Effect of Organic Alloy for Suppression of Polycrystallization in BCP Thin Film

Tatsuo Mori and Yusuke Masumoto

*Department of Electrical Engineering and Computer Science, Graduate School of Engineering,
Nagoya University, Nagoya, Aichi 464-8603, Japan*

Bathocuproine (BCP) is often used as a hole-blocking layer in organic light-emitting diodes (OLEDs) and as anti-migration layer of exciton in organic solar cells. However, BCP is easily polycrystallized after vacuum deposition immediately. We can suppress the polycrystallization of BCP thin film by means of organic alloy with the other material.

Keywords : organic alloy, polycrystallization, BCP, PBD, stability, thin film

1. Introduction

The organic light-emitting diodes (OLEDs) proposed by Tang and VanSlyke[1] are fabricated using low-molecular dyes and the vacuum vapor deposition method. Although they showed bilayer structure, commercialized devices have multilayers structure with more than five layers. In addition, Tang reported organic solar cell (OSC) with bilayer structure before then[2]. And in OSC complicated device structure is used to obtain high conversion efficiency. Bathocuproine (BCP) is often used as a hole-blocking layer in organic light-emitting diodes (OLEDs) [3-8] and as anti-migration layer of exciton in organic solar cells (OSLs)[9,10]. However, vaporized BCP thin films may be amorphous, but they are easily polycrystallized immediately after deposition by molecular migration due to room temperature. Although BCP is very useful for organic electronic devices, the stability of thin film structure of evaporated BCP is great issue to be resolved.

The authors reported the polycrystallization of naphthyl-substituted diamine derivative (NPD) on various indium-tin-oxide (ITO) substrates[11]. In these reports, polycrystallization is found to be suppressed in NPD thin film deposited on phthalocyanine copper (CuPc) thin film or sandwiched between two organic layers. Therefore, the authors speculate that each molecular migration can be suppressed by increasing hetero interface between two materials. One of the methods which

increase hetero interface by means of vacuum deposition method is to alternately deposit each

Fig. 1 The concept of organic alloy

organic thin layer. However, only horizontal interface increase in the alternate multi-layer structure. But it is very difficult to laterally fabricate the hetero interface by the vacuum deposition method. In general, a molecule easily aggregates with same molecules. Therefore, if co-evaporation method is used, the ideal film structure may be able to be fabricated under an optimum condition. The authors define organic alloy (structure) as the mixture with two hetero organic materials under amorphous or nanocrystalline structure.

For example, the author reported the EL properties of alternately deposited OLED with triphenyl diamine derivative (TPD) and 8-hydroxyquinoline aluminum (Alq3)[12]. Although this device shows interesting EL

phenomena, its device performance has higher threshold voltage of EL and poorer EL performance than conventional bilayer OLED with TPD and Alq3. Because the electron transport to recombination zone remarkably decreases by reason of alternate deposition of TPD with strong hole transportation and Alq3 with electron transportation. This shows that the selection of two pairing materials is fundamental to develop a desired function.

In the other case, the author reported the EL properties of OLEDs having various coevaporation layers with TPD and Alq3[13]. The pass formed by the aggregation of same molecules occurs by a coevaporation ratio of TPD and Alq3.

As mentioned the above, the authors select 2-(4-biphenyl)-5-(4-tert-butylphenyl)-1,3,4-oxadiazole (PBD). PBD is well-known as an electron transport material[14]. However, PBD also shows instable film structure. In this paper, the authors report the improvement of the polycrystallization phenomena by organic alloy films and EL properties of OLED with organic alloy layer.

2. Experimental

We used Bathocuproine (BCP) and 2-(4-biphenyl)-5-(4-tert-butylphenyl)-1,3,4-oxadiazole (PBD). Sublimated BCP and PBD were obtained from Nippon Steel Chemical Co., Ltd. and Ohjec Corp., respectively. The authors have used N,N'-di(1-naphthyl)-N,N'-diphenyl-1,1'-diphenyl-1,4'-diamine (NPD) as a hole transport layer, and 8-hydroxyquinoline aluminum (Alq3) as an emitting material. Sublimated NPD and Alq3 are obtained from Nippon Steel Chemical Co., Ltd. We used special ITO substrate for OLEDs: Giomatic Co. In general, ITO substrates were cleaned using UV-ozone treatment (5 min, Nihon Laser Electronics) after supersonic washing in pure water (5 min, two times), acetone (5 min, two times), 2-propanol (5 min, two times). The organic thin films were prepared using vacuum deposition at a pressure of $0.8-1 \times 10^{-3}$ Pa at room temperature. The deposition rates of BCP show Table 1.

Table 1 Fabrication conditions

Sample (ratio)		depo. rate [nm/s]	
BCP	PBD	BCP	PBD
1	0	0.2	-
1	0.5	0.2	0.1
1	1	0.2	0.2
1	2	0.1	0.2
0	1	-	0.2

We stored the specimens in Environmental chamber (LHL-113, ESPEC Co.), where temperature and relative humidity are controlled at atmosphere. Atomic force microscopy (AFM) was used with Nanoscale Hybrid Microscope, VN-8010, KEYENCE Co. We observed the NPD film prepared on an ITO substrate with a polarizing microscope, OPTIPHOTO-2 accompanied with a polarizing unit (Nikon Co.) and took photographs using Digital Sight, DS-L1 (Nikon Co.).

Efficiency-current-voltage characteristics were measured by a source measure unit (238 High Current Source Measure unit, Keithley Instrs., Inc.) and a luminance meter (BM-8; TOPCON Corp.). Measurements of luminance-current-voltage characteristics were carried out under vacuum of ~ 0.1 Pa. Electroluminescence spectra were obtained using a high-sensitivity spectro-multi-channel photo detector (MCPD-4500; Otsuka Electronics Co., Ltd)

3. Results and discussion

Figures 2(a) and 2(b) show the surface photo through ITO glass and the emitting photo for the OLED of ITO/NPD(50nm)/BCP(50nm)/LiF/Al, respectively. The cross area sandwiched by ITO electrode and Al cathode is 2×2 mm². The light-grey circle regions in Fig. 2(a) are thought to be the polycrystallization region of BCP. These regions correspond to the dark spots in Fig. 2(b). The polycrystallization of organic dyes is one of factors due to dark spot.

Fig. 2 (a) Surface photograph through glass, (b) Emitting image.

Fig. 3 Polarizing microscope images of 30 nm-thick BCP thin films on ITO: (a) as-depo. film; (b) after 3 hrs.

Fig. 4 Growth of polycrystallization regions in BCP (left column), BCP:PBD=1:1 (center) and PBD (right) films by polarizing microscopic photographs: top, time after deposition 3 hrs; middle, 1 days; bottom, 7 days.

Figures 3 show the polarizing microscope images of 30 nm-thick BCP thin films on ITO: 3a, as-deposited and 3b, after 3 hours. The thickness of 30nm is thought to be a standard thickness of BCP hole-blocking or anti exciton-migration films. BCP evaporated film is polycrystallized immediately after deposition in vacuum chamber. When a cathode metal is directly deposited on BCP film, one can observe slight polycrystallization of BCP in close proximity to evaporated cathode metal. BCP thin films have very instable film structure, although the film structure of BCP thin film is thought to be amorphous.

Figures 4 show the growth of polycrystallization regions in BCP, BCP:PBD=1:1 and PBD films by polarizing photographs. The polycrystallization of BCP film almost finishes after 3hrs. Once BCP thin films are polycrystallized, polycrystallized BCP film is stable. As PBD is also polycrystallized immediately after vacuum deposition, the polycrystallization of PBD film almost finishes

after 3hrs. The size of polycrystallization region in PBD is much smaller than that in BCP (diameter, ca. 600-700 μm). PBD shows microcrystalline structure. Bright (white) regions are growing microcrystals of PBD. In addition, PBD molecules are migrating and then they form the large filamentous crystalline structure after 7 days. There may be no PBD molecules in dark region after 7 days. In the other hand, the alloy films (BCP:PBD=1:1) are stable amorphous structure,

Fig. 5 Reflective microscopic images of BCP thin film before (a) or after (b) AFM measurement. Dashed square is a scan area by AFM probe (black arm in (b)).

Fig. 6 Reflective microscopic images of BCP:PBD (1:1) alloy film before (a) or after (b) AFM measurement. Dashed square is a scan area by AFM probe

although some small crystalline regions are generated. Organic alloy method is though to be very effective for the stability of organic morphology.

The authors demonstrate the improvement of mechanical durability of film structure. Figures 5 show the reflective microscopic images of BCP thin film before or after AFM measurement. Of course, the authors measured BCP thin film by non-contact AFM mode. Dashed square is a scan

area by AFM probe in Figs. 5. Although amorphous BCP thin film in square shows the same color as surrounding region in Fig. 5(a) before, it shows different color in Fig. 5(b) after. This suggests that BCP thin film in square damage by the weak interaction of AFM probe. Unfortunately, the authors are unsuccessful to obtain the AFM image of as-deposited BCP thin film. On another aspect, one can understand the rapid polycrystallization of BCP thin films from Figs. 5. The circular polycrystallization area has two different regions in coloration. The inside circular polycrystallization area grew under 40°C, 70%RH in the environmental chamber. The polycrystallization area enclosed between inside and outside circles grew during AFM measurement under ca. 22°C, 22%RH. One can understand that the morphology of BCP thin film is very instable.

Figures 6 show the reflective microscopic images of BCP:PBD (1:1) alloy film before or after AFM measurement. There is no difference between the image before AFM scan and that after AFM

Fig. 7 Growth of polycrystallization regions in BCP:PBD alloy film, 1:0.5 (left column), 1:1 (center) and 1:2 (right) by polarizing microscopic photographs: top, time after deposition 3 hrs; middle, 1 days; bottom, 7 days.

scan. Organic alloy method is confirmed to be very effective for the improvement of mechanical durability.

Figures 7 show the growth of polycrystallization regions in BCP:PBD alloy film, 1:0.5, 1:1 and 1:2 by polarizing microscopic photographs. Even if the PBD ratio decreases to 0.5, the polycrystallization of organic alloy film can be much suppressed. However, when the PBD ratio increases, PBD molecules with strong cohesion aggregate. The polycrystallization of BCP:PBD =1:2 alloy film after 7 days is similar to that of PBD thin film after 3 hrs or 1 day. The authors speculate that the white filamentary crystalline region may be formed by the aggregation of PBD molecules.

The authors succeed in the stabilization of BCP thin film by organic alloy technique. Next, the authors show the BCP alloy films are useful as hole-blocking layer. Figures 8 show The current density-voltage characteristics, (a) and Luminance-current density characteristics, (b) for

Figs. 8 The current density-voltage characteristics (a) and Luminance-current density characteristics for NPD(50nm)/BCP:PBD=1:1 alloy (50nm), open circles; NPD(50nm)/BCP(50nm), closed circles.

NPD(50nm)/BCP:PBD=1:1 alloy (50nm) and NPD(50nm)/BCP(50nm). The emissions from both specimens are due to NPD. The unexpected advantage on the use of BCP:PBD alloy layer is the lowering of operating voltage. The luminance per current density in NPD/BCP:PBD alloy is a little higher than that in NPD/BCP. Therefore, the improvement of film structure due to organic alloy is concluded to enhance the carrier transport in hole-blocking layer accompanied with strong hole-blocking property. Of course, the electron transportation of PBD molecules will contribute to the enhancement of carrier transport in BCP:PBD alloy film.

Although the authors cannot estimate the glass transition point of BCP, the temperature is speculated to be much low. It is reported that the suppression of molecular migration depends on the increase in glass transition point[15]. Two major method for increasing in glass transition point are reported: increase in molecular weight [16] and introduction of such a bulky substituent group as tert-butyl group. The former may be able to restrict molecular motion, but higher molecular weight will reduce its solubility in any solution. That is, it is difficult for higher molecular weight material to be purified with higher cost. As evidenced by PBD, the introduction of bulky group is not effective for low molecular weight materials.

In organic alloy technique, the molecular interaction between hetero molecules play an important role of the anchor effect due to suppression of molecular migration. Therefore, the compatibility between hetero molecules is very important. The authors have been investigating the organic alloying of BCP with various materials. Essentially, the compatibility between BCP and the other is not poor because the other materials do not have any hydrophilic group. Consequently, the stability of film structure is improved by organic alloying. However, the desired function of thin film is found to go down by some combinations.

4. Conclusions

Instable BCP thin films were improved to stable film structure by the organic alloy technique. The BCP:PBD(1:1) alloy film kept almost amorphous structure after 7 days from evaporation in spite of that BCP or PBD thin films were almost polycrystallized after 3 hrs. Hole-blocking property of BCP was not lost by organic alloying with PBD with good electron transportation. In addition, the BCP:PBD alloy layer showed enhanced electron

transport and injection from a cathode. Organic alloy technique is more convenient means for the suppression of molecular migration than the other.

Acknowledgement

A part of this study is supported by Research Foundation for the Electrotechnology of Chubu. We wish to thank Nippon Steel Chemical Co., Ltd. for the provision of NPD, Alq3, BCP.

References

1. C. W. Tang and S. A. VanSlyke, *Appl. Phys. Lett.*, **51**, 913 (1987).
2. C. W. Tang, *Appl. Phys. Lett.*, **48**, 183 (1986).
3. S. Kawami, K. Nanamura, T. Wakimoto, T. Miyaguchi, T. Watanabe, *PIONEER R&D* **11**, 13 (2000)[in Japanese].
4. R.C. Kwong et al., *Appl. Phys. Lett.* **81**, 162 (2002).
5. S. Tokito, T. Iijima, T. Tsuzuki, F. Sato, *Appl. Phys. Lett.* **83**, 2459 (2003).
6. M. Suzuki, S. Tokito, M. Kamachi, K. Shirane, F. Sato, *J. Photopolym. Sci. Technol.* **16**, 309 (2003).
7. S. Tokito, M. Suzuki, F. Sato, *Thin Solid Films* **445**, 353 (2003).
8. M. A. Baldo, S. Lamansky, P. E. Burrows, M. E. Thompson, S. R. Forrest, *Appl. Phys. Lett.*, **75**, 4 (1999).
9. J. Xue, S. Uchida, B. O. Rand, S. R. Forrest, *Appl. Phys. Lett.*, **84**, 3013 (2004).
10. S. Uchida, J. Xue, B. O. Rand, S. R. Forrest, *Appl. Phys. Lett.*, **84**, 4218 (2004).
11. T. Mori and Y. Iwama, *J. Photopolym. Sci. Technol.*, **18**, 59 (2005).
12. T. Mori, K. Obata, T. Mizutani, *J. Phys. D*, **32**, 1198 (1999).
13. T. Mori, H. Tsuge, T. Mizutani, *J. Phys. D*, **32**, 65 (1999).
14. C. Adachi, T. Tsutsui, S. Saito, *Appl. Phys. Lett.*, **55**, 1489 (1989).
15. B. E. Koene, D. E. Loy, M. E. Thompson, *Chem. Mater.*, **10**, 2235 (1998).
16. H. Tanaka, S. Tokito, A. Okada, Y. Taga, *Chem. Commun.*, 2175 (1996).