Strategies For Developing Barrier Films For Photovoltaics

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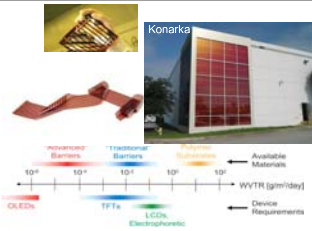
Background

The development of barrier films is a critical technology to reduce the susceptibility of photovoltaic systems to environmental degradation. These barrier films, which have effective water vapor transmission rates (WVTR) less than 10^{-4} g/m^2/day, often consist of multilayer films deposited by vacuum deposition. Methods which can be used to improve barrier properties while maintaining mechanical durability are critical for the packaging of flexible organic electronics.



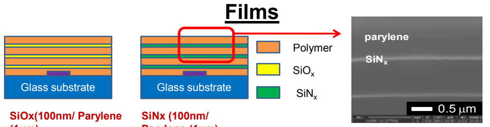
Barrier Issues

Barrier Layer WVTR	Barrier Layer Mechanical Performance
• Single layer vacuum deposited barrier films contain defects which limits their effectiveness. •The microstructure of the thin films controls their effective WVTR and is not well understood. •The impact of interfaces on the transmission properties has not received much attention.	•The mechanical properties of most barrier film are not known and are needed to model the stresses in the films. •Fracture toughness and adhesion are critical to mechanical reliability. •Methods to enhance mechanical reliability are needed.

Research Objectives

- Investigate the nucleation of thin films and interfaces and its impact on barrier layer performance.
- Investigate the mechanical adhesion in barrier films.
- Investigate edge sealants for high performance laminated barrier systems.

Multilayer Organic/Inorganic Barrier Films



SiOx(100nm/ Parylene (1µm)

SiNx (100nm/ Parylene (1µm)

FIB Microscopy image barrier

Barrier films consisted of:

SiO_x/Parylene

SiN_x/Parylene

SiNx/ PMMA

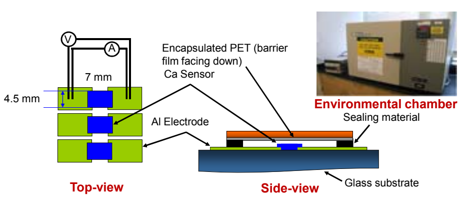
Al_2O_3/ Cytop

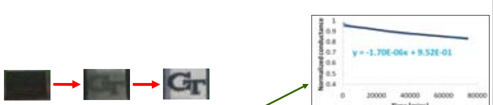
Al_2O_3, ZnO, or Al_2O_3/ZnO

Plasma ALD

Films were deposited on PET substrates at 110 C (flexible lids) or directly onto Ca samples for testing. Parylene, PMMA, and Cytop were deposited at room temperature and annealed at 110 C. Barrier films ranging from one to four dyads created and tested.

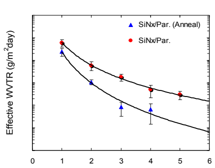
Ca corrosion test





$$WVTR[g/m^2/day] = 2\delta_{Ca} \times \rho_{Ca} \times \frac{dG_s}{dt} \times \frac{M(H_2O)}{M(Ca)} \times \frac{Ca\_Area}{Window\_Area}$$

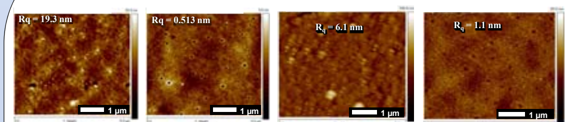
SiNx/ Parylene Results



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

Annealing of the polymer layer was found to result in an improvement in barrier performance.

Nucleation Of Barriers on PET



Bare PET

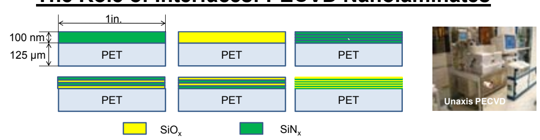
PMMA coated PET

SiN_x (100nm) on PET

SiN_x (100nm) on PMMA coated PET

Surface treatments play a large role in the quality of the barrier film. Amorphous SiN_x layer are smoother when grown on a PMMA buffer layer and has a smaller grain-like structure. This results in improved barrier performance.

The Role of Interfaces: PECVD Nanolaminates



Nanolaminates were created using PECVD deposition film (SiO_x/SiN_x) on PET lids. The film thickness was held constant at 100 nm while alternating layers of SiO_x and SiN_x were deposited. By reducing the thickness of each layer, the number of interfaces in the barrier films was increased.

Barrier performance of PECVD films

Number of dyads	Film structure/composition	WVTR [g/m²/day]
1	SiO_x(100nm)	3.26 10^{-2}
1	SiN_x(100nm)	2.03 10^{-3}
2	SiN_x(25nm)/SiO_x(25nm)	1.94 10^{-3}
2	SiO_x(25nm)/SiN_x(25nm)	1.04 10^{-3}
4	SiN_x(10nm)/SiO_x(10nm)	1.94 10^{-3}
2	SiN_x(25nm)/SiN_x(25nm)	2.27 10^{-3}

The Role of Interfaces: ALD Nanolaminates

AFM scan data of Thermal ALD films

	Al_2O_3	ZnO	Al_2O_3/ZnO nanolaminate
Roughness [nm]	0.236	1.07	0.488

Al_2O_3/ ZnO nanolaminate layers are deposited as 1:20 ratio with the total thickness of 100 nm. The Single Al_2O_3 and ZnO are also 100 nm.

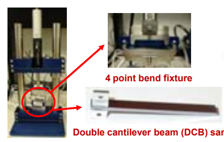
Comparison of ALD Nanolaminates to Organic/Inorganic Multilayers

Film structure/composition	WVTR [g/m²/day]
Al_2O_3	4x10^{-4}
ZnO	7x10^{-4}
3 dyads of PMMA(400 nm)/SiN_x(100 nm)	<5x10^{-5}
10 dyads of Al_2O_3(5 nm)/ZnO(5 nm)	<5x10^{-5}
Commercial Barrier	<5 10^{-5}
Glass Slides (sealant performance)	5x10^{-5}

Nanolaminates made from atomic layer deposition results in a synergistic effect which reduces the water vapor transmission rate beyond that of individual layers. This impact shows that ultrathin and ultrahigh barrier performance can be achieved.

Adhesion At Interfaces

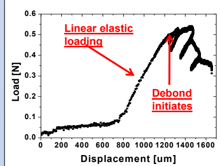
Delamination test with 4pt and DCB Samples



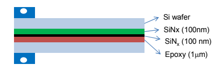
$$G < G_c \left[J/m^2\right]$$

Environment and stress accelerates defect evolution.

Test setup



Load vs. displacement curve with DCB sample



DCB experimental sample

$$G_c = \frac{12(1-\nu^2)P_c^2 a_c^2}{Eb^2h^3}$$

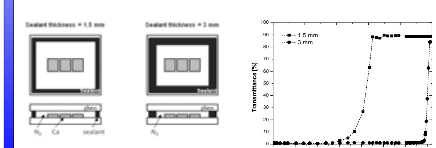
= 1.84 J/m²

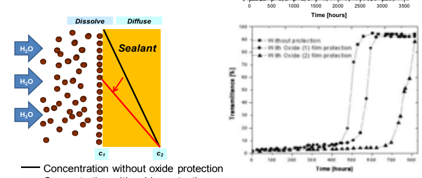
a_c = 29.94 mm

P_c = 0.3747 N

- The adhesion within the barrier layers is important to ensure the mechanical robustness of these films.
- SiNx/Parylene layers were shown to have an interfacial fracure energy of 1.5 - 4 J/m^2.
- SiNx PMMA layers were shown to have 30-36 J/m^2 showing vastly improved adhesion.
- Interface modification can be used to improve adhesion and resist environmental degradation effects.

Edge Sealant Performance





Concentration without oxide protection

Concentration with oxide protection

- Desiccant filled polyisobutylene edge have shown excellent performance. (WVTR < 10^{-3}g/m^2/day).
- A thin oxide layer (30nm) can be used to improve the sealing performance, increasing the Ca lifetime by 60%.

Conclusions

The structure of barrier films can play a large role in their effective WVTR. The use of nanolaminate inorganic or organic/inorganic films both provide excellent barrier performance. Adhesion in inorganic/organic laminates may provide some concern in long term performance in solar environments and must be addressed. Finally, edge sealants which utilize desiccant materials show promise for creating high performance laminated packaging for PV cells.

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