Reliability and degradation of organic light emitting devices

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We present a simple encapsulation technique for organic light emitting devices (OLEDs). By studying the degradation of a population of OLEDs, we show that the lifetime of encapsulated devices is increased by more than two orders of magnitude over that of unencapsulated devices. In both cases, degradation is primarily due to the formation of nonemissive regions, or dark spot defects. By studying the structure and evolution of the dark spots, we infer that the growth of electrode defects limits device lifetime. Hermetic packaging of OLEDs is essential if they are to be used in commercially viable flat panel displays. © *1994 American Institute of Physics.*

Since efficient green electroluminescence (EL) from an organic light emitting device (OLED) was first reported,[1,2] there has been considerable interest in utilizing OLEDs for full color flat panel display applications. However, there has been little mention of the lifetime limitations of OLEDs, and, to our knowledge, no systematic study of the degradation of a population of devices operating over extended periods of time in a room ambient.

Early investigations indicated that OLEDs have a limited lifetime, characterized by a decrease in EL efficiency and an increase in drive voltage. An OLED made using tris-(8-hydroxyquinoline)aluminum (Alq_3) as the active EL layer lost 50% of its initial EL intensity in 100 h,[1] when operated in dry Ar at a drive current I of 5 mA/cm^2. A later report[3] using distyryl arylene derivatives as the emitter layer in a blue OLED showed a decrease of 90% of initial EL intensity in 130 h, when operated in dry N_2 at I=6 mA/cm^2. In that case, the evolution of ''dark spots'' was identified as the principal degradation mechanism. Operating OLEDs in air[4] resulted in a 99% loss of EL intensity in as little as 150 min. Such short device lifetimes, even in inert atmospheres, render OLEDs useless for commercial applications. Although several recent patents describe means for protecting OLEDs from dark spot formulation,[5–6] the authors analyzed device lifetime only in terms of storage time in controlled temperature and humidity environments.

In this letter, we take the first step towards analyzing statistically significant device populations by presenting a methodology for fabricating and characterizing the lifetime of an array of OLEDs. We introduce a simple encapsulation technique to protect OLEDs from the deleterious effects of the atmosphere, and demonstrate a greatly enhanced lifetime (>1000 h of *continuous* operation) for encapsulated, as compared with unencapsulated, OLEDs. By microscopic analysis of OLEDs, we determine possible mechanisms leading to device failure.

The design for the encapsulated OLEDs (Fig. 1) is based on the established device structure.[1] Substrates are 5.5 cm×3 cm glass plates, precoated with indium tin oxide (ITO) with a sheet resistance of 15 Ω/square, and cleaned as described previously.[10] A 0.7 cm wide strip of 500 Å thick silicon nitride (SiN_x) is deposited over the ITO along the length of the substrate by plasma deposition from a mixture of 2% SiH_4 in N_2, 5% NH_3 in N_2, and N_2 in the ratio 120:35:100 at a substrate temperature of 250 °C. A 0.5 cm wide strip around the entire perimeter of the glass plate is then masked in preparation for the growth of the organic layers. A 250 Å thick layer of the preferentially hole-transporting organic material, *N*,*N*′-diphenyl-*N*,*N*-bis(3-methylphenyl)1,1′-biphenyl-4,4′diamine (TPD), is deposited on the substrates by thermal evaporation from a baffled Mo crucible at a nominal rate of 2–4 Å/s in a vacuum chamber with a base pressure of $<2\times10^{-6}$ Torr. A 370 Å thick layer of Alq_3 is then deposited on the TPD layer. An array of top electrodes consisting of a 1500 Å thick layer of Mg–Ag alloy is subsequently deposited by co-evaporation through a shadow mask of the two metals from separate Mo boats in a 10:1 Mg:Ag atomic ratio under a vacuum of 10^{-5} Torr. Without breaking vacuum, a 300 Å thick layer of Ag is deposited to inhibit atmospheric oxidation of the electrode. Each electrode in the array consists of a circular, 0.1 cm^2 contact, and a 0.7 cm, 0.5 mm wide lead, which brings the electrode onto the SiN_x margin. All thicknesses are nominal, as measured by a quartz crystal oscillator placed near to the substrate.

The completed array of devices is immediately transferred from vacuum to a glovebox under an overpressure of dry N_2 via a pass-through load-lock. A thin bead of epoxy adhesive[8] is applied from a syringe around the edge of the array, taking care not to make contact between the epoxy and

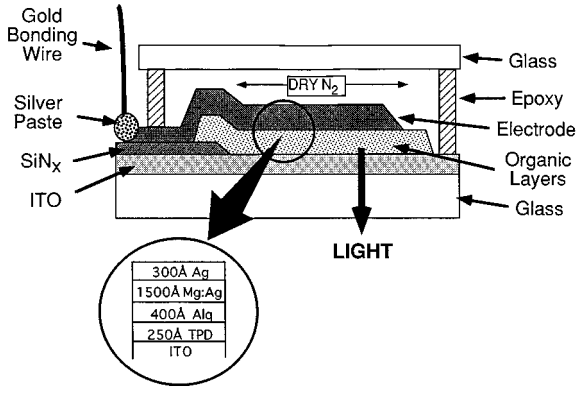

FIG. 1. Schematic side view of an encapsulated OLED.

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the organic layers. To complete the package, a clean glass plate is placed on top of the array, and left for the epoxy to fully cure at room temperature for 24 h. After removal from the glovebox, electrical connection to external circuits is made via a 25 μm Au bonding wire attached to the Mg–Ag electrode lead using a colloidal silver solution. Each device is placed in series with a 1 mA current regulator[9] and a 5 kΩ protection resistor. Approximately 30 V is applied across each device circuit. Periodically, the optical power output of each OLED is measured by placing a large-area Si photodiode over the device. Although this considerably underestimates the total optical power output due to reflection and waveguiding of light in the substrate, it accurately measures the output of each device relative to its output at the start of the experiment. The voltage drop across each device is also recorded. All measurements are taken at room temperature with no additional protection of the packaged device from exposure to the ambient atmosphere.

In Fig. 2(a) we show the time dependence of the optical output power of the encapsulated OLEDs. Each data point represents an average of approximately ten devices. The inset to Fig. 2(a) illustrates the behavior of a set of identical devices without any encapsulation. While the unencapsulated devices show little light output remaining after the first 10 h, the encapsulated devices maintain approximately 40% of their original light output even after $>$1000 h of continuous operation. In both cases, degradation is largely a result of the evolution of nonemissive regions, or dark spots,[3] which increase in both size and number with time. This is accompanied by a gradual increase in the voltage dropped across the devices [Fig. 2(b)]. This is consistent with an increase in device resistance due to a loss of working device area (due to the dark spots), and hence a higher voltage needed to maintain the same drive current. The improvement of more than two orders of magnitude in lifetime with device encapsulation indicates that reaction with the atmosphere, presumably from exposure to oxygen and water, is the limiting factor leading to device failure.

We note that when initially operating large area OLEDs, many devices are short circuits. After briefly running a current of several tens of milliamps through a new device, however, the short circuit opens, and the device emits light. During the extended lifetime tests, in some devices short circuits recur. However, a brief application of high current again opens the short. This behavior suggests the formation of microscopic conduction paths through the organic layers during extended operation which are burnt out on application of high current. Moreover, the initial existence of these paths suggests that nonplanarity exists at one or both of the organic/electrode interfaces, which may lead to nonuniform electric fields across the device resulting in the formation of high current ''hot spots'' or short circuits.

To illustrate the evolution of device failure, Fig. 3(a) shows the distribution of EL intensity from an operating, unencapsulated OLED, photographed through the ITO electrode. White areas of the image correspond to areas of bright EL. Figure 3(b) shows the same OLED approximately 4 min later. It is apparent that the area of bright EL (A) in Fig. 3(a) has become a dark spot in Fig. 3(b), and that the existing

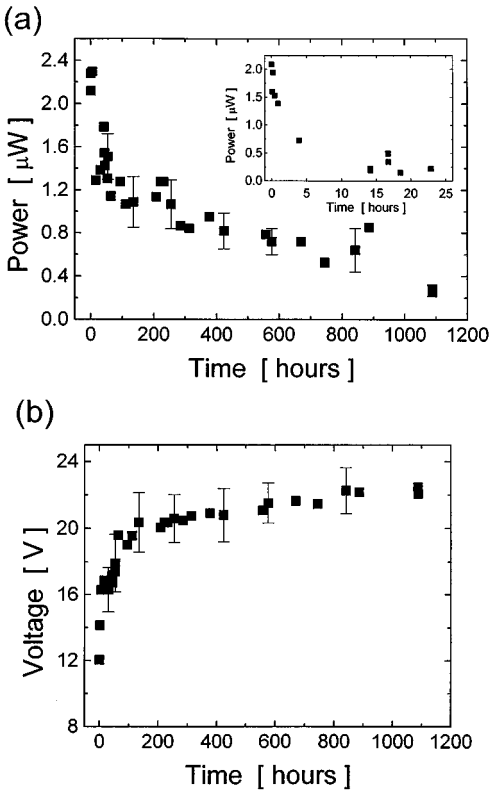

FIG. 2. (a) Time evolution of the average optical power output of a population of approximately ten encapsulated OLEDs. The inset shows the corresponding evolution of identical, unencapsulated devices. (b) Time evolution of the average voltage required to maintain a current of 1 mA through the OLEDs.

dark area (B) has expanded. A new bright area (C) is visible in Fig. 3(b), which also became a dark spot within a few minutes. Two important facts about OLED degradation are highlighted here; first, that dark spots originate as bright, presumably high current areas, and second, that once formed, dark spots tend to increase in area.

To further investigate the nature of dark spot defects, we show in Fig. 4 micrographs of an encapsulated device after several hundred hours of operation. Figure 4(a) shows the top of the Mg–Ag electrode, with a few defects highlighted by arrows. Examination of similar defects in other OLEDs with scanning electron microscopy and electron microprobe analysis reveal them to be deficient in both Mg and Ag as compared to surrounding areas, suggesting that these defects are holes in the top electrode. Figure 4(b) shows the corresponding area of the electrode viewed through the bottom ITO electrode, and shows several black spots, each surrounded by an extended discolored area which corresponds to a nonemissive region on the operating device. In many cases, there is a direct correspondence between the spots on the top of the Mg–Ag electrode and those seen through the ITO electrode, suggesting that the holes pass all the way through the electrode. The discolored regions indicate changes in the organic film or dewetting of the electrode surrounding these defects. Both surfaces of the Mg–Ag electrode are considerably degraded around the edge of the device, suggesting that edge effects, such as enhanced electric fields, accelerate the degradation process.

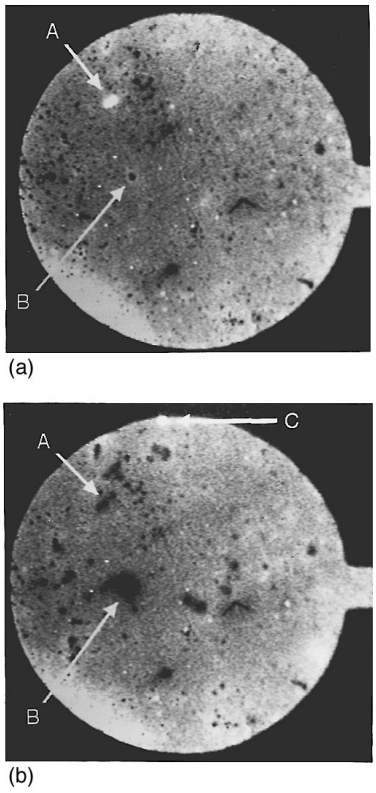

FIG. 3. (a) Distribution of EL photographed through the ITO electrode of an unencapsulated, operating OLED. (b) The same device, photographed approximately 4 min later, showing evolution of dark spot defects.

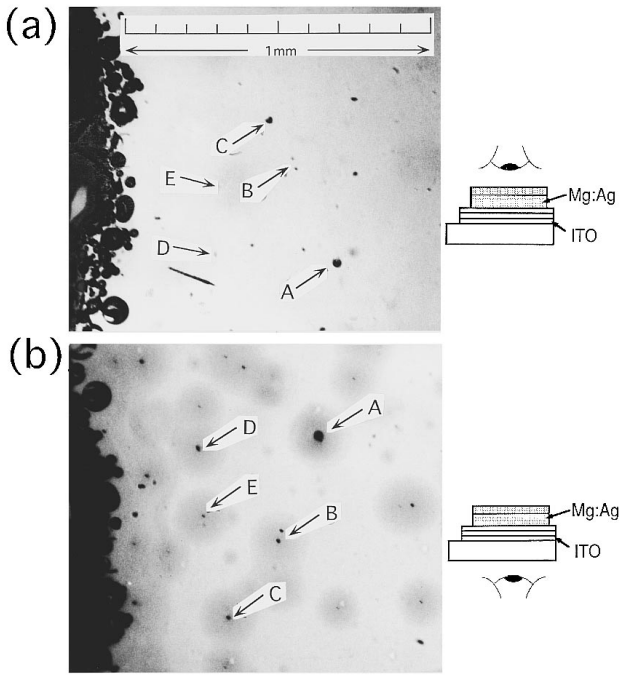

FIG. 4. Micrograph of an OLED after degradation showing (a) image of the top surface of the Mg–Ag electrode and (b) image taken through the bottom ITO electrode. Arrows highlight prominent defects visible on both surfaces of the electrode.

On the basis of these observations, we propose a model for the formation of dark spot defects in OLEDs. The electric field in an operating OLED is extremely high, typically in excess of 2 MV/cm, and it has been shown that the organic layers behave as insulators with low mobility and an extremely high density of traps.[10] Hot spots in the devices may be caused by even higher local fields in areas of electrode nonuniformity caused either by defects introduced during fabrication, recrystallization of the Mg–Ag top electrode, or changes in the degree of wetting of the organic surface by the Mg–Ag electrode. This may result in local rearrangement (leading to holes in the top electrode), enhanced oxidation, or total ablation of the top electrode. The defect thus formed steadily expands due to the enhanced electric field now present at its edge.

We note that the time evolution of the output power of the encapsulated devices is characterized by an initial rapid decay in the first 20 h, followed by a much slower, long-term decay. The initial, fast, decay may be due to reaction of the device with contamination introduced into the package at the time of construction; either water and oxygen adsorbed on to the surface of the devices or outgassed products of the epoxy cure. Once this initial contamination is scavenged by reactions at the contact, the subsequent degradation is slowed. Alternatively, the initial fast decay may be due to the growth of crystallites in the top electrode due to annealing or changes in the wetting properties between the electrode and the organic surface.

In summary, we have presented a systematic analysis of the lifetime of a population of green OLEDs under ambient atmospheric conditions. We have operated an array of devices in room ambient at constant current, and observed a decrease in the average optical power output and an increase in the drive voltage with time. We have proposed and demonstrated a simple encapsulation technique which increases the lifetime of OLEDs by a factor exceeding 100. The remaining degradation may be due to electric-field-induced reaction of nonuniformities in the Mg–Ag electrode, possibly with impurities diffusing into the package. The creation of devices with more than 1000 h of continuous operation using a simple epoxy package, however, demonstrates that with improved, hermetic packaging techniques and close attention to electrode uniformity, commercially viable OLEDs can be realized.

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