a pure Alq EML, as a function of Alq concentration

the PL spectra were observed at different temperatures for the same annealing time of 2 h. As shown in Figure 4, the PL intensities around 400 nm for TPD decreased and those around 500 nm for Alq increased with increasing the annealing temperature. From the results, we confirmed that the interdiffusion of the organic layers was accelerated with an increase in temperature. The PL spectral change was due to occurrence of energy transfer from TPD to Alq in the mixed organic layers formed by interdiffusion,[8-10] which was confirmed by co-deposited films.[11]

3. Thermal Stability of Organic Layers

TPD have been used as HTL in a large number of studies on organic EL devices, due to its high carrier mobility. However, as studied previously, the thermal instability of TPD layer was one of problems to overcome for practical use. Degradation of organic EL devices was mainly originated from lack of stability of organic films, which substantially affect the EL and the PL properties.

Topographic changes in the device surfaces were due to the change in morphology of the organic layers as shown in Figure 3. To clarify the thermal instability of the organic layers, we also measured roughness (Ra) of the organic layer by using AFM. Figure 5 shows the change in the observed roughness of the surfaces of bilayers in the form of a pure Alq film / a TPD-Alq mixed film as a function of Alq content in the mixed film. The roughness was decreased with the increase in the Alq content in the mixed film. It suggest that the thermal stability of the organic layers was increased by addition of Alq in the HTL.

CONCLUSIONS

We have studied thermal properties of organic EL devices by using an infrared thermal imaging radiometer, SEM, EDS, AFM, fluorescent spectroscopy. The following results were obtained: 1) The increase in current flow in the device leads to the increase in temperature which results in the morphological change in the EL device due to the thermal instability of the TPD layer. 2) Interdiffusion at the interface between the organic layers was accelerated by increasing temperature. 3) The thermal stability of organic layer was improved by the co-deposition of TPD-Alq as HTL.

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