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FAILURE MODES IN VAPOR-DEPOSITED ORGANIC LED's

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Abstract: A study of the main failure mechanisms in vacuum vapor-deposited organic light-emitting diodes (LED's) is presented. Three degradation modes were identified for a prototype bilayer ITO/TPD/Alq_3/Mg/Ag device: a) formation and growth of black non-emissive spots, b) abrupt ceasing of light emission associated with catastrophic failures caused by electrical shorts, and c) long term wearout associated with the decrease of quantum efficiency and luminance along with an increase in voltage, while the device is stressed under constant current.

INTRODUCTION

A comprehensive study of the main failure mechanisms in vacuum vapor-deposited organic light-emitting diodes (LED's) is presented. In this study a prototype bilayer organic device was used where the hole transporting layer (HTL) was TPD and the electron transport layer (ETL) was Alq_3.[1] In this device, due to the optimized charge injection and balance the recombination region is located far from both electrodes and light emission can occur at relatively low electric fields.[1] Thus, some commonly observed degradation modes usually seen in single layer devices, caused by Joule heating at high electric fields, or by quenching of the emissive species at the electrodes, are almost excluded.

Three distinct degradation modes were identified: a) formation and growth of black non-emissive spots, b) abrupt ceasing of light emission associated with catastrophic failures caused by electrical shorts, and c) long term wearout associated with the decrease of quantum efficiency

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and luminance along with an increase in voltage while the device is stressed under constant current. Characterization of post-stress devices by luminescent microscopy revealed that black spots result from delamination of the metal at the Alq_3/Mg interface which is initiated by pinholes on the cathode. Moreover the addition of a thin conductive polymer layer between the TPD and the ITO/glass substrate was found to suppress the leakage currents and eliminate the associated catastrophic failures.

EXPERIMENTAL

Bilayer organic LED's were vapor-deposited in a vacuum of about $2x10^{-7}$ Torr on indium-tin-oxide (ITO) glass substrates. The devices consisted of 600 Å of TPD (N,N´-diphenyl-N,N´-bis-(3-methylphenyl)-{1,1´-biphenyl}-4,4´-diamine) and 600 Å of Alq_3 (8-hydroxyquinoline aluminum). Organic LED's were also fabricated by incorporating a transparent conducting polymer layer between the ITO/glass substrate and the TPD layer. The conducting polymer was polyaniline (PANI) doped with camphor-sulfonic acid (CSA) which was spun on ITO/glass from *m*-cresol solutions prior to TPD deposition. The cathode was composed of 1000 Å of magnesium (Mg) and 1000 Å of silver (Ag). The deposition rates of the organic and metallic layers were approximately 3 - 5 Å/s and 10 - 20 Å/s, respectively. Substrate was close to room temperature during device fabrication. The device luminance-current-voltage characteristics were recorded by a HP semiconductor parameter analyzer, model HP-4155. Luminance was measured using a Graseby Optronics optometer, model S370. An electroluminescence (EL) and a photoluminescence (PL) microscope coupled with a CCD camera assembly (for image acquisition and storage) were used to study the black spots. All the experiments presented here were performed at room temperature.

RESULTS

1. Formation and growth of black spots

The formation and growth of black spots was studied under ambient conditions.[2] Imaging of the device was performed in-situ under constant low voltage stress (4.5 Volts) to eliminate any accelerated thermal degradation due to Joule heating. It was found that the *number* of black spots did not change with exposure to air, which suggested that the dark regions observed in the EL are created by initial conditions. Pinholes through the metal can provide entry points for water and oxygen. Particles and imperfections, preexisting on the ITO surface or introduced during device fabrication, are the best candidates for pinhole initiation. For particles of size exceeding the thickness of the organic layer, shadowing effects and lack of complete coverage is expected during deposition. However pinholes associated simply with grain-boundaries, due to the polycrystalline nature of the Mg/Ag film, induced during evaporation, can also yield the same effect. The black spot growth rate was mainly dependent on the ambient humidity content. No growth was observed in a dry N_2 chamber where water and oxygen existed only at parts per million levels. Moreover the growth was highly accelerated when 100 % relative humidity was introduced into the chamber.[3] Surprisingly, introduction of dry oxygen into the chamber did not affect noticeably the growth rate.

The EL dark spots were found to exhibit PL, which suggested that the organic part of the dark regions is still chemically intact.[2] Nomarski optical microscope images also revealed that the dark spots coincide with hemispheric dome-like textures centered around micron sized defects. These observations showed that EL black spots originate from lack of carrier injection, rather than from a PL quenching process.[4] Since the most likely cause of an injection barrier in these dark regions is a delamination process, the top (Mg/Ag) electrode was peeled away from the sample, with Scotch tape, in an attempt to isolate the interface at which the delamination might have occurred.[5] It was discovered that Mg delaminates very easily from Alq_3. In addition, very little Alq_3 was detected (with PL microscopy) on the Mg surface after removal of the electrode and the brighter circular regions in the PL (coincided with EL black spots) disappeared upon removal of the top electrode.

Furthermore, the PL of a stressed device was compared to that of an unstressed one, located on the same substrate, and it was found that the delaminated regions (black spots) of the stressed device had very similar sizes with those on the unstressed device. That was a clear evidence that the growth rate of black spots is not an electric field dependent process. In addition, the presence of microscopic ($< 20\ \mu m$) black specks appeared in the PL images of stressed devices. These

sites, which are located near the center of the delamination regions, represent areas where PL was severely quenched and in contrast to EL black spots their formation was electric field enhanced. Although the origin of these defects is not well understood, we can postulate that these are sites of leakage currents which lead to the generation of Joule heating within the Alq_3, and eventually oxidation reaction with the Mg electrode. Alternatively the black non-emissive areas may be regions where a thermally activated condensation reaction may be taking place, producing a non-emissive residue, as described by Papadimitrakopoulos *et al.*[6] Both types of reactions can induce volumetric rearrangements in the vicinity of the pinhole, thus opening pathways for the delamination of the poorly adhered Mg from Alq_3.

2. Catastrophic failures from leakage currents

2.1 Leakage current formation due to substrate imperfections

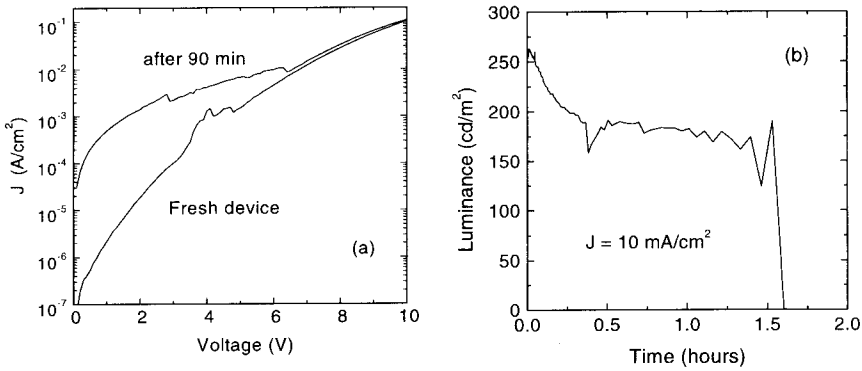

Fig. 1 (a) Current vs. Voltage characteristics for a device developing leakage currents, (b) Luminance vs. time showing catastrophic failure for a ITO/TPD/Alq_3/Mg device when stressed at constant current (10 mA/cm^2) in dry N_2.

When TPD is vapor-deposited directly on ITO it yields devices that fail catastrophically almost immediately, if electrically stressed under dry N_2 conditions. Furthermore, noisy leakage currents

are always formed prior to any failure. Figure 1(a) shows a commonly observed noisy current-voltage (J-V) behavior of an ITO/TPD/Alq_3/Mg/Ag device. After about 90 min. of stress (at constant current of 10 mA/cm^2) the device ceased to emit light and failed catastrophically as shown in Figure 1(b). A blister (of about 100 μm in diameter), indicating local melting of the organics, was detected on the active area of the device. Interestingly, the same device structure, if operated in air, showed less leakage and survived the continuous stress for several ten of hours without any catastrophic failure or leakage current formation.

The performance and reliability of the ITO/TPD/Alq_3/Mg/Ag device was significantly improved when 1000 Å of PANI:CSA was spin cast on the ITO/glass substrate prior to TPD deposition. The J-V characteristic was smoother with a much less noisy leakage current as shown in Figure 2(a). The use of conductive PANI also reduced dramatically the catastrophic events. Most devices lasted more than 1500 hours when stressed at constant current in dry N_2. These experiments suggested that preexisting particles or imperfections on ITO may be the cause for the formation of leakage currents. As shown in Figure 2(b) the evaporated thin TPD film does not cover large particles preexisting on the surface of ITO. The arrows in the figure indicate areas where the cathode could come in contact with the ITO. Very high electric fields could be formed locally around this imperfection and leakage currents can produce intense local heating which can melt the organics and establish an electrical short. The latter can be eliminated if a thin layer of a conductive material is used to cover the imperfection in a conforming way, as shown in Figure 2(c). Here, the conductive layer, sandwiched between the anode and cathode, will act as a "limiting resistor" suppressing the leakage current. Pani:CSA and other similar doped conductive polymers have been shown to work effectively.

The Pani:CSA layer was found to be an efficient hole injecting transparent electrode, where despite its considerable thickness the operational voltage of the devices was not affected and it was even reduced in some cases. Improvements in the EL quantum efficiency, from 1.4 % ph/el to 2.0 % ph/el, were also observed. Finally, it was found that transparent thin films of Pani:CSA can be used as a replacement for the ITO without much affecting the device characteristics. Our findings demonstrate that Pani:CSA could be used successfully, not only for polymer LED's,[7,8] as reported earlier, but also for the well established vapor-deposited LED's.

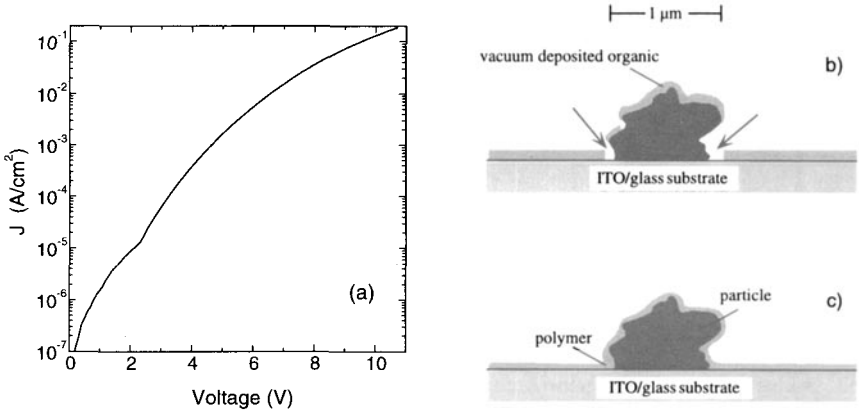

Fig. 2 (a) Current vs. Voltage characteristics for a device containing 1000 Å of Pani:CSA between the ITO and TPD, (b) drawing showing the incomplete coverage of a substrate particle by vacuum deposited TPD, (c) conformal coverage of a particle by the conductive polymer.

2.2 Leakage current formation due to crystallization

Crystallization of the organic layers can also initiate catastrophic failures. Particularly, small molecules like TPD having low glass transition temperature (T_g), tend to crystallize during operation or even storage.[9] Generation of local heat during electrical stress can cause crystallization and densification which disrupts the uniformity and continuity of the thin film. Crevices and pinholes[9] can then be the initiators for leakage currents which eventually evolve to short-circuit failures. Similar behavior is expected when a device containing a low T_g material is operated at elevated temperatures. The inclusion of a high T_g hole transporting layer (like star-burst amines) between the ITO and the TPD, which forms a uniform, smooth, amorphous and vitreous thin film, has been found to suppress leakage current formation.[10] In general, these types of organic "buffer layers" are essential to establish good device thermal stability.[11]

2.3 Long term leakage current formation

Finally, formation of leakage and eventual catastrophic failures have been observed at time scales much longer that the ones described above. For instance both type of devices having Pani:CSA or star-burst amines as buffer layers are prone to this failure. The nature of this kind of failure is not clear at present, however it may be related with the growth of conducting regions within the active area of the device. Slow ionic migration and accumulation within the device, driven by the electric field, may be providing the paths for these leakage currents.

3. Long term wearout

It is well known that organic LED's undergo continuous luminance degradation when stressed at constant current.[1,12] A typical example of this is shown in Figure 3 where an ITO/Pani:CSA/TPD/Alq_3/Mg/Ag device is stressed at 10 mA/cm^2. This experiment was performed under dry N_2 conditions to eliminate growth of black spots or other ambient related degradations. The observed luminance reduction is consistent with the quantum efficiency decrease with stress time. In addition to this an internal resistance is formed which subsequently increases the voltage across the device to maintain the externally applied current.

Although many different mechanisms can cause this long term wearout effect, we believe that a major part of the degradation is closely related to aspects of the interface between the organic layer, where emission occurs and where the barrier results in enhanced concentration of charge carriers. Impurities, which may be introduced during fabrication, formed as consequence of stress or drawn in by the applied electric field, will be the most detrimental if accumulated there. Mechanisms may include exciton quenching, charge trapping, or catalysis of degradative reactions. We have found that co-evaporation of 0.5 wt. % quinacridone (98 % nominal purity) with Alq_3 reduced the lifetime, shown in Fig. 3, by a factor of 10^4, together with a much faster voltage increase. However Alq_3 devices doped with quinacridone purified with train sublimation showed improved lifetimes similar to that shown in Fig. 3.

Modification in the chemical structure of the hole transporting molecule can also affect the device lifetime.[12,13] Due to their proximity to the emissive region, the hole transporting molecules can diffuse into the Alq_3 layer, chemically interact, and quench a portion of the emissive excitons. Finally, electrochemical degradation related to the interaction of the organics

with the electrodes can generate byproducts that can contribute to the long term reduction of quantum efficiency.

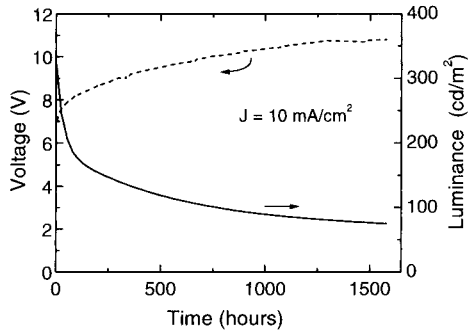

Fig. 3 Luminance and Voltage as a function of time when stressed at 10 mA/cm^2 for a ITO/Pani:CSA/TPD/Alq_3/Mg/Ag device.

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