Strategies for Developing Thin-Film Encapsulation for Organic Electronics

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ABSTRACT

In this work, we investigate several approaches to the development of encapsulation of organic electronics. A combination of plasma enhanced chemical vapor deposition, atomic layer deposition, and physical vapor deposition are used to make single layer and multilayer thin films and study the impact of structure on effective water vapor transmission rates. It was found that multilayer thin films consisting of organic and inorganic layers as well as inorganic nanolaminates provided the highest performance barrier films with effective water vapor transmission rates less than 5×10^{-5} g/m^2/day. Materials such as atomic layer deposition deposited Al_2O_3 also showed excellent initial performance, but were found to be susceptible to corrosion from water. Combining alumina with other materials was found to improve the long-term performance of the alumina films. Integration of these films into organic solar cell platforms was shown to effectively maintain shelf lifetime performance for more than 7000h.

INTRODUCTION

Organic electronic devices are rapidly moving towards commercialization due to the development of new organic materials with improved performance. These devices have presented themselves as a viable option in various applications such as organic light-emitting diodes (OLED’s), organic photovoltaics (OPV’s), organic field-effect transistors (OFET’s), and organic sensors [1-4]. In addition, the new active materials are expected to enable the development of large-area and flexible electronics at a low manufacturing cost [5, 6]. However, one primary technical challenge in all applications is the achievement of long lifetimes and high reliability. Common among most small molecule and conjugated semiconductor materials is the propensity for their electrical properties to degrade upon exposure to moisture and/or oxygen in the atmosphere. Furthermore, the low work function materials often used to form electrical contacts to the active layers are generally highly reactive and susceptible to degradation when exposed to water vapor and oxygen. Degradation of the electrical contacts results in decreased charge injection or collection in OLED’s and OPV’s, resulting in reduced device performance and efficiency [7]. Thus, developing thin-film encapsulation technologies that prevent or limit the exposure of organic electronic devices to water vapor and oxygen is imperative to the long term durability of these devices.

First, the processing temperature of the thin-film encapsulation must be compatible with the temperature limits of the organic and polymer substrate materials, typically being less than 120°C [8]. Often, low-temperature processing of inorganic layers using techniques such as plasma-enhanced chemical vapor deposition (PECVD) yields layers that are not perfect barriers due to many intrinsic defects in the films [9-13]. As a result, water vapor and oxygen diffuse primarily through these defects, which must be limited [13]. One solution is to use multilayer films consisting of alternating inorganic and organic layers so the defects in the inorganic layers are interrupted and do not channel continuously through the film structure. This creates a tortuous path resulting in a very long effective diffusion length lowering the overall permeability. [14, 15]. Another approach is to utilize high quality single layer films often made from atomic layer deposition (ALD). In this approach, very thin films (< 50 nm) are directly deposited onto devices or polymer substrates in order to create a high performance barrier with properties less than 10^{-4} g/m^2/day. This method avails itself to a wide range of oxides and other inorganics which can be synthesized by ALD processing. However, little has been done to study the use of multilayered inorganic materials to achieve synergistic properties as seen in the more common organic/inorganic barrier films. Such films hold promise for use in solar cell packaging where the degradation of organic layers in the barrier films from solar irradiation can be minimized.

In this article, we present the results of thin-film multilayer barriers consisting of PECVD-deposited SiN_x and SiO_x combined with polymer interlayers of parylene or PMMA. Contrasts in the performance of the organic/inorganic multilayers were made with single layers produced by ALD (ZnO and Al_2O_3) as well as PECVD inorganic multilayer nanolaminates (SiN_x/SiO_x) and ALD nanolaminates (ZnO/Al_2O_3) and a hybrid combination of PECVD and ALD inorganic films (SiN_x/Al_2O_3). Finally, the organic/inorganic multilayers and hybrid layers were combined with pentacene/C60 organic solar cells to demonstrate their impact on the shelf lifetime of organic solar cells.

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EXPERIMENTAL DETAILS

Thin-film fabrication

Barrier films were deposited on heat stabilized PET films 100 µm in thickness at temperatures of 110°C or less. Multilayer inorganic/organic barrier films were created using PECVD SiN_x and parylene C. Parylene thin films were deposited on the PET by vapor-phase deposition and polymerization of pary-xylylene in a Lab Coater PDS2. Parylene C was chosen as one of the organic layers due to its hydrophobic nature and the fact that it is a relatively flexible polymer that can be easily deposited by vacuum deposition at room temperature. Parylene dimers were loaded in the vacuum chamber and converted to a monomer vapor around 650°C. Condensation of the vapor on the sample at room temperature resulted in spontaneous polymerization and deposition on the PET substrate. The parylene thickness was measured with a KLA-Tencor P-15 profilometer to be 1 µm.

Inorganic layers of SiO_x and SiN_x were fabricated by PECVD using a Unaxis RF plasma system. The deposition was performed at 110°C for compatibility with the PET substrate and a total thickness of 100 nm was used. The barrier layers were fabricated by alternating layers of SiO_x or SiN_x with parylene layers. A 10 min annealing step was used prior to the deposition of the inorganic layers to improve the quality and performance of the films.

For single layer barrier films, atomic layer deposition was used to deposit Al_2O_3 or ZnO on heat stabilized PET (ST-505, DuPont). Both films were deposited in a FIJI ALD reactor (Cambridge Nanotech) at a temperature of 110°C. Alumina films, 60 nm in thickness, were deposited using Trimethylaluminum as the precursor and water as the oxidant. Zinc oxide was deposited using diethylzinc as the precursor and water as the oxidant. Film thickness was measured using a combination of profilometry and ellipsometry. Overall, the interest in ALD films is from their low defect density that allows the achievement of high performance barrier films in a single layer.

Next, nanolaminates from PECVD and ALD depositions were made. In the nanolaminates, films were deposited with alternating layers of inorganic materials to investigate the impact of interfaces on the barrier film performance. In the case of organic/inorganic barrier films, the organic layers interrupt the defect growth in the inorganic layer, resulting in an improvement in the overall barrier performance. In the case of the nanolaminates, an attempt was made to investigate if a similar effect can be achieved in inorganic films where susceptibility to UV irradiation in solar environments may be reduced by eliminating the organic layer. To create the nanolaminates, alternating layers of SiO_x and SiN_x were deposited by PECVD while increasing the number of dyads from 1 to 6 while keeping the total film thickness at 100 nm. This deposition was performed in the Unaxis PECVD chamber without breaking vacuum, but simply changing precursor gases. Nanolaminates were also created using the FIJI ALD system by alternating layers of ZnO and Al_2O_3. Here, the total film thickness was 60 nm while the number of dyads was varied from 1 to 10. Finally, a hybrid combination of PECVD deposited SiN_x along with a single layer of ALD deposited Al_2O_3 was investigated. The SiN_x was 100 nm while the Al_2O_3 layer was 50 nm. The concept behind this film was to utilize the rapid deposition of PECVD layers that are known to be more defective while sealing the defects using the high density ALD layer. Again, all depositions were performed at 110°C.

Effective WVTR Measurements

For the effective water vapor transmission rate (WVTR) measurements, Ca corrosion tests were performed by monitoring the change in electrical conductance as explained elsewhere [16, 17]. In this experiment, Ca sensors with an area of 4.5 × 7 mm^2 and aluminum (Al) electrical interconnects were used for conductance measurements as shown in Figure 1. Ca corrosion tests were performed in a controlled humidity chamber (Cincinnati Subzero Micro-Climate System) at 20°C and 50 % relative humidity (RH). To create the Ca test structure, the Al (100 nm) and Ca (310 nm) layers were deposited through shadow masks on glass substrates using a vacuum deposition system (Spectros, Kurt J. Lesker) connected to a nitrogen-filled glove box. The deposition rate and the thickness were monitored using a calibrated quartz crystal microbalance near the substrate. Al was deposited at a rate of 2 $Å\,s^{-1}$ and Ca at 2 - 3 $Å\,s^{-1}$ with a base pressure of ~ 8×10^{-8} Torr. Both depositions were made without breaking vacuum. After deposition of the Ca, the flexible barrier lids described in section 2.1 were sealed over the top of the Ca layer using a reactive desiccant filled polyisobutylene edge sealant (Helioseal PVS 101, Adco). Separated testing of this edge sealant revealed that it is possible to resolve WVTR rates as low as $5x10^{-5}$ $g/m^2/day$ using this approach. In a limited number of cases, the barrier films were directly deposited on top of the Ca layers that allowed WVTR measurements as low as $2x10^{-6}$ $g/m^2/day$.

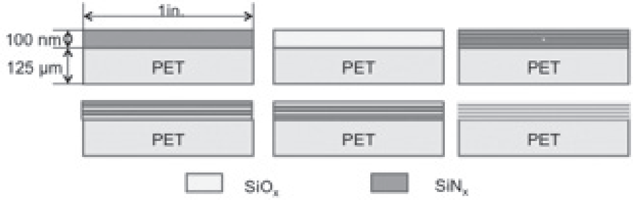


Figure 1: Depiction of the architecture of the PECVD nanolaminates made from SiO_x and SiN_x.

Shelf lifetime testing

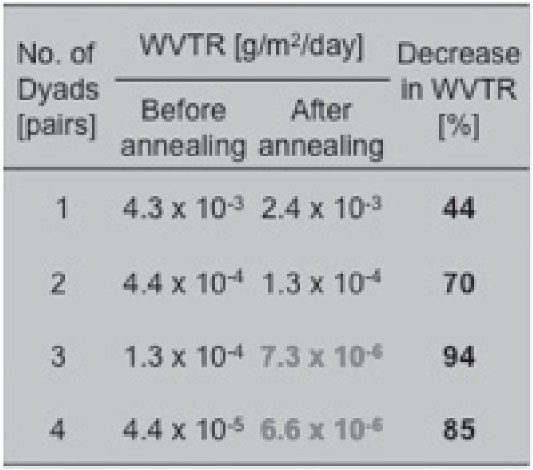
To demonstrate the performance of the barrier films, their integration with pentacene/C_{60}-based organic photovoltaic devices glass substrates [18] was performed. The devices had a geometry of indium tin oxide/ pentacene (50 nm)/ C_{60} (45 nm)/ bathocuproine (8 nm)/ Al with an active area of ~ 0.1 cm^2. First, a 400 nm-thick buffer layer of SiO_x was deposited on top of the solar cells. Then, the samples were encapsulated with one to three dyads of SiN_x and parylene and with a single dyad of the hybrid barrier film as described in section 2.1. To study the impact of the encapsulation process on the performance of the organic solar cells, the electrical characteristics of the devices were measured before and immediately after encapsulation in a nitrogen environment. A 175W Xenon lamp (ASB-XE-175EX, CVI) was used as a broadband light source with an irradiance of 73 mW/cm^2. Next, the encapsulated devices were stored for extended periods of time in air in an environmental chamber (20ºC, 50 % RH). The electrical characteristics were measured periodically in the lab environment under a solar simulator (91169, Oriel) to investigate the device degradation as a function of time. Three devices on a single substrate were tested for each encapsulation. The performance averaged over three devices was then compared to that of a bare unencapsulated sample used as a reference device.

RESULTS

SiN_x/Parylene Multilayers

The effective WVTR of the SiN_x/parylene multilayers is shown in Table 1. The data show that the effective WVTR decreases with increasing number of dyads of SiN_x/parylene. The WVTR varies by two orders of magnitude between 1 dyad and 4 dyads when the parylene layer is not annealed. In this case, the best performing WVTR achieved is on the order of 4 x 10^{-5} g/m^2/day. However, the annealing step is seen to reduce the WVTR, resulting in an improvement in overall barrier performance. For a single dyad, over a 40 % reduction is seen in WVTR. With 4 dyads, an 85 % reduction is observed with the best performing films showing an effective WVTR of 6 x 10^{-6} g/m^2/day. To measure these values, direct encapsulation experiments were utilized. The improvement in the WVTR is a result of annealing the parylene layer above the glass transition temperature that allows some reorganization of the polymer chains and reduction in surface roughness. While this may lead to some improvements in the SiN_x quality, additional benefit may also be derived from the removal of any residual water vapor which enters the film during the transfer from the parylene chamber to the PECVD chamber. The reduction in residual water stored in the film results in a lower effective WVTR in the transient measurement regime. Thus, measurements which do not go beyond the lag time effect which was found to be as high as 1400 h in some films, an apparent drop in effective WVTR was observed.

Table 1: Performance of SiN_x/Paryalene Multilayers.



No. of Dyads [pairs]	WVTR [g/m²/day]		Decrease in WVTR [%]
	Before annealing	After annealing	
1	4.3 x 10^{-3}	2.4 x 10^{-3}	**44**
2	4.4 x 10^{-4}	1.3 x 10^{-4}	**70**
3	1.3 x 10^{-4}	7.3 x 10^{-6}	**94**
4	4.4 x 10^{-5}	6.6 x 10^{-6}	**85**

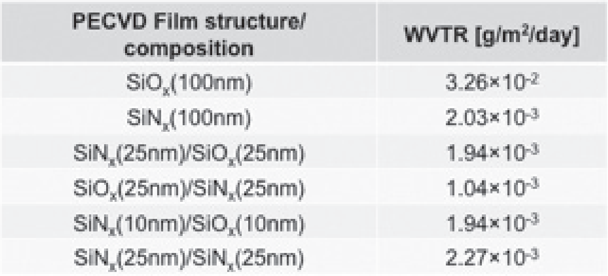
Hybrid Multilayer Barrier Films

The effective WVTRs of SiO_x (100 nm)/Al_2O_3 (50 nm)/ parylene (1 μm) and SiN_x (100 nm)/Al_2O_3 (50 nm)/parylene (1 μm) were measured to be 3.4 × 10^{-5} g/m^2/day and 2.6 × 10^{-5} g/m^2/day, respectively, at 20°C and 50 % RH. While SiN_x deposited by PECVD has been reported to show better barrier performance than SiO_x [19, 20], our results show that there is no significant difference between two films when combined in the hybrid architecture. These results suggest that the water permeation through the defects and pinholes of both the SiO_x and SiN_x films deposited by PECVD are well passivated by the ALD deposited Al_2O_3. Using PECVD, the deposition rate of SiO_x is three times faster than that of SiN_x, so SiO_x is more favorable in terms of processing speed. The thickness of the ALD deposited Al_2O_3 was decreased to 10 nm, and the effective WVTR of SiO_x (100 nm)/Al_2O_3 (10 nm)/parylene (1 μm) was measured to be 2.3 × 10^{-5} g/m^2/day. Therefore, a 10 nm thick Al_2O_3 film deposited by ALD is enough to cap the pinholes and defects in the SiO_x film.

ALD and Inorganic Nanolaminate Barrier Films

Figure 1 shows the architecture of the PECVD inorganic nanolaminates measured in this study and the results are shown in Table 2. As expected, the 100 nm SiO_x layer shows inferior barrier performance when compared with the 100 nm SiN_x, being on the order of 3 x 10^{-2} and 2 x 10^{-3} g/m^2/day, respectively. The creation of a nanolaminate film by mixing the SiN_x with SiO_x or even interrupting and renucleating the growth of the SiN_x film resulted in WVTR values which were on the order of 2 x 10^{-3} g/m^2/day, regardless of architecture. This result suggests that the WVTR of these films is controlled by the barrier performance of the SiN_x layer. In essence, the defect structure in the SiN_x layer is not mitigated and is the limiting factor in the overall barrier performance of the inorganic nanolaminate films by PECVD. Thus, while PECVD is a rapid method for depositing such inorganic films, the defect level in these materials makes it difficult to achieve ultrahigh barrier performance (< 10^{-5} g/m^2/day) required for organic electronics and solar cell applications.

Table 2: Performance of PECVD Nanolaminates.



PECVD Film structure/ composition	WVTR [g/m^2/day]
SiO_x(100nm)	3.26×10^{-2}
SiN_x(100nm)	2.03×10^{-3}
SiN_x(25nm)/SiO_x(25nm)	1.94×10^{-3}
SiO_x(25nm)/SiN_x(25nm)	1.04×10^{-3}
SiN_x(10nm)/SiO_x(10nm)	1.94×10^{-3}
SiN_x(25nm)/SiN_x(25nm)	2.27×10^{-3}

Inorganic nanolaminates made from Al_2O_3 and ZnO are shown in Table 3. Here, the WVTR of the 60 nm thick layer of ZnO and Al_2O_3 were shown to be on the order of 6 x 10^{-4} and 8 x 10^{-4} g/m^2/day, respectively. The combination of the films into a 10 dyad nanolaminate, however, showed a change in the effective WVTR. The decrease in WVTR was below the detection limit of the experimental setup (< 5x 10^{-5} g/m^2/day). These data suggest that the combination of ZnO and Al_2O_3 using ALD can result in the passivation of defects or the creation of a barrier at the interface between the two layers that limits water vapor diffusion. If such layers have higher density and more interfaces are introduced in the barrier via the nanolaminate architecture, it is possible to result in the order of magnitude improvement or greater in the WVTR. Thus, controlling the reactions at the interface between organic and inorganic layers along with reduction in defect density allows for improvements in the WVTR of barrier films.

Table 3: Performance of ALD Nanolaminates.

ALD Film structure/composition	WVTR [g/m^2/day]
Al_2O_3(60nm)	6×10^{-4}
ZnO(60nm)	8×10^{-4}
Al_2O_3(3nm)/ZnO(3nm)	$<5\times10^{-5}$

SOLAR CELL SHELF LIFETIME TESTING

Due to the time involved in testing the shelf lifetime, comparisons where made between the conventional organic/inorganic multilayer barrier film encapsulation and the hybrid barrier film encapsulation for integration with the Pentacence/C60 solar cells. In this study, the barrier films were directly deposited on top of the solar cells rather than the flexible lids in order to reduce side permeation as a result of the limiting performance of the edge sealant. The main performance parameters of the solar cells such as the open-circuit voltage V_{OC}, short–circuit current density J_{SC}, fill factor *FF*, and power conversion efficiency η were compared before and after encapsulation to investigate the impact of processing the barrier films on the device. When averaged over 12 devices (6 for the multilayer barrier, 6 for the hybrid barrier), η was 3.4 % before encapsulation and changed to 3.3 % after encapsulation. While there were small increase in η and V_{OC} and reduction in J_{SC} and *FF* due to the thermal annealing effect as reported previously [21, 22], it can be concluded that there is no significant negative change in the device performance after encapsulation.

Next, the main performance parameters were compared with their initial values as a function of exposure time to atmosphere (20°C/ 50 % RH) to investigate the effectiveness of the encapsulation. In this experiment the barrier films consisted of: SiO_x (100 nm)/Al_2O_3 (50 nm)/parylene (1 μm) and SiN_x (100 nm)/ Al_2O_3 (50 nm)/parylene (1 μm) and SiN_x (100 nm)/parylene (1 μm) ranging from 1-3 dyads. Figure 2 shows the normalized η changed with exposure time for the two different types of encapsulation structures and one reference sample without encapsulation. As generally expected in organic devices, the unencapsulated solar cells degraded very fast (Figure 2). The η dropped to less than 20 % of their initial values within 50 hrs. This fast degradation of the unencapsulated solar cells stresses how important it is to encapsulate organic devices for practical application of organic solar cells. For the hybrid encapsulation layers, there was no appreciable reduction in η for the first 7000h. This corresponds to an effective WVTR of on the order of 10^{-5} g/m^2/day based on our Ca corrosion tests. Some fluctuations in the performance parameters are expected due to the slight variation in irradiance power and electric contact resistance during each measurements. For the multilayer barrier structures, the solar cells encapsulated with 1 and 2 dyads show a degradation in performance over the time measured, reaching 50 % of the original conversion efficiency within 1500 and 250 h. However, the solar cells encapsulated with 3 dyads show virtually no degradation over the first 7000h. Again, these films have a WVTR on the order of 10^{-6} g/m^2/day. Over the time tested, these films show similar peformance as the hybrid layers. However, the hybrid architecture reduces the use of polymer layers which can loose adhesion or degrade in solar environments. In addition, it is a simple and scalable process which can lead to high performance barrier films while reducing the complexity of the architecture.

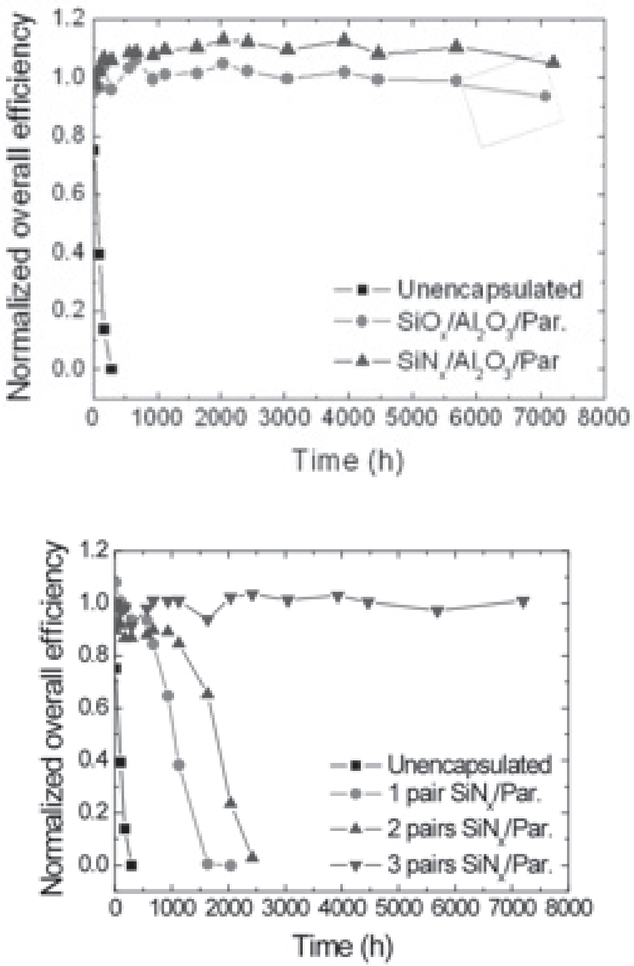


Figure 2: Data showing the normalized efficiency vs time for hybrid encapsulated solar cells (top) and multilayer encapsulated solar cells (bottom).

CONCLUSIONS

The use of ALD to create inorganic nanolaminates or the hybrid combination of PECVD and ALD films was shown as an effective way of creating high performance barrier films without the use of polymer interlayers. These films are expected to be less susceptible to degradation in solar environments and can simplify the architecture of the barrier films. Additional understanding of the interaction that occurs at the interfaces of ALD deposited films is necessary to elucidate the performance enhancements seen in their application to nanolaminate films.

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REFERENCES

1. Lewis, J.S., *Material challenge for flexible organic devices*. materials today, 2006. 9(1): p. 38-45.

2. Yoon, M.H., et al., *Low-voltage organic field-effect transistors and inverters enabled by ultrathin cross-linked polymers as gate dielectrics.* Journal of the American Chemical Society, 2005. 127(29): p. 10388-10395.

3. Dennler, G., et al., *A new encapsulation solution for flexible organic solar cells.* Thin Solid Films, 2006. 511-512: p. 349-53.

4. Yoon, Y.S., et al., *Effects of parylene buffer layer on flexible substrate in organic light emitting diode*. Thin Solid Films, 2006. 513(1-2): p. 258-263.

5. Weaver, M.S., et al., *Organic light-emitting devices with extended operating lifetimes on plastic substrates.* Applied Physics Letters, 2002. 81(16): p. 2929-31.

6. Gu, G., et al., *Vacuum-deposited, nonpolymeric flexible organic light-emitting devices*. Optics Letters, 1997. 22(3): p. 172-174.

7. Wuu, D.S., et al., *Water and oxygen permeation of silicon nitride films prepared by plasma-enhanced chemical vapor deposition*. Surface & Coatings Technology, 2005. 198(1-3): p. 114-117.

8. Ghosh, A.P., et al., *Thin-film encapsulation of organic light-emitting devices*. applied physics letters, 2005. 86(2): p. 223503.

9. Chatham, H., *Oxygen diffusion barrier properties of transparent oxide coatings on polymeric substrates.* Surface & Coatings Technology, 1996. 78(1-3): p. 1-9.

10. Marra, D.C., et al., *Silicon hydride composition of plasma-deposited hydrogenated amorphous and nanocrystalline silicon films and surfaces*. Journal of Vacuum Science & Technology a-Vacuum Surfaces and Films, 1998. 16(6): p. 3199-3210.

11. Sobrinho, A.S.D., et al., *Defect-permeation correlation for ultrathin transparent barrier coatings on polymers.* Journal of Vacuum Science & Technology A, 2000. 18(1): p. 149-157.

12. Erlat, A.G., et al., *SiO_x gas barrier coatings on polymer substrates: Morphology and gas transport considerations.* Journal of Physical Chemistry B, 1999. 103(29): p. 6047-6055.

13. Tropsha, Y.G. and N.G. Harvey, *Activated rate theory treatment of oxygen and water transport through silicon oxide poly(ethylene terephthalate) composite barrier structures.* Journal of Physical Chemistry B, 1997. 101(13): p. 2259-2266.

14. Affinito, J.D., et al., *A new method for fabricating transparent barrier layers.* Thin Solid Films, 1996. 291: p. 63-67.

15. Affinito, J.D., *Hybridization of the polymer multi-layer (PML) deposition process.* Surface & Coatings Technology, 2000. 133: p. 528-534.

16. Nisato, G., et al. *Evaluating high performance diffusion barriers: The calcium test.* in *Proc. Int. Display Workshop/ Asia Display*. 2001.

17. Paetzold, R., et al., *Permeation rate measurements by electrical analysis of calcium corrosion.* Review of Scientific Instruments, 2003. 74(12): p. 5147-5150.

18. Yoo, S., B. Domercq, and B. Kippelen, *Efficient thin-film organic solar cells based on pentacene/C-60 heterojunctions.* Applied Physics Letters, 2004. 85(22): p. 5427-5429.

19. Vogt, M. and R. Hauptmann, *Plasma-deposited passivation layers for moisture and water protection.* Surface & Coatings Technology, 1995. 74-75(1-3): p. 676-681.

20. Robles, S., E. Yieh, and B.C. Nguyen, *Moisture Resistance of Plasma-Enhanced Chemical-Vapor-Deposited Oxides Used for Ultralarge Scale Integrated Device Applications*. Journal of the Electrochemical Society, 1995. 142(2): p. 580-585.

21. Potscavage, W.J., et al., *Encapsulation of pentacene/C-60 organic solar cells with Al_2O_3 deposited by atomic layer deposition.* Applied Physics Letters, 2007. 90(25): p. -.

22. Yoo, S., et al., *Analysis of improved photovoltaic properties of pentacene/C-60 organic solar cells: Effects of exciton blocking layer thickness and thermal annealing.* Solid-State Electronics, 2007. 51(10): p. 1367-1375.