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Development of highly flexible and ultra-low permeation rate thin-film barrier structure for organic electronics

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ABSTRACT

A flexible thin-film encapsulation architecture for organic electronics was built and consisted of a silicon oxide/alumina and parylene layer deposited over Ca sensors on a barrier-coated polyethylene terephthalate substrate. The film's effective water vapor transmission rate was $2.4 \pm 1.5 \times 10^{-5}$ g/m^2/day at 20 °C and 50% relative humidity. Flexural tests revealed that for films deposited on the polyethylene terephthalate substrate, the barrier layer failed due to cracking at a curvature radius of 6.4 mm, corresponding to a strain of 0.8%. Adding an epoxy top coat of suitable thickness shifted the neutral axis toward the encapsulation layer, reducing the induced strain. Barrier performance was maintained under the 6.4 mm radius of curvature in this encapsulation structure. Thus, shifting the neutral axis via device structural design is an effective method of extending the flexibility of thin-film encapsulation structure without compromising the performance loss as a barrier layer.

1. Introduction

One of the unique advantages of organic semiconductor materials is their potential for creating flexible electronics. The paradigm shift from wafer-based technology to roll-to-roll printing, which is enabled by the use of polymer substrates, promises flexible electronics at a much lower cost. The use of flexible polymer substrates as opposed to more rigid support, however, introduces greater risk in terms of mechanical reliability in these devices. At present, brittle materials such as the transparent conducting oxide (TCO) electrodes and oxide and/or nitride films found in encapsulation barrier layers play critical roles in the performance of organic light emitting devices and organic photovoltaics. Much research has been dedicated to discovering more flexible replacements for TCO electrodes, primarily in the form of carbon nanotube film electrodes [1–4]. These potential TCO replacements have enabled dramatic improvements in mechanical reliability, but a number of technical challenges must still be resolved. It remains unclear whether the brittle thin-film encapsulation oxides and nitrides can be replaced with flexible materials that exhibit commensurate barrier performance.

There have been a number of investigations into the brittle failure of indium tin oxide used as transparent electrode in organic devices [5,6]. The performance of encapsulation films under static and fatigue deformation has been studied by a limited number of groups. Grego et al. [7] examined the onset of mechanical failure of a 100-nm-thick SiO_xN_y film, which is also widely used as an encapsulation material, on a 130-μm-thick polyethylene naphthalate substrate using the X–Y–θ bending system, which enables testing at well-defined curvature radii. They reported crack initiation in the film at a bending radius of 7 mm (~0.9% strain) and noted that the crack density increased as the radius decreased. Gartside et al. [8] developed a barrier layer by plasma-enhanced chemical vapor deposition (PECVD) from hexamethyl disiloxane and oxygen source gases. This layer had good flexibility, with initial cracks occurring at 0.4% nominal tensile strain, equivalent to a bending radius of 7 mm, and maintained its barrier performance after 58,000 cycles of loading to ~0.2% nominal tensile strain. Additional research is needed, however, to improve barrier layer flexibility, especially for applications involving tensile strains. In general, the strain limitation of these brittle encapsulation materials lies between 0.5 and 2% [9–12]. Thus, to increase the flexibility of these barrier films, it is necessary to improve the critical strain of the barrier films or to reduce the strain to which they are subjected during flexure. Strain is proportional to the distance from the neutral surface, so placing the brittle barrier layers close to the neutral surface minimizes the strain they experience. This basic concept has been employed in the fabrication of thin-film transistors (TFT). Sekitani et al. [13] showed that an organic TFT, when laminated, remains functional at an extremely small bending radius. The device was fabricated on a 13 μm thick polyimide film and covered with a 13 μm thick poly-chloro-para-xylylene encapsulation layer, effectively embedding the device at the neutral surface. For this geometry, bending does not add any strain to the

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TFT; thus, the failure strain of the TFT materials does not limit the bending curvature.

In this study we created an encapsulation structure for flexible organic electronics that is both a good barrier and highly flexible. For flexibility, a 100-μm-thick polyethylene terephthalate (PET) substrate was used. It is known that PET itself is highly permeable to water vapor and oxygen, so additional barrier coatings on the PET substrate are required to satisfy the stringent requirements of organic device encapsulation. The performance of our encapsulation structure as a barrier layer was investigated through Ca corrosion testing, and its flexibility was examined with a bending test. To overcome the mechanical limitation of the barrier layers, the encapsulation structure proposed here shifts the neutral surface to the barrier layer. This approach allows for a highly flexible encapsulation structure as well as superior barrier performance.

2. Theoretical background for thin film mechanics

The strain in a thin-film encapsulation structure under flexural deformation is given by the following equation.

$$\varepsilon_z = \left(\frac{z - z_n}{R}\right) \tag{1}$$

where z_n is the neutral layer position, known as the zero strain surface, and R is the bending radius of curvature. In addition to the strain caused by bending, thin-film fabrication also introduces an intrinsic mismatch strain following

$$\varepsilon_m = \varepsilon_0 + \varepsilon_{th} + \varepsilon_{ch} \tag{2}$$

where ε_0, ε_{th}, and ε_{ch}, are the built-in strain during fabrication, thermal mismatch strain, and humidity mismatch strain, respectively. These are insignificant, however, compared to strain induced by bending. Hence, only bending strain is considered in this study. The bending strain on a device or encapsulation layer can be reduced by shifting the neutral surface toward the device layer, namely, placing the encapsulation layer closer to the neutral surface. When both the film and substrate have similar moduli, the neutral surface lies at the geometric mid-surface of the structure and the strain on the top surface, ε_{top}, follows

$$\varepsilon_{top} = \frac{d_1 + d_2}{2R} \tag{3}$$

where d_1 and d_2 are the thickness of film and substrate, respectively and R is the bending curvature radius. A more general structure for thin-film encapsulation involves a thin film with high modulus on a low modulus substrate. In this case, the strain on the top surface of the thin film is given by

$$\varepsilon_{film} = \left(\frac{d_1 + d_2}{2R}\right)\frac{\left(\chi\eta^2 + 2\eta + 1\right)}{(1+\chi\eta)(1+\eta)} \tag{4}$$

where $\chi = Y_1/Y_2$ and $\eta = d_1/d_2$. E_1 and E_2 are the film and substrate moduli, respectively. Eq. (4) accounts for the neutral axis shifting toward the encapsulation layer, which is common when a high modulus film is placed on a flexible, low-elastic modulus substrate [14]. While the strain is reduced compared to that in Eq. (1), this arrangement does little to reduce the bending radius of curvature before failure for the encapsulation layer. In the case of barrier layers on a polymer substrate, flexibility of the barrier layer can be improved by applying another layer of suitable thickness on the top of the barrier. This added layer shifts the strain-sensitive barrier layers toward the neutral surface, where the strain is reduced. If the cross-section is symmetric about the horizontal axis, then the neutral surface lies halfway between the top and bottom, as illustrated in Fig. 1(a). However, for asymmetric geometries or laminated structures consisting of multiple materials, the neutral surface location, n_c, can be determined by

$$n_c = \frac{\sum_{i=1}^{n} n_i E_i A_i}{\sum_{i=1}^{n} E_i A_i} \tag{5}$$

where n_i, E_i, and A_i are the location of the centroid, the modulus of elasticity, and the cross sectional area of the ith material. For lamination of two different materials, as illustrated in Fig. 1(b), the location of neutral surface is given as follows:

$$n_c = \frac{\frac{d_1}{2}E_1 d_1 + \left(d_1 + \frac{d_2}{2}\right)E_2 d_2}{E_1 d_1 + E_2 d_2}. \tag{6}$$

If the neutral surface is located at the interface between two materials ($n_c = d_1$), the thickness of the added layer (d_2) should satisfy

$$E_1 d_1^2 = E_2 d_2^2. \tag{7}$$

Therefore, the flexibility of the encapsulation structure can be improved by placing the brittle layer at the neutral surface, as demonstrated in this work.

3. Experimental details

3.1. Fabrication of encapsulation structure

As previously reported, a hybrid layer consisting of SiO_x or SiN_x, fabricated by PECVD, and Al_2O_3, added by atomic layer deposition (ALD), on a glass substrate has an effective water vapor transmission rate (WVTR) of $2.0 \pm 1.0 \times 10^{-5}$ g/m^2/day at 20 °C and 50% relative humidity (RH) [15]. To use this barrier layer in an encapsulation structure for flexible organic devices, the glass substrate is replaced by a flexible PET substrate. PET itself is permeable to water vapor and oxygen, so a hybrid layer must be employed to create a barrier. The process temperature for both PECVD and ALD was kept under 110 °C to remain compatible with organic electronic devices [15–17]; conventional PET substrates can withstand temperatures up to 120 °C [18]. Detailed process parameters such as reactant flow rate, pressure, and RF power can be found in reference [15]. For this

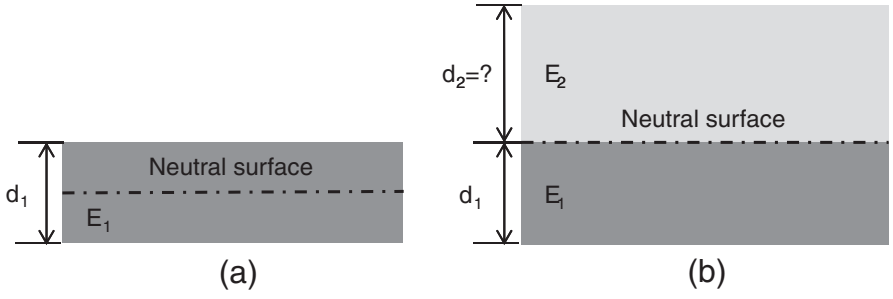

Fig. 1. (a) Neutral surface for a homogeneous material. (b) Neutral surface for a laminated structure containing two different materials.