National Renewable Energy Laboratory

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Plasma Surface Modification of Polymer Backsheets: Origins of Future Interfacial Barrier/Backsheet Failure

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Abstract

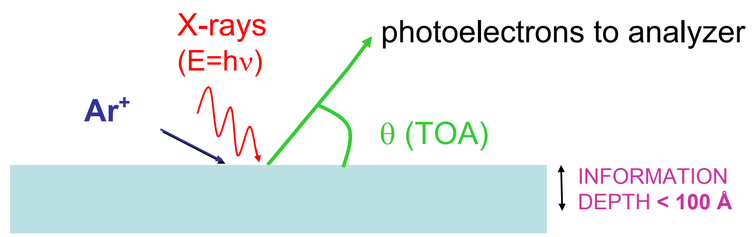
Flexible polymer substrates coated with inorganic oxide moisture barriers are a potential replacement for glass backsheets in thin-film PV (photovoltaic) modules. Silicon oxynitride (SiO_xN_y) deposited by plasma enhanced chemical vapor deposition (PECVD) on polyethylene terephthalate (PET) represents one potential new backsheet candidate. Barrier deposition runs at NREL have included a nitrogen-rich plasma pretreatment prior to barrier deposition with the intention of cleaning the PET surface and enhancing adhesion of the SiO_xN_y barrier film to PET; however, test coupons of PET/barrier/EVA/TPE failed after damp-heat exposure. (EVA is ethylene vinyl acetate and TPE is Tedlar®-PET-EVA). PET substrates exposed to plasma conditions similar to those used in pretreatment were examined by X-ray photoelectron spectroscopy (XPS) to reveal that new low molecular weight PET fragments were created at the PET surface. These fragments are responsible for barrier/PET interfacial failure and barrier transfer to the EVA encapsulant side following damp heat exposure.

Objectives

- Glass is typically used in thin film PV modules as both the frontsheet and backsheet material.[1]
- Polymer films are an alternative backsheet: advantages are decreased weight, cost and better handleability.
- Unlike glass, polymer films are ***not*** inherently impervious to moisture and need a moisture barrier.
- Silicon oxynitride (SiO_xN_y) coatings can provide moisture intrusion protection.
- PET was coated with SiO_xN_y moisture barrier films using a Pernicka PECVD deposition system at NREL.[2]

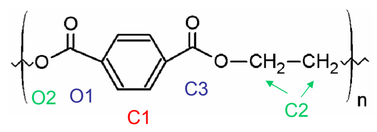
X-ray Photoelectron Spectroscopy

- Surface sensitive – information depth is <100 Å.
- Qualitative and quantitative information – elements identified by the photoelectron binding energies and signal is proportional to concentration.
- Chemical state information – binding energy sensitive to valence state and chemical environment.
- Depth profiling – sequential sputtering and analysis.
- Angle resolved XPS (ARXPS) – grazing take-off angle (TOA) enhances information from near-surface species.

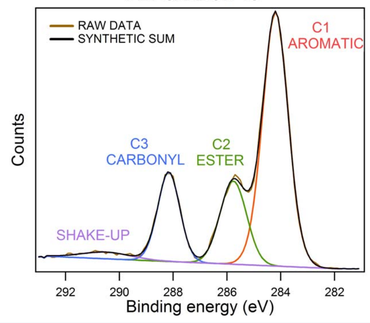


XPS of Polyethylene Terephthalate

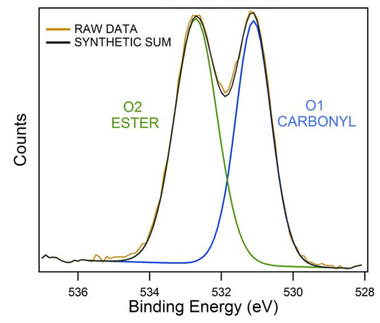
- High resolution XPS scans show various carbon and oxygen functional groups resolved in expected 3:1:1 and 1:1 ratios.



PET CARBON 1S

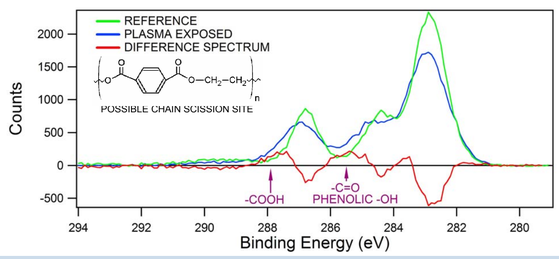


PET OXYGEN 1S



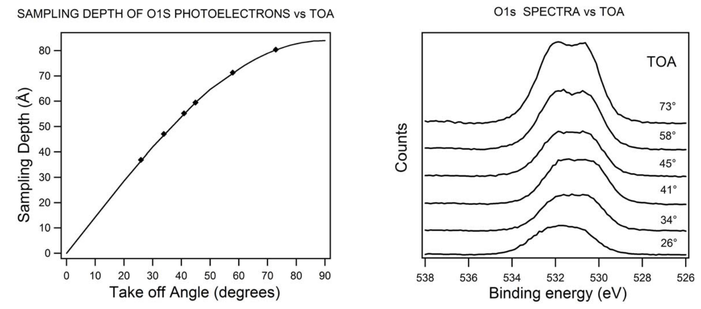
Plasma Treatment of PET

- PET was exposed in the Pernicka PECVD deposition chamber to 60W plasma power, 500 sccm N_2 and 100 sccm N_2O (14% N_2O in N_2) for 10 min @ 40ºC.
- Samples were sealed in vials in a glove bag attached to the Pernicka load-lock and then mounted and transported to the XPS instrument under inert/vacuum conditions.
- Terminal carbonyl, carboxylic acid and phenolic –OH groups appeared in plasma treated PET consistent with a **chain scission mechanism** resulting in low molecular weight PET fragments.
- Approximately 5 atomic percent nitrogen was also detected.



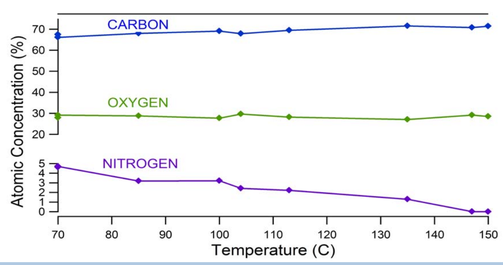
Angle Resolved XPS of Plasma-Treated PET

- Variation of photoelectron take off angle (TOA) alters XPS sampling depth and is non-destructive.
- Sampling depth varied from approximately 36 Å to 80 Å.
- Grazing TOA spectra contain significant contribution to oxygen lineshapes from the PET fragments. High TOA shows predominantly bulk, native PET.
- Plasma-modified layer layer is less than ~ 55 Å.



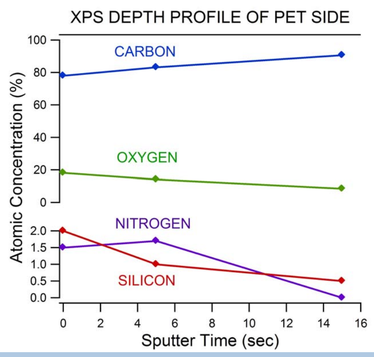
Thermal Desorption XPS of Plasma-Treated PET

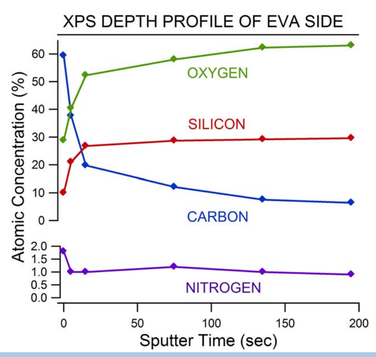
- Plasma-treated PET sample was heated in the XPS chamber with periodic scanning of carbon, oxygen and nitrogen.
- Nitrogen concentration decreased beginning at 70ºC and C1s and O1s lineshapes gradually resembled those for pure PET.
- Nitrogen was non-detectable by 148ºC and C1s and O1s lineshapes were identical to those for pure PET.
- PET fragments are volatile or diffuse into bulk indicating low molecular weight; soaking sample in water achieves same results indicating fragments have a high polarity.



Interfacial Failure Analysis of PET/SiO_xN_y/EVA/TPE

- Barriers were grown using a nitrogen-rich plasma pretreatment.
- Test coupons demonstrated reasonable initial adhesion but delaminated after 100 hours of damp heat exposure (85ºC/85%RH).
- XPS analysis suggests barrier transfer to EVA encapsulant side.

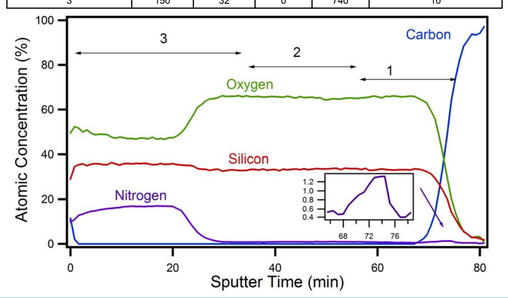




Depth Profile of SiO_xN_y Barrier Film

- SiO_xN_y barrier coated PET sample as used for laminate coupon was analyzed by XPS depth profiling.
- A N_2O/N_2 plasma pre-treatment was used. Nitrogen incorporation at the PET/barrier interface is evident.
- Only trace levels of **nitrogen** incorporation during phases 1 and 2 of the deposition despite N_2O and N_2 presence during these phases.

Phase	SiH_4	N_2O	O_2	N_2	Time (min)
Plasma pre-treat	0	100	0	500	10 (60 Watts)
1	150	8	8	740	6
2	150	12	4	740	6
3	150	32	0	740	10



Conclusions

- Plasma treatment of PET induces chain scission to occur resulting in formation of nitrogen-containing, low molecular weight, polar PET fragments (thickness < 55 Å).
- Fragments are either thermally desorbed or diffused into bulk PET at elevated temperature.
- PET fragments are water soluble.
- Depth profiles show retention of PET fragments at the barrier/PET interface due to low substrate temperature conditions.
- Depth profiles show a 2:1 oxygen to silicon ratio at the PET/phase 1 interface similar to that found for the EVA side of delaminated coupons indicating failure near the PET/phase 1 interface.
- Damp heat exposure of coupons causes failure at the PET/barrier interface with barrier transfer to the EVA side. This is consistent with the water soluble nature of polar PET fragments at this interface.

Conclusions *(cont.)*

- *Note: Moisture barriers to date have yielded reasonable water vapor transmission values; it is adhesion at the PET/barrier interface that fails. Depth profiles of barriers produced without plasma pretreatment do not show enhancement of nitrogen at the barrier/PET interface by nitrogen-containing PET fragments and adhesion of coupons after damp heat exposure is improved.*

Future Directions

- Utilize higher substrate temperatures to thermally desorb PET fragments produced via intentional or incidental plasma exposure.
- Conduct mapping experiments to determine compositional and thickness uniformity for current Pernicka conditions.
- Examine relationship between film composition and barrier efficacy and adhesion.
- Evaluate impact of film thickness on barrier efficacy.
- Evaluate thermal properties of polymer substrates and impact on adhesion.

Acknowledgements

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[1]G.J. Jorgensen, et al., "Moisture transport, adhesion, and corrosion protection of PV module packaging materials"; paper to be submitted to Progress in Photovoltaics.

[2]S.H. Glick, J.A. del Cueto, K.M. Terwilliger, G.J. Jorgensen, J.W. Pankow, B.M. Keyes, L.M. Gedvilas, F.J. Pern, "Silicon oxynitride thin film barriers for PV packaging", DOE 2005 Program Review Proceedings.

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