Silicon Carbide Barrier Technology to Enable Flexible OLED Displays

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Abstract

This paper provides an overview on the characteristics of a-SiC:H barrier film deposited for flexible display applications. Key characteristics such as high crack resistance, high thermal/hydro stability, excellent adhesion to the polymer substrate, as well as very low permeance has been demonstrated. The excellence of this barrier film has been shown from competitive analysis compared with other barrier coating materials. Finally, flexible Polymer Light Emitting Diode (PLED) test pixels have been fabricated on the barrier coated plastic substrate, demonstrating the viability of the device with lifetime data.

1. Introduction

Flexible displays offer many potential benefits over other technologies such as impact resistance, light weight, thinness, conformability, and potential cost effectiveness. In order to realize flexible Organic Light Emitting Diodes (OLEDs), several flexible substrates need to be evaluated among which polymers, metal foils and ultrathin glass are considered as leading candidates as substrate materials [1]. Polymer substrates especially have compelling reasons to be more popular than the other two owing to excellent flexibility and lightweight nature. The key issue in fabricating reliable OLEDs on polymer substrate is then narrowed down to the discussion on how to protect the device from moisture and oxygen with good flexibility.

Dow Corning's barrier coating on polymer substrate is based on an amorphous silicon-carbon alloy (*a*-SiC:H) thin film deposited by low temperature Plasma Enhanced Chemical Vapor Deposition (PECVD) using trimethylsilane as an organosilicon precursor. The silicon-carbide alloy films act as protective barriers and have been used as a bottom side barrier and a top encapsulant on flexible plastic substrates (Fig. 1).

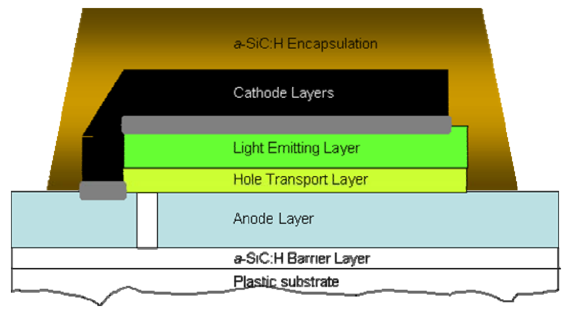

Fig. 1. A crosscut diagram of a polymer light emitting diode on flexible substrates showing *a*-SiC:H barrier coatings used in the scheme.

Zambov et al. discuss the development of improving plasma efficiency of PECVD at low temperatures to accommodate processing plastic substrates while simultaneously forming dense films [2]. The barrier coatings in a composite multilayer stack have been applied to a Polymer LED (PLED) on a glass test vehicle as a direct thin film encapsulation. Weidner et al. discuss the thin film encapsulation elsewhere [3].

In this study, we have analyzed the barrier coated film essential in making a reliable flexible device and focusing on flexibility as one of the key characteristics. The flexibility has been tested by measuring water vapor transmission rate (WVTR) after flexing samples in a harsh environment. Additionally, we have compared *a*-SiC:H barrier films with other barrier films for competitive analysis. One of our barrier films has been chosen to fabricate flexible PLED test pixels to demonstrate the viability of the device with electrical characteristics and lifetime data at the end.

2. Experimental

A blank plastic substrate was processed through a proprietary web cleaning method to improve the barrier coating performance. This cleaning is based on a hypothesis that defect mitigation by web cleaning is critical and it is largely determined by defects that originate pinholes in a layer [4]. Two PECVD process conditions have been selected to prepare 8 different pieces of barrier coating on plastic polymer substrates. Process condition A has demonstrated to exceed the sensitivity limit of Aquatran® by MOCON® that is less than 5E-4 g/m^2·day. All of the barrier films were flexed over two different mandrel sizes with some samples also receiving a boiling water treatment as well. All samples proceeded to WVTR measurement. The experimental details are listed in Table 1.

TABLE 1. Experimental matrix used to evaluate the performance of the barrier films

Experimental Matrix	
Process conditions used for Barrier coated films	A and B
Mandrel flex test	½” and ¾”
Boiling water test	Yes and No

Flexibility testing has been performed using a manual cylindrical mandrel tester in conjunction with a boiling water treatment to determine the crack resistance of attached barrier coatings. Each test piece is placed over a mandrel with the uncoated side in contact so the barrier coating is elongated. Using a steady pressure of the fingers a piece is bent approximately 180° around the mandrel at a uniform velocity and held for 1 minute. A Differential Interference Contrast (DIC) microscope is used for initial crack inspection. Boiling water treatment is a simple but effective procedure that accelerates adhesive failures by completely immersing a piece of barrier coated film framed and clamped in a plastic frame in boiling deionized water for 1 hour. The test is used to analyze toughness and thermal stability of thin film coatings. Barrier performance of a sample after such treatments is confirmed by measuring WVTR using Permatran-W® Model 3/33 to determine whether any deterioration occurs. Typically, a low performance film delaminates resulting in a high WVTR, or it curls to very small radius of curvature after the boiling water treatment.

As a benchmark study, several competitive barrier films were acquired and analyzed. PVD based SiON:H and AlO based barrier coated films have been chosen to compare with Dow Corning PECVD based SiC:H. Permeance, transparency, thermal/ hydro stability, adhesion and surface roughness measurements were performed by Permatran-W®, a UV-Vis spectrometer, boiling water treatment, standard tape test, and Atomic Force Microscopy (AFM), respectively. Unfortunately, the flexibility test by the mandrel flex tester was not conducted for the competitive barrier films.

Finally, flexible PLEDs were fabricated through a multi-element array on a 15cm×15cm plastic substrate. The barrier films function both as a substrate as well as an encapsulation on top of the entire structure. The PLED test pixels have been fabricated with a transparent conductive oxide coating on which several thin film layers were deposited. Those consisted of a hole transport layer from H.C. Starck, light emitting polymer from Sumation and cathode metals such as Ca and Al. Once the device had been packaged by Dow Corning’s *a*-SiC:H Thin Film Encapsulation, lifetime data were measured and defect imaging data were collected to provide an assessment of the barrier coatings used in the fabricated device. Defect analysis was performed using a digital video camera and custom software to optically track the appearance and growth of defects on the luminous field.

3. Results and discussion

1. Flexibility testing under accelerated conditions

All eight samples were below the sensitivity limit of Permatran-W® that is 5E-3 g/m^2·day prior to any test. Especially, condition A used in the test is proven to provide WVTR less than 5E-4 g/m^2·day that is the sensitivity limit of Aquatran®. Based on previous boiling water treatment, barrier coated films showed good thermal stability at temperatures up to 100°C. From the flexibility test using samples 1, 2, 5, and 6 without boiling water treatment, it is shown that the crack resistance threshold is between ¾ and ½ inch in diameter as samples 2 and 6 have been increased WVTRs by one order of magnitude or more.

TABLE 2. Water Vapor Transmission Rate of the eight different pieces of sample before and after boiling water test and flexibility test.

Condition	Sample ID	Pre-treated WVTR, mg/m^2·day	Boiling water test	Bending diameter	Post-treated WVTR, mg/m^2·day
A	#1	<5	No	¾ in.	<5
	#2	<5	No	½ in.	30 – 70
	#3	**<5**	Yes	¾ in.	**<5**
	#4	<5	Yes	½ in.	<5 – 9.9
B	#5	<5 - 11.4	No	¾ in.	<5
	#6	<5 - 11.4	No	½ in.	53.4
	#7	<5 - 11.4	Yes	¾ in.	18.3
	#8	<5 - 11.4	Yes	½ in.	24 – 49

The other samples such as 3, 4, 7, and 8 that were both boiled and bent at different mandrels have been shown to be deposition process dependent. Samples 3 and 4 deposited by condition A have maintained WVTR successfully after both of the tests in series. Especially, WVTR of the sample 3 was not changed indicating that the coating had an excellent crack resistance. Interestingly, barrier films subjected to the boiling water treatment tend to have higher crack resistance as they have lower WVTR after they were bent. A possible hypothesis is that the layers composed of ceramic hard coating on top and viscoelastic polymer layers underneath are coupled to have higher fracture toughness through the harsh condition with heat cycle. WVTR data of the samples before and after subsequent treatments are summarized in Table 2.

2. Comparison between Dow Corning's barrier films and other barrier coated films

For the benchmark study, several barrier films were analyzed including silicon nitride and aluminum oxide based films. WVTR varied greatly across all samples used in the comparison study. Lowest levels of WVTR were achieved with the Dow Corning's barrier coated films. One important characteristic to note is that PECVD based barrier is capable of accommodating much greater thicknesses than PVD grown film. Due to the intrinsic brittle attribute of PVD based films preventing them from being thicker [5], the thickness of the PVD films used in the study was their extreme limit of the growth condition. Therefore, these values of WVTR are the practical limits for their barrier application.

Table 3. Comparison of the figure of merit among the commercially available barrier coatings and Dow Corning's barrier coating systems.

	Film X	Film Y	Film Z	Dow Corning	Dow Corning
Coating material	SiON:H	SiON:H	AlO	SiC:H	SiOC:H
Thickness, nm	200	200	550	400	350 - 750
WVTR, mg/(m^2·day)	530 - 1158	32 - 47	15 - 30	<5 - 6.1	<5 - 8.4 or <0.5
T@530nm, %	85	86	89	55	68 - 87
Boiling water test	Delam. /crack	Delam. /crack	Pass	Pass	Pass
Standard tape test	Pass	Pass	Delam. /crack	Pass	Pass
RMS (5µm), nm	2.5	3.6	0.6	5.2	3.3 – 6.8

Except for Dow Corning's barrier films, all samples have been delaminated and cracked either after boiling water test or standard tape test as shown in Figure 2. Especially, the defect found in a sample from company Y is caused by buckling effect that would be typical for SiN coating due to a biaxial-residual compressive stress in layers. While AlO-based films passed without any crack or delamination at the boiling water test, the samples failed during the standard tape test.

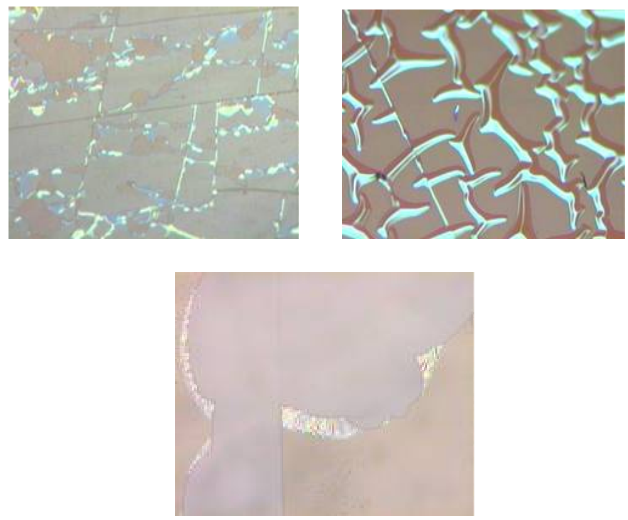

Fig. 2. Optical microscope images of commercially available films showing delamination and cracking of coatings. (Top left: severe crack and delamination of Film X after boiling water test; Top right: Delamination caused by buckling of Film Y after boiling water test; Bottom: Delamination of Film Z after standard tape test.)

All of the SiC:H-based coatings simultaneously possess good barrier performance, good adhesion strength, and remain thermally stable. We hypothesize that the interface between polymer and ceramic coating of the *a*-SiC:H is more stable to simultaneous extremes in temperature and humidity. Table 3 shows the comparison summary of the samples between the different materials and the test results.

3. PLED device performance

Flexible PLEDs were fabricated using a multi-element array on a 15cm×15cm plastic substrate. The PLED arrays have been used to evaluate the a-SiC:H layer directly on plastic substrate as a barrier and on top of the device as a direct thin film encapsulation, respectively, as shown in Fig. 1. Defect imaging analysis and lifetime measurement of the PLED pixels were conducted. The PLED pixel lit up on the barrier coated film is shown in Figure 3.

Fig. 3. PLED device pixels on barrier coated film substrates.

The lifetime of the PLED devices is represented by plotting the area of defect regions (black area) with time. Black spot growth has been analyzed up to 400 hours of pixel arrays of PLEDs on plastic substrate as a storage lifetime test in Figure 4, showing that the best performing flexible PLED scheme has defect area of as low as 11% at the time of 400 hours.

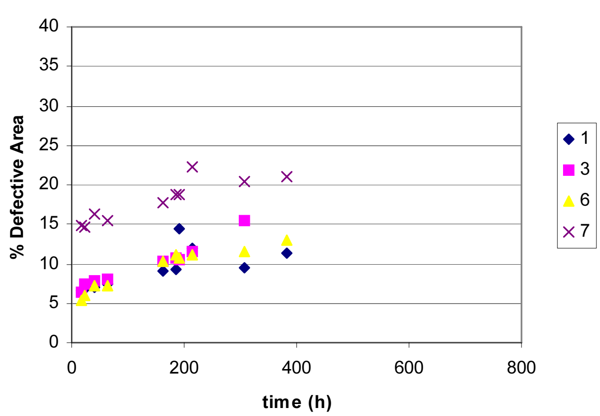

Fig. 4. Defective area vs. storage time (not operational time) up to 400 hours of pixel arrays of PLEDs with thin film encapsulation on plastic substrate. The legend denotes each pixel used in the measurement.

4. Summary

We have studied the flexibility of the PECVD silicon carbide barrier thin film enabling flexible displays. The permeance of the barrier coatings on polymer substrates has not been deteriorated after mandrel bending test and boiling water treatment. This demonstrates that they have excellent thermal/hydro stability and crack resistance at ¾ inch and possibly ½ inch mandrel in diameter. From the competitive analysis we have shown that the *a*-SiC:H barrier films have excellent moisture barrier properties, combined with markedly superior adhesion and toughness to the other barrier materials. Overall, Dow Corning's barrier technology of which WVTR gets lower than 5E-4 g/m^2·day is shown to be robust and extremely competitive in critical performance specifications. Finally, we have successfully fabricated polymer light emitting diodes as test structures to evaluate compatibility of the barrier films, characterizing light output and lifetime of individual pixels.

5. Acknowledgements

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6. References

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