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Laboratory Thin-Film Encapsulation of Air-Sensitive Organic Semiconductor Devices

Samuel P. Subbarao, *Student Member, IEEE*, Matthias E. Bahlke, *Student Member, IEEE*, and Ioannis Kyriassis, *Member, IEEE*

Abstract—We present an approach, which is compatible with both glass and polymer substrates, to in-laboratory handling and intra-laboratory shipping of air-sensitive organic semiconductors. Encapsulation approaches are presented using polymer/ceramic and polymer/metal thin-film barriers using commercially available materials and generally available laboratory equipment. A technique for depositing an opaque vapor barrier, a transparent vapor barrier, and an approach to storing and shipping air-sensitive thin-film organic semiconductor devices on both polymer and glass substrates are presented. Barrier performance in air was tested using organic light-emitting diodes (OLEDs) as test devices. The half-life performance of OLEDs on plastic substrates in air exceeded 700 h, and that on glass exceeded 500 h. Commercially available heat-seal barrier bag systems for device shipping and storage in air were tested using a thin film of metallic calcium to test water permeation. More than four months of storage of a metallic calcium film in a heat-sealed foil bag was demonstrated in the best storage system. These approaches allow for the encapsulation of samples for longer duration testing and transportation than otherwise possible.

Index Terms—Encapsulation, lifetime, organic, organic light-emitting diode (OLED), oxide, polymer, semiconductor.

I. INTRODUCTION

ORGANIC semiconductors are used in a variety of devices, including organic light-emitting diodes (OLEDs), organic photovoltaics, organic photodetectors, and organic field-effect transistors (OFETs). These semiconductors are often sensitive to water vapor and oxygen and need to be encapsulated [1]–[3]. For devices on transparent polymer flexible substrates, which are not natively impermeable to water vapor and oxygen, it is also important that any barrier used be mechanically flexible and transparent to visible light on the light-emitting side. Traditional epoxy/getter approaches, which have been effective on glass-substrate-based devices, are not suitable for transparent flexible organic devices. Mechanically flexible thin-film approaches are required.

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There are generally two goals for any barrier: to improve storage lifetime and to enhance continuous-use lifetime. This paper focuses on storage lifetime—i.e., a device's ability to maintain its performance after a certain storage time. The acceptable lifetime will vary based on the type of device and the tester's performance needs. In this paper, we use an OLED as the test device and measure the time to 50% of the initial brightness. This is a common measure of OLED life and has been used to evaluate other barriers in the literature [4], [5].

Several methods have been presented in the literature to encapsulate OLEDs and other organic-semiconductor-based devices that use a glass substrate. Burrows *et al.* [5] presented an epoxy and glass seal. This is a serial process in which the adhesive is applied by a syringe and can be detrimental to the device if the epoxy contacts the semiconductor layers. Al–Li and HDPE multilayer barriers have also been used with half-lives of 63 h on glass [6]. Other groups have used a combination of oxide, polymer, and epoxy seals [7] for OLEDs on glass with a half-life of over 1000 h. More recent barriers have produced significantly better performance. Using a plasma-deposited silicon oxide/silicone hybrid barrier on glass, Mandlik *et al.* [4] demonstrated an accelerated (65 °C and 85% RH) measured half-life at 7500 h, using active area rather than light intensity as the metric.

There are also a number of encapsulation techniques that are suitable for flexible substrates. Polymer film encapsulation using CVD poly-p-xylylene (Parylene N) and/or poly-2-chloro-p-xylylene (Parylene C) was shown to improve lifetime by four times over that of unencapsulated [8] samples. Vitex has presented a proprietary barrier coating on PET with more than 2000-h half-life [9]. A lamination process for encapsulating OLEDs on plastic (PES) has shown a half-life at 230 h [10].

Despite the aforementioned work, it has been proven challenging for groups to find a satisfactory encapsulation solution that can be deployed in a laboratory setting using commercially available substrates and equipment, particularly for testing and analysis of sensitive devices. There are no commercially available solutions that are accessible to research and development laboratories for encapsulating thin-film organic devices. Commercial solutions typically require specialized equipment and intellectual property licenses, and laboratory-equipment-based solutions to date have exhibited inadequate performance.

There is a significant demand for techniques that are able to preserve device characteristics for air-sensitive devices in the laboratory during testing and also for exchanging samples between laboratories for cross-testing. This has been proven to be a particularly important issue for organic-solar-cell and

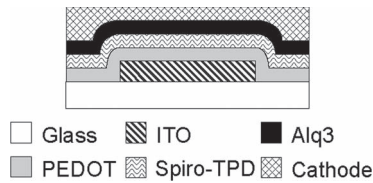


Fig. 1. OLED stack: PEDOT:PSS (85 nm), spiro-TPD (50 nm), Alq3 (50 nm), and Mg:Ag/Ag (50/50 nm).

organic-solid-state-lighting efficiency testing, in which testing at centralized laboratories is a requirement for device validation. In these centralized facilities, devices are often placed in a queue for several weeks before evaluation. Storage and shipping solutions that are accessible to R&D groups and that are able to preserve device characteristics during that time are essential.

II. OLED FABRICATION AND TESTING

To test encapsulation performance, we use the efficiency of an OLED driven with a low duty cycle. The length of time until the OLED output intensity halves determines the half-life performance of encapsulation. The stack used is shown in Fig. 1 and consists of an 85-nm layer of poly(3, 4-ethylenedioxythiophene):poly(styrenesulfonate) (PEDOT:PSS, Baytron P VPCH 8000 purchased from H.C. Starck), which is spun on and baked at 110 °C prior to transport layer evaporation: 50 nm of spiro-TPD (E105 purchased from Luminescence Technology Corporation). Fifty nanometers of aluminum tris-hydroxy quinolate (AlQ3: LT-E401 from Luminescence Technology Corporation), and a Mg:Ag (10:1)/Ag (50-nm/50-nm) cathode are then evaporated to complete the stack.

Two sizes of OLEDs were fabricated: a 40 × 40 mm OLED on a 50 × 50 mm substrate, and a set of 4, 5 × 5 mm OLEDs on a 50 × 50 mm substrate. The smaller OLEDs were used for testing lifetime. The larger OLEDs were used to test large-area coverage.

III. OLED ON GLASS SUBSTRATE

A. Substrate Processing and Cleaning

The indium tin oxide (ITO)-coated glass (40 Ω/square) was purchased from Luminescence Technology Corporation. The substrate was spin cleaned first with acetone, isopropanol, and methanol and then coated with HMDS and AZ4620 photoresist. The resist was exposed, developed, and postbaked at 110 °C for 15 min. The ITO was then etched using aqua regia (3:1, hydrochloric acid:nitric acid). The ITO was then cleaned using acetone, isopropanol, methanol, and treated with an O₂ plasma for 2 minutes.

B. OLED Stack

Immediately after the plasma treatment, the ITO was coated with PEDOT:PSS and baked at 110 °C for 15 min inside a glove box with direct access to the evaporation and CVD chambers. The organic semiconductors were then deposited on the substrate: 50 nm of spiro-TPD, followed by 50 nm of Alq3. The cathode used was 50 nm of 10:1 Mg:Ag alloy, followed by 50 nm of Ag.

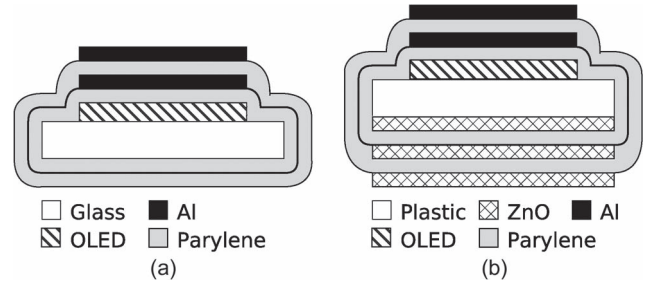


Fig. 2. OLED encapsulation for (a) glass and (b) plastic. ZnO (50 nm), Parylene C (2 μm), and Al (50 nm).

C. Encapsulation

The glass substrate on which the OLED is fabricated is an excellent water vapor and oxygen barrier. The cathode area, however, is permeable to water vapor and oxygen. To protect the organics against attack from the cathode side, the sample was coated with 2 μm of Parylene C and then 100 nm of Al (masked so that the device is not shorted). Parylene deposition does not significantly degrade OLEDs and has been used in similar multilayer barrier stacks for OLEDs and other device architectures [7], [11]. This parylene–Al stack is repeated twice. The encapsulation cross section is schematically shown in Fig. 2(a).

D. Testing Method

A low-duty-cycle test was performed in order to determine the storage performance of the barrier. The OLEDs were turned on for 1 s (sampled ten times during this 1 s) and then turned off for 10 min (0.166% duty cycle). Prior to testing, the OLEDs were burned in for 30 s to minimize the increase in brightness immediately after turn-on. The low-duty-cycle testing allowed us to separate coulombic OLED degradation from degradation by water and oxygen penetration. Lifetime testing of 100% duty cycle and 400 cd/m² was also conducted in parallel in encapsulated devices and devices stored in the glove box, and both were found to be limited by the OLED lifetime, which, in this case, is shorter than the storage lifetime. The tester was a homemade voltage-controlled current source in a light-absorbing enclosure, which was connected to a data acquisition controller (LabJack U3-HV) controlled by LabView. The bias current was set prior to the collection of data so that the OLED intensity was 350 cd/m² as measured by a Konica-Minolta LS-100 Luminance Meter.

E. Results

The lifetime of the OLED on glass is shown in Fig. 3. Half-life was measured with respect to the 75-h mark, which would correspond to 390 cd/m² starting out. Half-life occurs at 600 h at 196 cd/m². This gives a half-life of 525 h.

IV. OLED ON PLASTIC SUBSTRATE

A. Substrate Processing and Cleaning

To fabricate OLEDs on polyethylene naphthalate (PEN, Dupont Teijin Films), the process followed was similar to

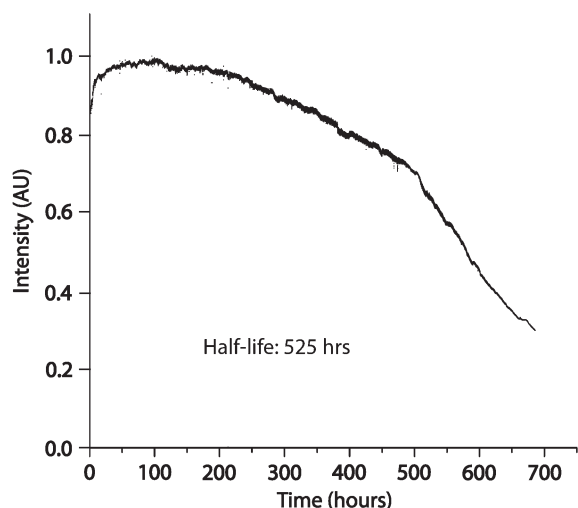


Fig. 3. Lifetime of OLED on glass with encapsulation. Half-life at 525 h.

that used to fabricate OLEDs on glass. PEN coated with ITO (Techni-Met) with a sheet resistance of $60 \Omega/\text{square}$ was used. PEN offers several benefits over most other plastic substrates, including thermal tolerance well over 100°C [12]. The same solvent-cleaning procedure as used on glass was employed. The substrate was treated with UV/ozone for 5 min after solvent cleaning. Aqua regia for the etch step was diluted 3:1 water:etchant; concentrated aqua regia etched too quickly. The OLED fabrication was identical.

B. Encapsulation

PEN is a poor water vapor and oxygen barrier. The parylene–Al double layer on the cathode side, which is used for devices on glass substrates, is therefore not sufficient to protect devices on plastic. Many barriers to oxygen and water vapor are opaque, however, which is problematic in a bottom-emitting OLED. A transparent ceramic/polymer multilayer was used for protection on the exterior of the sample, which allowed the use of a commercially available substrate. After OLED fabrication, a layer of ZnO (50 nm) was sputtered onto the plastic side of the sample (this step can also be performed after the dehydration bake and before the OLED deposition). Then, the sample was coated with Parylene C ($2 \mu\text{m}$). Al (100 nm) was then deposited on the cathode side through a shadow mask. This entire process was repeated (ZnO on the front side, Parylene C over the whole sample, and Al on the cathode side). A final layer of ZnO was then deposited on the front side. In total, the barrier on the plastic side consists of three ZnO layers and two parylene layers, while the barrier on the cathode side consists of two Al layers and two parylene layers. The OLED on plastic with the encapsulation stack is shown in Fig. 2(b).

C. Results

The lifetime of the OLED on PEN is shown in Fig. 4. Half-life was measured with respect to the 10-h mark, corresponding to $397 \text{ cd}/\text{m}^2$. The projected half-life, based on the first 500 h of data, is 760 h.

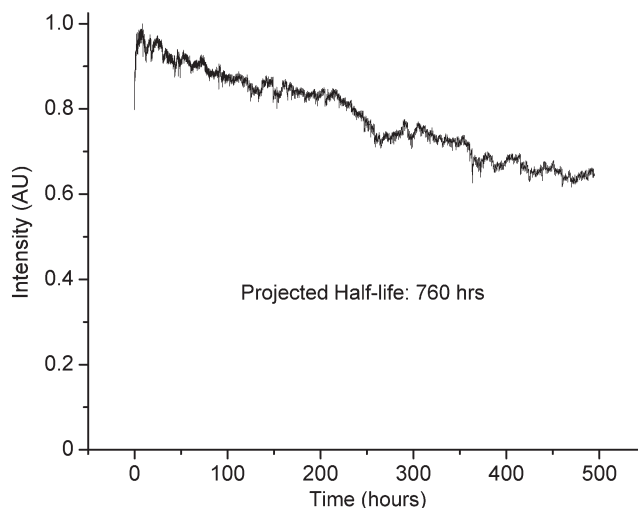


Fig. 4. Lifetime of OLED on plastic with encapsulation. Projected half-life at 760 h.

TABLE I
STORAGE LIFE

Package	Time
Laminated foil bag	175,000+ minutes (4+ months)
Metallized MET/PET bag	1,080 minutes (18 hours)
Polyethylene sandwich bag	33 minutes
Direct exposure to air	3 minutes

V. STORAGE AND SHIPPING

Storage and shipping of sensitive organic semiconductor devices are a critical issue. One approach is to heat seal sensitive devices in a laminated foil bag in an inert-gas environment (a glove box with $< 0.1\text{-ppm}$ oxygen and water vapor). Several candidates were analyzed, and the tests show that laminated foil bags form a good barrier, which is far superior to that of metallized film bags (Table I). Results are presented using metallic calcium films (50 nm) on glass slides as indicators for oxygen and moisture permeation. A polyester film bag (KSP-150-1MB), a silver MET/PET film bag (602B-1M) (both obtained from Ampac Packaging, LLC), and a plain polyethylene bag (Webster Industries WBIZIPSAND) were tested, with the sample being sealed inside a glove box, which communicated with the evaporator. The laminated foil bag sample likely has additional lifetime, but because the sample was exposed when it was examined, a limited number of data were available, and the four-month mark represents the opening of the last sample. Opening and resealing the sample inside the glove box were considered but may not offer a fair comparison because the atmosphere will be flushed with new dry nitrogen at each examination interval.

VI. CONCLUSION

The encapsulation of polymer-substrate-based organic-semiconductor-based electronic devices has been a pressing

concern for the OLED community in both commercial settings and research laboratories. While laboratory uses, such as shipping incomplete samples and testing, do not often require the extended lifetimes that commercial products demand, degradation can be an obstacle to sample processing in multiple laboratories or measuring device performance in a calibrated environment, such as a national standard laboratory or cross-checking laboratories.

This paper has presented a straightforward approach to handling air-sensitive organic-semiconductor-based devices on both glass and plastic substrates using generally available laboratory equipment. Devices that can tolerate an opaque and conducting barrier (e.g., devices on glass and the back of polymer-substrate-based devices) can be encapsulated using a multilayer polymer/metal film. Devices that require a transparent or insulating barrier (e.g., OLEDs on plastic or OFETs) can be protected using a polymer/ceramic film. A combination of approaches can also be employed. We have demonstrated that it is possible to use a commercially sourced ITO film and apply encapsulation on the front side to form a flexible transparent barrier in conjunction with the opaque barrier on the rear of the device. Encapsulation performance was tested using OLEDs, and performance in air was extended to more than 500 h for both devices, which is adequate for most laboratory efficiency performance testing. A commercially available laminated foil barrier bag for storing and shipping devices has also been presented and tested using a calcium film. A lifetime extension of more than four additional orders of magnitude has been achieved with this storage system.

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