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Considerable improvement in the stability of solution processed small molecule OLED by annealing

GuiLin Mao[a], Zhaoxin Wu[a,*], Qiang He[a,c], Bo Jiao[a], Guojin Xu[a], Xun Hou[a], Zhijian Chen[b], Qihuang Gong[b]

[a] Key Laboratory of Photonics Technology for Information, Key Laboratory for Physical Electronics and Devices of the Ministry of Education, School of Electronic and Information Engineering, Xi'an Jiaotong University, Xi'an, 710049, PR China
[b] State Key Laboratory for Mesoscopic Physics and Department of Physics, Peking University, Beijing, 100871, PR China
[c] Department of UAV, Wuhan Ordnance Noncommissioned Officers Academy, Wuhan, 430075, PR China

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ABSTRACT

We investigated the annealing effect on solution processed small organic molecule organic films, which were annealed with various conditions. It was found that the densities of the spin-coated (SC) films increased and the surface roughness decreased as the annealing temperature rose. We fabricated corresponding organic light emitting diodes (OLEDs) by spin coating on the same annealing conditions. The solution processed OLEDs show the considerable efficiency and stability, which were prior or equivalent to the vacuum-deposited (VD) counterparts. Our research shows that annealing process plays a key role in prolonging the lifetime of solution processed small molecule OLEDs, and the mechanism for the improvement of the device performance upon annealing was also discussed.

1. Introduction

Organic light emitting devices are a promising electronic display and solid state lighting technology due to the excellent properties such as light weight, self emitting, wide view angle and flexibility [1,2]. Currently, the main method for fabricating small molecule OLEDs is vacuum-deposition, however, the manufacturing costs must be reduced so that the small molecule OLEDs can be accepted in the general illumination and display market. It is well known that the vacuum-deposition process has critical drawbacks including considerable loss of the expensive materials during evaporation, complex manufacturing process and high manufacturing costs. Hence, solution processed OLEDs is attracting much attention as potential candidates for large area flat panel displays and solid state lighting, owing to their simple processing route and low manufacturing cost. Although the significant progress has been made to obtain highly efficient solution processed small molecule OLEDs [3–5], The stability of these devices compared with vacuum deposition processed devices are rarely reported. Recently, Lee et al. [6] investigated the distinctive characteristics of solution processed small organic molecule films and devices, and indicated that the lower density of the solution processed films can be a major cause for the short lifetimes. Later, in our group, Wang et al. [7] also reported the considerable efficiency and stability of solution processed OLEDs compared with the vacuum deposited counterparts. However, how to improve the stability of solution processed OLEDs is still unknown. Therefore, it is necessary to investigate the distinctive nature of the spin-coated films and find the approach to improve the stability.

This paper presents a blue emitting small molecule OLEDs by solution processing using mixed-host (MH) of N,N′-diphenyl-N,N′-bis(1-naphthyl)(1,1′-biphenyl)-4,4′diamine (NPB) and 2-(t-butyl)-9,10-bis(2′-naphthyl) anthracene (TBADN)(6:4) doped with 4,4′-bis[2-{4-(N,N-diphenylamino)Phenyl}vinyl] biphenyl, (DPAVBi) as the emitting material, the coated emitting material layer (EML) were annealed with various conditions. It was found that the densities of the spin-coated films increased and the surface roughness decreased as the annealing temperature rose. We fabricated corresponding OLEDs by spin coating on the same annealing conditions. The solution processed OLEDs show the considerable efficiency and stability, which were prior or equivalent to the vacuum-deposited counterparts. The obtained results are compared herein with the characteristics of vacuum-deposited counterparts (in terms of luminous efficiency and operational lifetime).

* Corresponding author.
E-mail address: zhaoxinwu@mail.xjtu.edu.cn (Z. Wu).

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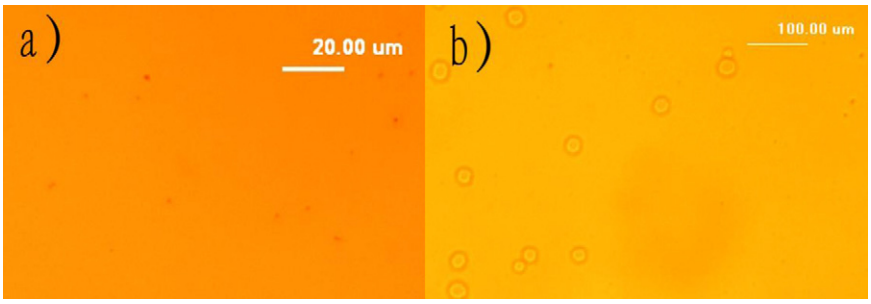

Fig. 1. The optical microscope images of organic films spin-coated on top of ITO. (a) All the images of the film annealed on the following conditions (90 °C, 40 min), (140 °C, 10 min), (140 °C, 20 min), (140 °C, 30 min), (180 °C, 10 min), (180 °C, 20 min) like the same, So one image was given to represent them; (b) annealing condition (220 °C, 10 min).

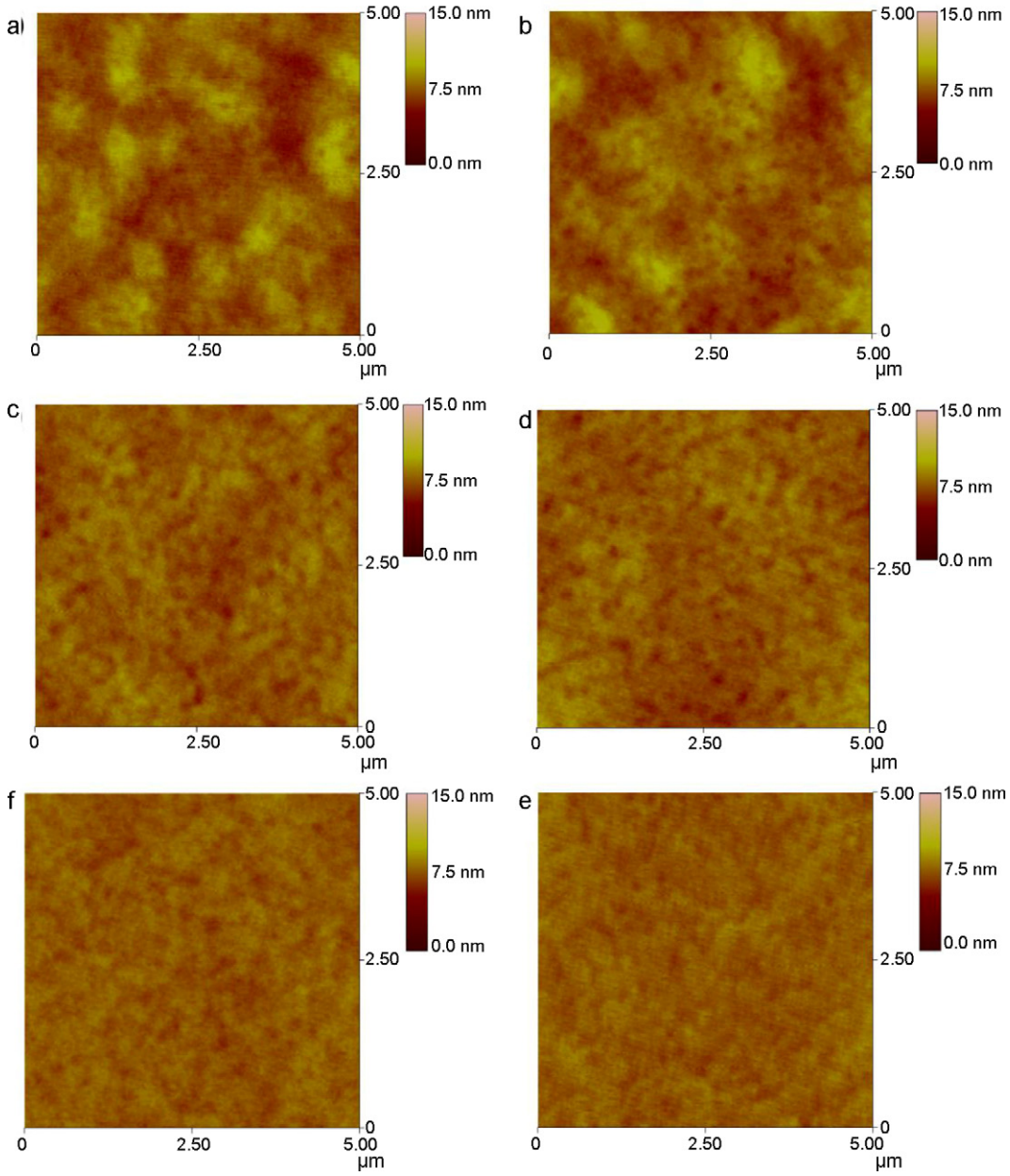

Fig. 2. The AFM images of spin-coated films with annealing condition of (a) 90 °C, 40 min (RMS = 0.883 nm), (b) 140 °C, 10min (RMS = 0.870 nm), (c) 140 °C, 20 min (RMS = 0.574 nm), (d) 140 °C, 30 min (Ra = 0.596 nm), (e) 180 °C, 10 min (Ra = 0.412 nm), and (f) 140 °C, 20 min (Ra = 0.406 nm) (scan size: 5 μm × 5 μm).

2. Experimental

2.1. Spin-coated molecular films

To investigate the annealing effect on the density of solution processed small organic molecule films, we compared the morphology of the solution processed films with different annealing conditions at first. To do this, we first spin-coated a water-dispersed poly(ethylenedioxythiophene):poly(styrenesulfonate) (PEDOT:PSS) film on the indium–tin–oxide (ITO) glass with a thickness of 45 nm, after spin coating, the films were annealed at 120 °C under ambient atmosphere for 15 min, then a 40 nm thick film (EML) i.e. NPB and TBADN mixed host (6:4) doped with DPAVBi (4%) was later spin-coated on the PEDOT:PSS layer, the spin-coated EML were then baked on a hot plate at 90 °C for 40 min; at 140 °C for 10 min, 20 min and 30 min; at 180 °C for 10 min and 20 min; and at 220 °C for 10 min under ambient atmosphere, respectively. Fig. 1 shows the morphology images (by optical microscope) of both types of film, it can be clearly found that the distinctive crackles developed at the film annealed at 220 °C for 10 min, hence, relatively high annealing temperature than the glass-transition-temperature (T_g) of MH (NPB T_g = 99 °C, TBADN T_g = 126 °C) was not suitable for fabricating OLED devices.

In order to illustrate how the annealing temperature affects the surface morphology of the films, the AFM images were given as follow. Fig. 2 shows the AFM images of both annealed films, the root-mean-square (RMS) roughness values of spin-cast films were 0.883 nm, 0.870 nm, 0.574 nm, 0.596 nm, 0.412 nm, and 0.406 nm, respectively. The AFM investigations indicate that the spin-coated films show a smoother and pin-free surface morphology as the annealing temperature increased.

We then investigated the refractive indices of these spin-coated films by performing spectroscopic ellipsometry measurements, the refractive indices can be used to evaluate the porosity of the films, The refractive index (n_f) of the film can expressed as $n_f = n_s(1-q) + n_p q$, where n_s and n_p are the mean indices of skeleton of the film and the pore space, respectively, and q is the porosity, or the fractional volume of the pores in the film [8]. So the refractive index, n_f, is reversely in proportional to q, the porosity of films. Fig. 3 shows the ordinary refractive index versus the photon energy for the different types of films. It was found that the refractive index increased as the annealing temperature rose, these images showed that the spin-coated films annealing at 90 °C were more porous and had lower density than the 180 °C annealed ones.

It is generally acknowledged that the molecules in the solution processed films are not as closely packed as those in the vacuum deposited film, there are an abundance of solvent impurities remain

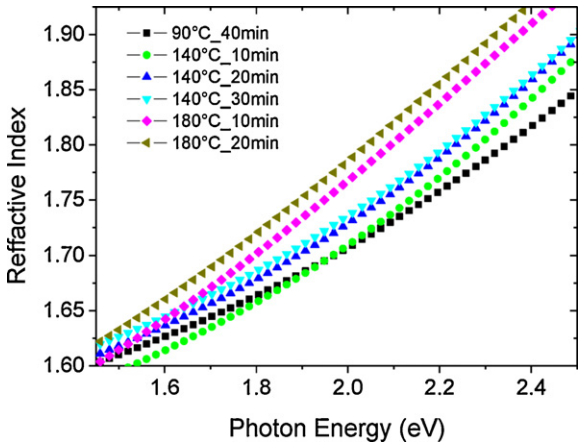

Fig. 3. The refractive indices of solution processed TBADN + NPB:DPAVBi films.

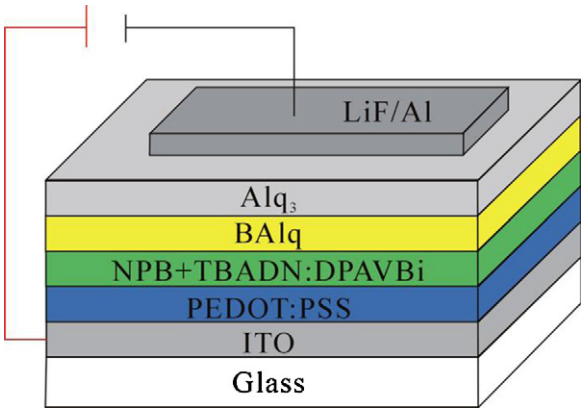

Fig. 4. The schematic structure of devices.

inside the unannealed solution processed films, besides, oxygen also can diffuse into the films more easily, so after annealing at a temperature (<T_g (NPB)), the solvent impurities will partly escape from the films, and leave some holes inside the films. However, when the annealing temperature raised more than glass transition temperature of the MH (>T_g (TBADN)), the organic solutes will change into glassy, and the holes will become smaller as the thermal motion of organic small molecular become faster. As a result, the film density was improved.

2.2. OLED fabrication and measurements

Based on the spin-coated films with different annealing conditions, corresponding OLED devices were fabricated. The devices structure studied is ITO/PEDOT:PSS (50 nm)/EML (45 nm)/BAlQ (15 nm)/Alq_3 (25 nm)/LiF (1 nm)/Al (80 nm) (see Fig. 4). Here, a 50 nm PEDOT:PSS was spin-coated on the patterned ITO substrates and then dried using a hot plate at 120 °C for 15 min to remove the solvent completely. Then the emitting layer was deposited either by spin coating or by vacuum evaporation on the PEDOT:PSS layer to obtain a thickness of 45 nm; the spin coating and annealing process were carried out in atmosphere ambient. Subsequently, the Hole-blocking-layer (HBL) Bis(2-methyl-8-quinolinolato-N1,O8)-(1,1′-Biphenyl-4-olato)aluminum (BAlq) and electron-transporting-layer (ETL) aluminumtris(8-hydroxyquinoline) (Alq_3) with a thickness of 10 nm and 30 nm separately were deposited by vacuum deposition. LiF (1 nm) and Al (80 nm) films were sequentially deposited on the electron transporting layer as cathode. The detailed fabrication of spin-coated devices can also be found in our previous report [9].

The current–voltage–luminescence (*I–V–L*) characteristics and lifetimes were analyzed by Keithley 2602 source meter and luminance meter.

3. Results and discussion

Fig. 5 shows the *I–V–L* characteristics of the devices. Sepeai et al. [10] and Lee and Park [11] have demonstrated the possibility of improving the OLED performance by an annealing process. So we found that the solution processed devices showed comparable property with the vacuum-deposited ones after annealing.

We also studied the stability of the solution processed devices, Fig. 6 presented the comparison of stability of solution processed OLEDs and the vacuum deposited one, unlike the results reported by Lee et al. [6], which present significantly shorter lifetimes for the solution processed devices (1 h for Alq_3 as ETL and 3 h for TPBi as ETL) than for the vacuum processed ones (30 h for Alq_3 as ETL) with a structure of ITO/PEDOT:PSS/TBADN + DPAVBi/Alq_3 (or

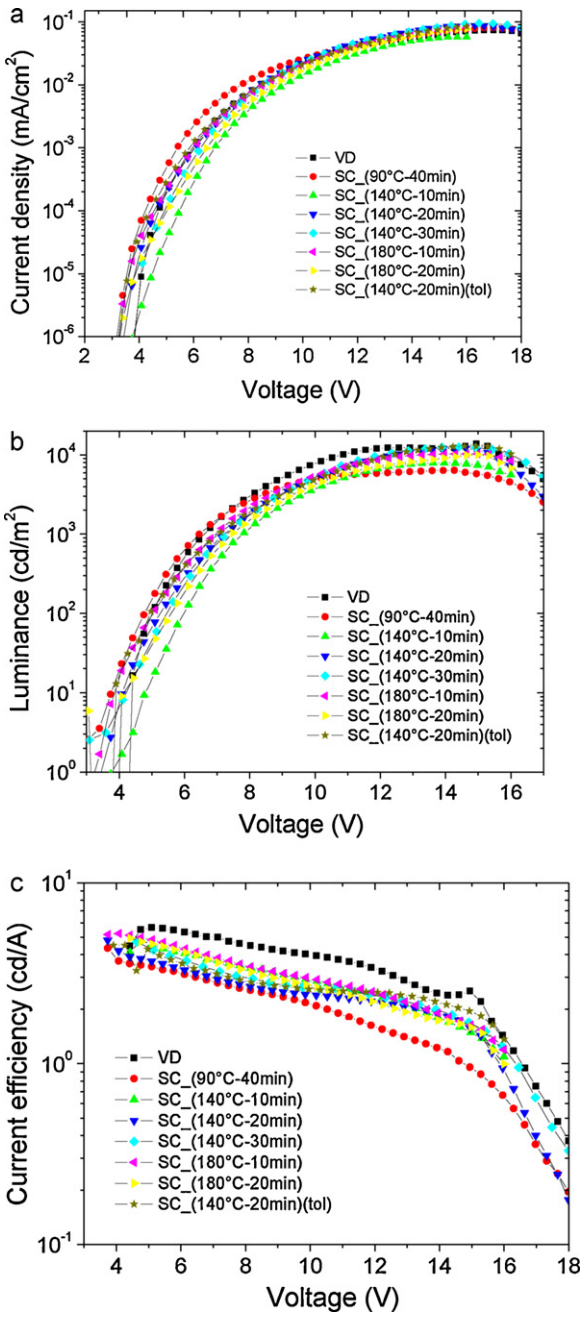

Fig. 5. Characteristics of solution processed and vacuum-deposited devices of ITO/PEDOT:PSS/TBADN + NPB:DPAVBi/BAlQ/Alq3/LiF/Al, respectively. (a) Current–density voltage, (b) luminance–voltage, and (c) current efficiency–voltage.

TPBi)/LiF/Al under an electrical current stress (at an initial brightness of 600 cd m^{-2}). In our structure, we adopted the MH system and introduced HBL, which effectively dispersed carriers and presented a good charge balance [12]. Even more important, it can be found that the lifetimes of the solution processed devices were significantly improved as the annealing temperature rose, a previous study reported that changes in the surface, either chemical (oxidation) and or physical (reduced roughness), are not likely the main reason for the OLED performance improvement [13]. So the improvement should be attributed to the enhanced density of the EML film (see Section 2.1).

Our measurements indicate that an optimum annealing condition is required for the best device stability. The lifetime of the device first increases with increased annealing temperature and

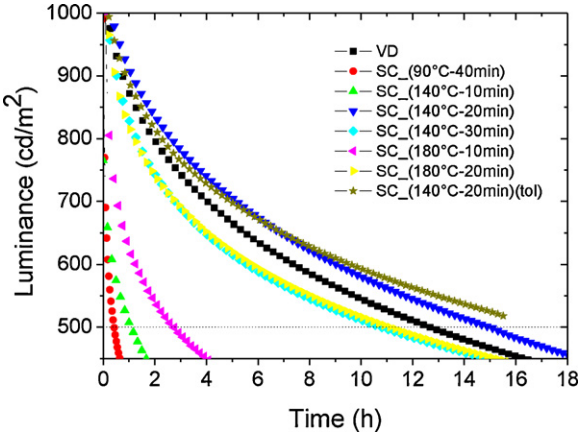

Fig. 6. Luminance decay versus time characteristics of solution processed (chlorobenzene and toluene (tol)) and vacuum-deposited devices of ITO/PEDOT:PSS/TBADN + NPB:DPAVBi/BAlQ/Alq3/LiF/Al structure (at an initial brightness of 1000 cd/m^2).

prolonged annealing time up to a certain critical condition (i.e., 140 °C and 20 min for device, respectively), after which the lifetime decreases. The decrease in lifetime seems to have originated from the high annealing temperature induced crystallization and crackle. The crystallization is due to the low T_g of NPB and TBADN during the following annealing process [14].

The change in the devices performance with different annealing time and temperature indicates that there exists an optimal annealing condition ensures the complete removal of residual solvent of chlorobenzene, in the same time less crystallization and crackle. Besides, we used the toluene (tol) as solvent and annealed on the condition (140 °C, 20 min), corresponding device shows the same stability as using chlorobenzene, which explains that the solvent evaporates completely as well.

4. Conclusions

In this work, we have investigated the annealing effect on solution-processed small organic molecule films. The more compact films of the mixed host of TBADN:NPB doped with DPAVBi can be obtained by an annealing process. We demonstrated corresponding OLEDs With the spin-coated films of TBADN:NPB doped with DPAVBi, which serves as the EML. The solution processed OLEDs show the considerable efficiency and stability, which were prior or equivalent to the vacuum-deposited counterparts. This simple and versatile solution processed small organic molecular method can be used to fabricate inexpensive large scale OLEDs with significant impact to reduce manufacture cost and avoid the complexity of the vacuum co-deposition process.

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