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Description	



Improved initial drop in operational lifetime of blue phosphorescent organic light emitting device fabricated under ultra high vacuum condition

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A blue phosphorescent organic light emitting device fabricated under the ultra high vacuum (UHV) condition of 6.5×10^{-7} Pa decreases the initial luminance drop upon lifetesting under a constant dc current of 15 mA/cm² by 3 times compared to a device fabricated under a high vacuum (HV) condition of 7.6×10^{-6} Pa resulting in a 23% increase in half lifetime. We calculate a water content of 10^{-4} mol. % in the UHV device emissive layer (EML) and 10^{-2} mol. % in the HV device EML. We discuss the effects of water on luminance loss and voltage rise for the devices. © 2011 American Institute of Physics. [doi:10.1063/1.3610998]

Phosphorescent organic light emitting devices (PHOLEDs) have demonstrated internal quantum efficiencies of nearly 100% and have now achieved commercialization in displays and are also targeted for solid state lighting applications.¹ Excellent operational half lifetimes have been achieved through molecular and device architecture design.²⁻⁴ To meet commercial targets, manufacturers typically focus on maximizing lifetime to a luminance drop of less than ~5% for displays and ~30% for lighting applications.^{5,6} Therefore, a better understanding of device degradation mechanisms particularly those that cause the initial luminance drop within the first few hours of operation are integral to improving device operational lifetime.

Luminance loss in organic light-emitting devices (OLEDs) can be categorized into intrinsic and extrinsic degradation processes. Intrinsic degradation has been widely discussed in the literature. It is a commonly-accepted view that materials can electrochemically degrade during the application of electrical excitation resulting in the formation of charge trapping and excited state quenching defect states.⁷ To further explore the mechanisms responsible for degradation, Giebink modeled blue PHOLED device degradation and proposed that exciton-polaron annihilation was the primary defect producing mechanism.⁸

Extrinsic degradation factors are attributed to impurities and environmental contaminants,⁹ i.e., migration of mobile ions,¹⁰ metal diffusion,¹¹ and water which is a primary residual gas in high vacuum (HV) device fabrication processes.¹² Ikeda has reported that lowering the vacuum pressure during device fabrication results in longer operational lifetimes for the simple fluorescent bilayer structure, tris(8-hydroxyquinolino)aluminum (III) (Alq₃) and 4,4'-bis[*N*-(1-naphthyl)-*N*-phenyl-amino]-biphenyl (α -NPD). The improvement in device stability was associated with a decrease in the electrochemical reaction between Alq₃ and residual water.¹² Although water has been identified as a potential degradation cause, the quantity of residual water in a device has not been discussed; nor has its effect on the shape of the device lifetime curve and

voltage rise as a function of time. Ultra high vacuum (UHV) conditions are not currently used in OLED manufacturing. However, in this paper, we fabricated OLEDs under UHV conditions in order to determine the impact of water impurities on device performance under current OLED HV manufacturing conditions. We calculate and compare the quantities of residual water based on the fabrication condition for the archetype blue phosphorescent device containing a blue phosphorescent emitter, *fac*-tris[3-(2,6-dimethylphenyl)-7-methylimidazol[1,2-f] phenanthridine] Iridium(III).⁸ We further discuss the influence of vacuum pressure on the operational lifetime curve and drive voltage.

In order to fabricate the blue PHOLEDs, a 2 mm wide patterned indium-tin-oxide anode coated glass substrate was cleaned using a three step 10 min ultrasonication process first using an organic base cleaner (SEMICO-CLEAN 23: Furuuchi Chemicals), then distilled water, and finally isopropanol. The substrate was exposed to UV-ozone for 30 min and loaded into a vacuum chamber with a base pressure of 10^{-6} to 10^{-7} Pa. The base pressure was lowered by adjusting the chamber baking conditions. In order to obtain UHV conditions, the vacuum chamber was baked at 120 °C for 6 h, 180 °C for 6 h, and then left for 12 h to cool to room temperature. After cooling, the deposition system turbo vacuum pumps were left to pump for 6 days. In order to obtain HV conditions, the chamber was pumped down without baking for 12 h. The pressure was monitored with a cold cathode gauge (Pfeiffer Vacuum: IKR 270). The residual gas components were monitored using a quadrupole mass spectrometer (INIFICON: model H300M).

Prior to device fabrication 200 nm of each material used in the device was evaporated to reduce the amount of volatile impurities present. The devices were made by the sequential deposition of a 10 nm hole injection layer (HIL), a 30 nm α -NPD hole transport layer (HTL), an emissive layer (EML) consisting of a 30 nm (4,4'-bis(3-methylcarbazol-9-yl)-2,2'-biphenyl) (mCBP) layer doped with 9 wt. % of the blue phosphor,⁸ a 5 nm mCBP blocking layer (BL), a 40 nm Alq₃ electron transport layer (ETL), a 1 nm LiF electron injection layer (EIL), and a 100 nm Al cathode. The deposition rates were 0.1 nm/s for the EML, BL, and ETL, 0.03 nm/s for the HIL,

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0.15 nm/s for the HTL, 0.01 nm/s for the EIL, and 0.3 nm/s for the cathode. The total deposition time from the HIL to the cathode was 2 h. After fabrication, the PHOLEDs were transferred to a dry nitrogen gas glovebox (<1 ppm H₂O and O₂). The devices were encapsulated using a glass lid, a commercial moisture getter and a UV cured epoxy edge seal.

Current density—voltage—luminance characteristics were measured with a source measure unit (Keithley, 2400) and a luminance meter (Topcon, BM-9). Electroluminescent (EL) spectra and EL transient times were obtained using a spectroradiometer (Konica-Minolta: CS-2000) and a femto-second streak camera (Hamamatsu photonics: FESCA-200), respectively. Device operational lifetime measurements were performed at a constant dc current of 15 mA/cm² at room temperature with drive voltage and light output monitored as a function of time.

The base pressure was monitored before heating the organic sources. For device A, the pressure reached 6.5×10^{-7} Pa, defined as the UHV region.¹³ Device B was fabricated under a HV condition of 7.6×10^{-6} Pa. Water at a partial pressure of 2.9×10^{-6} Pa was observed to be the primary residual gas under HV conditions. Under UHV conditions, the amount of water was significantly smaller with a partial pressure of 8.7×10^{-9} Pa. The Hertz-Knudsen formula [Eq. (1)] is used to determine how much residual gas impinges on a surface.¹²

$$J = \frac{P}{\sqrt{2\pi kMT}} \quad (1)$$

where P is the partial pressure of a gas, k is the Boltzmann constant, M is the molar mass of the gas, and T is temperature. Equation (1) shows that the impingement rate is directly proportional to the partial pressure of water.

The impingement rates of deposited molecules i.e., mCBP host and the blue phosphor, were estimated based on the deposition rates of 0.091 nm/s and 0.009 nm/s, respectively, using density values and molecular weights of 1.7 g/cm³, 485 g/mol for mCBP, and 1.8 g/cm³ and 1198.48 g/mol for the blue phosphor.

The adsorption rate (R_{ads}) in the EML can be estimated by Eq. (2).

$$R_{\text{ads}} = S \times J \quad (2)$$

Here, the sticking coefficient, S , is defined as the rate of impinging molecules depositing on a given surface. The sticking coefficient of water on stainless steel is accepted to be approximately 10^{-2} at 300 K under vacuum levels of 10^{-6} to 10^{-7} Pa.¹⁴ The sticking coefficient of water on a thin film surface of mCBP has not been measured. However, based on the relative non-polarity of the organic host and reports that related derivatives such as 4,4'-bis(N-carbazolyl)biphenyl have a contact angle for water of 96°, i.e., much greater than that of stainless steel with a contact angle of approximately 58°,^{15,16} we assume that the S will be at least an order of magnitude less for the EML surface, compared to that of stainless steel, i.e., approximately 10^{-3} . From Eq. (2), the calculated adsorption rates of water for the UHV (A) is 3.1×10^7 molecules/cm²/s and HV (B) devices is 1.0×10^{10} molecules/cm²/s. Assuming the sticking co-efficient of the blue phosphor and mCBP is 1, the calculated adsorption rate for the blue phos-

phor is 8.2×10^{11} molecules/cm²/s and for the mCBP is 1.9×10^{13} molecules/cm²/s based on the deposition rates. The molar percentages of water incorporated within the devices are estimated to be approximately 10^{-4} mol. % for device A and approximately 0.05 mol. % for device B.

At all current densities, the normalized EL spectra for both devices are identical to the spectra shown in the inset of Fig. 1. The peak wavelength and 1931 Commission Internationale d'Éclairage (CIE) color co-ordinates are 464 nm and (0.151, 0.246), respectively, characteristic of the blue phosphor. Figure 1 shows the luminous efficacy versus current density characteristics of devices A and B. It is observed at current densities less than 10 mA/cm² that there is an approximate 1 cd/A difference. EL transient times before operational lifetime testing are identical, 0.96 μs at 10 mA/cm². Unlike oxygen, water does not have a low energy triplet ground state, therefore, it is not expected that water contained within the EML will markedly affect the exciton lifetime prior to electrical aging.

Figure 2 shows the normalized luminance of devices A and B as a function of operational time at a constant dc drive current of 15 mA/cm². The initial luminance (L_0) for device A is 1880 cd/m² and device B is 1774 cd/m². After the first 5 h of testing, the luminance of device A drops by 6% compared to an 11% drop for device B. The normalized luminance difference between device A and device B as a function of time (ΔL_{AB}) is shown in the inset of Fig. 2. The magnitude of ΔL_{AB} increases for the first 5 h of lifetime test. Figure 3 shows the operational voltage of devices A and B as a function of lifetime. The initial driving voltages (V_0) are not significantly different with values of 9.25 V and 8.97 V for devices A and B, respectively. However, within the first few hours, the voltage rise required to maintain a constant current density becomes 0.25 V larger for device B compared to device A. As shown in the inset of Fig. 3, the voltage difference between devices B and A (ΔV_{AB}) displays a similar trend compared to the initial luminance drop. The electric field across the device at this lifetest condition is 8×10^5 V/cm at $t = 0$ h. An electric field of this magnitude is great enough to electrochemically reduce water, resulting in the generation of hydroxide and hydrogen ions (OH⁻ and H⁺).¹⁷ These ions may act as both deep charge traps in the EML and chemically reactive agents and are expected to be

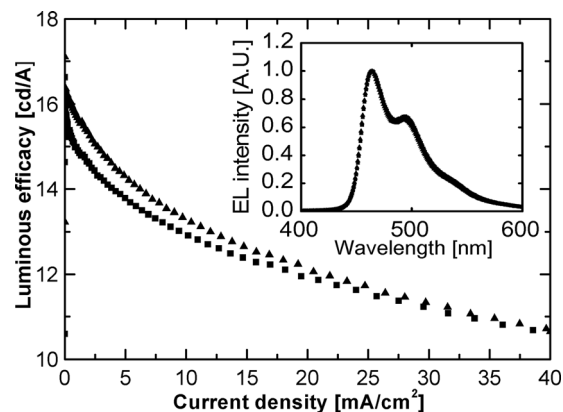


FIG. 1. Luminous efficacy versus current density of devices A (triangles) and B (squares). Inset: Normalized EL spectra of devices A and B at 10 mA/cm².

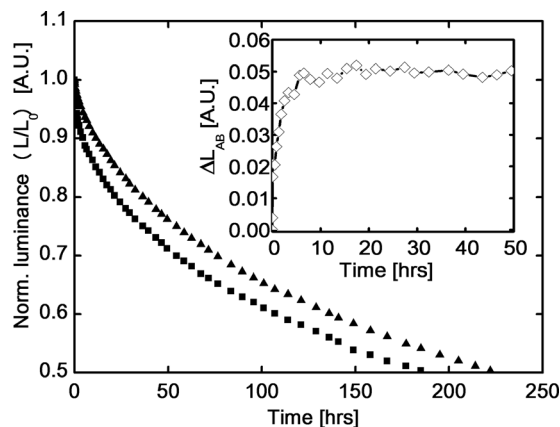


FIG. 2. Normalized luminance (L/L_0) loss of devices A (triangles) and B (squares) as a function of time. Devices are driven at constant dc current density of 15 mA/cm^2 . The initial luminance (L_0) for devices A and B is 1880 cd/m^2 and 1774 cd/m^2 , respectively. Inset: Normalized luminance difference ΔL_{AB} between devices A and B as a function of time.

detrimental to the sensitive components and electrochemical processes occurring in the EML. Based on a polaron-exciton degradation model, a defect density of 10^{18} cm^{-3} , or approximately 0.1% of the molecular density, is presumed to lead to a >50% loss in luminance.^{8,18} Therefore, we speculate that the addition of small quantities of ionic materials in the EML in the form of electrochemically reduced water will advance the degradation process.

Within the first 5 h of device life test, the number of charge carriers injected into device B was calculated to be 7×10^{19} . In the total organic layers of the HV device, the calculated number of water molecules is 3×10^{15} including 1×10^{11} molecules in the EML. Therefore, enough charge is available to ionize all of the water within this time frame. The relative ratio of water in devices A and B is 1:300; therefore, the water contained in device A can be ionized within the first few minutes of operation. We estimate that a 10^{-9} Pa partial pressure of water in the VTE chamber might eliminate the initial luminance drop for the blue PHOLED. However, if the assumption is made that device luminance loss has a linear relationship with a defect density, the presence of as little as

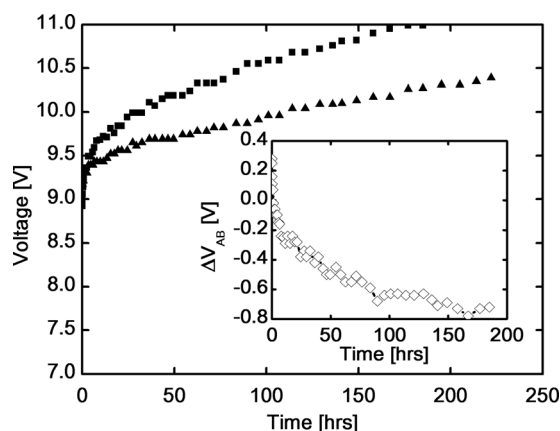


FIG. 3. Operational voltage of devices A (triangles) and B (squares) as a function of time. Devices are driven at constant dc current density of 15 mA/cm^2 . Inset: voltage difference (ΔV_{AB}) between devices A and B as a function of time.

0.01% of the molecular defect density would be enough to cause the initial luminance drop for the HV device.⁸

After the first 5 h of lifetime test, we observe that ΔL_{AB} does not further change and the lifetime curves for both devices track the intrinsic degradation model used by Giebink. Device A achieves a half lifetime of 225 h, a 23% increase compared to device B as shown in Fig. 2. Assuming an acceleration factor⁸ of 1.8, a constant luminance lifetime test on device A at an initial brightness of 1774 cd/m^2 results in a calculated half lifetime of 253 h, i.e., 37% greater than device B. The voltage rise as a function of time for device A results in an increase of approximately 1 V after 188 h of continuous operation. As shown in Fig. 3, this contrasts with the voltage rise of 2 V for device B. It is noted that ΔV_{AB} does not appear to trend with ΔL_{AB} after the first 5 h of lifetime test. We speculate that if water is being electrochemically reduced into ionic states, the initial effect will be severe with respect to luminance loss and voltage rise. The further reduction of water in the transport layers may result in the formation of traps that increase the voltage for the duration of the time test, reflecting the differences between ΔL_{AB} and ΔV_{AB} after the initial degradation event.

In summary, we demonstrate that a blue PHOLED fabricated under UHV conditions improved the lifetime initial LT_{95} luminance drop by a factor of 3 compared to a HV device. We calculate a 10^{-4} mol. \% and 0.05 mol. % water content in the UHV and HV device EMLs respectively. We demonstrate that reducing the partial pressure of water during fabrication can significantly reduce the initial luminance drop and voltage rise. This can be achieved by fabricating devices in UHV conditions or by redesigning the organic materials in the EML so that, in their neutral or excited state, they are less susceptible to reactions with water. This will be the focus of future studies.

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