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Sudden death of organic light-emitting diodes

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ABSTRACT

The degradation in light output of an Organic Light Emitting Diode (OLED) has been studied extensively and has been explained by different mechanisms, such as formation of chemical defects or electrical traps and by thermally induced inter-diffusion of dopants. However, there is an overlooked type of degradation, where the light output decreases rapidly with time. This catastrophic failure can often be attributed to a hard electrical short due to local defects. Here, we show that this "sudden death" can also occur in the absence of a hard electrical short. We investigate this phenomenon by current–voltage characteristics and small-signal impedance measurements on typical OLEDs with a LiF cathode interlayer. We show that in a short period of time the built-in voltage of the diode vanishes; the *J–V* characteristics become symmetric. The origin is a dramatic increase in the work-function of the LiF interlayer. The interlayer changes from an electron-injecting contact to a quasi-Ohmic hole-injecting contact. The pristine bipolar diode does not become electrically shorted, but suddenly transforms into a unipolar hole-only diode. Upon applying a high voltage the original diode is restored, manifesting the dynamic switching of the LiF contact.

1. Introduction

Organic light emitting diodes (OLEDs) have a bright future in mobile phone displays, television screens and large-area lighting [1–9]. The practical application has initiated numerous studies on their reliability. The light output has been measured as a function of time under constant current stress. The degradation, or decrease in light output, has been thoroughly investigated [10–22] and the experimental data obtained have been summarized in numerous reviews [23–26]. Degradation in OLEDs is typically classified into three categories: Dark spot formation, intrinsic degradation and catastrophic failure. Dark spot formation is the increase of non-emissive regions with time. The dark spot growth is strongly related to oxidation reactions of the organic or electrode materials with the environment. Protection from the ambient, by proper encapsulation, is effective in suppressing dark spot growth and therefore increases the OLED lifetime [24,27]. Intrinsic degradation occurs when the OLED brightness decreases without any obvious change in the OLED's appearance. Under continuous operation the light output gradually decreases with time. The required driving bias then concomitantly increases gradually. The degradation rate increases with increasing set current value and temperature. This type of degradation has been attributed to

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processes as diverse as formation of defects in the chemical structures, formation of electrical traps, and thermally induced diffusion of dopants [12,28–30]. In this contribution we focus on the third type of degradation; catastrophic failure, in which the light output vanishes almost instantaneously and, simultaneously, the bias voltage drops abruptly. This type of failure constitutes a severe reliability problem as it occurs at an unpredictable moment, hence the name "sudden death".

The phenomenon has been typically associated with the presence of local defects, such as dust particles [27,31,32]. In this case, the failure is inevitably accompanied by the formation of a hard electrical short. Controlled processing conditions, such as increasing the thickness of the carrier transporting layers [33], reduction of the working temperature [34] and improved encapsulation have succeeded in increasing the OLED lifetime. However, even for state-of-the-art OLEDs, the phenomenon can still persist. Here we show that sudden death can occur in the absence of a hard electrical short, which implies a different origin. We investigate OLEDs with a LiF cathode interlayer. We show that under prolonged operation, the LiF contact is transformed from an electron- to a hole-injecting contact.

To that end, we measure the light output as a function of time and characterize the degraded diodes simultaneously by *J*–*V* and small-signal impedance measurements. We show that the catastrophic failure is due to the disappearance of the built-in voltage. The pristine bipolar diode is not electrically shorted but is suddenly transformed into a hole-only unipolar diode. During operation, spikes in current and luminescence are observed, the occurrence of which is related to memristive switching. Upon applying a high voltage the original diode is restored. We argue that upon degradation the work-function of the LiF interlayer is raised, as supported by recently reported electroluminescence (EL) of symmetric LiF/polymer/LiF diodes, measured in both bias polarities [35]. To demonstrate hole injection by LiF contacts we reproduced the symmetric ITO/LiF/P3HT/LiF/Al diodes.

2. Experimental

The typical OLED stack we used is schematically presented in Fig. 1a. The encapsulated OLED is composed of

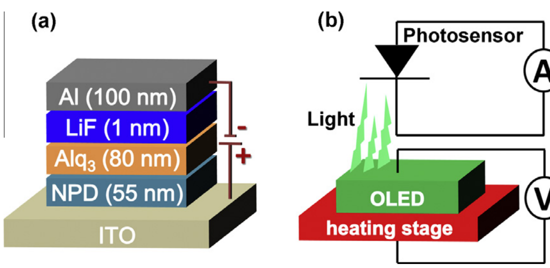

Fig. 1. (a) Schematic of the used OLED stack. The device area is typically 5.5 cm^2 (b) Schematic of the experimental setup. The OLED is in thermal contact with a heating stage and in series with a voltage source. The light output is captured with an ammeter through a silicon photo-sensor located directly above the OLED.

an 80 nm thin emissive layer of tris-(8-hydroxyquinoline) aluminum (Alq_3). To enhance the efficiency, a 55 nm thick hole transport layer of N,N′-di(1-naphthyl)-N,N′-diphenyl-(1,1′-biphenyl) 4,4′-diamine (NPD) is used. As cathode a 1 nm thin film of LiF endcapped with Al is used.

As schematically shown in Fig. 1b, the light output was measured as a function of time using a silicon photo-sensor connected to a Keithley 487 picoammeter. Temperature dependent measurements were carried out in a liquid helium cryostat (Advanced Research Systems, ARS – HC2). The degraded OLEDs were characterized by *J*–*V* measurements and by small-signal impedance measurements. *J*–*V* measurements were performed using an Agilent semiconductor parameter analyzer 4156C. Small-signal admittance measurements over the range of 50 Hz to 1 MHz were carried out with a Fluke PM 6306 RCL meter. In all the measurements the LiF/Al electrode is grounded, while the bias is applied to the ITO electrode.

To demonstrate hole injection by LiF contacts we also fabricated symmetric ITO/LiF(5 nm)/P3HT(70 nm)/LiF(5 nm)/Al diodes. The ITO substrates were cleaned, using in order, acetone, soap scrubbing, and isopropanol. LiF (Sigma Aldrich, 99.9%) was deposited by vacuum sublimation from an alumina crucible under 10^{-6} mbar. P3HT (>98% head to tail, M_n = 54000 to 75,000 g mol^{-1}, Plextronics, purchased from Aldrich) was dissolved in o-dichlorobenzene with a concentration of 15 mg/ml and cast at 800 rpm. The diodes were prepared, kept and characterized in inert N_2 atmosphere (O_2, H_2O < 1 ppm).

3. Results and discussion

A typical example of light output as a function of time is presented in Fig. 2a. The diode is continuously operated at a current of 20 mA/cm^2. The initial luminance is 680 Cd/m^2. The light output slowly decreases with time to reach 600 Cd/m^2 after 400 h, or approximately 16 days. The voltage to sustain the current concomitantly rises from 4.5 V to 6 V. During this time the appearance of the OLED does not change. The light output degrades gradually with small fluctuations, as can be seen in Fig. 2a.

After 400 h a catastrophic failure occurs. The light output measurements are expanded in Fig. 2b. The light output first rapidly decreases with time; it is halved in two days. The light output becomes increasingly noisy before it drops to zero. At the same time the voltage to sustain the current drops by almost an order of magnitude. Simultaneously the current transport is changing. The *J*–*V* characteristics are presented in Fig. 3a. The black curve represents the pristine OLED. The *J*–*V* curve is typical for a bipolar rectifying diode. The built-in voltage is around 2 V, equal to the difference in work-function between the ITO anode and the LiF/Al cathode.

After sudden death the built-in voltage disappears and the *J*–*V* characteristics become symmetric (red *J*–*V* curve in Fig. 3a). At very low bias the current is Ohmic; at higher bias the current increases becoming super-linear with bias, which is indicative of space-charge limited current.

The capacitance as a function of bias is presented in Fig. 3b. The black line represents the pristine OLED. Below