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ABSTRACT

Dielectric thin-film barrier and adhesion-promoting layers consisting of silicon oxynitride materials (SiO_xN_y , with various stoichiometry) were investigated. For process development, films were applied to glass (TCO, conductive $\text{SnO}_2\text{:F}$; or soda-lime), polymer (PET, polyethylene terephthalate), aluminized soda-lime glass, or PV cell (a-Si, CIGS) substrates. Design strategy employed de-minimus hazard criteria to facilitate industrial adoption and reduce implementation costs for PV manufacturers or suppliers. A restricted process window was explored using dilute compressed gases (3% silane, 14% nitrous oxide, 23% oxygen) in nitrogen (or former mixtures, and 11.45% oxygen mix in helium and/or 99.999% helium dilution) with a worst-case flammable and non-corrosive hazard classification. Method employed low radio frequency (RF) power, ≤ 3 milliwatts per cm^2 , and low substrate temperatures, $\leq 100^\circ\text{C}$, over deposition areas $\leq 1000 \text{ cm}^2$. Select material properties for barrier film thickness (profilometer), composition (XPS/FTIR), optical (refractive index, %T and %R), mechanical peel strength and WVTR barrier performance are presented.

1. Objectives

Technical efforts to address challenges of delivering quality, cost-effective, successful long-term device performance, for a majority of all electrical components, and most specifically PV devices and systems characteristically require not only well engineered active core elements but also competitive, skillfully designed integrated support packaging. Exceedingly efficient state of the art devices, which rapidly deteriorate without adequate protections, serve little benefit. A practicable high performing PV encapsulation was the goal of this work, in which moisture barriers of dielectric SiO_xN_y thin films were applied to various substrates using a low temperature plasma enhanced chemical vapor deposition (PECVD) coating method. From the outset, process restrictions consistent with facilitating eurytopic industrial adoption were imposed. In harmony with contemporary conventional encapsulation methods, one line of investigation pursued augmentation of low-cost polymeric packaging back films supplemented with these dielectric SiO_xN_y thin film moisture ingress barriers. For fast barrier quality screening sputtered aluminized soda-lime glass substrates were subsequently directly coated by thin-film deposition prior to damp heat exposure. Other less conventional approaches applied either thin film barriers directly onto various bare active CIGS thin-film devices (work in progress) or applied similar external barrier coatings over commercially available pre-encapsulated a-Si

PV mini-modules. To assess efficacy of the resultant film barriers various properties of interest for resultant package composites were characterized before or following damp heat exposure. Long-term research goals target improving module performance and PV system reliability, and service life, concerns cited in Section 4.1.1.1 of the DOE Solar Energy Technologies Research program Multi-Year Technical Plan.

2. Technical Approach

Compressed PECVD reactant gases cited were diluted (in nitrogen or helium, to below the lower pyrophoric limit of 4% silane) reducing storage concerns, operator handling risks and their related costs (no bunker, fewer haz-mat controls, alarm support requirements minimized) and used in conjunction with additional compressed N_2 , and He or Ar sources (all 99.999%). A relatively simple material handling approach was adopted where straightforward precautions were taken to minimize ordinary particulate introduction (but stringent and costly clean room mitigation and filtering were never imposed). The vacuum system consists of load lock, deposition, and backup chambers interconnected (via pneumatic VAT slit valves), individually turbo pumped (Pfeiffer TMU 1000 PM PO2 280) with assist from three separate rotary vane mechanical pumps (Leybold DB40 BCS Trivac, running fomblin), controlled by one Pfeiffer TCP 380 or two 600 electronic drives respectively. Process gases were distributed via mass flow control (MKS 647B, MKS 1179A or 1159B combination) with system pressures monitored by either baratron (MKS120 capacitance manometer) and pirani gauges (Granville-Phillips 256 convectron) or ion gauges at appropriate points during the deposition cycles.

Background pressures were typically on the order of 10^{-7} Torr, while process pressures ranged between 10^1 to 10^3 mTorr, during depositions, (with turbo throttled at ~ 250 to 400 Hz). Plasmas were generated via a 600 W, 13.56 MHz RF system (Advanced Energy RFX 600 generator and ATX 600 tuned matching network). Thin film depositions were performed at relatively low power (often 8 to 16 W, with some runs up to 200 W) and at low temperature (T), (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) substrate materials. To our knowledge, little work has been reported under restricted conditions such as these (i.e. ease industrial use, low-T $\leq 97^\circ\text{C}$), thus some resulting materials properties required characterizations such as barrier film thickness (profilometer), composition (XPS/FTIR), optical (refractive index, %T and %R), mechanical peel strength/adhesion and WVTR barrier performance.

3. Results and Accomplishments

Process control was monitored by resultant film layer thicknesses (Veeco Dektak³ profilometer). Deposition rates typically range between 70 ± 20 angstroms per minute. Most coating thicknesses were on the order of three to four thousand angstroms. Thickness uniformities achieved for the process (over areas of roughly 1000 cm^2) were evaluated to be just over $\pm 15\%$, (based on five deposition runs, with nearly identical gas flows. Thickness uniformity appeared to improve when plasma power was reduced (probably by permitting greater diffusion within the reaction chamber before gas molecules react at the substrate surface). Slight adjustments made on the RF electrode alignment and good tuning for the matching network likely contribute to improved thickness uniformity for the deposited thin films.

Pre-deposition plasma exposures were varied (between 0.8 and 70 J/cm^2 , for 15s to 20 min) to study effects on polymer/SiO_xN_y interfacial adhesion (subsequent SiO_xN_y deposition conditions were unchanged). Resulting barriers were tested for water vapor transmission rates (WVTRs).¹ Some selected characteristics for three better performing barrier film coatings on polymer substrates (PET, both -2A's or PEN, 050505-1B) produced to date are shown in Table 1. Barrier performance increased inversely as etch dose (related peel tests also revealed interfacial failure occurred at the polymer thin film interface following damp heat exposures). An accompanying publication by J. Pankow addresses this inverse relation and interfacial effects regarding water vapor exposure and loss of adhesion in more detail.²

Combined packaging experiments serve to quantify the relative effectiveness for various packaging strategies and components. Reduced etch dose demonstrated water vapor transmission rates (for our best performing barrier film on PET, to date) of 0.2, 0.5, and $13.45 \text{ g/m}^2/\text{day}$, at respective temperatures of 37.8, 59, and 85°C , and 100% relative humidity (RH), for abbreviated times, where activation energy, $E_a = 0.84 \text{ eV}$. Exposure to 100% RH for ~eight days led to barrier failure at the thin film/polymer interface. Peel strength measurements¹, for a similar film made under 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 ($85^\circ\text{C} / 85\% \text{ RH}$), the PET thin-film interface failed (film remained on EVA) and subsequent peel tests could not be performed. Under these SDCs at 85°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 SiO_xN_y and SiO_x barriers, nitrogen based plasma deposition gases were altered (He and O₂/He); associated WVTR measurements suggest only small differences in barrier performance result from the related variations in plasma chemistry and film stoichiometry.

In addition, we are currently testing a variety of thin-film CIGS, and a-Si PV cells coated with barrier thin film layers. Damp heat exposure aggressively corrodes aluminum so we have coated thin-film Al (sputtered onto soda-lime glass)

and used these for rapid visual screening for thin film SiO_xN_y barrier coatings. FTIR spectra of the SiO_xN_y thin films suggest similar bonding is present whether films were PECVD deposited at room temperature or near 85°C . IR bands were tentatively identified as: (N-H) 3300 cm^{-1} , (Si-H) strong 2250 to 2050 cm^{-1} (Si-O) relatively weak 1210 to 1150 cm^{-1} , (Si-N) strongest 915 to 850 cm^{-1} , (Si-H wag) $\sim 660 \text{ cm}^{-1}$. The higher frequency of the Si-H stretch centered at 2160 cm^{-1} has been proposed to be due to the greater electronegativity of N atoms attached to back bonded Si-Si species.³ Numerous authors have reported shifts can occur in these IR band frequencies due to variations in bond stress.^{4,5} Analyses along these lines may help to correlate the FTIR results with film density and barrier performance characterizations.

Table 1. PECVD Coated SiO_xN_y polymer backsheets.

Sample ID	40°C WVTR (g/m ² /d)	60°C WVTR (g/m ² /d)	85°C WVTR (g/m ² /d)	Activation Energy E _a (eV)
PET (neat)	3.98	13.80	69.50	0.55
040105-2A	1.17	4.01	21.95	0.63
052605-2A	0.37	2.23	16.02	0.81
PEN (neat)	1.74	7.40	31.60	0.59
050505-1B	0.41	1.61	6.19	0.58

4. Conclusions

Thin film PECVD deposited barrier coatings will need further improvement to provide adequate protection for PV devices. Evaluations determining the effectiveness of packaging modifications will likely need to remain a priority to help deliver long-term reliable PV service either through modified encapsulation or direct device applications.

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