Material challenge for flexible organic devices

Outside of the active device layers, there are a variety of requisite functional layers in flexible organic electronic devices. Whether the application is in displays, lighting, integrated circuits, or photovoltaics, there are materials challenges in implementing flexible and/or organic devices into practical applications. We highlight two topics that are common to most flexible electronic technologies. First, we describe the difficulty in developing suitable permeation barriers on polymer substrates, the approaches being taken to solve this problem, and their current status. Second, we highlight the limited mechanical ruggedness of brittle inorganic films and present approaches for improving overall device flexibility.

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The unique characteristics of organic electronic devices offer the promise of widespread adoption in numerous technology areas, including displays, lighting, photovoltaics, radio-frequency identification (RFID) circuitry, and chemical sensors. The various topics in this issue of *Materials Today* demonstrate the potentially revolutionary promise of organic electronic devices with their inherently low-temperature, large-area processing compatibility and mechanical flexibility. These compelling aspects of the device performance are primarily the result of the active layers, i.e. the semiconducting layers and the electrical contacts to them. There are a variety of materials challenges outside the active device layers that pose problems for large-scale production and implementation[1]. Depending on the application, issues arise from processing temperature limitations for polymer substrates, the performance of low-temperature TFTs and transparent conductors, dimensional stability of the substrate with changes in temperature and humidity, as well as processing and handling techniques for flexible substrates.

Flexible electronic devices are used most commonly for optoelectronic applications (light-emitting or photovoltaic diodes) or for thin-film transistors (TFTs) for integrated circuits (ICs) or active-matrix displays, but there are a variety of others. This article will focus on two issues that are both major technical challenges and common to a variety of technologies, device types, and applications. The first involves one of the most challenging issues for the development of emissive, mechanically flexible devices for display or lighting

ISSN:1369 7021 © Elsevier Ltd 2006

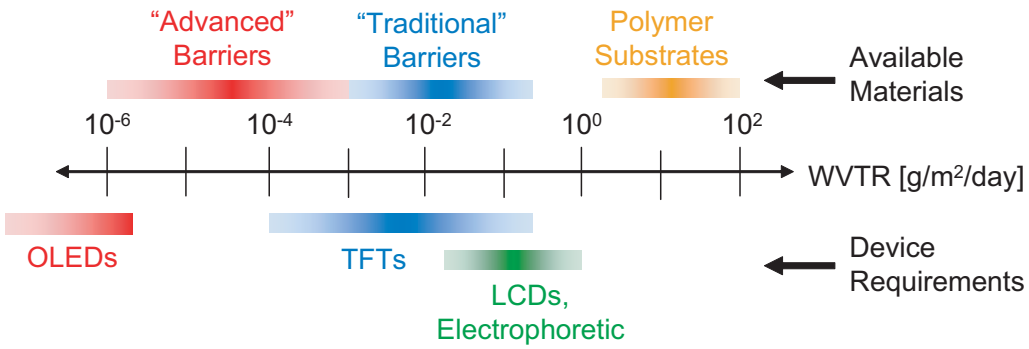

Fig. 1 WVTR requirements for common flexible electronic devices and the barrier performance provided by available materials.

applications, namely the production of a suitable thin-film permeation barrier. The second focus area, common to most flexible electronics applications, is on the mechanical limitations of inorganic films used in flexible devices.

Thin-film permeation barriers

Most high-performance semiconducting organic compounds show degraded performance when exposed to environmental moisture. Encapsulation is thus required. There is a wide range of permeation requirements for different materials and applications. Generally, devices such as organic light-emitting devices (OLEDs) that use chemically reactive electrodes have the highest sensitivity to moisture, and degradation is observed at the organic layer/electrode interface[2,3]. Unlike glass, polymer substrates do not provide sufficient protection to permeants, and a thin-film barrier deposited on the substrate is required. Traditional encapsulation involves attaching a glass or metal lid to the substrate using a low-permeation epoxy. This approach is not compatible with flexible devices, so thin-film encapsulation is required. Moreover, at least one of these encapsulating layers must be transparent. Much of the fundamental understanding of permeation barrier technology has its origins in food or pharmaceutical packaging.

The widely quoted[4] requirement for water vapor transmission rate (WVTR) for an OLED lifetime of >10 000 hours is 1 x 10^{-6} g/m²/day. For organic TFT applications, the higher performing active layer materials tend to also have greater stability problems. The WVTR requirements for TFTs[5] are not as strict as those for OLEDs, and are generally in the range of 1 x 10^{-3} g/m²/day to 1 x 10^{-1} g/m²/day. For liquid crystal displays (LCDs) and electrophoretic displays[6,7], the WVTR requirement is ~1 x 10^{-1} g/m²/day. Fig. 1 shows the order of magnitude of protection required for various organic electronic devices and provided by various materials (described later).

Permeation barrier requirements for OLEDs exceed the minimum sensitivity of 5 x 10^{-4} g/m²/day from traditional permeation rate measurement techniques by over two orders of magnitude[8] and so novel approaches have to be applied to aid the development of thin-film barriers. The most widely used approach is a Ca thin film, typically 50-100 nm, deposited on the barrier-coated substrate[9-11]. The Ca film is encapsulated and becomes transparent as oxygen and moisture penetrate the barrier film. Monitoring the film optically allows the measurement of the Ca depletion rate, which can be converted to the permeation rate. Alternative approaches use radioactive tritiated water as the permeant to mimic moisture permeation[12,13] or an ultrahigh vacuum residual gas analyzer to monitor the permeation of various species[14].

Permeation through inorganic thin films

Thin-film permeation barriers have traditionally been formed from Al or Al or Si oxides. Bulk oxides and Al are effectively impermeable to oxygen and water[15], as are perfect SiO_2 films[16,17]. But traditional thin-film single barrier layers provide at best only two to three orders of magnitude improvement over the oxygen transmission rates (OTR) of polymer substrates, whether deposited by plasma-enhanced chemical vapor deposition (PECVD), sputtering, or evaporation[16,18-23]. This limit is the result of permeation through defects or nanoscale pores rather

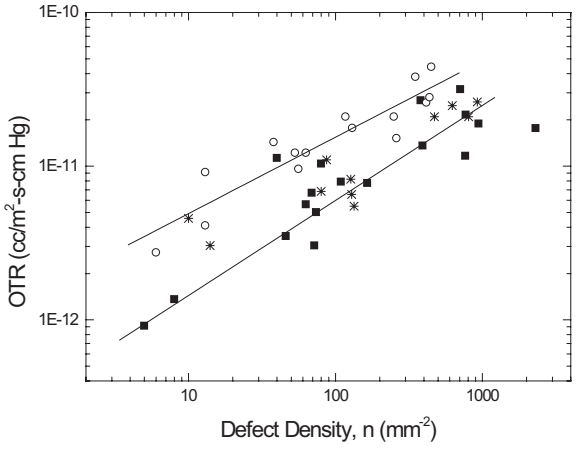

Fig. 2 OTR as a function of defect density for Al (o), SiO_x (*), and SiN_x (■) films. Note that 1.5 x 10^{-12} cc/m²/s/cm Hg is the equivalent of 0.1 cm³/m²/day. (Reproduced with permission from[16]. © 2000 American Institute of Physics.)

than the bulk of the barrier film. Fig. 2 shows the correlation of film defect density with OTR for SiO_x, SiN_x, and Al-coated polyethylene terephthalate (PET), demonstrated by da Silva Sobrinho *et al.*[16]. The source of defect-driven permeation has been primarily attributed to pinhole defects[16,19,24] though more recent studies have shown that in the absence of pinhole defects permeation rates are still reduced by less than three orders of magnitude over the substrate alone[22]. The remaining permeation is shown to be the result of pores in the subnanometer to several nanometer range, produced by surface roughness and/or low density of the films[22,25-28]. More detailed reviews of permeation mechanisms and the performance of various permeation barriers have been given elsewhere[19,29].

Many barrier studies measure only OTR or WVTR, but it is important to note that barrier performance can be dependent on the permeant species. Permeation in polymers occurs by different mechanisms for nonpolar, noninteracting molecules such as oxygen than for polar, condensable molecules such as water, which may interact with the polymer[22,30]. Moreover, there is evidence that the permeation pathways through barrier films can be different for oxygen and moisture[28].

Two approaches to improve barrier performance significantly have been explored: increased film density and multilayer structures. It has been shown that increased film density reduces permeation through nanoscale pores[28]. Using this approach, promising results have been demonstrated recently by Symmorphix by means of a proprietary high plasma density sputtering technique. The films exhibit exceptionally high density and are amorphous. From these single-layer films, WVTR rates of 8 x 10^{-5} g/m^2/day have been measured using the Ca test under accelerated conditions of 60°C/90% RH (relative humidity), indicating excellent performance at room temperature[31,32]. Similarly, General Atomics has reported excellent permeation barrier performance from sputtered amorphous Al_2O_3, with a WVTR of 5 x 10^{-5} g/m^2/day at 38°C/100% RH[33]. Researchers from the University of Colorado have reported Al_2O_3 films deposited by low-temperature atomic layer deposition with a WVTR of 1 x 10^{-3} g/m^2/day[13].

Multilayer permeation barrier structures

Given the difficulty of producing a single-layer permeation barrier with sufficiently high film density and sufficiently low defect density, a popular alternative has been to use a multilayer structure comprised of alternating polymer and inorganic layers. The polymer multilayer (PML) process was first demonstrated at GE, and polymer smoothing layers were subsequently developed elsewhere[34]. The smoothing layers were shown to be effective at reducing defects related to surface flaws for several types of films, including reactively sputtered and electron-beam evaporated Al_2O_3[34,35]. The smoothing effect of the polyacrylate is a result of the deposition process in which the liquid acrylate monomer first condenses on the substrate surface and is subsequently cured. This

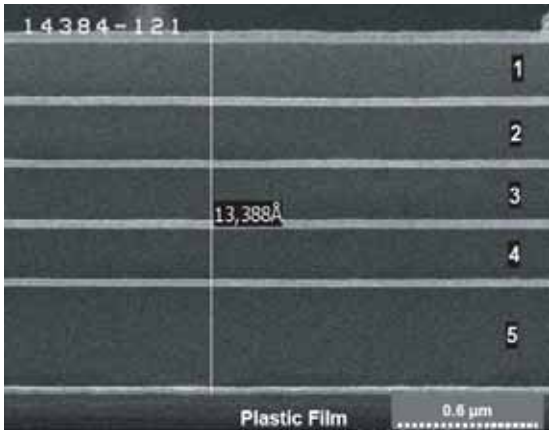

Fig. 3 Organic/inorganic multilayer structure from Vitex Systems. (Reproduced courtesy of Vitex Systems.)

reduces the effect of surface flaws in the polymer substrate[35,36]. Similar planarization has been achieved with spin-coated resins.[37,38]

Multilayer barrier coated polymers from Vitex have demonstrated a WVTR estimated to be equivalent to 2 x 10^{-6} g/m^2/day at ambient conditions using the Ca test[10]. A cross-sectional micrograph of a Barix™ sample from Vitex is shown in Fig. 3. The company has also shown a combination of barrier-coated substrate and top encapsulation with a WVTR of 8 x 10^{-6} g/m^2/day at ambient conditions[39]. In other efforts, GE has reported a permeation barrier structure deposited by PECVD with graded junctions between multiple organic and inorganic regions, with WVTR results in the 10^{-5}-10^{-6} g/m^2/day range, calculated from accelerated measurements at 50°C/95% RH[40].

The mechanism by which multilayer structures improve barrier performance has been a subject of significant discussion. Among the explanations given are the smoothing effect of the polymer layers, the 'decoupling' of defects in neighboring films by the polymer layers, the increase of the diffusion path length, and the improved likelihood of having one 'perfect' layer in the structure when multiple layers are used. More recently, Graff *et al.*[41] have shown that multiple barrier layers should not improve the steady state permeation rate by orders of magnitude. Rather, using reasonable figures for defect densities, their calculations show that the lag time could increase to several years. This implies that multiple layers simply delay a significant amount of permeation, but this delay may be sufficient for many applications. This explanation seems to be supported by recent measurements[33].

Mechanical limitations of inorganic films

Many demonstrations of electronic devices on flexible substrates involve the fabrication of traditional devices substituting only the substrate material. Often smoothing layers are employed and, if necessary, the processing temperatures are reduced. However, there has been relatively little attention paid to the limits of flexibility of these devices. Mechanical failure in a device is determined by the

weakest component. For those devices that use inorganic thin films, these brittle layers are likely to be the source of failure. More recently, there has been an effort to develop devices with no brittle components whatsoever[42-45]. However, certain devices such as flexible OLEDs require inorganic films[29] and it is, therefore, important to understand and improve the mechanical limits of these materials.

We will begin with a general overview of thin-film strain in electronic devices and which device configurations and components are of concern. We will briefly address the various techniques employed for bend testing and give an overview of the most common materials used in flexible electronic devices: transparent conductors, thin-film permeation barriers, semiconductors for TFTs, and metal interconnects.

Mechanics of films on flexible substrates

The mechanics and brittle failure mechanisms of single and multilayered films on flexible substrates have been described in detail elsewhere[46-54], but we will give a brief description here.

When a sheet is bent, the outer surface experiences tensile stress and the inner surface compressive stress, while a plane inside the sheet (in the middle if the sheet is homogeneous) – defined as the neutral plane – experiences no uniaxial stress at all. Films deposited on one or both sides shift the stress and strain distribution, but for many flexible electronics devices where the films are very thin relative to the substrate one can make the following simple approximation for the relationship between film strain and radius of curvature:

$$\varepsilon_f = d/2r \qquad [1]$$

where d is the thickness of the substrate and r is the radius of curvature. To make a rough estimate of the radius of curvature at failure, we can see that for a 100 μm substrate and for a typical failure strain of 0.5-1.0% for brittle films in tension, the minimum radius of curvature is 5-10 mm.

Failure modes of layered materials involve the growth of microcracks under stress[55] and the details of the fracture mode depend on the substrate modulus, film adhesion, and film cohesion among other things. The most common failure modes for brittle films on flexible substrates are film cracking/channeling and debonding[53], as

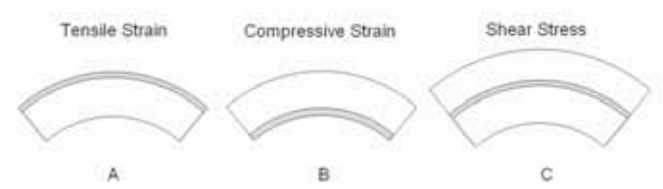

Fig. 5 Geometries for flexible electronic devices. Devices (shaded) experience tensile strain, compressive strain, or shear stress depending on the bending geometry of the substrate.

depicted in Fig. 4. The former is more common for films in tension with good adhesion between layers, while the second mechanism is more common for films in compression or when adhesion is poor.

Early failure in brittle films is caused by preexisting defects. For oxide films on polymer substrates, these are often caused by defects in the substrate morphology. The failure curvature can, therefore, be reduced by minimizing such defects with a smoothing layer. In addition, defects can occur from scratches or edge defects. It is preferable to keep films from extending to the substrate edge as stress can be concentrated near the edges.

Given these considerations, what structures are most advantageous for flexible electronics? Fig. 5 shows several possibilities. Structure A has the device layers on the convex surface, placing the layers under tensile strain when the device is bent and is, therefore, most prone to failure. Structure B has the device layers on the concave surface under compressive strain and is, therefore, preferred. Often, structure A versus B is determined not by mechanical considerations but by the device structure (e.g. top- or bottom-emitting OLEDs). Structure C is different in that the device layers are encapsulated by a second polymer film that is comparable to the substrate. In this structure, the device layers are at the neutral plane and can, therefore, be curled to a very tight radius[54]. However, for higher modulus substrates shear stress can be significant and challenging for interlayer adhesion.

Mechanical test methods

Many types of mechanical deformation geometries can be used to study film failure. One of the most common is the tensile test[48-50,55-58]. *In situ* microscopy is used to monitor the formation and

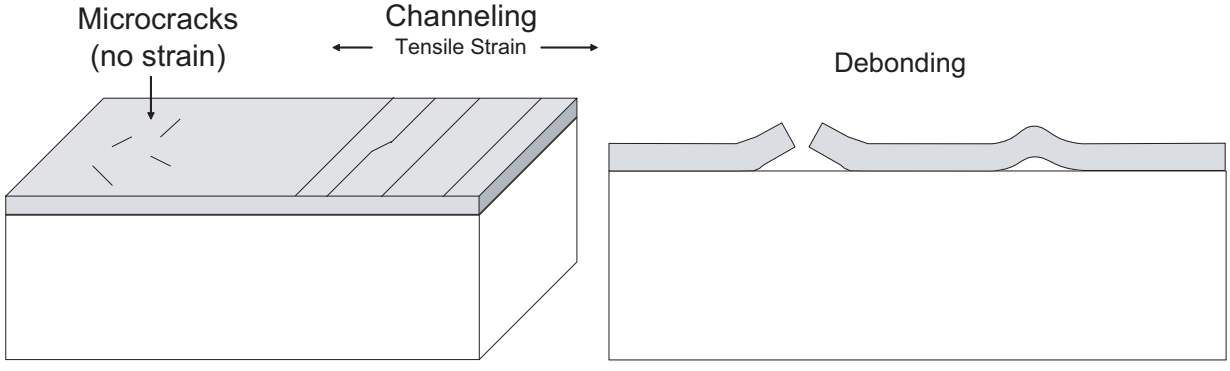

Fig. 4 Primary failure modes for brittle films on polymer substrates.

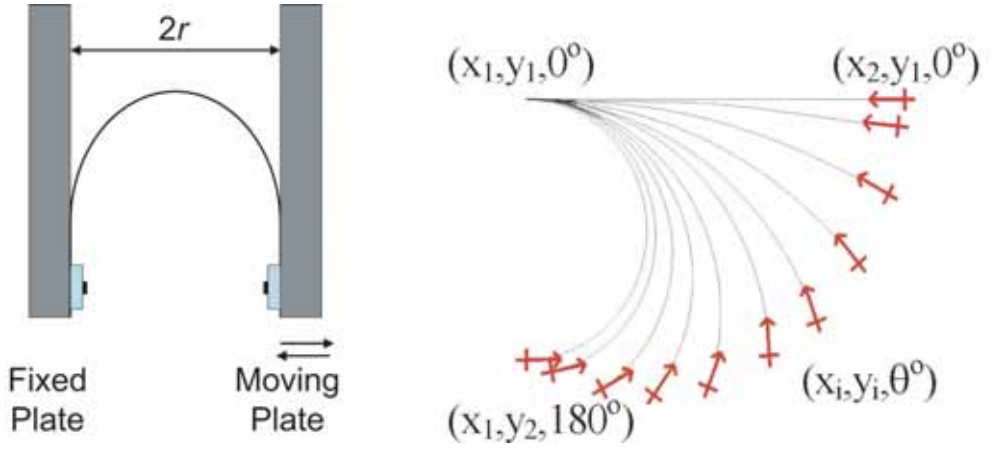

Fig. 6. Two common bend test methods for evaluating mechanical failure in films on flexible substrates are the collapsing radius test (left) and the X-Y-θ test (right).

density of cracking failure in the film. This technique is very effective, but is time consuming and potential errors may be introduced by clamping compliant substrates. Other types of tests include bulge and indentation tests[51,52,59,60]. The most direct and appropriate for evaluating films for flexible electronics is bending the sample to a given radius *r*[61-63]. For this type of bend test the most common technique is the collapsing radius test, while recently a more sophisticated technique called the X-Y-θ test has been developed. Both are depicted in Fig. 6. The respective advantages of each method have been discussed in detail elsewhere[61].

Mechanical failure of display components

Transparent conductors

Of particular concern for display and photovoltaic devices is the mechanical integrity of transparent conductors. The transparent conductors used most often are transparent conducting oxides (TCOs), the most common of which is indium-doped tin oxide (ITO). As such, ITO has been the most frequently studied of the TCO materials. ITO fails under tensile strains typically in the range of 0.8-1.2 %, though the use of buffer layers and built-in stress can be used to increase this value somewhat[64]. Fig. 7 shows a typical failure curve for ITO. As shown, much of the conductivity can be recovered when the sample returns to a flat position, but this is a time-dependent effect, and gradual loss of conductivity occurs with cycling[61].

Several alternative materials have been evaluated to provide improved mechanical robustness over that of ITO. Conductive polymers are suitable for some applications. They provide outstanding mechanical durability in terms of both strain and cycling. However they are generally less transparent and conductive. For example, the most commonly used conductive polymer, poly(3,4-ethylenedioxythiophene) poly(styrenesulfonate) or PEDOT:PSS, typically has a maximum conductivity[65] of ~10^{-2} Ω^{-1}cm^{-1} compared with ~10^{-4} Ω^{-1}cm^{-1} for ITO[66], and PEDOT:PSS is partially absorbing in the red portion of the spectrum[67]. Composites of carbon nanotubes embedded in a polymer matrix have also been evaluated for flexible transparent conductor applications. As a result of the large extent of overlap between nanotubes, these provide excellent mechanical robustness. The challenge for these nanocomposites lies in simultaneously providing sufficient conductivity and transparency. Currently films with sheet resistance R_s < 100 Ω/sq are possible with optical transmission of ~85%[67].

An interesting alternative is the use of transparent multilayers composed of ITO-metal-ITO (IMI) layers, particularly using Ag as the metal layer. These are commonly used as cold mirrors or shielding for electromagnetic interference (EMI) because of their high conductivity and good optical transparency. It was recently shown that IMI films can exhibit >80% average visible transmission with R_s < 10 Ω/sq[68]. Most importantly for flexible applications, it has been shown that IMI films offer a significant improvement in mechanical durability over ITO

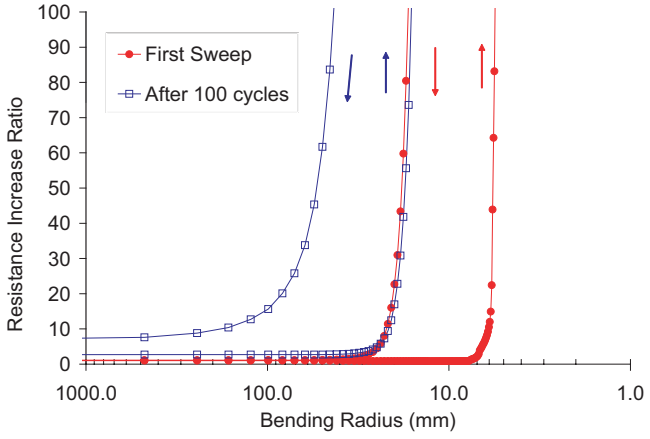

Fig. 7. Change in resistance for ITO on a polyethylene naphthalate (PEN) substrate as a function of bending radius, before and after 100 cycles to 5 mm.

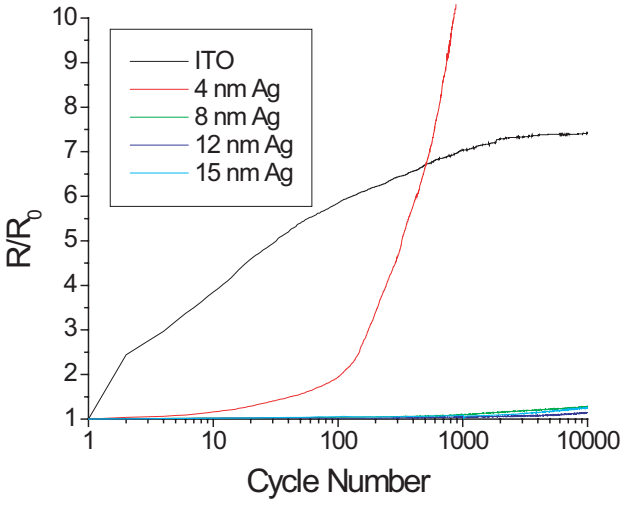

Fig. 8 Change in sample resistance for a series of ITO-Ag-ITO multilayer TCOs with different Ag layer thicknesses. The samples were cycled to a radius of 6 mm[69].

films[69]. Fig. 8 shows the improved mechanical robustness for IMI films compared with ITO under cycling to a radius of 6 mm.

Permeation barriers

We have already discussed the challenges in fabricating permeation barriers that are sufficient for long-lived OLED devices. Implicit in this application is the use of inorganic thin films because the density of organic materials is not sufficient. This brings the added risk of cracking under bending conditions. Given the stringent barrier requirements for OLEDs, a single cracking failure would be catastrophic for a device. To date, there have been relatively few reports of the mechanical durability of permeation barriers. One reason is the difficulty in characterizing failure in a statistically significant manner. One option is to perform permeation tests on samples with and without bending. This requires a large number of samples, is very time consuming, and does not provide quantitative data on the failure density.

A method was recently developed that highlights cracking defects in permeation barrier films, even when a polymer top-coat is used. The technique is rapid and can be performed in batches, allowing convenient statistical studies. Previous reports have shown that oxygen plasma can be used to highlight pinhole defects in barrier films[18]. The barrier film is inert to the oxygen plasma, but the polymer substrate is rapidly etched, leading to undercut of the film. The substrate feature quickly becomes visible under a microscope. This process is shown schematically in Fig. 9.

This simple plasma etching procedure does not work for cracking defects because of the much larger aspect ratio of the defect for a 10 nm crack (approximately 10:1) than for a micron-scale pinhole (approximately 1:10). It was recently shown that a partial etch of the barrier film reduces the thickness and, therefore, the aspect ratio of the defect. It also causes preferential etching at the defect site, widening the defect and further decreasing the aspect ratio. Fig. 10

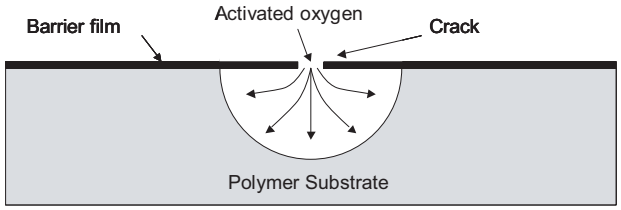

Fig. 9 Schematic diagram of oxygen plasma highlighting of defects in barrier films. The plasma etches large features in the substrate while leaving the barrier film intact.

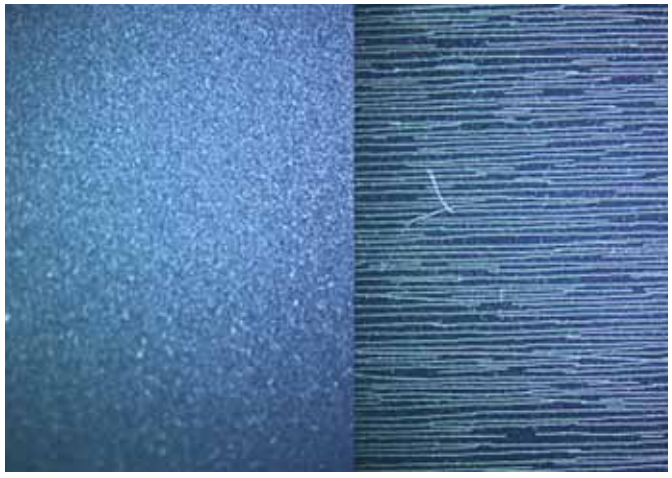

Fig. 10 Dark-field optical microscopy images of permeation barrier films that have undergone the plasma defect-highlighting process, either unbent (left) or bent beyond the failure radius (right).

shows dark-field microscope images of two etched samples, one with cracking defects and one without. This highlighting technique was used to perform one of the few systematic studies of barrier performance[70]. Furthermore, it was demonstrated that by removing the polymer top-coat in the same plasma chamber and subsequently highlighting the defects, the technique can be used to study mechanical failure of organic/inorganic multilayer barrier films a layer at a time.

Amorphous Si TFTs

Organic TFTs currently do not match the performance attained by inorganic devices, and the performance for low-cost, solution-processable organics is even lower. Therefore, for the near future, devices such as flexible, active-matrix OLED displays will use TFTs based on amorphous Si (a-Si) or nanocrystalline Si. Not only is mechanical cracking in Si-based TFTs a concern, but strain effects on device mobility must also be considered. Gleskova *et al.*[62] showed that the failure limit for a-Si TFTs is ~0.5% in tension, which is slightly lower than for the TCO and barrier films, and up to 2% in compression, which is comparable to other inorganic materials.

Hsu *et al.*[71] have shown that patterning the blanket a-Si layer into islands on the polymer substrate reduces the local strain on the islands, which is compensated in the polymer substrate between them.

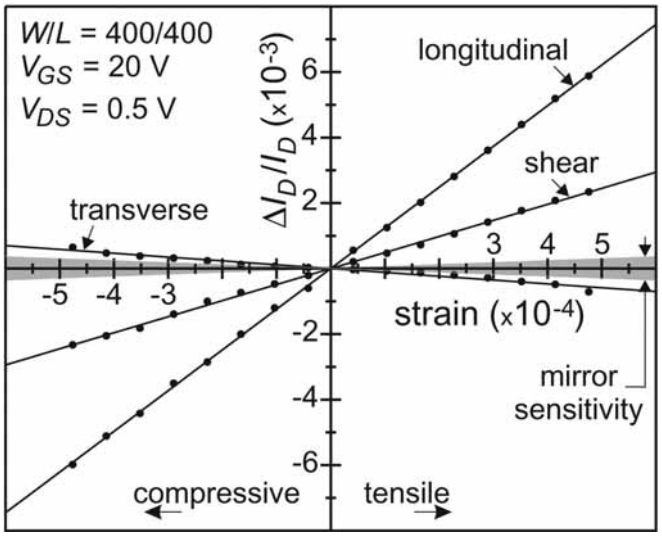

Fig. 11 Effect of mechanical strain on drain current (I_D) for a-Si TFTs with different orientations relative to the strain vector. Also shown is the range of sensitivity for current-programmed mirror circuits, which have suppressed dependence on strain. (Reproduced with permission from[55]. © 2005 American Institute of Physics.)

The islands must be electrically interconnected, but this could be a useful approach for extending the mechanical limits in flexible electronics.

The mobility of TFTs is also affected by strain. However, Servati and Nathan[55] have shown that for predictable, uniaxial strain, orienting the TFTs such that the channel current flows perpendicular to the applied stress reduces the drain current sensitivity by an order of magnitude relative to the parallel orientation. This is demonstrated in Fig. 11, which shows the change in drain current for a-Si TFTs as a function of strain. Moreover, the authors show that if current mirror circuitry is used to account for the variation in the TFT threshold voltage, this can suppress strain effects to negligibly small values for any TFT orientation. Contact-printed crystalline Si ribbons, an interesting alternative to a-Si, have recently been shown to have good mechanical and electrical properties, but this technology is in an early stage of development[72].

Metal and polymer conductors

As mentioned previously, if transparency can be sacrificed, conductive polymers and polymer composites can provide high conductivity with excellent mechanical durability[67,73]. But for some applications, the higher conductivity of metals is required. Metal films do not exhibit brittle failure like oxide materials, but rather fail by localized deformation whereby a neck is formed and elongated, leading to rupture. It has been shown that the most critical parameters determining the rupture strain are the modulus of the substrate and film adhesion[74]. For example, a Au film on a low modulus silicone substrate begins to fail at 3% strain, which is comparable to a freestanding film. In this case, the substrate does not confine the elongation of the neck. However, on a higher modulus substrate such as polyimide, deformation is more uniform and films can survive strains >10% assuming there is good adhesion between the film and substrate.

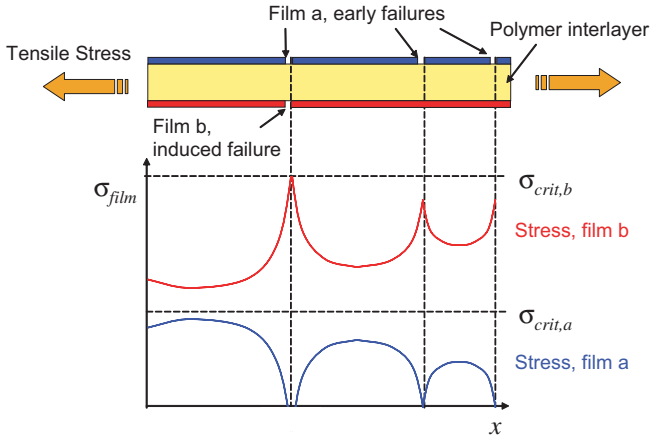

Fig. 12 Schematic demonstration of layer interactions in thin films. In this case, film a has a lower critical stress and fails before film b. However, the stress relief in film a is transferred through the polymer to film b, where induced failures can occur.

Interlayer effects

While it is important to understand the failure limits of individual device layers, it is also important to understand the interactions between layers in a device. When a failure occurs in a thin film, stress is relaxed locally and transferred to adjacent layers. This means that while a device layer may withstand a uniform stress when tested alone, the same layer in a multilayer device may fail because of a failure in another layer of the stack[75]. This effect is shown schematically in Fig. 12. The result is that, for example, while a single crack may not be catastrophic for an ITO layer, it may result in premature failure in a neighboring TFT or permeation barrier layer that does result in catastrophic failure. The degree of interaction is specific to different materials and organic interlayers, and will require significantly more attention as the limits of flexibility are pushed for commercial devices.

Conclusions

Flexible electronics have the opportunity not only to revolutionize an industry, but to create entirely new ones. Notwithstanding the advances in device performance, there are traditional materials challenges in the enabling structures that must be addressed. Components such as permeation barriers, transparent conductors, smoothing layers, and interconnects must all be evaluated for flexible devices. For many applications that require permeation barriers, such as lighting and displays, barriers with sufficient performance at a cost that is compatible with large-scale, low-cost manufacturing have not yet

been identified. Still, the progress demonstrated by multilayer structures and high-density, amorphous single layer films is encouraging. There is also implicit concern in using brittle inorganic films in flexible applications. Efforts to understand the failure limits and mechanisms have been gaining momentum. These mechanical failures make it likely that the introduction of commercial products will progress from less challenging, conformable devices eventually to rollable and even foldable devices. mt

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