UV-polymerized Films
Enable Ultra-Barrier Coatings for Thin-Film Photovoltaics and Flexible Electronics

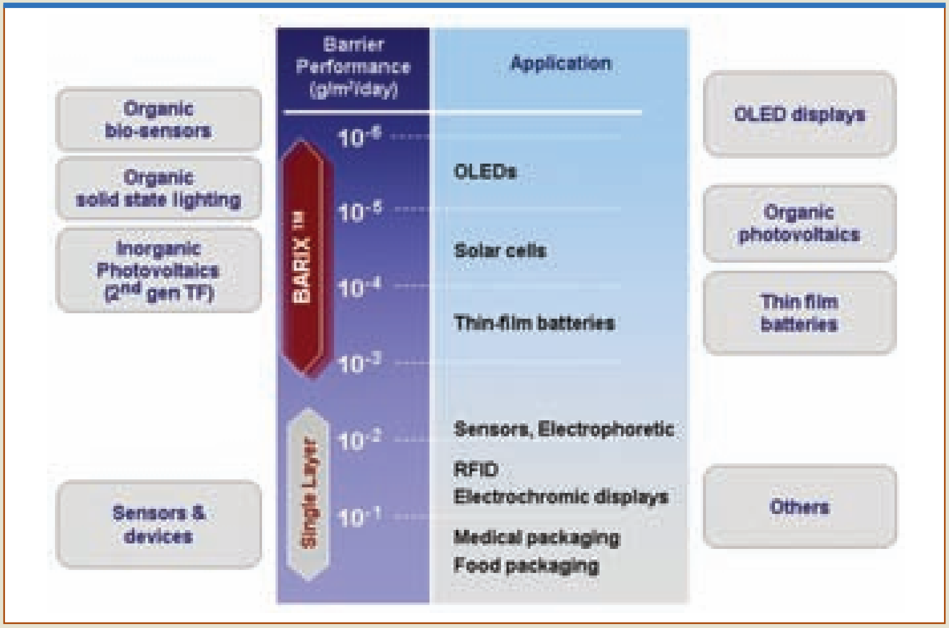
By Martin P. Rosenblum, Steve Lin and Xi Chu

Many of the new and exciting developments in flexible electronics and thin-film photovoltaics require a robust, transparent and flexible encapsulation material to protect devices and materials sensitive to water vapor or oxygen. The conventional encapsulation method is to use glass for its transparency and barrier performance. This sacrifices the important advantages of flexibility and weight. To overcome these limitations requires a flexible and transparent material that is an effective barrier to water vapor and oxygen. The use of UV-polymerized, vacuum-deposited films has enabled the development of multilayer barrier coatings that meet these demanding requirements.

There are many polymer films, such as polyethylene teraphthalate (PET) and polyethylene naphthalate (PEN), that are flexible and have good transparency in the visible spectrum. These films provide little effective

FIGURE 1

Barrier performance and applications



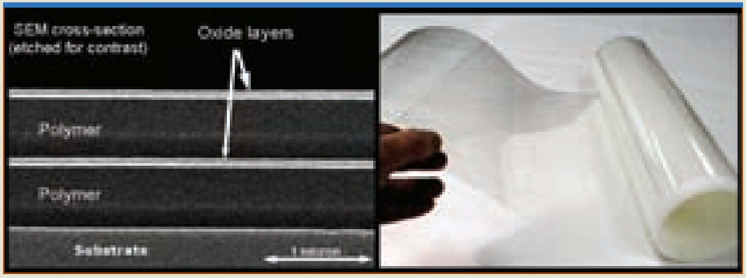
barrier to water vapor or gas. Typical values for water vapor transmission rates (WVTR) for polymer films range from 1 to 10 g/m^2/day at ambient (20°C and 50%RH) conditions. A large industry exists that deposits thin films of materials onto plastic film to improve its barrier performance. This is a common technique used throughout the food and beverage industries. These single-layer barrier coatings can reduce WVTR to less than 1 g/m^2/day and, in some cases, to less than 0.1 g/m^2/day. The requirements for protecting organic light emitting diode (OLED) displays and lighting are many orders of magnitude more stringent as shown in Figure 1.

The specifications for OLED devices, depending on the required lifetime, range from 1x10-4 g/m^2/day to less than 1x10-6 g/m^2/day. Thin-film photovoltaic cells are less sensitive to water vapor but can require lifetimes of 20 years or more for residential and commercial installations. These barrier requirements cannot be obtained by a single-layer barrier coating. Although fundamental properties of conventional barrier coating materials (such as aluminum oxide and silicon oxide) have inherent barrier performance that exceed these requirements, thin films always contain both intrinsic and extrinsic defects that act as short-circuit paths for water vapor.

Intrinsic defects are those arising from the imperfections or discontinuities of the processes of film nucleation and growth. These defects are typically characterized by microscopic pores or boundaries of reduced physical density. Local variations in the surface energy due to contamination or material non-uniformity can lead to differences in film nucleation that coalesce to form defective regions. Surface roughness and topography will also influence the uniformity of nucleation and the character of the film growth process. Often these defects, once formed during the initial stages of film growth, propagate through the thickness of the growing film. The result is that barrier performance cannot be indefinitely improved simply by increasing the thickness of the deposited film. Barrier layers are typically brittle materials, so thick coatings are subject to cracking and detrimental to flexibility.

FIGURE 2

Multilayer structure and barrier film



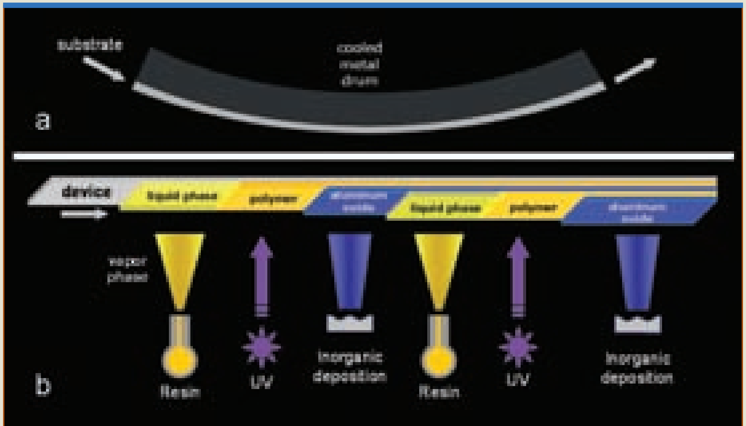
Extrinsic defects are classified as those arising from foreign objects, debris and mechanical damage that disturb the formation and continuity of the thin-film barrier layer. The sources for these defects occur at all points in the manufacturing process. Polymer films are typically not fabricated or converted under clean room conditions. Particulate-generating paper cores are used for winding. To avoid high friction between film layers on the roll, slip coatings and treatments are commonly applied to the back surface of the film. There may be some degree of material transfer to the front surface or print-through if the roll is wound tightly. This is a particular danger in vacuum web coating because of the tendency of atmospheric pressure to crush the roll when removed from the vacuum. Particles are attracted to static charges on the surface of the plastic as it is unwound. The deposition process can create particles from flaking of the coating on surfaces or from mechanical abrasion of moving parts.

To overcome many of these problems and fabricate a flexible, transparent film with ultra-barrier properties, we have developed a patented system (Barix™) which uses thin polymer layers that are deposited alternatively with thin barrier layers. This multilayer organic/inorganic structure, as seen in Figure 2, has several unique features that enable superior barrier performance.

The polymer layer, typically between 250 nm and 1,000 nm in thickness, is deposited by flash evaporation of a multicomponent proprietary acrylate-based resin system. The design of the resin system is a complex balance of properties, performance and process. For the encapsulation of top-emission OLEDs, the requirements include high transparency throughout the visible spectrum; low shrinkage (<15%) to minimize stress; and low water solubility for barrier performance and compatibility with plasma-based deposition of the barrier layer. While several of these criteria are applicable for the protection of thin-film solar cells, additional requirements include long-term stability against UV degradation (weatherability); high interfacial adhesion for robust

FIGURE 3

Multilayer deposition configurations



a) Deposition on polymer web b) Direct encapsulation

mechanical performance; and structural stability at elevated temperatures and humidity (i.e., 85°C and 85% RH for >2,000 hours).

The vapor is directed onto the substrate through a narrow slit over which the substrate passes. The vapor condenses as a liquid onto the substrate planarizing and smoothing the surface. Particles or other topographic features on the surface can be coated over and smoothed by the liquid. Through surface tension, a thin layer of liquid is able to smooth particles or features with dimensions many times that of the average polymer layer thickness. While in the vacuum, the liquid resin on the surface is converted to a solid polymer by exposure to an ultraviolet light source. Thermal curing is not an option for direct encapsulation of temperature-sensitive OLED devices. Speed of curing is important for maintaining high productivity for short cycle times and high line speeds in roll-to-roll fabrication. Electron beam curing has been used successfully in roll-to-roll coating, but UV curing has proven to be both cost effective and simpler to implement. In laboratory experiments, we have demonstrated that UV curing is capable of supporting line speeds of greater than 20 meters/minute.

Deposition of the barrier layer takes place immediately after the polymer deposition process as shown in Figure 3. The barrier layer deposition method commonly used with this multilayer process is the reactive magnetron sputter deposition of aluminum oxide. This deposition process is well established and has been scaled commercially for large area deposition in the window glass coating industry. The target material is low-cost aluminum metal. The refractive index of the aluminum oxide (1.65-1.67) is a reasonable match to that of the polymer layer (1.49-1.51). This minimizes the amount of interference created by the multilayer structure and maintains high transparency without color shift. This has been verified by several OLED display makers. If an even better match is required, silicon may be alloyed with the aluminum to reduce the refractive index of the barrier layer without compromising barrier performance.

A key enabling feature of the polymer deposition process is the smoothing of the substrate and the formation of a clean and highly uniform surface for subsequent deposition of the aluminum oxide barrier layer. The in situ creation of the fresh polymer surface provides for a consistent and uniform nucleation of the aluminum oxide film. The result is the formation of a dense, continuous, high-quality barrier layer at thicknesses between 20 and 50 nm. The thinness of the layer allows for faster process throughput.

A second feature of the multilayer structure performed by the polymer layer is the decoupling of defects between barrier layers. The polymer separates the barrier layers from one another and prevents defects in the bottom oxide layer from propagating to the top oxide layer. This decoupling of defects avoids the short-circuiting through the barrier layers by forcing the water vapor to diffuse throughout the polymer layer to reach a defect

FIGURE 4

Calcium barrier test structure

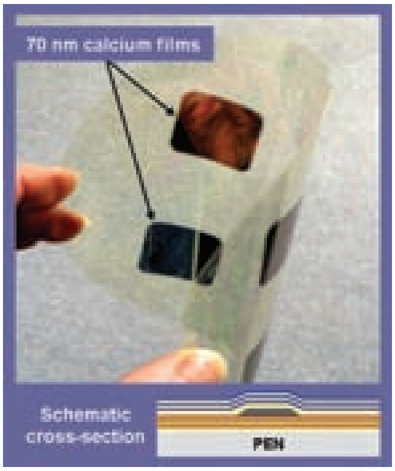
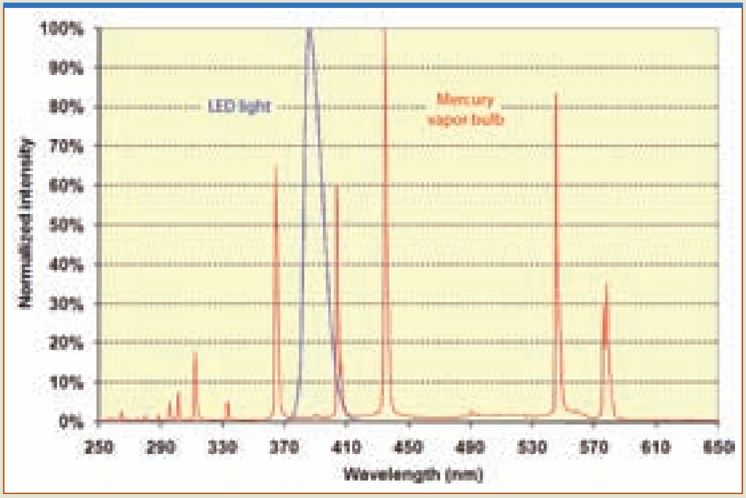


FIGURE 5

UV source spectra



before it can penetrate the next barrier layer. The net effect is to create a very long lag time, greater than the life of the device, for the water vapor to reach the device. This lag-time mechanism of the multilayer structure contrasts with the more commonly measured steady-state transmission rate measured by commercial instruments, such as the MOCON Permatran™ and Aquatran.™

To measure the barrier performance of these multilayer coatings, it was necessary to develop a technique that had greater sensitivity than what was available with commercial equipment. The method used is the precise measurement of the change of light transmission with time through a thin film of calcium metal protected by the barrier coating (Figure 4).

Calcium is a highly reactive metal that becomes transparent when oxidized. By precisely measuring the relative change in light transmission through the calcium, it is possible to calculate the amount of water vapor that has reached the calcium. In conjunction with accelerated testing by exposure to elevated temperature and humidity, the calcium method is capable of determining room temperature "effective" transmission rates on the order of 10-6 $g/m^2/day$. The current "standard" barrier test criterion at Vitex is to measure less than a 10% relative change in light transmission through a 70 nm calcium film after 1,000 hours exposure to 85°C at 85% relative humidity. We calculate this to be equivalent to an effective water vapor transmission rate of less than 1x10-6 $g/m^2/day$ at 20°C and 50% relative humidity.

The formation of the oxide barrier layer onto the preceding polymer layer makes up a layer pair, referred to as a dyad. The number of dyads is determined by the specific nature of the surface, material to be coated and the required lifetime of the device. The number of dyads and polymer thicknesses required are also influenced by the density and size of particles that need to be coated. Cleaner surfaces require thinner and fewer dyads. As processes, vacuum hardware and materials have improved over time, it has been possible to reduce the number of dyads required from six to two or three for the sensitive OLED devices, while retaining a barrier performance of less than 10-6 $g/m^2/day$.

The majority of the development of the resin system and polymer deposition process used a microwave-excited mercury vapor lamp for the ultraviolet source. This source reliably provides ample ultraviolet power and a multi-wavelength spectrum. Recently,

TABLE 1

Qualification criteria for resin system and light source

Criterion	Status	Comment
Adhesion	✓	Equivalent
Barrier performance	✓	Equivalent
Chemical supply	✓	Licensee qualified
Cure optimization	✓+	Large process margin
Desorption / extraction	✓+	Less outgassing
Handling and safety	✓	Ambient light sensitive
OLED compatibility	✓+	Improved on sensitive devices
Photoinitiator stability	✓+	Greater thermal stability
Shelf life	✓	Minimum 6 months
Shipping	✓	Requires opaque packaging
Shrinkage	✓+	Relative shrinkage reduced by 20%
Visible transmission	✓	No change

a new light-emitting diode (LED) ultraviolet source has been qualified and implemented in Guardian™ thin-film encapsulation systems. A modification of the photoinitiator in the resin system was required to accommodate the longer wavelength of the LED UV source.

The shift to a solid-state UV source was motivated by several technical and commercial factors. In addition to the desired output in the UV, the microwave-excited mercury source generates large amounts of visible and infrared radiation. Even with the use of a 'cold' reflector and 'hot' mirror, there is considerable heating of the substrate or device. For higher throughput, a higher UV power causes the bulb temperature to rise and increases, as T^4, the infrared radiation impinging on the substrate or device. This makes scaling for manufacturing more difficult and expensive as further heat-mitigating hardware must be used. In contrast, the water-cooled LED UV source generates a narrow spectrum centered near 395 nm with negligible extraneous heat load to the device. Figure 5 shows a comparison of the spectra of the two UV light sources.

The qualification of the new resin system and UV light source consists of an extensive set of evaluation criteria. These are shown in Table 1.

Several of the evaluations demonstrated that the new resin system and UV light source provided improved performance and processing. Studies of the conversion percentage and UV dose revealed full curing, greater than 90% conversion as determined by Fourier transform infrared spectroscopy, at energy densities of less than 200 mJ/cm^2. The longer UV wavelength extended the process compatibility to more sensitive OLED materials and displays. Additional care is required to protect the new resin system from exposure to ambient light because of increased sensitivity to longer wavelengths. This is easily accomplished with opaque packaging.

The multilayer barrier structure is applied with two distinct methods as shown in Figure 3. The multilayer coating can be directly deposited onto the device to be protected. This method provides immediate protection when incorporated as part of the device fabrication process. It provides the thinnest and lowest weight flexible, transparent barrier. The world's thinnest active matrix OLED display using direct encapsulation with multilayer barrier coating was shown by Samsung SMD at the 2008 Society for Information Display Conference as shown in Figure 6. This method is used to encapsulate OLED displays in situ after the device deposition, since even the shortest exposure of most unprotected OLED displays to the atmosphere is not acceptable. It is also suitable for other thin-film devices such as lithium batteries and OLED lighting.

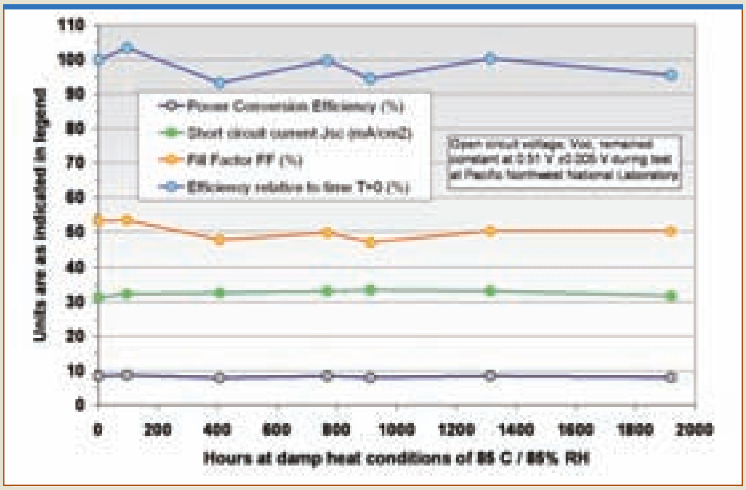
The other method for applying the multilayer barrier coating is through its incorporation onto a carrier or base film, such as PET or PEN. The

Figure 6

Flexible AM-OLED display with direct multilayer encapsulation

Figure 7

Damp heat test of multilayer encapsulated CIGS solar cell



resulting flexible barrier material can be used as a carrier or substrate for subsequent device fabrication and by lamination onto the surface of the device for encapsulation. Thin-film copper indium gallium (di)selenide (CIGS) photovoltaic cells that have been encapsulated by the lamination process with a 2-dyad barrier coating on PEN have greatly exceeded the IECE 61646 damp heat test that requires less than 5% reduction in power conversion efficiency after exposure for 1,000 hours at 85°C and 85% relative humidity as shown in Figure 7. The use of lamination encapsulation with the multilayer barrier coating allows for significant cost reduction through the use of high-volume, roll-to-roll manufacture of the barrier coating on base film.

Conclusion

The use of vacuum-deposited, UV-polymerized films advances the application of thin-film coatings for the demanding requirements of the new era of flexible and organic electronics. As a key component in the fabrication of multilayer barrier coatings, it has been demonstrated to be the enabling technology for flexible, transparent and light weight encapsulation of OLED displays and thin-film solar cells.

Acknowledgements

Vitex Systems acknowledges the cooperation of the Pacific Northwest National Laboratory for evaluation of the barrier performance of encapsulated solar cells.

—Martin P. Rosenblum is vice president, operations and engineering; Steve Lin is director, polymer technology; and Xi Chu is director, process engineering at Vitex Systems Inc. in San Jose, Calif.