Barrier Layer Technologies

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Abstract: The realization of flexible electronic devices will open the door to new, low cost commercial products. There are many technological hurdles that must be overcome to commercialize flexible electronic devices and even more challenges to achieve roll-to-roll processing. Significant progress has been made in many areas. However, due to the stringent requirements on the barrier layer, no clear technological leader has emerged. This document will review the requirements for a successful barrier layer and examine the progress made in each material currently being researched.

Introduction

One of the main difficulties in commercializing electronic organic molecules is lifetime. Electronic organic molecules and polymers can degrade in a few hours under normal environmental conditions. Devices are therefore fabricated in an inert environment and encapsulated to protect them from oxygen, water and ultraviolet light. In this manner lifetimes on the order of ten thousand hours or higher are possible.\textsuperscript{1} Organic light-emitting devices (OLEDs) are being investigated as an alternative to liquid-crystal displays (LCDs). While LCDs require heavy and brittle glass panels, OLEDs can be deposited on flexible plastic rolls. This makes OLEDs an attractive technology for low cost, light-weight, flexible displays.\textsuperscript{1}
All electronic organic molecules have different technical issues. Even among OLEDs each color has its own strengths and weaknesses. Blue OLEDs have particularly poor lifetimes. This makes full color display lifetimes a particularly large hurdle that must be overcome to make flexible electronics a reality.²

OLEDs have two degradation modes. The first is intrinsic loss of efficiency over long periods of time. The second mode is the growth of dark spots. It is the later that is responsible for the rapid degradation of OLEDs. The mechanism for dark spot growth is due to the presence of water and oxygen. Rapid OLED degradation can be prevented through encapsulation.³⁴⁵

Flexible barrier layers are required for flexible electronic devices. Flexible displays have the added burden of requiring transparency. In order to achieve sufficient lifetimes the barrier layer must transmit less than 10⁻⁶ g/m²/day of water vapor and less than 10⁻⁵ mL/m²/day of oxygen.⁶

Different applications require different degrees of flexibility. An OLED display for a soldier’s visor or a pilot’s cockpit only needs to be flexible during fabrication.⁷ Once fabricated, the device can be inserted between two shaped, inflexible panels that have sufficient barrier properties. Other applications will require the device to be flexible during operation. These will require transparent, flexible barrier layers. Polymers⁶, glass⁸ and composites⁹¹⁰ are being investigated, as are stable organic semiconductors.¹¹ No barrier layer technology has shown commercial viability at the time of this writing.
Evaluating Barrier Layers

Transmittances less than $10^{-6}$ g/m$^2$/day of water vapor and less than $10^{-5}$ mL/m$^2$/day of oxygen are two small to be measured with conventional techniques. A testing technique has been developed in which a thin film of calcium is deposited on the sample. As water permeates through the sample the calcium reacts to form a calcium salt. Optical transmission can measure the presence of the calcium salt. Measurements can be taken over the course of several days. In this manner the cumulative water uptake can be plotted versus time. The slope of a best fit line will reveal the rate at which water is transmitted through the barrier layer. This measurement technique is known as the “calcium test.”

The effectiveness of a barrier layer is often determined by defects. This can lead to localized degradation, which is worse for a product than uniform degradation. An advantage of the calcium technique is that it allows for the evaluation of localized transmission rates allowing one to study the effects of defects in the barrier layer.

In addition to directly measuring the transmittance of water through the barrier it can be useful to make in-situ measurements on the device as it ages. Electrical characteristics can be measured during thermal annealing using a high resolution in-situ electrical measurement technique. Light output is measured as a function of time, giving an Arrhenius relation and the corresponding activation energy of failure.

FT-IR and UV-Vis spectroscopy experiments can also be performed in-situ while the device is heated. This enables the study of reaction mechanisms and kinetics. Furthermore,
observing the degradation of characteristic peaks with time can result in an Arrhenius plot, revealing the activation energy for a mechanism.¹⁴

Finally, Photothermal Deflection Spectroscopy is a useful technique for measuring oxygen content. Oxygen will react with organic semiconductors forming defects. These defects can be measured by modulating the intensity of an incident light beam resulting in periodic heating. Index of refraction is temperature dependant and can be reliably measured.¹⁴

**Metal Foil Barriers**

Flexible electronic applications that do not require transparency can utilize metal foil barrier layers. Metal foil barriers have superior mechanical properties and are easier to process than glass. Additionally metal foil barriers have excellent barrier properties. Metal foil barrier layers have low cost, excellent thermal conductivity properties, deform predictably and have high operating temperatures. Unlike other barrier materials, metal foil has a rough surface. Furthermore the coefficient of thermal expansion of a metal foil substrate is mismatched with the coefficient of thermal expansion of organic electronic components. Most importantly metals are opaque, making them unsuitable for flexible displays except as a backplane.¹⁵

**Polymer Barriers**

Polymer films are highly desirable materials for flexible electronics. Polymers can be low cost, are relatively smooth and are transparent. Furthermore mechanical properties can be fine tuned for desired flexing and the coefficient of thermal expansion is a good match for organic electronic
devices. However, plastic substrates have limited operating temperatures and poor thermal conductivity. They also have very poor barrier properties.\textsuperscript{15}

Two polymers have been heavily investigated as barrier materials: polyethylene terephthalate (PET) and polyethylene naphthalate (PEN). Both polymers have superior barrier properties compared to other polymer substrates. PET transmits 20 g/m\textsuperscript{2}/day of water vapor while PEN transmits only 3.6 g/m\textsuperscript{2}/day of water vapor. However, even these films are six orders of magnitude off from being an effective barrier layer for organic electronics.\textsuperscript{6}

Achieving six orders of magnitude improvement in barrier performance would require a major technological breakthrough. Despite this immense challenge polymers are still being examined because they have other desirable properties. In particular, polymers display the correct mechanical properties in terms of tensile strength and stiffness. Finally, they have compatible coefficients of thermal expansion with other organic components.\textsuperscript{6}

Polymers are highly temperature sensitive. This can be engineered around. Compared with PET, PEN has a higher $T_g$ but a similar $T_m$, allowing it to be melt processed but have a higher operating temperature. PEN retains its strength for long periods of time at elevated temperatures.\textsuperscript{6}

Polymers are an attractive substrate material that industry has experience using. If any significant progress has been made towards achieving barrier polymers it is proprietary. Baring a major breakthrough polymers will not be used as barrier materials.
**Glass Barriers**

At thicknesses thinner than 100 microns glass films are flexible. A bending radius of 30 mm has been achieved. Sheets as thin as 30 microns can be fabricated using a downdraw process. Like optical fibers, flexible glass sheets have poor mechanical properties unless they have pristine surfaces. Polymer coatings are necessary to preserve the integrity of the surface and therefore the mechanical properties. In addition to having excellent barrier properties, glasses also have superior thermal stability in comparison with plastics.  

The fiber optics industry has made flexible glass a common part of everyday life. It may seem obvious to simply transplant the technology from the fiber optics industry to develop flexible glass barrier layers. However, the mechanical properties of glass are dependant on the surface area. A geometric calculation reveals that a single square foot glass sheet has almost the same surface area as half a kilometer of 125 micron diameter fiber. This implies that small panels of flexible glass are feasible with a high degree of surface control.

A major goal for the flexible electronics industry is roll-to-roll processing. Geometric surface area calculations show that small panels of flexible glass are feasible. Rolls of flexible glass have considerably more surface area. A commercial flexible glass plant, operating on the same scale as a fiber optic draw tower, would deal with a much greater surface area of material. This translates into requiring a much cleaner operating environment.

Geometric surface area calculations reveal that for every inch of roll width, there is 130 times the surface area as a
125-micron diameter optical fiber. Since optical fiber is often fabricated in a class 10 clean room environment (ISO 4) a 7 inch width roll would require an ISO 1 clean room environment to maintain the same numbers of contaminants on the roll. This would greatly add to the fabrication cost of any flexible electronic device, but it is not an insurmountable hurdle.

**Multilayer Composite Barriers**

Further lessons can be learned from the fiber optics industry. It is well known that the mechanical properties and optical transparency of fiber optics degrade over a period of time in the presence of water. Hermetic coatings are used to offset the start of a fatigue knee that is associated with rapid aging after many years. Thin hermetic coatings, such as 20-50 nm amorphous carbon, can greatly increase the lifespan of the material. Amorphous carbon is opaque and therefore unusable for flexible displays. However, the lesson to be learned here is that barrier layers do not need to be thick.\textsuperscript{16}

It is therefore unsurprising that there has been significant interest in the Barix\textsuperscript{TM} vapor barrier film manufactured by Vitex Systems Inc. Barix\textsuperscript{TM} is a multilayer technology using alternating layers of organic polyacrylate and thin inorganic barrier materials. Possible inorganic materials include SiO\textsubscript{2}, Si\textsubscript{3}N\textsubscript{4}, Al\textsubscript{2}O\textsubscript{3} and ITO.\textsuperscript{9}

Tests of these barrier materials show promising results. Rates of $8 \times 10^{-5}$ g/m\textsuperscript{2}/day water vapor transmission have been reported from calcium tests.\textsuperscript{12} Less quantitative testing has been performed showing that OLEDs protected with multilayer composite barriers continue to function after being submerged in water for a week and subsequently
allowed to age for one month. However, these tests illustrate the problem with multilayer films. While the majority of the OLEDs continue to function, dark spots are clearly visible.\textsuperscript{10}

The main problem with using thin inorganic barrier layers is that roughness or defects compromise barrier performance. Barix\textsuperscript{TM} barrier layers use a technique to smooth the polymer surface to preserve the integrity of the inorganic layers. Additionally, Barix\textsuperscript{TM} uses multiple inorganic layers to “decouple” defects.\textsuperscript{9}

Vitex Systems Inc. was in the process of developing an inline barrier layer vacuum deposition tool called The Guardian Tool. In 2003 Vitex Systems Inc. received an award for Excellence in Technology in Thin Films from Frost and Sullivan for its Barix\textsuperscript{TM} films. The award document even states that “Vitex has overcome this key bottleneck with its Barix moisture barriers.” It was believed that Barix\textsuperscript{TM} was the solution to the barrier layer problem. However, within a couple years development of the Guardian Tool stopped and the company became an IP company.

\textbf{Stable Organic Semiconductors}

In addition to improving the quality of barrier layers there is additional research into the stability of organic semiconductors. More stable organic molecules could lessen the demand on barrier properties opening up possibilities for other barrier materials.

An organometallic semiconductor has been reported with remarkable stability. In one test, the material was heated in water over 80°C for twelve hours without showing a significant degradation of electronic properties. This is considerably better than organic
electronics that rapidly degrade in white light, air or water.\textsuperscript{11} The organometallic material is soluble in common organic solvents meaning it could be adapted for ink printing. Unfortunately this particular material is platinum based giving it a prohibitive cost. However, it does demonstrate that the stability of organic electronic molecules can be significantly improved.\textsuperscript{11}

Another promising technology utilizes organic phosphors. Reaction kinetics are dependant on the concentrations of the reactants. In the degradation reaction of OLEDs, the organic molecule must be in an excited state to become oxidized. If the molecule can be kept in equilibrium with a ground state then the concentration of excited molecules can be kept low. This decreases the kinetics of the degradation reaction leading to more stable molecules. Phosphor emitters can theoretically last hundreds of thousands of hours in an inert environment.\textsuperscript{1}

**Conclusion**

Research to date has successfully identified the transmission requirements for a successful barrier layer. Additionally, techniques capable of measuring these low transmissions in samples have been invented. There have been no major advances in barrier layer materials.

Of the materials being examined as barrier layers there is no clear winner. Metal foil layers are not transparent making them unsuitable for flexible displays. Polymers do not have the required barrier properties. Flexible glass sheets are challenging to fabricate. Multilayer composite materials are costly due to the number of layers required to decouple defects. There is
no barrier layer technology that will meet the demands of the upcoming flexible electronics industry.

The future of the flexible electronics industry hinges on the development of a successful barrier layer. Advances in barrier layer technology will most likely occur on two fronts: improvements to the barrier layer materials and improvements to the stability of organic electronic materials. Until significant improvements have been achieved on both ends flexible electronic devices will not become commercial products.

References


