

# “Packaging” of Moisture Sensitive Materials Used in Wearable Devices

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## Introduction

Vacuum deposition of thin film gas diffusion barriers have been in high volume manufacturing for over 60 years particularly in the food packaging industry. This has typically involved the high rate thermal evaporation of thin Aluminum layers onto PET, polypropylene or polylactic acid based substrate materials. However, transparent barriers are also required for applications where product viewing, x-ray screening and microwaveability are of importance. Materials such as  $\text{SiO}_x$ ,  $\text{SiN}_x$ ,  $\text{AlO}_x$  and  $\text{TiO}_x$  are therefore often used. However, as this industry is highly commoditized, the layer cost is critical and the barrier performance plays an almost secondary role. Consequently, deposition tool sets employ rapid substrate handling systems (meters per second) with ultra-high deposition rate source technologies in order to meet these aggressive cost/performance targets. Organic electronic devices however, operate at the other end of the layer performance spectrum. Within an organic light emitting diode (OLED) device, the small molecule organic semiconductors used to generate light and the low work function metals (e.g. Ca and Li) used for efficient electron injection from the cathode to the organic luminescent layers are extremely sensitive to the presence of water vapor. Cathode hydrolysis in particular is known to create non-conductive channels in the electrode resulting in non-emissive black spots and pixel distortion (Graff et al 2005). Direct or non-direct encapsulation of the device is therefore required to achieve the required 10 year lifetime at room temperature with water vapor transmission rate requirements a million-fold lower than in food packaging industry ( $< 10^{-6}$  g/m<sup>2</sup> day c.f.  $> 1$  g/m<sup>2</sup> day).

## Vacuum Deposition of Coatings for Ultra High Barrier Used in Wearable Devices

High density inorganic layers are utilized for OLED barrier film applications. The deposition technologies utilized must be compatible with low deposition temperature ( $< 110^\circ\text{C}$ ) as many of the materials utilized in barrier film fabrication are sensitive to thermal, UV or ion bombardment based degradation (Morrison et al. 2015). Semi-crystalline heat stabilized substrates are often required as a consequence of their relatively high glass transition temperature, low coefficient of thermal expansion, low shrinkage and high solvent resistance. These substrates can also be commercially obtained with planarization layers at the surface, reducing the barrier layer defect density and hence enhancing barrier performance (McDonald et al. 2005).

Atomically dense barrier layers can be produced by using deposition technologies with a semi-energetic deposition flux to the growth surface either in the form of ions or neutral species (Graff et al 2005). As such, high rate thermal and e-beam evaporation technologies are not able to produce films of sufficient density and quality for barrier layers in organic electronics. Some improvements can be made by utilizing either ion or plasma assistance, albeit with limited extendibility. Both PVD and CVD processes are more commonly used for high density barrier layer production, but require markedly different defect mitigation strategies to ensure the requisite balance between performance and cost. Typically, sputtered  $\text{SiO}_x$ ,  $\text{SiN}_x$ ,  $\text{AlO}_x$  and  $\text{TiO}_x$  are produced using a reactive mid-frequency process using “metallic” targets. Particle and molten droplet contamination during thin film processing represents a major source of yield

reduction in barrier production (Morrison et al. 2015). Such contamination has been shown to occur as a consequence of arcing during processing (Daalder 1976, Juettner 1987, Sproul 1997, Koski et al. 1999, Wickersham et al 2001, Wickersham et al 2002, Anders 2006). Consequently the principal route towards reducing this source of defectivity has involved controlling not only the arc density but also the arc energy. The most common form of arc, the plasma-target arc, is initiated by the breakdown of an insulating region on the target surface, by the release of trapped gas from the target or the presence of a field emission point on the target (Anders 2006). This type of arc can be extinguished by switching off the power supply. The second form of arcing, known as shield-substrate arcing, occurs when a voltage develops between either a shield or mask and the substrate resulting in damage at the substrate surface itself. The third and final form of arc, known as a target-shield arc, occurs when a low impedance path is formed between the shield and the target. This form of arcing is observed in either a “dirty” system or alternatively when there is a geometrical change in position between the shields, the dark space protection and/or the targets.

The generation of these defects during PVD barrier processing has been attributed to the highly localized absorption of arc energy at the target surface resulting in rapid heating (Juettner 1987). Under these conditions the target surface immediately under the arc root is heated within a  $\mu\text{s}$  timescale resulting in a change of phase. Large droplets are ejected as a consequence of vapour bubble formation and motion in the melt once the boiling temperature has been attained (Wickersham et al. 2001, Wickersham et al. 2002). This is analogous to water droplet loss during boiling. Particle formation typically takes place via an alternative mechanism. When the arc energy induced thermal stresses exceed the dynamic tensile strength of the target material, mechanical fracture and ultimately spallation and ballistic ejection of fragments of the target surface takes place (Daalder 1976, Wickersham et al 2001, Wickersham et al 2002). In PVD, these defects have radii typically of the order of 1-3  $\mu\text{m}$  with densities of the order of several hundred per  $\text{mm}^2$  (Graff et al 2005). Key to reducing the spatial density and size of these defects is the close control of the arc frequency and arc energy. This is most commonly achieved through the use of a low cathode power density, but at the consequence of low deposition rate and hence throughput and significantly increased fully burdened layer cost. One further disadvantage of PVD is its inherent line of sight deposition capability. Small asperities either directly on the substrate surface, arising from substrate (web) slitting, or as a consequence of arcing during processing cannot be conformally covered. As such, small pinholes in the deposited layer are typically observed and the barrier performance deviates from that expected when considering only the bulk layer material. PECVD however is a deposition technology that overcomes these issues. Dense  $\text{SiN}_x$  layers can be deposited under process conditions utilizing moderate to high levels of ion bombardment with the same type of Silane chemistry used for gate dielectric deposition for TFT's. Low pressure processing is typically utilized to ensure the ion content in the deposition flux is sufficient to reduce the overall hydrogen content of the layer and eliminate weakly bound  $\text{SiH}_2$  and  $\text{NH}_2$  moieties within the film. The ion bombardment also has the advantage of increasing the adsorbate mobility and enhances the layer conformality over defects or asperities on the substrate surface itself. Particulates generated during deposition are small and more widely spaced than observed in PVD with radii and densities more typically of the order of  $\sim 0.5 \mu\text{m}$  and in the tens of defects per  $\text{mm}^2$  respectively (Graff et al 2005). Consequently, intrinsic material barriers measured with test methods like the so-called Calcium test deliver barrier performance values for single  $\text{SiN}_x$  layers in the  $5 \times 10^{-5} \text{ g/m}^2 \text{ day}$  range (Morrison et al. 2015), whereas permeation analysis using MOCON like test methods yield permeation rates more than an order of magnitude higher.

## Implications for R2R Processing

Unlike thin film encapsulation (TFE), barrier film processing involves the utilization of so-called roll-to-roll (R2R) processing. This involves the use of a manufacturing platform that processes substrates in a continuous fashion in rolls up to a few kilometers in length. Depending upon the process itself, this imposes a limitation in terms of the mean time before cleaning and in some cases the particle management strategy. This has led to the implementation of “sputter-up” configurations in PVD tool designs and vertical/deposit-up process zones in CVD tool configurations. An example of such a R2R CVD production platform is shown in Figure 1 (Applied Materials R2R CVD tool). In its simplest form it consists of an unwinder module, a process module and a rewinder module. Each process module can be equipped with a number of high rate linear plasma sources in separately pumped process compartments. The number of process modules required is determined by a combination of the layer stack structure and the desired tool productivity. The standard platform employs a tempered coating drum to accurately control the substrate temperature and temperature uniformity within the coating zone. This configuration also has the advantage of permitting the use of a very small gap between the coating drum/substrate and the chamber separation walls resulting in pressure separation (several orders of magnitude) between individual process compartments in each process module. One further advantage of dynamically moving the substrate through the coating zone is found in terms of coating uniformity. In batch coating systems the coating thickness and property uniformity must be optimized in two dimensions, often leading to an increase in cathode design complexity and cost. Within a R2R tool, the uniformity is optimized in a single dimension only, thereby simplifying the tool design and reducing cost per unit area. As the process is continuous, the process gas and substrate material is more efficiently utilized (no significant substrate to substrate gas stabilization time influence as found in typical cluster tool based batch processing).

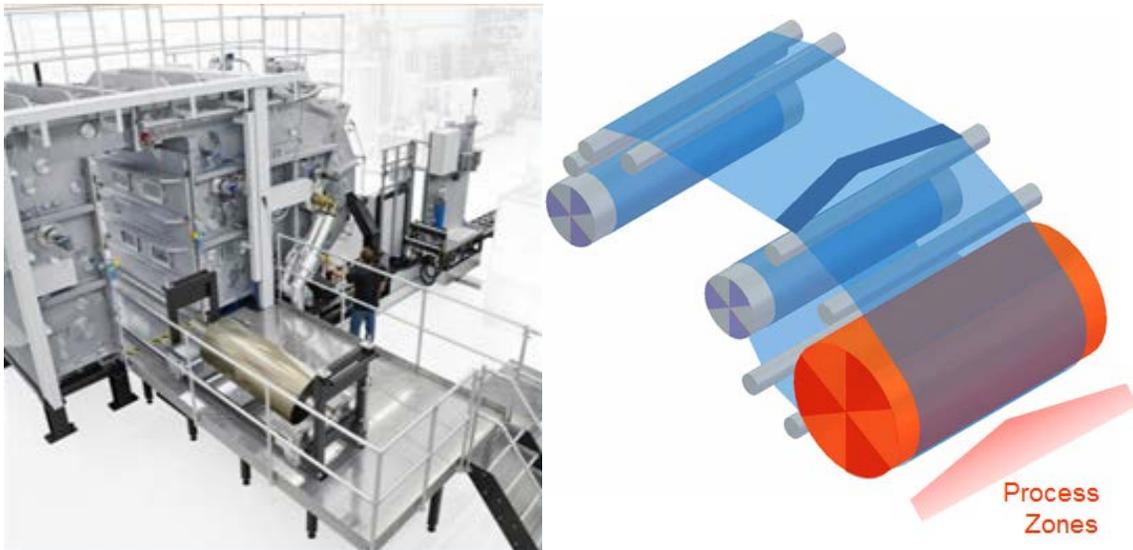


Fig. 1. Applied Materials R2R CVD tool & schematic winding path.

Significant demands exist in terms of winding different types and thicknesses of substrate within the same production tool. The tension applied to the substrate during winding (transport) may dramatically differ depending upon the tensile yield, substrate temperature and substrate thickness. Consequently, these R2R tools are equipped with online tension measurement and control systems to ensure stable substrate transport through the deposition system. Mechanical

contact between both transport and tension rollers and the coated substrate is also intentionally minimized, or where possible eliminated (see Figure 1), to reduce the risk of both scratch formation and particulate inclusion. Indeed new manufacturing platforms have recently been developed where removal of all front surface roller contact has been shown to dramatically reduce the defect density and significantly improve the resultant barrier performance. The winding path of these tools has further been optimized to ensure the minimum level of backside contact again reducing the defect creation rates arising from substrate conveyance. A series of low friction roller bearings coupled with dual bearing roller architecture also ensure roller parallelism and the elimination of transverse web “wandering” during transport. One final innovation used to reduce the impact of particles on the production yield involves the use of electrostatic charge mitigation devices to prevent the substrate rolls from charging during unwinding and the subsequent attraction of particulate material from the unwinder chamber to the surface. This helps to limit the level of extrinsic contamination at the substrate surface.

Multilayer deposition capability is required for OLED applications with the barrier and optical performance requirements depending upon the final integration scheme within the final product. This is enabled in a R2R production tool through the use of the aforementioned gas separated linear plasma deposition sources. Process based particle control is also enabled by confining the plasma to the deposition zone and by rigorous fluid dynamic optimization ensuring laminar gas flow, uniform pressure distribution and no dead or recirculation zones within deposition zone itself. High density plasma source technologies are also implemented at excitation frequencies greater than 13.56MHz to ensure efficient power coupling to the plasma and low thermal budget, high quality inorganic layer processing. Liquid precursor handling capability also permits the deposition of multilayer structures utilizing quasi-organic buffer layers (interlayers). Further uptime advantages can also be obtained by using fluorinated gases for in-situ plasma cleans to remove side-wall deposits eliminating the need to open the tool to the atmosphere for cleaning and maintenance at the end of each roll.

### **Defect Metrology & Substrate Cleaning Strategies**

As R2R systems process substrates continuously over long time period, accurate process monitoring and control systems are required for quality and yield optimization. Optical transmission and reflection measurements are typically used for inline layer thickness monitoring and control. Scratch, particulate and pinhole defects down to 500 nm can be detected using CCD or CMOS camera based systems processing (Oerley 2014, Rooms et al. 2014), whereas defects between 100 nm and 1000 nm in size, particularly relevant for OLED barrier processing segment are better detected using Coherent Fourier Scattering (CFS) methods (Oerley 2014). These line camera systems utilize multiple wavelength LED light sources to illuminate the surface of the substrate with either diffuse or focused light in order to distinguish between different types and positions of defect either within the substrate itself or orientated on its surface. Further measurement sensitivity is gained in moving from bright field measurement (looking for contrast differences between the defect and the substrate) to near dark field and finally dark field measurement (looking for scattering differences between defect and the substrate) to more accurately detect the position and shape of the abnormality. Transmission and reflection modes are possible with both bright field and dark field depending upon whether the substrate and coating couple remains transparent or opaque respectively. This permits accurate defect

detection and classification of inclusions, macroscopic scratches & pinholes with bright field techniques and arc traces, microscopic scratches and particles with dark field detection.

### **Multilayer Concepts for Ultra High Barrier Production**

Defect control in barrier processing is of vital importance as the influence of the low diffusivity dense inorganic layer can significantly be offset by the presence and spatial density of cracks and pinholes in the layer. Consequently mitigation strategies often employ the use of multilayer structures where the dense, inorganic layers are separated by planarizing organic/polymeric layers. The barrier performance of the organic itself is low, typically of the same order of magnitude as the substrate, but the multilayer structure forces water vapor or oxygen to move laterally after penetration through a crack or pinhole to the next available permeation channel in the subsequent inorganic layer rather than travel vertically through the stack. This so-called “tortuous path” approach therefore permits defect decoupling from the final barrier performance.

Figure 2 schematically illustrates the effect of defect spacing and defect size on effective diffusivity calculated using the so-called “Crank” diffusion model (Graff et al 2005). As the pinhole defect size increases for a constant spacing, there is an initial rapid increase in diffusivity followed by saturation. However, if the defect spacing is reduced, there is a quadratic increase in diffusivity and the barrier performance is dramatically reduced. Consequently, substrate and tool cleanliness, quality of substrate conveyancing and initial quality and roughness of the substrate all play a critical role in high volume manufacturing of barrier film using R2R processing technologies by ultimately minimizing the total defect density.

From a practical and economic perspective, the organic/polymer layer is seldom processed under vacuum conditions when combined with PVD. Typical flash evaporation technologies are difficult to integrate within a R2R PVD deposition tool due to mismatches between mean time to clean and the processing line speed. A more cost effective and productive manufacturing solution involves atmospheric processing of the organic layer prior to further PVD deposition. Slot die coaters prove to be an excellent tool for this purpose, offering layers of micron level thickness, good thickness uniformity, web speeds in the tens to hundreds of meters per minute range and a low capital cost (Frontier 2015). However, the necessity of bringing the substrate in and out of vacuum in addition to the complex fluid rheology of the organic, make defect mitigation more complex and confirm the necessity to work in a clean room. Economy of scale is also important, as low volume organic material synthesis results in coating costs similar to that of the inorganic layers produced by PVD.

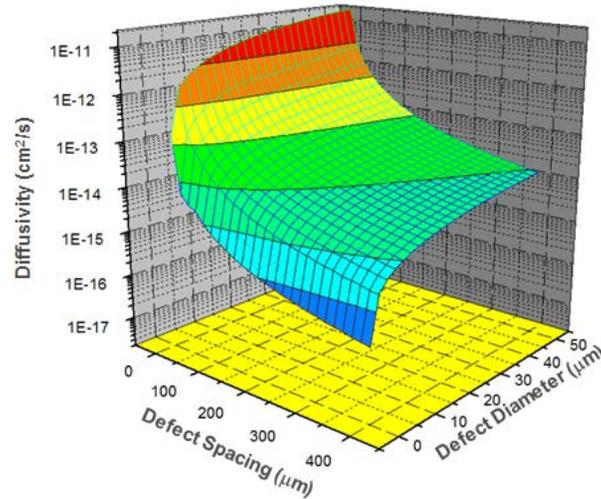


Fig. 2. Influence of defect spacing and diameter on diffusivity for an  $\text{AlO}_x$ /polymer based double layer system.

These multilayer systems can also be deposited using CVD (described previously in this chapter). Following deposition of the barrier quality  $\text{SiN}_x$  layer, an organic layer is deposited using non-silane based chemistry in a so-called “initiated CVD” mode. This involves activation of a gas phase chemical initiator, prior to reaction with semi-organic monomer species at the substrate surface. The surface reactivity is controlled primarily by the dissociated initiator concentration, the partial pressure of the monomer and the substrate temperature and permits tuning of the process between conformal growth and planarizing growth structures. Under optimized conditions, the level of planarization is appropriate for underlying nitride defect mitigation via pore filling, thereby preventing the nucleation of through-layer nodule shaped defects. Furthermore, an additional advantage of this CVD process is the ability to deposit these decoupling or “buffer” layers in an optically transparent, mechanically resilient form (Coclite et al 2010). Optimized barrier performance can therefore be achieved by using a layer thickness large enough to embed and bury defects and thin enough to ensure maximized optical transmission and color neutrality in combination with two  $\text{SiN}_x$  barrier layers. Barrier performance levels approaching  $5 \times 10^{-6}$  g/m<sup>2</sup> day have been demonstrated in 60°C/90% RH Calcium tests based upon this approach (Spee 2013) using a layer stack design similar to that shown in Figure 3.

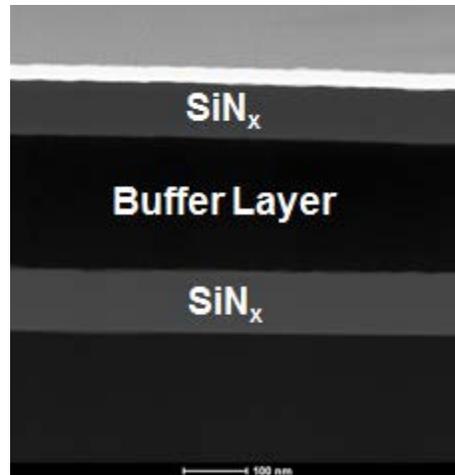
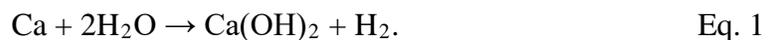


Fig. 3. Multilayer CVD stack on PEN substrates for ultra-high barrier applications.

### Barrier Measurement

A wide variety of different barrier performance measurement technologies are now available in order to characterize both the defect averaged and the intrinsic material performance levels respectively both for water vapour (WVTR=Water Vapour Transmission Rate) and for oxygen (OTR = Oxygen Transmission Rate). However, despite the presence of a limited number of standards for these permeant species (ASTM F1249 for H<sub>2</sub>O and ASTM D3895 for O<sub>2</sub>), there is still little consensus on the most suitable method for validation of barrier performance (Graff et al 2005). Defect averaged barrier measurement technologies are typically operated in the form of a steady state transmission test. This involves the use of a membrane mounted within a flow cell where the barrier coated side of the substrate is exposed to a known concentration of permeant loaded test gas (Maixner 2002, Stevens et al 2005, Graff et al 2005, Erlat et al. 2009). The opposing surface of the barrier film is exposed to a constant flow of dry, oxygen free sweep gas to ensure that a concentration gradient is generated over the thickness of the barrier film test sample providing the constant driving force for diffusion. The detection of the desired permeant can be performed using optical absorption in the infra-red (MOCON), mass spectrometry and the detection of the dose of radioactive tritium through the use of tritiated water vapour (Erlat et al 2009). When steady state conditions are reached the barrier value can be provided and referenced together with the temperature and relative humidity levels used during testing. Ultimately, the sensitivity of these permeation based steady state measurements is limited by the test sample edge leakage and the nature of the sensor technology used to detect the permeant.

The most commonly used test for determining the intrinsic quality of the inorganic barrier layer materials used in barrier film manufacture is called the “calcium test” (Nisato et al 2001, Nisato et al 2003). This test involves the deposition of a thin layer of calcium metal on a glass substrate and its lamination to the barrier film under test using an appropriate adhesive. The subsequent package is placed within a climate chamber under, typically 85°C/85% RH conditions and the resultant stack optical density is monitored as a function of time. Calcium metal, whilst weakly reactive with oxygen under ambient conditions, reacts more aggressively with water vapour:-



As such, determination of the rate of change in the optical transmission of the test package provides a path to the determination of the WVTR for the barrier layer via

$$WVTR = -2A \frac{M_{H_2O}}{M_{Ca}} \rho_{Ca} \frac{L_{Ca} W_{Ca}}{L_S W_S} \frac{d(OD)}{dt}, \quad \text{Eq. 2}$$

where A is a scaling factor relating calcium thickness and the optical density, M represents the molar mass of the named chemical species,  $\rho_{Ca}$  is the density of calcium,  $L_{Ca}$  &  $W_{Ca}$  are the length and width of deposited calcium area and  $L_S$  &  $W_S$  are the length and width of the permeation area bounded by the edge perimeter seal (Erlat et al. 2009). The gradient,  $d(OD)/dt$ , finally describes the rate of change of the optical transmission. This test, whilst providing detailed information on the intrinsic quality of the inorganic layer, can also be used to provide some spatial defect size and density information by imaging using standard microscopic techniques, providing key information on tool hygiene and general process stability. Electrical calcium tests can also be performed by replacing the rate of optical density change of the calcium layer with the rate of electrical resistivity increase (Paetzold et al 2003). However, edge sealing is considerably more difficult and no information on barrier film defectivity levels can be obtained.

## **Summary**

Innovative manufacturing solutions for R2R multilayer stack deposition have been made through elimination of the principle sources of defects affecting barrier performance. This has culminated in high speed processing equipment where all front surface roller contact has been eliminated and layer metrology systems that demonstrate micron level defect detection even in dynamic operation modes. Key to the success of these tools, has been the transfer of hardware, processes and substrate handling methodologies pre-existent in the multi-billion dollar, large area LCD display industry. Consequently, display grade barrier layers and stacks have been demonstrated at low cost. This manufacturing inflection has therefore enabled the processing of a range of next generation mobile and large area display based devices.

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