

Ultraviolet-assisted synthesis of encapsulating adhesives and their application for lifetime improvement of organic light emitting diodes

Chen-Ming Chen^a, Ming-Hua Chung^a, Tsung-Eong Hsieh^{a,*}, Bohr-Ran Huang^b, Huai-En Hsieh^b, Fuh-Shyang Juang^c, Yu-Sheng Tsai^c, Mark O. Liu^d, Jen-Lien Lin^d

^a Department of Materials Science and Engineering, National Chiao-Tung University, Hsinchu 30010, Taiwan, ROC

^b Graduate School of Optoelectronics Engineering, National Yunlin University of Science and Technology, Yunlin 640, Taiwan, ROC

^c Institute of Electro-Optical and Materials Science, National Formosa University, Huwei, Yunlin 63208, Taiwan, ROC

^d Material and Chemical Research Laboratories, Industrial Technology Research Institute, Hsinchu 300, Taiwan, ROC

ARTICLE INFO

Article history:

Received 7 May 2008

Received in revised form 16 June 2008

Accepted 4 July 2008

Available online 24 July 2008

PACS:

73.90.+f

72.80.Le

87.15.Mi

85.60.Jb

Keywords:

Electrical properties and measurements

Polymers

Luminescence

OLEDs

ABSTRACT

The lifetimes of organic light emitting diodes (OLEDs) have been successfully enhanced with the modulation of LiF thickness and the utilization of encapsulating adhesives, which have been successfully and quickly synthesized with UV irradiation. Experimental results demonstrate that LiF and lab-made encapsulating adhesives can block the invasion of moisture as well as oxygen in the atmosphere into the OLEDs so that the lifetimes of devices with their encapsulation are 18-folds longer than those without encapsulation.

© 2008 Elsevier B.V. All rights reserved.

1. Introduction

Organic light emitting diodes (OLEDs) have attracted much attention because of their widespread applications such as displays, illuminations, and so on. Compared with other competitors (e.g. liquid crystal displays, mercury lamps, etc.), OLEDs exhibit the predominance of lower cost, less power consumption, higher contrast ratio, faster response time, better brightness, and larger viewing angles [1–5]. However, the lifetime has recently become a crucial obstacle to the commercialization of OLEDs since moisture and oxygen in the air corrode the metal electrode and organic materials, causing dark spots while the device is lighted up and drastically decreasing the lifetime [6,7]. Although the literatures about the lifetime promotion for the encapsulation of OLEDs with metal or glass can have been reported [8–10], the process of package is inconvenient and expensive. Recently, inorganic materials (e.g. SiO₂, Al₂O₃, etc.) [11], polymers (e.g. polyacrylics, PET, poly(*p*-xylylene), etc.) [12,13] and their combinations (i.e. organ-

ic/inorganic hybrid composites) [14] have also been utilized for the gas barrier application. Nevertheless, the lifetimes of OLEDs with the packages of these materials are not satisfactory. Therefore, we have tried to encapsulate OLEDs with multi-layer structures to meet the requirements of long lifetimes.

In this paper, we have firstly fabricated the OLEDs and deposited lithium fluoride (LiF) as the protection layer on the metal electrode to increase the lifetimes of OLEDs. In order to further improve the lifetimes, the encapsulating adhesives have been rapidly prepared with ultraviolet (UV) irradiation and spin-coated on the LiF layer. Experimental results manifest that introduction of lab-made encapsulating adhesives can substantially prolong the lifetimes of devices and effectively avoid the corrosion of the organic layers and metal electrodes.

2. Experimental

2.1. Materials

Naphthyl phenyl benzidine (NPB; hole transport material), tris-[8-hydroxyquinoline] aluminum (Alq₃; light emitting material),

* Corresponding author. Tel.: +886 3 5712121x55306; fax: +886 3 5724727.
E-mail address: tehsieh@cc.nctu.edu.tw (T.-E. Hsieh).

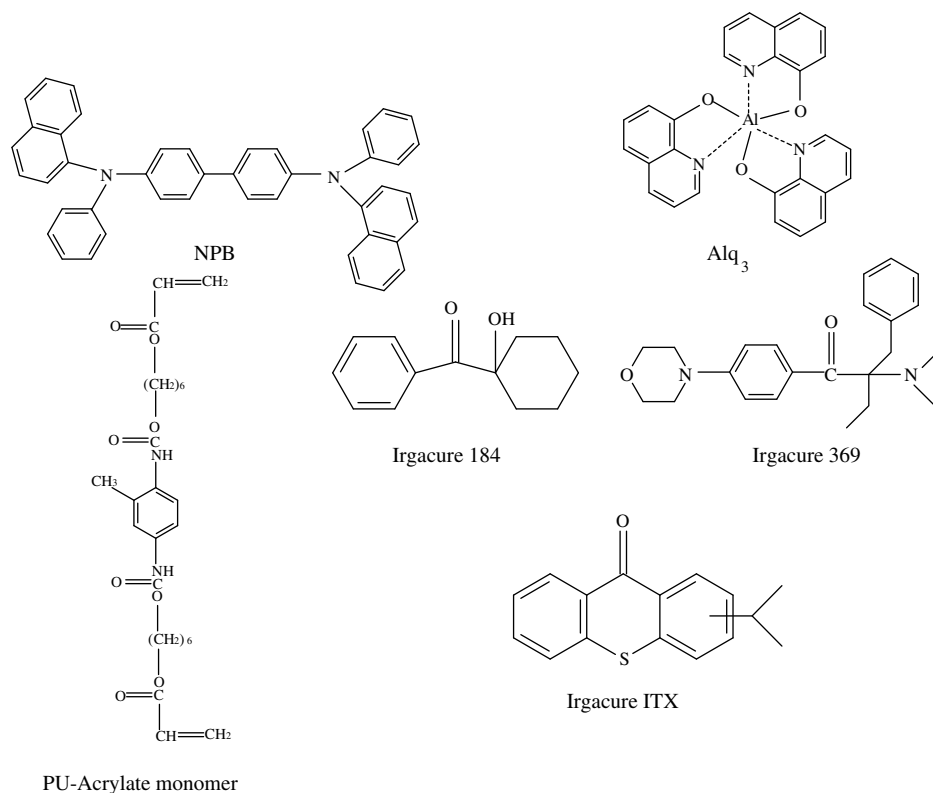


Fig. 1. The chemical structures of used materials.

lithium fluoride (LiF; electron injection/protection material), and silica (filler) were purchased from Aldrich Co. (Fig. 1). The monomers of encapsulating adhesives (PU-Acrylate) and the photoinitiators (Irigacure 184, Irigacure 369, and Irigacure ITX) were obtained from UCB Co. and Ciba Co., respectively (Fig. 1). All the materials in this study were used without further purification.

2.2. Instruments

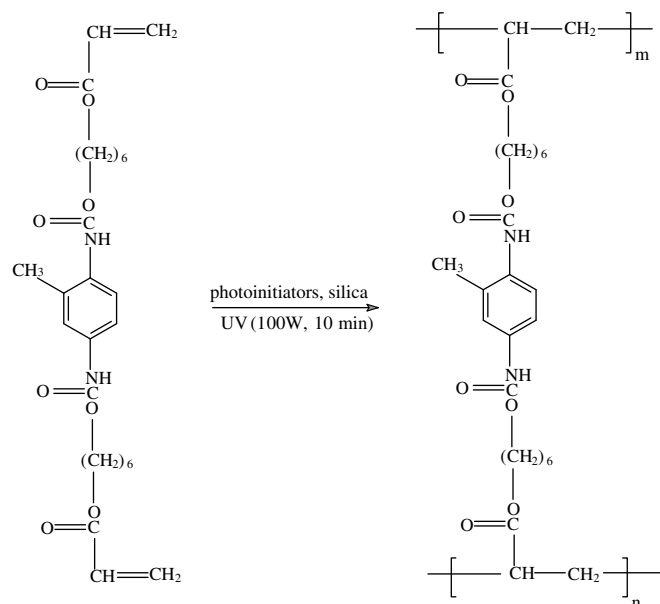
The molecular weight and viscosity were measured with a Waters Alliance GPC V200 and a Viscolite 700, respectively. Moreover, we recorded the electroluminescent properties and lifetimes of OLEDs by Keithley 2400 and Spectrascan PR650, respectively.

2.3. Synthesis of UV curable encapsulating adhesives (PU-Acrylate)

PU-Acrylate monomer (90 g), silica (10 g), Irigacure 184 (1 g), Irigacure 369 (0.5 g), and Irigacure ITX (0.5 g) were stirred and irradiated by a UV lamp (100 W) for 10 min (Scheme 1). The weight-average molecular weight (M_w), number-average molecular weight (M_n), M_w/M_n ratio, and viscosity of PU-Acrylate were 153,000, 72,600, 2.11, and 16,300 cps, respectively.

2.4. Fabrication of OLEDs

The fabrication of OLEDs was executed in a glove box. Firstly, the ITO glass ($5 \Omega/\square$) was ultrasonically washed with the acetone, methanol, and de-ionized water for 5 min. After dried with a stream of nitrogen as well as the oven and treatment of O₂ plasma for 90 s, we deposited NPB (hole transport layer; 50 nm), Alq₃ (light emitting layer; 50 nm), LiF (electron injection layer; 3 nm), Al (cathode; 80 nm) layer by layer onto the ITO glass with vacuum evaporation (Type 0 of Fig. 2a). Then the protection films (LiF) with



Scheme 1.

two different thicknesses (i.e. 80 and 100 nm) were deposited onto the Al layer (Type I of Fig. 2b) in order to investigate the gas barrier effect for the thickness of the protection layer. The similar process was used in the fabrication of Type II (Fig. 2(c)). The encapsulation of Type II was executed with spin-coating of lab-made encapsulating adhesives on the LiF protection layer (stage I: 1500 r.p.m. for 20 s; stage II: 3500 r.p.m. for 30 s) and curing by UV illumination for 10 s (Fig. 2c). The thickness of encapsulating adhesives was 100 μm , measured by a surface profiler.

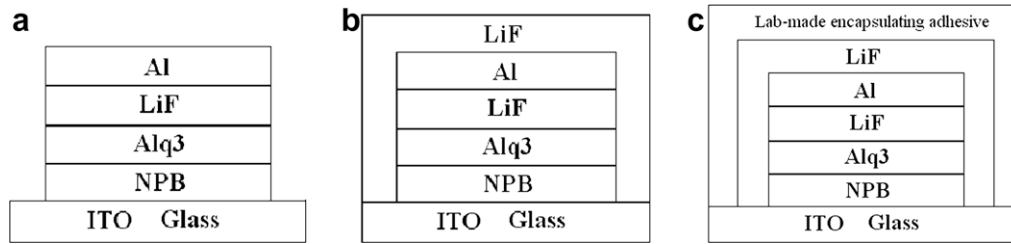


Fig. 2. The structures of lab-made OLEDs. (a) Type 0: ITO glass/NPB(50 nm)/Alq₃(50 nm)/LiF(3 nm)/Al(80 nm); (b) Type I: ITO glass/NPB(50 nm)/Alq₃(50 nm)/LiF(3 nm)/Al(80 nm)/LiF(80/100 nm); (c) Type II: ITO glass/NPB(50 nm)/Alq₃(50 nm)/LiF(3 nm)/Al(80 nm)/LiF(100 nm)/encapsulating adhesive (100 μm).

3. Results and discussion

3.1. UV-assisted synthetic procedure

UV is the electromagnetic radiation of 180–400 nm and possesses high energy. The main principle of UV-assisted synthetic procedure is to induce the dissociation of photoinitiators, generating free radicals to result in initiation, propagation, and termination for free radical polymerization [15]. Scheme 1 represents UV-assisted synthetic procedure of encapsulating adhesives. In this study, the reaction of PU-Acrylate with UV-assisted synthetic procedure takes only 10 min, while that with conventional thermal methods takes several hours for completion. Moreover, the viscosity for PU-Acrylate prepared by UV irradiation (16,300 cps) are larger than that prepared by conventional thermal methods (8500 cps; reaction duration = 16 h) and no solvent is necessary in the UV-assisted synthetic procedure. These advantages fit the requirements for the low-cost and clean production of encapsulating adhesives or other polymeric materials.

3.2. Lifetime enhancement

As shown in Fig. 3a, the lifetimes of lab-made OLEDs are deeply influenced by the thickness of the protection layer, LiF. Without LiF, the luminance sharply drops when the device is lighted up and the half-lifetime, defined as the duration while the luminance decays from the original amount to its half, is only 4 h, revealing the oxygen and moisture in the air deteriorates the corrosion of metal electrodes and organic layers. When LiF is deposited, however, the half-lifetime drastically rises to be 20 (LiF = 80 nm) and 31 h (LiF = 100 nm), respectively, representing the LiF has the resistance of the oxygen and moisture in the air and thus the lifetimes of lab-made OLEDs are prolonged. Experimental results manifest that the lifetimes of OLEDs can be modulated with the LiF thickness and the devices with thicker LiF films exhibit better barrier effects.

Although the half-lifetimes of lab-made OLEDs have been promoted to reach 31 h, we are still not satisfied. In order to further improve the lifetimes, we have tried to spin-coat lab-made encapsulating adhesives and cure it with UV illumination as shown in Fig. 2c. The LiF layer inserted between the cathode and the encapsulating adhesives not only exhibits a little gas barrier capability as described above but also avoids the corrosion of encapsulating adhesives (i.e. PU-Acrylate), which are slightly acidic, on the cathode (Al layer). As shown in Fig. 3b, utilization of lab-made encapsulating adhesives dramatically enhances the half-lifetimes of devices to achieve 72 h, which are 2.3-folds to those of Type I (LiF = 100 nm) and 18-folds to those without encapsulation (Type 0). This result shows that the polymer matrix (PU-Acrylate) and the filler (silica) can further block the entry of moisture and oxygen in the air into the OLEDs, suppressing the degradation of organic materials and metal electrodes. In comparison with commercial UV curable epoxy-based encapsulating adhesives (EPO-TEK OG112-4; Epoxy technology Inc.), lab-made encapsulating adhesives exhibit longer lifetimes and shorter curing duration since the half-lifetimes and curing times of EPO-TEK OG112-4 are 35 h and 2 min, respectively. This represents that PU-Acrylate are alternative polymer matrices to epoxy resins for the encapsulation of electric devices via the appropriate prescription of photoinitiators and dispersion of fillers. Compared with the literature data for the lifetimes of OLEDs [12], lab-made electroluminescent devices with multi-layer encapsulation exhibit better gas blocking capability since the half-lifetimes of devices with packages reported in the literature are only 3.1-folds to those without packages.

Experimental results have proved that LiF and lab-made encapsulating adhesives for OLEDs encapsulation have better lifetime enhancement than other known materials because PU-Acrylate exhibit more excellent water proof propensities than other polymers [16] and high adhesion strength with LiF [17]. Moreover, LiF has tougher chemical resistance to encapsulating adhesives than other inorganic materials [18]. Consequently, the encapsulation with the

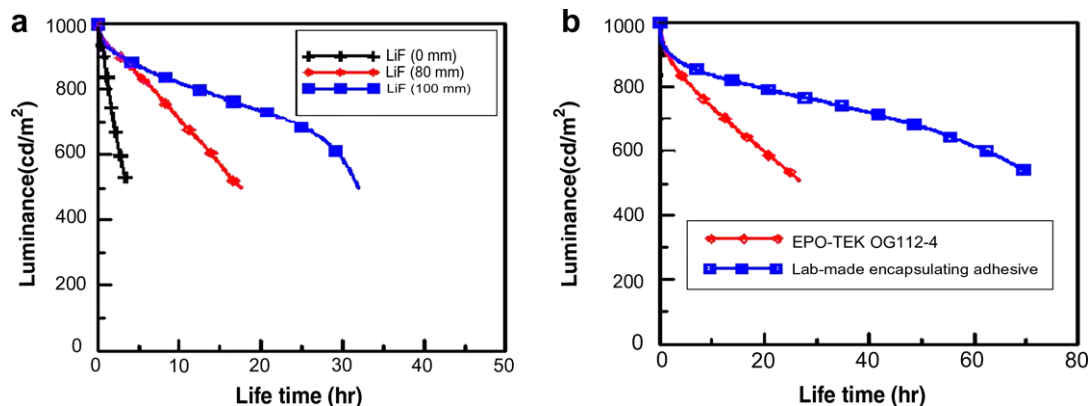


Fig. 3. The lifetimes of lab-made OLEDs (a) Type 0 and I (b) Type II.

association of LiF and PU-Acrylate can effectively reduce the gas permeability. In the near future, we will keep on synthesizing other excellent encapsulating adhesives with different polymer matrices and fillers by UV process to further improve the lifetimes of OLEDs, accelerating the commercialization.

4. Conclusions

We have successfully increased the lifetimes of OLEDs by the introduction of protection layer (LiF) and encapsulating adhesives, which can be synthesized by swift UV procedure. With LiF and encapsulating adhesives, the half-lifetimes of devices can be heightened to 18 times longer than those without encapsulation.

Acknowledgement

Financial support by ITRI 7354DC4300 is highly appreciated.

References

- [1] K. Müllen, U. Scherf, *Organic Light Emitting Devices: Synthesis, Properties and application*, Wiley-VCH, New York, 2006, p. 410.
- [2] A. Bettencourt-Dias, *Dalton Trans.* 22 (2007) 2229.
- [3] C.H. Chen, J. Shi, *Coord. Chem. Rev.* 171 (1998) 161.
- [4] S. Wang, *Coord. Chem. Rev.* 215 (2001) 79.
- [5] H. Meng, Z.R. Li, *Organic Light-Emitting Materials and Devices*, RSC Press, London, 2006, p. 672.
- [6] S.F. Lim, W. Wang, S.J. Chua, *Mat. Sci. Eng. B* 85 (2001) 154.
- [7] L.M. Do, K. Kim, T. Zyung, H.K. Shim, J.J. Kim, *Appl. Phys. Lett.* 70 (1997) 3470.
- [8] S.K. Kim, B.H. Hwang, J.H. Lee, J.I. Kang, K.W. Min, W.Y. King, *Curr. Appl. Phys.* 2 (2002) 335.
- [9] B.M. Henry, F. Dinelli, K.Y. Zhao, C.R.M. Grovenor, O.V. Kolosov, G.A.D. Briggs, A.P. Roberts, R.S. Kumar, R.P. Howson, *Thin Solid Films* 355 (1999) 500.
- [10] E.M. Moser, R. Urech, E. Hack, H. Kuenzli, E. Mueller, *Thin Solid Films* 317 (1998) 388.
- [11] A.G. Erlat, B.M. Henry, J.J. Ingram, D.B. Mountain, A. McGuigan, R.P. Howson, C.R.M. Grovenor, G.A.D. Griggs, Y. Tsukahara, *Thin Solid Films* 388 (2001) 78.
- [12] G.H. Kim, J. Oh, Y.S. Yang, L.M. Do, K.S. Suh, *Polymer* 45 (2004) 1879.
- [13] Y.S. Jeong, B. Ratier, A. Moliton, L. Guyard, *Synth. Met.* 127 (2002) 189.
- [14] C. Charton, N. Schiller, M. Fahland, A. Hollander, A. Wedel, K. Noller, *Thin Solid Films* 502 (2006) 99.
- [15] H.R. Allcock, F.W. Lampe, *Contemporary Polymer Chemistry*, second ed., Prentice Hall, Englewood Cliffs, New Jersey, 1990, p. 51.
- [16] H.R. Allcock, F.W. Lampe, *Contemporary Polymer Chemistry*, second ed., Prentice Hall, Englewood Cliffs, New Jersey, 1990, p. 156.
- [17] A.V. Pocius, *Adhesion and adhesive technology: an introduction*, Munich/Hauser publishers, New York, 1997, p. 326.
- [18] J.T. Lutz Jr., R.F. Grossman, *Polymer Modifiers and Additives*, Marcel Dekker, New York, 1988, p. 260.