

# Silicon oxynitride thin film barriers for PV packaging

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## 1. Abstract

Dielectric, adhesion-promoting, moisture barriers comprised of silicon oxynitride thin film materials ( $\text{SiO}_x\text{N}_y$ , with various material stoichiometric compositions  $x,y$ ) were applied to: 1) bare and pre-coated soda-lime silicate glass (coated with transparent conductive oxide  $\text{SnO}_2:\text{F}$  and/or aluminum), and polymer substrates (polyethylene terephthalate, PET, or polyethylene naphthalate, PEN); plus 2) pre-deposited photovoltaic (PV) cells and mini-modules consisting of amorphous silicon (a-Si) and copper indium gallium diselenide (CIGS) thin-film PV technologies. We used plasma enhanced chemical vapor deposition (PECVD) process with dilute silane, nitrogen, and nitrous oxide/oxygen gas mixtures in a low-power ( $\leq 10$  mW/cm<sup>2</sup>) RF discharge at ~ 0.2 Torr pressure, and low substrate temperatures  $\leq 100^\circ\text{C}$ , over deposition areas ~1000 cm<sup>2</sup>. Barrier properties of the resulting PV cells and coated-glass packaging structures were studied with subsequent stressing in damp-heat exposure at  $85^\circ\text{C}/85\%$  RH. Preliminary results on PV cells and coated glass indicate the palpable benefits of the barriers in mitigating moisture intrusion and degradation of the underlying structures using  $\text{SiO}_x\text{N}_y$  coatings with thicknesses in the range of 100–200 nm.

## 2. Design Strategy

Safety & economic considerations motivate a process choice that reduces implementation costs and eases industrial adoption of fabricated coatings. Plasma-enhanced chemical vapor deposition (PECVD) process was chosen, whose features and precautionary issues are noted:

- > High deposition rate
- > Low process temperatures
- > Commercially feasible to scale to very areas (~ 1m<sup>2</sup> or more)
- > Employ de-minimus hazard criteria for process gases:
  - worst-case flammable and non-corrosive hazard classification
    - ❖ restricted process window explored using only dilute compressed gases:
      - ❖ 14% nitrous oxide in N<sub>2</sub>,
      - ❖ 23% oxygen in N<sub>2</sub>,
      - ❖ 3% silane in N<sub>2</sub>,
      - ❖ 11.45% oxygen in helium and/or
      - ❖ 99.999% helium dilution.

## 3. Deposition System

Five chamber in-line system featuring:

- > Load lock + 4 deposition chambers,
  - ❖ 2 PECVD chambers,
  - ❖ Thermal evaporation,
  - ❖ Sputtering.
- > 1000 cm<sup>2</sup> deposition area
- > Turbo-pumped vacuum process;
- > Isolated chambers & interconnection via pneumatic slit valves;
- > Process gases distributed via mass flow controllers;
- > Process pressures in the 0.1-1.0 Torr range monitored with capacitance manometers;
- > Base vacuum and foreline pressures sensed with pirani gauges and/or ion gauges;
- > Temperatures controlled with resistive heaters in feedback loops with PID controllers
- > Motorized transport of substrate.

## 4. In-Line Deposition System



[http://www.nrel.gov/ncpv/performance\\_reliability/indoor\\_testing.html#coating](http://www.nrel.gov/ncpv/performance_reliability/indoor_testing.html#coating)

## 5. Processing

Typical background pressures were on the order of  $10^{-7}$  Torr. Process pressures ranged from 40 to 800 mTorr, during depositions, (with turbo throttled at ~ 250 to 400 Hz). Plasmas generated via 600-W, 13.56 MHz RF (Advanced Energy RFX 600) generator and matching network (AE ATX 600). Thin film depositions performed at relatively low power (often 8 - 16 W, with some runs up to 200 W) and low temperatures, (ambient to  $\leq 97^\circ\text{C}$ ) using either soda-lime, TCO ( $\text{SnO}_2:\text{F}$ ) coated soda-lime glass, or Melinex® ST504 (Dupont-Teijin) PET, or Kaladex® 1000 PEN (polyethylene naphthalate), and the PV cells (a-Si, CIGS) substrate materials.

## 6. Conventional -vs.- Modified Packaging Polymer Barriers

Water Vapor Transmission Rates\* (WVTRs) (g/m<sup>2</sup>/d) for some conventional packaging materials and resulting PECVD coated  $\text{SiO}_x\text{N}_y$  modified polymer backsheets.:

----- WVTRs (g/m<sup>2</sup>/d) -----

Sample ID	40°C	60°C	85°C
PET (neat)	3.98	13.80	69.50
073004-1	0.20	0.50	13.45
040105-2A	1.17	4.01	21.95
052605-2A	0.37	2.23	16.02
PEN (neat)	1.74	7.40	31.60
050505-1B	0.41	1.61	6.19

\* (measured on Mocon Permatran-W 3/31 MG) <sup>1</sup>

## 7. Moisture Transport/Activation Energy

WVTRs allow diffusivity (D) and solubility (S) to be obtained.<sup>1</sup> From permeability ( $P = D \cdot S$ ), and Arrhenius relation  $P = P_{\text{exp}} \cdot \exp(-E_a/k_B T)$ , measurements for WVTRs (as function of temperature) yield estimates for activation energy of moisture transport by barrier/substrate.

Sample ID	E <sub>a</sub> Activation Energy (eV)
PET (neat)	0.55
073104-1	0.84
040105-2A	0.63
052605-2A	0.81
PEN (neat)	0.59
050505-1B	0.58

<sup>1</sup> (per ASTM F1770-97e1).

## 8. Damp Heat Exposures & Mechanical Peel Tests

Exposure to 100% Relative Humidity (RH) for eight days (~190 hr) led to barrier failure at the thin film/polymer interface. Peel strength measurements<sup>1</sup>, for a similar film made under the same deposition conditions (SDCs) and laminated to glass with EVA (pseudo-module construct) had initial peel strength in excess of 11.1 N/mm (when test was halted). Following 112 hours of damp heat exposure ( $85^\circ\text{C} / 85\%$  RH), the PET thin-film interface failed [thin film remained on EVA, (by XPS) and subsequent peel tests could not be performed.

## 9. Barrier Film Stoichiometry

Under SDCs at  $85^\circ\text{C}$ , a second film (on TCO) had composition evaluated (by XPS) at  $\text{Si}_{1.0}\text{O}_{0.25}\text{N}_{0.34}\text{C}_{0.04}\text{Ar}_{0.04}$ ; following a 4 min Argon sputter, (where carbon is adventitious, and trace Ar is likely an artifact from sputtering). To investigate both  $\text{SiO}_x\text{N}_y$  and  $\text{SiO}_2$  barriers, nitrogen based plasma deposition gases were altered (He and O<sub>2</sub>/He); associated WVTR measurements suggest only small differences in barrier performance result from the related variations in plasma chemistry and film stoichiometry. Barrier performance increased inversely with etch dose. Inverse relation and interface adhesion/water details were addressed in more detail by XPS study.<sup>2</sup>

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Conference Title: CIJ Energy Initiative/NREL Symposium  
Conference Location: Boulder, Colorado  
Conference Dates: October 3, 2006  
NREL report number - NREL/PO-5200-40682

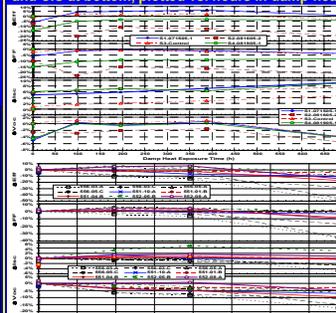
## 10. Coated Mirrors: results

Pre-sputtered Al metal coatings on soda-lime glass substrates were over-coated with  $\text{SiO}_x\text{N}_y$  barrier films. Where defects allow penetration, moisture will rapidly corrode the Al metal. Note however, the coated scribe line at far right side, has survived ~940 hours exposure to damp heat ( $85^\circ\text{C}/85\%$  RH). (More easily seen in right image, with substrate on light box).



## 11. Coated Cells: I-V results

Amorphous silicon (a-Si) and copper indium diselenide (CIS) cells were coated with  $\text{SiO}_x\text{N}_y$  and then exposed to the  $85^\circ\text{C}/85\%$  RH damp-heat stress. I-V power parameter results for select cells are shown below, for a-Si at top and CIS at bottom, plotted vs. hours in damp-heat:



a-Si Cells:

- > best resistance to moisture-induced degradation is shown by coated coupon S1
- > control S3, next best

CIS Cells:

- > Most of SiOxNy coated coupons (colored symbols & lines) exhibit enhanced moisture-durability over the uncoated ones (black lines & symbols)

## 12. Conclusions

Current recipes for thin film barrier coatings provided enhanced protection to PV cells against degradation in damp-heat stress, albeit further improvements are still needed. Adhesion of the coatings to polymeric sheets was acceptable before damp-heat stress, but failed after at most 100 hrs thereafter. More tests are in progress to evaluate the effectiveness of packaging modifications using dielectric thin-film barriers to mitigate water ingress and help deliver long-term reliable PV service either through modified encapsulation or direct device applications.

Acknowledgements:

Work was performed under DOE contract DE-AC36-GO10337.

References:

- <sup>1</sup> G. J. Jorgensen, et al., "Moisture Transport, Adhesion, and Corrosion Protection of PV Module Packaging Materials", Solar Energy Materials & Solar Cells 90 (2006) 2739.
- <sup>2</sup> J. W. Pankow and S. Glick, "Plasma surface modification of polymer backsheets: origin of future interfacial barrier/backsheets failure", NREL 2006 Program Review Proceedings.