

Gas Permeation and Lifetime Tests On Polymer-Based Barrier Coatings

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ABSTRACT

We describe a flexible, transparent plastic substrate for OLED display applications. A flexible, composite thin film barrier is deposited under vacuum onto commercially available polymers, restricting moisture and oxygen permeation rates to undetectable levels using conventional permeation test equipment. The barrier is deposited under vacuum in a process compatible with conventional roll-coating technology. The film is capped with a thin film of transparent conductive oxide yielding an engineered substrate (Barix™) for next generation, rugged, lightweight or flexible OLED displays. Preliminary tests indicate that the substrate is sufficiently impermeable to moisture and oxygen for application to moisture-sensitive display applications, such as organic light emitting displays, and is stable in pure oxygen to 200°C.

Keywords: Organic, Thin Film, LED, Moisture Barrier, Polymer Deposition, Vacuum Deposition, Flexible, Display.

1. INTRODUCTION

Organic light emitting devices (OLEDs) now achieve low-voltage operation [1] and have recently demonstrated the potential for luminous efficiencies in excess of 40 lm/W [2]. Furthermore, the intrinsic properties of organic semiconductors render them ideal candidates for novel display applications. Many of the materials used in polymeric OLEDs [3] are intrinsically flexible and similar flexibility has been shown to occur in small molecule, vacuum deposited OLEDs (FOLEDs) [4] due to relatively weak intermolecular bonding. Small molecule materials also enable the fabrication of complex, multi-layer devices on a wide range of substrates to create novel, transparent displays [5] and high resolution, stacked pixels [6]. A typical large area, vacuum-deposited, passive matrix FOLED, grown on a 175 µm thick ITO-coated polyester substrate, is shown in Fig. 1.

The efficiency and operating lifetime of OLEDs has reached the point where limited commercial production of displays on glass is commencing. On glass or Si, isolation of the OLED from atmospheric oxygen and moisture is typically accomplished with a glass or metal lid, attached to the display substrate using a bead of UV-cured epoxy. Such an encapsulation technique is not viable for a flexible display, since low moisture permeability epoxies are rigid. Even on rigid displays, a lid requires additional bracing or standoffs for sizes > 12 cm diagonal. The high moisture permeation of plastic substrates has therefore limited their potential for use in FOLEDs.

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The ideal substrate for FOLED manufacture would combine the barrier, thermal and scratch resistant properties of glass with the flexibility, toughness and processability of plastic.

In this paper, we describe composite barrier layers on plastic substrates, generally referred to as Flexible Glass™, deposited by a roll-coating technique. The barriers exhibit moisture barrier performance below the limit of MOCON [7] detection instruments (5×10^{-3} g/m²/day) at 25°C and 38°C. Preliminary measurements indicate that these engineered substrates are sufficiently impermeable to atmospheric contaminants to form the basis for long-lived FOLED displays.

2. MOISTURE BARRIERS ON PLASTIC.

Simple barrier films, consisting of metal or ceramic oxide layers vapor deposited on polyester or polypropylene, have been developed and successfully utilized in flexible food packaging applications. However, substrate roughness and defects intrinsic to these materials limit their barrier performance. Vapor permeation rates fall as a function of deposited barrier film thickness due to the covering of substrate roughness and the filling of pinholes, but the propagation of grain boundary defects results in no significant gain beyond a critical thickness, which is typically 100 - 300 Å, resulting in a lower limit transmission rate of ~ 0.05 g/m²/day. [8] Furthermore, most vapor deposition techniques are conformal, reproducing the substrate texture. Breaks in continuity as the film traverses high aspect ratio features on rough substrates can also limit the effectiveness of vapor-deposited coatings on plastic.

The barrier performance required for OLED displays is unclear, since the mechanism of long-term degradation is still the subject of debate. An order of magnitude upper limit on acceptable moisture permeation is calculable by making the simple assumption that oxidation of the low work function (Mg or Ca) cathode limits the operating lifetime of "leaky" devices. For example, assuming a Mg cathode thickness of 500 Å, density 1.74 g/cm³ and molar mass 24 g, an OLED contains 3.6×10^{-7} mol/cm² of metallic Mg. Such a cathode is completely oxidized by $\sim 6.4 \times 10^{-6}$ g of water. To achieve a device lifetime of a year, therefore, we obtain a maximum leak rate of 1.5×10^{-4} g/m²/day. Severe device degradation will likely be observable after 10 % of the cathode is oxidized (indeed, if the damage occurs at the organic-metal interface the loss of only 5 Å of metal may be significant). Furthermore, the calculation ignores potential degradation of the organic semiconductor itself, which some believe is catalyzed by water. [9] However, it is clear that long lived OLEDs require a moisture barrier which transmits $< 10^{-5}$ g/m²/day of water. All conventional vapor barrier films are therefore inadequate for FOLED applications by several orders of magnitude. Furthermore, a need is identified for a test which is sensitive to water vapor and oxygen permeation in the required range. A schematic illustration of the vapor barrier scale and the efficacy of available coatings is shown in Fig. 2.

The Barix™ vapor barrier[§] film is a vacuum-based process which allows the development of multi-layer organic-inorganic barrier architectures. These building blocks allow specific performance to be tailored into almost any substrate to satisfy the requirements of various display applications. The process also has excellent economics because the individual chemical components (organic and inorganic materials) can be applied in a single processing sequence using vacuum technology. In addition, because Barix™ is a vacuum-based process, products can be made at the highest level of cleanliness and in rapid throughput, roll-coating systems. We therefore expect that these engineered barrier substrates would be comparable in price to the glass substrates currently purchased for use in flat panel displays.

3. BARIX™ MULTILAYER COATINGS.

In Fig. 3a, we show an atomic force micrograph (AFM) of a commercially available [10] polyethylene terephthalate (PET) film. Spikes higher than 150 Å are observed. On heat-stabilized PET substrates (required for dimensional stability during processing steps such as photoresist baking) similar spikes up to 1500 Å in height are observed. Such spikes are not fully planarized by sputter-deposited ITO, but rather protrude

[§] Barix is a trademark of Vitex Systems, Sunnyvale, CA

through the ITO anode yielding dark spots in an OLED built on the substrate and compromising vapor-barrier performance.

Our vacuum multilayer deposition technique [11] offers a flexible technique to overcome the effects of substrate non-uniformities on a vacuum-deposited ceramic vapor barrier. The technique involves the flash evaporation of an acrylic monomer onto a cooled substrate; either in a planetary or roll-coating configuration. Immediately subsequent to condensation the monomer is cured, yielding a highly cross-linked polyacrylate film. This evaporation technique enables extremely high deposition rates (up to 1 $\mu\text{m/s}$) for roll-coating applications. More importantly for vapor barrier applications, the deposition and curing of the *liquid* monomer results in a flexible, transparent polymer film which is non-conformal to the substrate, effectively decoupling non-uniformities from a barrier layer which can be deposited in the same vacuum system. For example, in Fig. 3b we show an AFM of a PET substrate, identical to that in Fig 3a, after deposition of a 0.25 μm thick layer of polyacrylate. The surface roughness of the coated sample is $< 10 \text{ \AA}$. Up to $\sim 5 \mu\text{m}$ thick layer of polymer can be applied to a substrate in one pass. Using multiple passes in a vacuum system or roll-coater, films of arbitrary thickness can be built up with similar surface roughness.

BarixTM utilizes such “decoupling” layers of vacuum deposited polyacrylate between multiple layers of vapor-barrier material such as SiO_2 , Si_3N_4 , Al_2O_3 or conducting oxides such as ITO. The generic structure of an engineered barrier substrate is shown in Fig. 4. By this technique, the effect of the multiple barrier layers is additive, and O_2 and H_2O permeation rates of $< 0.005 \text{ cc/cm}^2/\text{day}$ and $< 0.005 \text{ g/cm}^2/\text{day}$, respectively, have been achieved at 38°C . This measurement is limited by the sensitivity of the MOCON measurement technique, which directly measures the molar quantity of oxygen or moisture diffusing across a 100 in^2 edge-sealed membrane of material. More sensitive, quantitative moisture permeation tests are required to independently judge the adequacy of our barrier for long-term FOLED applications, however in this paper we present preliminary evidence for their efficacy using operating lifetime results from OLEDs built on inorganic substrates with BarixTM top encapsulation. (The vacuum-compatibility of the BarixTM process allows for the potential incorporation of both substrate sealing, OLED deposition and OLED encapsulation in the same production line.) A schematic illustration of an encapsulated FOLED is shown in Fig. 5.

Early results from an encapsulated OLED built on a Si substrate are shown in Fig. 6, where we show the same pixel immediately after encapsulation (a) and after 13 weeks storage with no further measures to isolate the device from the atmosphere. One week of this period involved device operation under water. Several small dark spots present on the device immediately after encapsulation grew during storage but it is clear that the OLED suffered minimal overall degradation. Comparable devices operated in air show significant degradation in a period of days. We therefore conclude that the moisture permeation rates of the encapsulation layer are $< 10^{-5} \text{ g/cm}^2/\text{day}$.

4. PERFORMANCE OF BARIXTM SUBSTRATES FOR FOLED APPLICATIONS.

The room temperature deposition of indium tin oxide on plastic substrates is extensively described in the literature, and we have demonstrated ITO coatings on BarixTM substrates with a sheet resistance of $\sim 30 \Omega/\square$ and transparency $> 80\%$ across the visible spectral region. In Fig. 7, we demonstrate that our engineered substrate can be used for the growth of FOLEDs with similar operating characteristics to OLEDs grown on ITO-coated glass substrates. The current-voltage characteristic of both devices follows the power-law dependence indicative of space-charge-limited conduction in the presence of deep traps. Therefore injection from the contacts does not limit the current flow in either case. At an injected current above 50 mA/cm^2 we observe a small increase in drive voltage on the BarixTM substrate. This is due to series resistance in the long ITO anode which could be eliminated using thicker ITO, wider electrodes or metallic bus bars in parallel with the anode.

In the inset we show the brightness of each device measured through (and normal to) its respective substrate. Here, the FOLED has a higher external quantum efficiency due to better refractive index matching between the substrate and the organic semiconductor layers. We conclude that low voltage FOLEDs built on the Barix flexible engineered substrates show improved efficiency over conventional glass OLEDs.

5. THERMAL STABILITY OF BARIX™ FILMS

Extended operation of OLEDs above 100 °C has not been reported. For the present generation of FOLEDs grown on heat stabilized polyester, the glass transition temperature (T_g) of the substrate (~ 78 °C) is likely to limit high temperature applications. However, for encapsulated glass or Si top emitting OLEDs and the next generation of high T_g polymer substrates, it is important to understand the temperature stability of Barix™ layers. This was assessed by differential scanning calorimetry (DSC) and thermal gravimetric analysis (TGA). In Fig. 8 we show the simultaneously run DSC and TGA traces for a 10µm thick layer of polyacrylate grown on and subsequently removed from an Al foil substrate. In an atmosphere of pure O₂, mass loss commences at 200 °C and is accompanied by an exothermic peak in the DSC. We observe a two-stage decomposition in the DSC at ~ 200 °C and 350 °C, which we interpret as decomposition of different functionalities in the cross-linked network. Higher stability is observed under an N₂ atmosphere. In either case, the barrier layer and thin film encapsulation is stable up to conventional photoresist processing temperatures (typically 120 °C) and to higher temperatures than known small molecule OLED materials.

6. CONCLUSION

The availability of new engineered substrates now make FOLED displays a realistic possibility. Composite organic-inorganic coating technologies can potentially decrease the moisture and oxygen permeability of a wide range of flexible substrates to the range required for long-lived FOLED operation. Furthermore, an OLED can potentially be fabricated and encapsulated in the same vacuum system, eliminating the need for a glued lid. We expect this technology to radically expand the range of flexible substrates available for a variety of moisture and oxygen-sensitive applications.

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Figure 1: Photograph of a flexible OLED (FOLED) display built in UDC's pilot line facility in Ewing, NJ. This passive matrix, 128 x 64 pixel display (400 x 500 micron pixel pitch), operating at a conventional video brightness of 100 nits, is fabricated on heat stabilized polyethylene terephthalate (PET) film (0.18 mm thick).

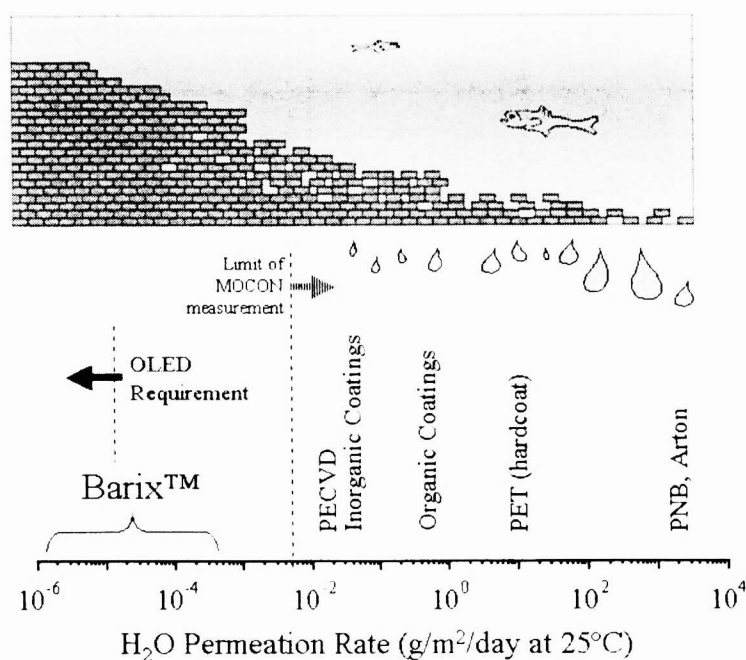


Figure 2: Barrier scale showing the relative levels of oxygen permeability of typical polymers and coatings and the sensitivity limits of the current MOCON test equipment. Also shown is the level of permeability expected to be needed for long lifetime OLED displays.

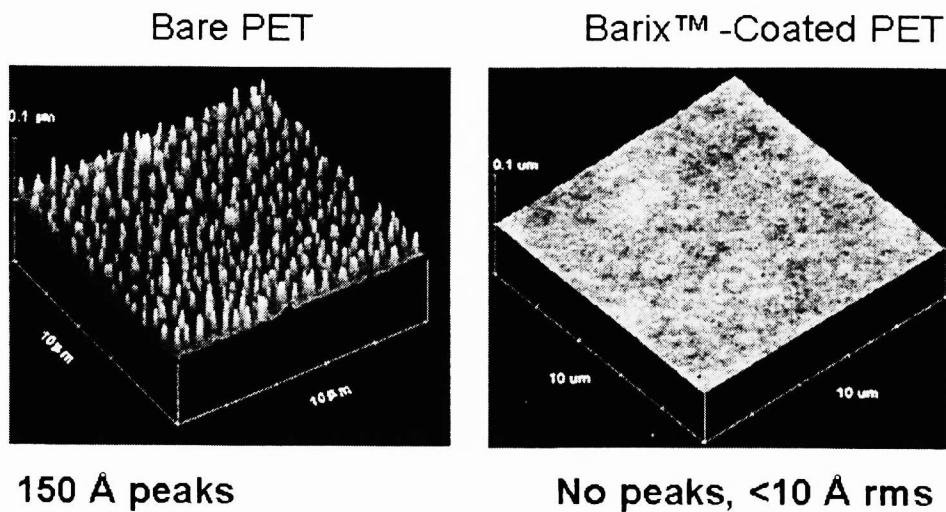


Figure 3 left: Atomic force micrograph of a commercially available polyester substrate showing typical surface roughness. **right:** an identical substrate with a 0.25 μm thick planarizing layer of polyacrylate deposited via vacuum deposition.

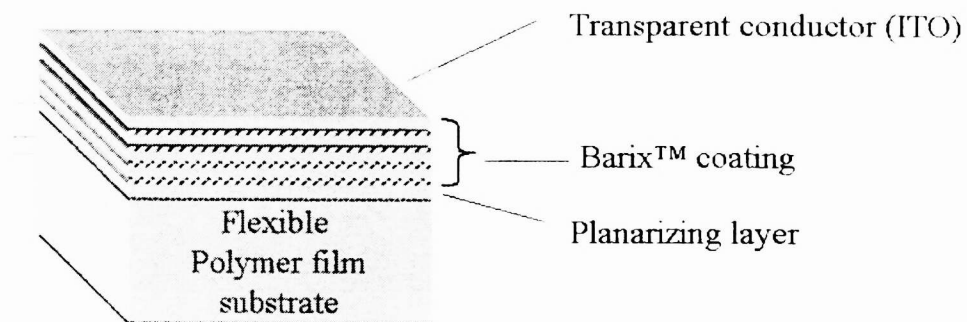


Figure 4: Schematic cross section of a Barix™ flexible engineered substrate.

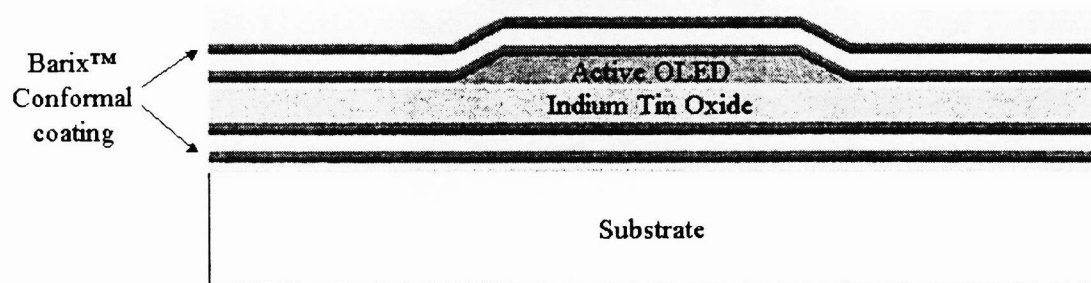


Figure 5: Schematic cross section of a Barix™ encapsulated OLED. The substrate may be either rigid or flexible. Since the encapsulation is transparent across the visible spectral region, opaque substrates utilizing top-emitting OLEDs are also useable.

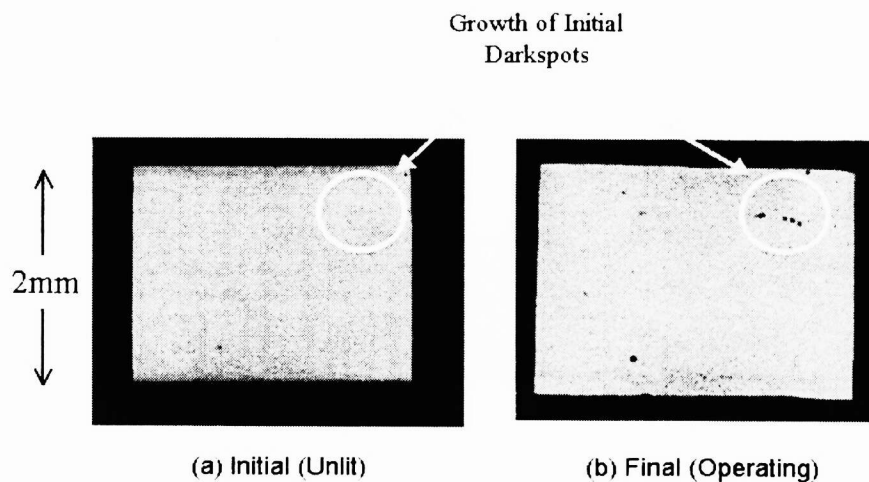


Figure 6: Top emitting OLED grown on a Si substrate and encapsulated using a Barix™ layer. **Left:** ambient light photograph immediately after encapsulation. **Right:** Operating device after 13 weeks of storage and immersion in water as described in the text. (Courtesy of eMagin Corp.)

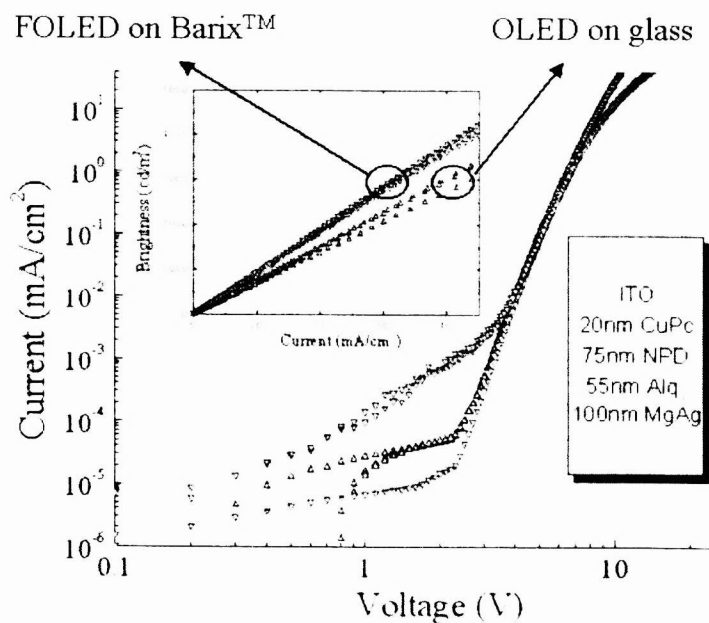


Figure 7: Current-voltage characteristics of a vacuum-deposited FOLED grown on the Barix engineered substrate. Inset: Brightness of the FOLED as a function of drive current.

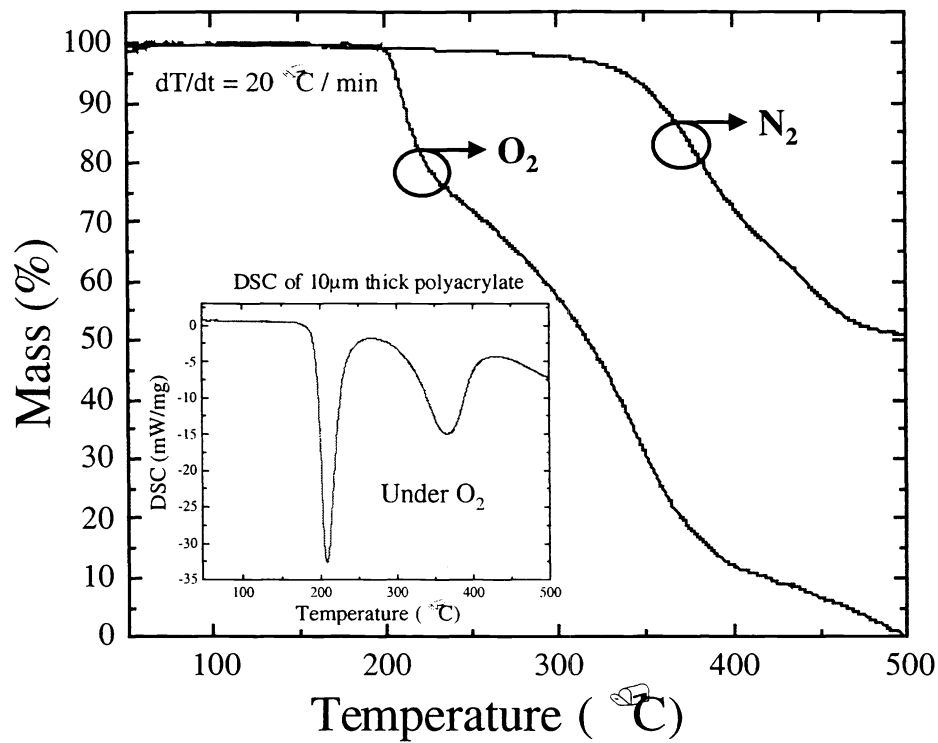


Figure 8: Thermal gravimetric analysis of a 10 mm film of polyacrylate; the lowest melting point component of Barix™. Significant mass loss occurs at 200°C under pure oxygen and 350°C under pure nitrogen. The heating rate was 20°C/min. Inset: Differential scanning calorimetry of the same film showing a two stage decomposition beginning at 200°C.