

Surface Analysis of Stressed and Control Tin Oxide Thin Films on Soda Lime Glass

J.W. Pankow

*Presented at the National Center for Photovoltaics and Solar Program Review Meeting
Denver, Colorado
March 24-26, 2003*



NREL

National Renewable Energy Laboratory

1617 Cole Boulevard
Golden, Colorado 80401-3393

NREL is a U.S. Department of Energy Laboratory
Operated by Midwest Research Institute • Battelle • Bechtel

Contract No. DE-AC36-99-GO10337

NOTICE

The submitted manuscript has been offered by an employee of the Midwest Research Institute (MRI), a contractor of the US Government under Contract No. DE-AC36-99GO10337. Accordingly, the US Government and MRI retain a nonexclusive royalty-free license to publish or reproduce the published form of this contribution, or allow others to do so, for US Government purposes.

This report was prepared as an account of work sponsored by an agency of the United States government. Neither the United States government nor any agency thereof, nor any of their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States government or any agency thereof. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States government or any agency thereof.

Available electronically at <http://www.osti.gov/bridge>

Available for a processing fee to U.S. Department of Energy
and its contractors, in paper, from:

U.S. Department of Energy
Office of Scientific and Technical Information
P.O. Box 62
Oak Ridge, TN 37831-0062
phone: 865.576.8401
fax: 865.576.5728
email: reports@adonis.osti.gov

Available for sale to the public, in paper, from:

U.S. Department of Commerce
National Technical Information Service
5285 Port Royal Road
Springfield, VA 22161
phone: 800.553.6847
fax: 703.605.6900
email: orders@ntis.fedworld.gov
online ordering: <http://www.ntis.gov/ordering.htm>



Surface Analysis of Stressed and Control Tin Oxide Thin Films on Soda Lime Glass NCPV and Solar Program Review 2003

Joel W. Pankow
National Renewable Energy Laboratory
1617 Cole Blvd., Golden, CO 80401

ABSTRACT

Surface analysis techniques have been used to investigate tin oxide-coated soda lime glass specimens prior and subsequent to their exposure to DC bias, heat, and humidity. All specimens reported here comprise the following layered structure: tin oxide/silicon oxycarbide/glass. Depth profiling using X-ray photoelectron spectroscopy (XPS) clearly shows the interfacial regions in both control samples and samples exposed to the above-mentioned conditions (stressed). Control samples show distinct and relatively compact interfacial regions as well as an intact silicon oxycarbide diffusion barrier. Stressed films, however, show more diffuse interfacial regions and a physically and chemically altered silicon oxycarbide diffusion barrier. This deterioration of the diffusion barrier is proposed to be a pre-requisite event to enable tin oxide delamination.

1. Introduction

Thin-film PV success depends on the viability of modules under long-term exposure to widely varying environmental conditions. Temperature and humidity are two of the most important environmental conditions, and the performance of PV modules subjected to these conditions ultimately determines module reliability. Recent observations of both deployed modules and modules subjected to accelerated lifetime testing to simulate long-term environmental exposure seem to indicate, that under certain combinations of temperature and humidity as well as operational or applied voltages, delamination of the tin oxide thin film from the glass substrate can occur.[1] A definitive and experimentally proven mechanism responsible for tin oxide delamination has yet to appear in the literature, however, it seems that heat, humidity, and operational or applied voltage, either separately or in combination, are active in the mechanism. Since sodium is a major component of soda lime glass, many researchers believe that sodium migration is involved in the delamination mechanism. The most likely explanation for this link is based on the exchange of sodium counterions in glass for hydrogen from water to create silanol (SiOH) groups accompanied with the formation of sodium hydroxide. The sodium hydroxide further attacks the glass Si-O-Si network structure to form additional silanol end groups.[2] This in turn can lead to tin oxide-glass delamination.

There have been few reports of the application of surface analysis techniques toward understanding the mechanism behind tin oxide-glass delamination. A fair amount of basic surface analysis has been performed on tin oxide films and glass substrates; however, most of this work has not been

PV related. Furthermore, relatively little surface analysis has been performed on laboratory PV specimens subjected to accelerated lifetime testing or on actual deployed modules for that matter. Examination of delaminated tin oxide-glass structures seems to be limited to utilization of scanning electron micrographs that, while qualitatively providing an image of the delaminated surface, do not provide for surface chemical element compositional information or information regarding chemical bonding structure/environment. Surface analysis techniques such as XPS are well suited for these investigations. As well as qualitative and quantitative surface information obtained from XPS, binding energies of ejected photoelectrons are sensitive to chemical valence state and local chemical environment. In addition to providing true surface analysis of the specimens with an information depth of about 50-100 Å, an argon sputter gun can be used to controllably sputter through the film to reveal information beyond the first 50-100 Å and provide a true chemical element depth profile. Depth profiles are then particularly useful for examination of materials that contain interfacial regions such as the tin oxide/silicon oxycarbide/glass system.

Finally, although the structure and composition of glass and tin oxide have received a reasonable amount of attention in the literature, there seems to have been little focus on exploring the composition, integrity, and intended role of the silicon oxycarbide (SiO_xC_y) layer.

2. Experimental

Samples from NREL and Energy Photovoltaics (EPV) were used in these studies. EPV has developed a procedure for stressing transparent conductive oxide (TCO) films that is described in a recent paper.[3] First, electrical connections are established to the samples by soldering copper wire to the TCO and soldering an indium contact pad to the glass side. The sample is placed glass side down on an electrically conductive pre-heated metal hot plate at 180° to 225°C with the TCO contact connected to the negative side of a DC power supply and the electrically conductive hot plate (in contact with the glass contact) connected to the positive side of the supply. 10 to 100 VDC are applied for upward of 15 minutes. Finally, the sample is allowed to cool either in air, under dry conditions, or in a humid environment. An apparatus currently under construction at NREL is similar to the EPV design, but will involve certain unique features such as alternative methods for connections to the glass and tin oxide as well as utilization of ultra low humidity glove box storage conditions. Control and

stressed samples were all examined using a PHI 5600 XPS spectrometer equipped with a monochromatic aluminum X-ray source. A base vacuum level of approximately 5×10^{-10} torr ensures a negligible amount of additional moisture exposure once samples are placed in the instrument. Finally, an argon sputter gun is used to sputter the samples in a controllable fashion by alternating data collection and sputter cycles.

3. Results and Discussion

Figure 1 shows the XPS depth profile for a commercial sample of tin oxide/glass that was not subjected to the above-described stressing procedure. The y-axis displays atomic concentration of the corresponding elements, and the x-axis is sputter time in minutes. Through proper calibration of the instrument, this axis may alternatively be plotted as thickness. An initial survey scan of this sample revealed only tin, oxygen, and adventitious carbon within the first 50-100 Å of analysis depth. The tin oxide layer is estimated to be over 8000 Å, and, consequently, only tin and oxygen are determined for the first 190 minutes of sputter time. Due to the thickness of the tin oxide and its uniform composition, the first 100 minutes of the profile are not shown in Fig. 1. One peak for oxygen 1s photoelectrons derived from oxygen in tin oxide is observed at a binding energy of 530.6 eV. As the sputter crater reaches a depth wherein photoelectrons from additional oxygen-containing layers are detected, a second broad O1s peak begins to appear. This peak is centered at 533.0 eV and is well resolved from the tin oxide oxygen peak. By using oxygen 1s scans from the beginning and end of the depth profile, linear least squares analysis (LLS) is used to fit the two forms and then plot the corresponding contributions from these forms as a function of sputter time. The peak at 533.0 eV is due to photoelectrons from oxygen in glass as well as oxygen in the silicon oxycarbide layer in proportions dependant on sputter depth. Photoelectrons from oxygen in both the glass and silicon oxycarbide layer occur at a higher binding energy than oxygen in tin oxide due to their more electropositive environment compared to their environment in tin oxide; and assignments are consistent with literature values.[4] Using a smaller pass energy on the XPS analyzer in future studies may resolve the glass and oxycarbide oxygen forms.

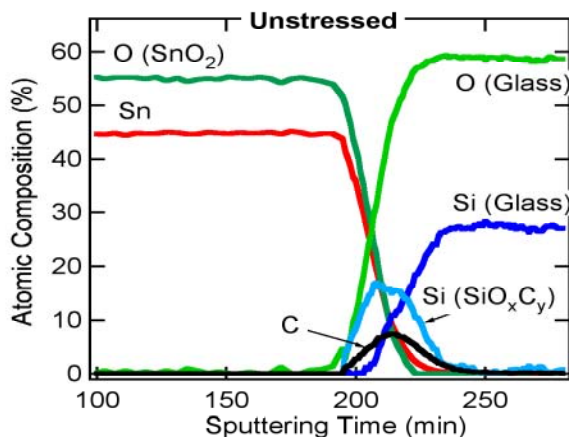


Figure 1. XPS depth profile of control sample

Occurring almost simultaneously with the appearance of the second oxygen peak in the depth profile was the appearance of silicon, which persisted throughout the completion of the depth profile. Unlike the oxygen spectra, the silicon spectra did not have two well-resolved components. Rather, the peak seemed to shift from 103.0 eV at the onset of detection, to about 103.6 eV as bulk glass was approached. Figure 2 shows a stack plot of selected silicon spectra as a function of increasing sputter time. Target factor analysis (TFA) was conducted to determine that two individual silicon species were responsible in varying proportions for the peaks – one centered at 103.0 eV occurring early in the profile, and the other at 103.6 eV dominating later in the profile. In TFA, principal component analysis (PCA) is first used to determine the number of component spectra required to reproduce the original spectra data within a certain amount of experimental error. In the next stage, spectral target factor analysis is performed to test each suspected component spectrum from the profile itself. Finally, once all the component spectra are identified, TFA will display the atomic concentration of each component as a function of sputter time. Figure 3 illustrates the two silicon-containing components determined by TFA for this depth profile. By displaying the resultant silicon components in the depth profile, the silicon species at 103.0 eV appears within a distinct window in the profile from about 180 to 230 minutes and is clearly due to Si in SiO_xC_y . The assignment of this component to Si from SiO_xC_y is further substantiated by the appearance of carbon within this same window (see below). The second Si-containing component at 103.6 eV begins to appear at about 210 minutes and eventually dominates the silicon species throughout the rest of the profile. This species is clearly due to Si in glass. The binding energies of these two Si peaks are consistent with the local chemical environments of Si in SiO_xC_y vs. Si in glass and is consistent with literature values.[4,5] Within the same window of sputter time that the SiO_xC_y silicon peak dominates, a single carbon peak centered at 284.0 eV also appears, consistent with carbon from SiO_xC_y . The Si (glass) peak is accompanied by the appearance of the alkali metal components of glass (Na, Mg and Ca), which are not shown.

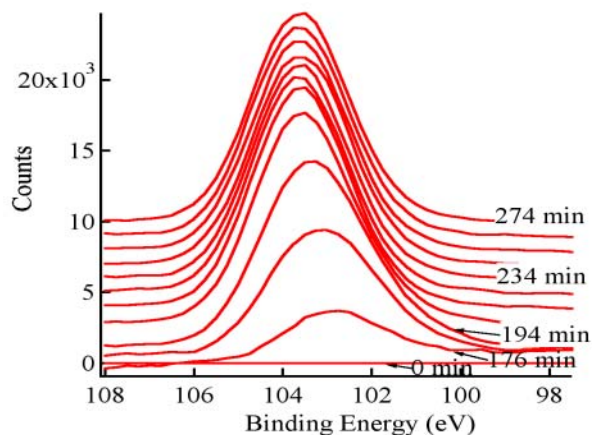


Figure 2. Silicon stack plot

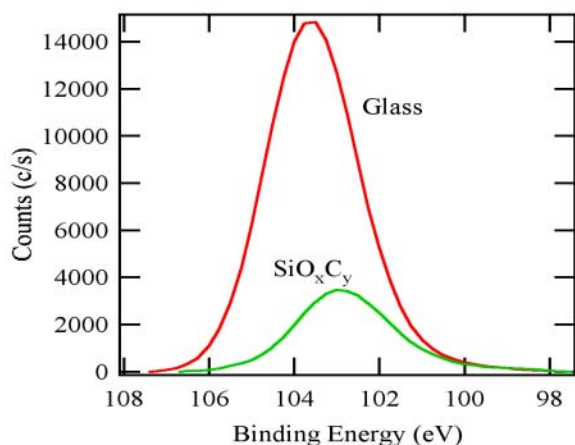


Figure 3. Principal silicon components (control)

The XPS depth profile of the EPV stressed sample is shown in Figure 4. The sample was stored in desiccant prior to analysis in an attempt to delay or avoid tin oxide delamination. EPV has found that if samples are subjected to the final step of the procedure (humidity exposure), the tin oxide will delaminate. As in Fig. 1, the first 100 minutes of the profile have been truncated. Oxygen 1s peaks and assignments are identical to those of the control sample. The maximum for carbon concentration was found to occur at a slightly higher sputter time than for the control sample, which may be due to slightly different sputtering rates of the instrument since the samples were analyzed several days apart. For comparison purposes, the profiles for Figs. 1 and 4 have been time adjusted to align this carbon peak. As the profile first approaches and then extends into the bulk glass, sodium, magnesium and calcium begin to appear, and eventually, steady state concentrations of these elements as well as silicon and oxygen from glass are reached. Note that sodium, magnesium, and calcium are not shown in the profile.

The profile for the stressed sample in Fig. 4 is markedly different from the control profile in Fig. 1. First of all, the interfacial regions are not as sharply defined as in the control. Although the sample was stored in desiccant by EPV, it is possible that the delamination process has started. The degree to which this has potentially occurred would depend on a multitude of variables, including desiccant condition, threshold levels of humidity required for delamination, and exposure time to ambient prior to loading the sample in the instrument etc. A previously compact tin oxide layer that deteriorates and detaches from the SiO_xC_y layer or along with SiO_xC_y with the creation of voids would explain the qualitative differences in the tin profiles. Unlike the control sample, the stressed sample does not exhibit two distinguishable silicon components as tested by TFA. This means that even though Si 2p photoelectrons may arise from multiple silicon-containing species, all the silicon atoms exist in indistinguishable valence states or chemical environments, resulting in one peak centered at about 103.2 eV. This indicates that there has been a chemical breakdown of the silicon oxycarbide diffusion barrier, and the extended window over which carbon detection occurs may be an indication of a deterioration of SiO_xC_y physical

integrity, such as interfacial failure within the SiO_xC_y layer. In fact, additional analyses of EPV delaminated samples were conducted but are not illustrated here.[3] In areas where no visible tin oxide remains, XPS survey scans detected only carbon, silicon, oxygen, and alkali glass metals. Furthermore, depth profiles revealed that the carbon detected was due only negligibly to surface-confined adventitious carbon, since depth profiles revealed steady state carbon concentrations upward of 20 atomic percent for over 20 minutes. These observations are consistent with complete or partial interfacial failure at or within the silicon oxycarbide layer for both this and the sample represented by Fig. 4, respectively.

At this time, we have seen no reliable differences in the degree of sodium migration for control and stressed samples. However, a chemical and physical breakdown of the diffusion barrier would certainly allow for a sodium-rich glass surface to interact with diffused water to create a caustic alkali environment capable of destroying the -Si-O-Si- network structure and the associated interfacial bonds.

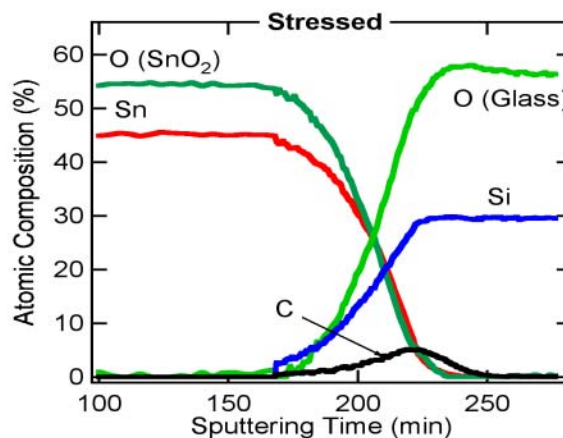


Figure 4. XPS depth profile of stressed sample

4. Conclusions

XPS depth profile investigations of control and stressed tin oxide thin films on glass have proven to be a useful tool toward better understanding interfacial failure mechanisms and resulting delamination events. Various data reduction techniques were employed to carefully examine the depth profile data including linear least squares fitting and target factor analysis. Depth profiles of the samples were consistent with a layered structure described as $\text{SnO}_2/\text{SiO}_x\text{C}_y/\text{glass}$, and all of the interfaces of the samples were clearly evident. In both control and stressed samples, linear least square fitting of the oxygen profile was employed by using scans from early and late in the profile to define representative oxygen forms. As a result, oxygen from tin oxide can easily be distinguished from oxygen in glass and SiO_xC_y . Although it was not possible to deconvolve oxygen as silicon oxycarbide from oxygen as glass, future studies will employ higher resolution detection and angle-resolved XPS techniques in combination with data reduction techniques to try to distinguish these forms. A separation of their respective contributions may in fact not be possible

due to the similar chemical environments of oxygen in both of these forms.

Of particular interest in the samples was the clear indication of the silicon oxycarbide layer. Over the course of the profile for the non-stressed control sample, target factor analysis revealed two unique silicon-containing components. The lower binding energy component coincided with the appearance of a carbon peak within the same sputter time window, and this lower energy Si component was assigned to Si from the silicon oxycarbide layer. Somewhat later in the profile, a higher binding energy form of Si begins to dominate the Si signal and is assigned to Si from glass. Identification of the diffusion barrier layer in the control was found to be critical toward comparing this same layer in stressed samples where an apparent physical and chemical breakdown of the diffusion barrier seems to occur. This breakdown is believed to be a critical event during interfacial failure that ultimately may enable the delamination event.

Ongoing studies are focused on the examination of a multitude of other tin-oxide-coated glass samples by XPS as well as other surface analysis techniques. Samples are being prepared by a variety of techniques, and stress parameters are thoroughly varied and examined. In addition, data collection parameters are under investigation, including varied sputter interval times/rates, detector pass energy, and sample tilt angle (angle resolved).

5. Acknowledgements

The author would like to acknowledge Mr. Kai Jansen of Energy Photovoltaics for various samples as well as Mr. Christopher Cording of AFG Industries for background information on glass fabrication. Dr. Andrew Back of Physical Electronics is acknowledged for several informative communications regarding target factor analysis. Dr. Sally Asher of NREL is acknowledged for her assistance with preparation of the figures presented in this paper. DOE supported this research under contract no. DE-AC36-99GO10337.

REFERENCES

- [1] C.R. Osterwald, T.J. McMahon, J.A. del Cueto, "Electrochemical Corrosion of SnO₂:F Transparent Conducting Layers in Thin Film Photovoltaic Modules," *Solar Energy Materials and Solar Cells.*, in press, 2002.
- [2] D.E. Clark, C.G. Pantano, L.L. Hench, *Corrosion of Glass* (Books for Industry, New York) 1979.
- [3] K.W. Jansen, A.E. Delahoy, "A Laboratory Technique for the Evaluation of Electrochemical Transparent Conductive Oxide Delamination from Glass Substrates," *Thin Solid Films*, **423** (2003) pp. 153-160.
- [4] J.F. Moulder, W.F. Stickle, P.E. Sobol, K.D. Bomben, *Handbook of X-ray Photoelectron Spectroscopy* (Physical Electronics, Inc., Eden Prairie, Minnesota) 1995.
- [5] C. Önnby, C.G. Pantano. "Silicon Oxycarbide Formation on SiC Surfaces and at the SiC/SiO₂ Interface," *J. Vac. Sci. Technol. A* **15(3)** (1997) pp. 1597-1602.

REPORT DOCUMENTATION PAGE			Form Approved OMB NO. 0704-0188	
Public reporting burden for this collection of information is estimated to average 1 hour per response, including the time for reviewing instructions, searching existing data sources, gathering and maintaining the data needed, and completing and reviewing the collection of information. Send comments regarding this burden estimate or any other aspect of this collection of information, including suggestions for reducing this burden, to Washington Headquarters Services, Directorate for Information Operations and Reports, 1215 Jefferson Davis Highway, Suite 1204, Arlington, VA 22202-4302, and to the Office of Management and Budget, Paperwork Reduction Project (0704-0188), Washington, DC 20503.				
1. AGENCY USE ONLY (Leave blank)	2. REPORT DATE May 2003	3. REPORT TYPE AND DATES COVERED Conference Paper		
4. TITLE AND SUBTITLE Surface Analysis of Stressed and Control Tin Oxide Thin Films on Soda Lime Glass			5. FUNDING NUMBERS PVP3.3301	
6. AUTHOR(S) J. W. Pankow				
7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES) National Renewable Energy Laboratory 1617 Cole Blvd. Golden, CO 80401-3393			8. PERFORMING ORGANIZATION REPORT NUMBER NREL/CP-520-33602	
9. SPONSORING/MONITORING AGENCY NAME(S) AND ADDRESS(ES)			10. SPONSORING/MONITORING AGENCY REPORT NUMBER	
11. SUPPLEMENTARY NOTES				
12a. DISTRIBUTION/AVAILABILITY STATEMENT National Technical Information Service U.S. Department of Commerce 5285 Port Royal Road Springfield, VA 22161			12b. DISTRIBUTION CODE	
13. ABSTRACT (<i>Maximum 200 words</i>) Surface analysis techniques have been used to investigate tin oxide-coated soda lime glass specimens prior and subsequent to their exposure to DC bias, heat, and humidity. All specimens reported here comprise the following layered structure: tin oxide/silicon oxycarbide/glass. Depth profiling using X-ray photoelectron spectroscopy (XPS) clearly shows the interfacial regions in both control samples and samples exposed to the above-mentioned conditions (stressed). Control samples show distinct and relatively compact interfacial regions as well as an intact silicon oxycarbide diffusion barrier. Stressed films, however, show more diffuse interfacial regions and a physically and chemically altered silicon oxycarbide diffusion barrier. This deterioration of the diffusion barrier is proposed to be a pre-requisite event to enable tin oxide delamination.				
14. SUBJECT TERMS delamination; x-ray photoelectron spectroscopy; transparent conducting oxides; thin films			15. NUMBER OF PAGES	
			16. PRICE CODE	
17. SECURITY CLASSIFICATION OF REPORT Unclassified	18. SECURITY CLASSIFICATION OF THIS PAGE Unclassified	19. SECURITY CLASSIFICATION OF ABSTRACT Unclassified	20. LIMITATION OF ABSTRACT UL	