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STUDY OF DELAMINATION IN ACCELERATION TESTED PV MODULES

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ABSTRACT: The average adhesional shear strength at silicon cell/EVA interface in damp-heat, acceleration-tested modules was ~27% of that measured in new modules. The average carbon concentration at the surface of samples extracted from acceleration tested modules was 15 atomic % or ~30% of that measured in new modules. Surface concentrations of sodium on Si-cell samples from the acceleration tested modules ranged from 4.9 to 22.0 atomic % while those of phosphorous ranged from 4.3 to 7.1 at. %. These are very high impurity concentrations. Often small concentrations of phosphorous were detected at the interface between titanium oxide antireflection coating and silicon cell. All the samples, that showed low surface concentrations of carbon, had low adhesive strengths. Moreover, high sodium and phosphorous concentrations always correlated with low adhesional strengths. There was clear evidence of a direct correlation between carbon concentration and adhesional strength and an inverse correlation between sodium and phosphorous concentrations and adhesional strength. Similar correlation has been observed, at FSEC, in earlier studies on field deployed PV modules.

Keywords: PV Module Durability - 1: Damp-Heat Acceleration Tested - 2: C-Si EVA - 3

1. INTRODUCTION

Delamination, resulting from the loss of adhesion must be addressed in order to achieve 30-year lifetime for photovoltaic (PV) modules. Delamination has occurred to varying degrees in a small percentage of modules from all manufacturers. For example, last winter, semitransparent façade, crystalline silicon, glass-to-glass building integrated PV (BIPV) modules installed in 1998 on the office building of the Federal Ministry of Economic Affairs in Berlin began to turn partly milky with spots growing continuously [1]. All modules in the 100 kW array were replaced at an estimated cost of US$ 900,000. Delamination has occurred in BIPV modules at Bremen, Rheinbach, and PV systems at Troisdorf and Munich, all in Germany [1]. Earlier, all the modules fabricated by another company and installed on a segment of a 1 MW plant at Toledo, Spain delaminated. Delamination is more frequent and severe in hot and humid climates.

Over the last six years, FSEC has accumulated wealth of data through systematic and detailed study of module durability concentrating on the solar cell/encapsulant composite with an objective to lay the scientific basis for improvement of PV module manufacturing technology [2-6]. Crystalline silicon PV modules deployed at the Sandia National Laboratories (SNL), FSEC and other locations in the US and around the globe are being studied whenever possible with their respective control modules.

Present acceleration testing of PV modules usually does not reproduce yellowing and browning of encapsulant, delamination, solder de-bonding, cracking of glass or backing sheets, and some other slowly occurring degradation phenomena. Therefore, FSEC is participating in the SNL Module Long Term Exposure (MLTE) project.

This paper presents the study of loss of adhesion and impurity precipitation at Si/EVA interface in damp-heat acceleration-tested PV modules fabricated by two manufacturers, one in Europe and the other in USA with an aim to improve the durability of PV modules. Some of the modules had shown partial delamination in a few cells after 1000 hours of damp-heat acceleration test.

2. EXPERIMENTAL TECHNIQUE

Sample extraction process developed by SNL and further improved at FSEC was employed for sample extraction. Nuts or bolts were attached directly to the samples. The maximum torque and the corresponding angle of rotation required to extract samples were measured. Recently FSEC has developed a process for extraction of samples from glass-to-glass PV modules. Over one hundred silicon cells samples and corresponding EVA samples were extracted from four new and four damp-heat acceleration-tested PV modules of the two manufacturers. Adhesional shear strength was calculated from the maximum torque required to extract ~1.7 cm diameter samples. After application of torque, the failure always occurred at the silicon cell/EVA interface. Morphology of freshly extracted Si cell and EVA samples was examined by optical microscopy, scanning electron microscopy (SEM), Auger electron spectroscopy (AES) using a Perkin Elmer PHI 660 Scanning Auger Multiprobe, and X-ray photoelectron spectroscopy (XPS) using PHI model 560 Multi Technique XPS system.

3. RESULTS

Two acceleration tested modules were analyzed because of problems of partial delamination in a few cells after 1000 hours of damp-heat acceleration testing. Thorough visual inspection of each module was carried out under daylight and UV light in dark room from the front glass side. A narrow strip of peripheral regions in majority of cells of acceleration tested modules showed a hazy i.e. whitish appearance under UV illumination. When seen under daylight, couple of cells had bubbles around the bus line. Complete delamination of the middle region of the silicon cell/EVA interface was observed for one or two cells in each module. The average adhesional shear strength for all the samples in the acceleration-tested modules was 1.74 MPa or ~31% of that in contemporary new modules.

Results of analysis of a representative sample #14B2 extracted from the busline region having adhesional strength of 0.45 MPa equivalent to the maximum torque for extraction of 0.42 Nm are provided in the following. Faceted bluish multi-crystalline silicon cell was visible over most of the sample area while thin EVA coverage was seen only on some isolated areas by optical microscopy of the sample from the bus line region.

AES survey of the sample carried out over a faceted silicon cell area approximately near the middle between two grid lines is shown in Figure 1. AES peak energies and atomic concentrations obtained from AES survey in Figure 1 were phosphorous 112 eV, 4.22%, carbon 269 eV, 13.41%, titanium 380 and 415 eV, 22.72%, oxygen 510 eV, 45.66% and sodium 951 and 989 eV, 14.1%. Substantially high concentrations of the impurities: phosphorous and sodium, and low concentration of carbon are consistent with the measured low adhesional strength.

An AES line scan was carried out on Si cell sample surface for Ti, O, Si, C, Na, and P. No correlation could be inferred from elemental peak heights because of the lack of distinct compositional or geometrical features within the scanned distance. The line scans showed uniform coverage of oxygen, carbon, titanium, and sodium while substantial portion of the impurity, phosphorous was located in isolated spots. The concentration of silicon was too low to infer any correlation.

A depth profile was carried out at a rate of approximately 100 Å min^{-1} to a depth of ~2350 Å using the three-point method. Variation of peak heights with the depth for the elements Ti, O, C, Si, Na and P are given in Figure 2. The depth profile clearly shows the initial rise, plateau and gradual decline of titanium signal arising from the TiO_x AR layer having a thickness of ~1450 Å. Initially the carbon concentration arising from EVA coverage of the cell sample fell off rapidly and then gradually became negligible at higher depths. Sodium concentration also fell off rapidly at first. Phosphorous concentration decreased rapidly and was negligible within the TiO_x AR layer. However, there was substantial phosphorous concentration at the TiO_x/Si cell interface over the depth range of 1400-1750 Å. This constitutes a higher than the usual maximum n-type dopant concentration in silicon added to prepare the p-n junction. The substantial sodium concentration dropped rapidly. Only a part of the sodium concentration detected within the TiO_x AR layer may be attributed to noise. Oxygen concentration showed a narrow peak near the surface followed by a plateau and a decline corresponding to the titanium oxide layer. The oxygen peak near the surface may be the result of oxygen in EVA and in compounds formed with the impurities phosphorous and sodium. Similarly oxygen concentration continues to remain significant beyond the TiO_x AR layer because of a silicon oxide layer at that interface.

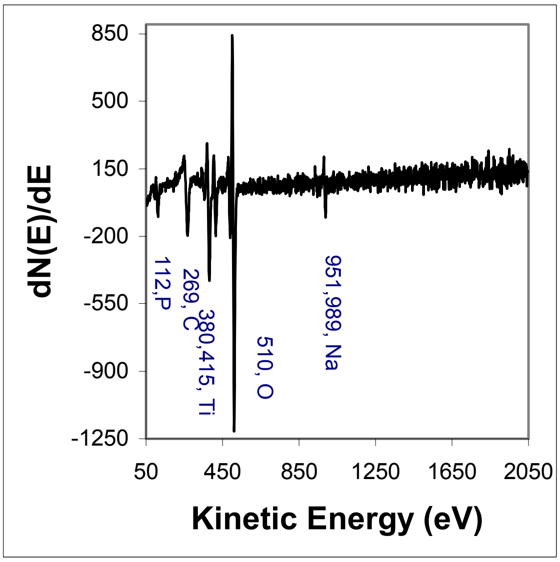

Figure 1: AES survey of a sample #14B2 from a busline area.

AES depth profile was suspended at the interface between TiO_x AR layer and Si p-n layer and AES survey of the chosen area was carried out. AES energies and atomic concentration of elements calculated from an AES survey of the spot at the interface were as follows: silicon 91, 1556, and 1615 eV, 73.86%, phosphorous 120 eV, 9.15%, titanium 382, 418 eV, 6.20%, and oxygen 510 eV, 10.79%. It should be noted that the phosphorous concentration is very high. Moreover, the peak-to-peak method measures the atomic concentrations more accurately.

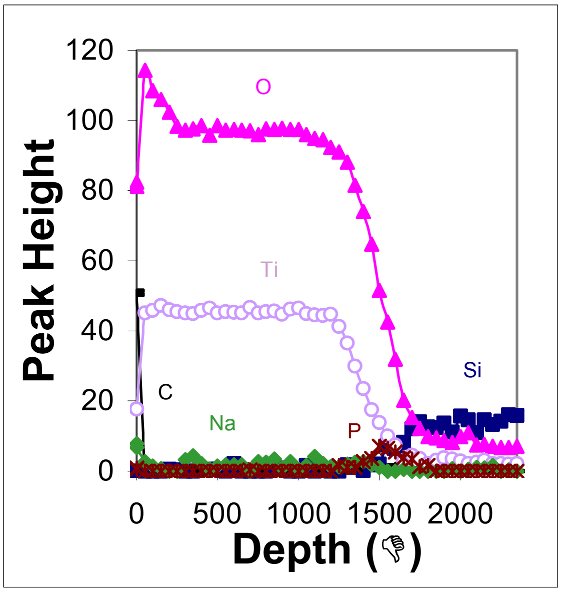

Figure 2: AES depth profile showing elemental peak heights of sample #14B2.

AES line scan carried out at the TiO_x/Si cell interface for elements Si, O, C, Ti, Na and P showed a reasonably uniform coverage of the elements except for a higher oxygen concentration in an isolated region.

The XPS survey of the EVA sample is given in Figure 3. XPS peak positions and corresponding atomic concentrations calculated using the areas under XPS peaks and elemental sensitivities, were as follows: silicon Si2P3, 101.5 eV, 1.5 at. %, carbon C1s, 284.5 eV, 59 at. %, silver, Ag3d5, 367 eV, 0.1 at. %, titanium Ti2P3, 458.5 eV, 0.8 at. %, oxygen O1s at 531 eV, 22.4 at. %, and sodium Na1s, 1072 eV, 16.3 at. %. The substantially high sodium concentration arose from sodium diffusing from front sodalime glass. Titanium is from titanium oxide delaminating from the cell surface or possibly from surface contamination. A minute bluish patch on EVA surface was observed by optical microscopy indicated that delamination has taken place at the TiOx/Si interface.

Figure 4 provides a compilation of adhesional strengths and concentrations of carbon, sodium and phosphorous of samples extracted from acceleration tested modules in this study. It clearly shows that the adhesional strength is higher when carbon concentration at the Si/EVA interface is high and the concentration of sodium and phosphorous is low and vice versa. Similar correlation has been observed in the case of modules deployed in hot and humid and hot and dry ambients [6].

4. DISCUSSION

The middle portions of one or two cells from damp-heat acceleration-tested modules had delaminated. The average adhesional shear strength for all the samples in the acceleration-tested modules was 1.737 MPa. This is 31% of the typical adhesional shear strength of contemporary new modules. All the samples that showed low surface concentrations of carbon had low adhesional strengths. The average carbon concentration at the surface of Si samples extracted from acceleration tested modules was 10 at. %. Carbon signal at the surface of Si samples results from EVA clinging to the surface after sample extraction. Experience has shown that the adhesional strength is reduced drastically even leading to complete delamination whenever the concentration of carbon at the surface drops to ~10%.

The high concentrations of precipitated impurities sodium and phosphorous have resulted in significant loss of adhesion and even complete delamination. The maximum concentration of n-type dopant phosphorous in the p-n junction silicon cell is usually expected to be ~1%. Often substantially higher concentrations of phosphorous were detected at the interface between titanium oxide and silicon p-n junction signifying a higher than expected maximum n-type dopant concentration in silicon. Experience has shown that the adhesional strength is reduced to 50% whenever the concentrations of phosphorous and sodium exceed 3% and 5% respectively.

Some line scans indicated considerably higher than average phosphorous concentrations within narrow localized regions. This may have resulted from uneven distribution of the dopant over the silicon wafer. It would be useful to analyze the distribution of phosphorous from region to region on as-doped; and as-doped and etched silicon wafers both without antireflection coating or grid contacts by AES secondary ion mass spectroscopy.

Excessive amounts of sodium are detrimental to adhesion. Most probably the high concentration of sodium on EVA surface is from sodalime glass. During the 90's glass manufacturers added more soda ash so as to replace dolamite in glass sheets used in PV modules. Dolamite is a greyish white natural mineral with a vitreous lustre and

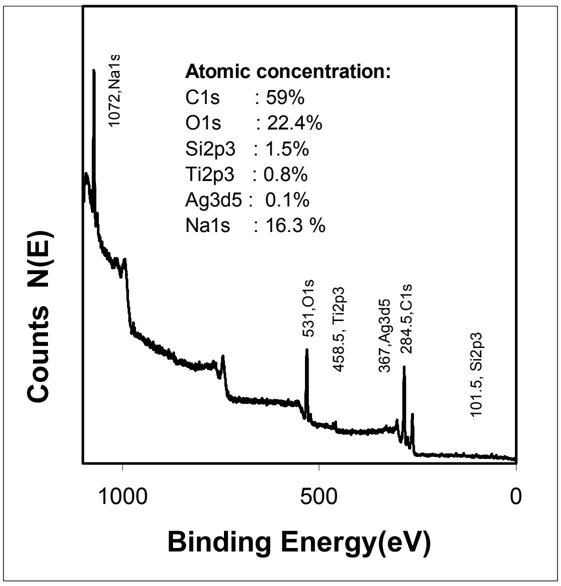

Figure 3: XPS survey of an EVA sample

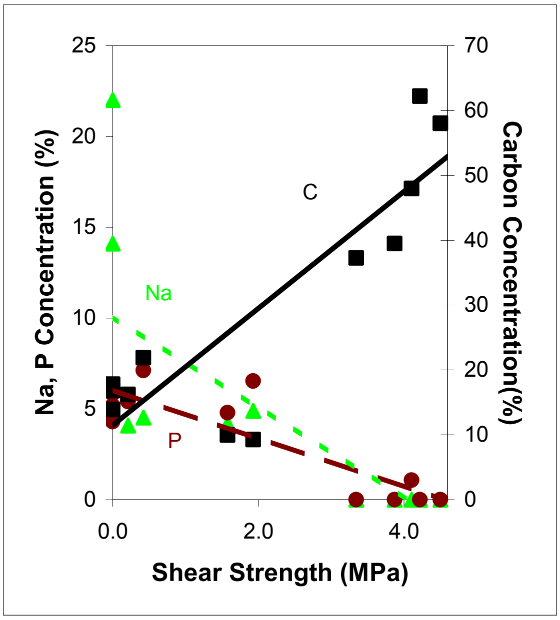

Figure 4: Correlation between adhesional strength at Si/EVA interface with concentration of C, Na and P

a chemical composition, $CaMg[CO_3]_2$. Because of the added soda ash, Na_2O cocentration in typical glass sheets used in PV modules increased to 14%. The increased soda ash content can result in a reactive surface layer. Studies at FSEC have shown that reduction of soda ash content can reduce moisture ingress in PV modules. Recently, glass manufacturers have begun reducing the soda ash content to 10%. It should be remembered that sodium from coastal ambient can also diffuse into the PV modules in the hot and humid climate.

In a few cases, non-negligible sodium and carbon concentrations were detected at titanium oxide/silicon cell interface. It should be verified if a part of sodium at that interface is arising from surface contamination.

In addition to sodium concentrations comparable to those measured on corresponding silicon cell samples, small quantities of titanium were detected on the surface of some EVA samples from the acceleration-tested module. Titanium may have resulted because of corrosion, delamination, or possibly from surface contamination. Small concentrations of tin and silver were detected on samples from bus line region of acceleration-tested module possibly due to corrosion of grid lines and solder bond.

An understanding of the systemic problems could be developed and correcting measures could be taken by establishing a base line for the adhesional shear strength, morphology and interface composition. This will also assist in pinpointing occasional problems caused by out-of-spec materials, improper handling, and process modification.

It is suggested that the process of phosphorous diffusion should be improved for limiting the concentration and also for guaranteeing uniform distribution over the surface; as-doped; and as-doped and etched silicon wafers both without antireflection coating or grid contacts should be analyzed for obtaining a better estimate of the maximum concentration and uniformity of the dopant as well as dopant depth profile; lower sodium content superstrate glass should be used; and a more detailed investigation of adhesional strength, interface morphology and composition should be undertaken with an aim of establishing a base line and developing an understanding of the systemic problems.

5. CONCLUSIONS

The average adhesional shear strength at silicon cell/EVA interface in damp-heat, acceleration-tested modules was ~27% of that measured in new modules. The average carbon concentration at the surface of samples extracted from acceleration tested modules was 15 atomic % or ~30% of that measured in new modules. Surface concentrations of sodium on Si-cell samples from the acceleration tested modules ranged from 4.9 to 22.0 atomic % while those of phosphorous ranged from 4.3 to 7.1 at. %. These are very high impurity concentrations. Often significant concentrations of phosphorous were detected at the interface between titanium oxide antireflection coating and silicon cell. All the samples, that showed low surface concentrations of carbon, had low adhesive strengths. Moreover, high sodium and phosphorous concentrations always correlated with low adhesional strengths. There was clear evidence of a direct correlation between carbon concentration and adhesional strength and an inverse correlation between sodium and phosphorous concentrations and adhesional strength. Similar correlation has been observed, at FSEC, in earlier studies on field deployed PV modules.

The phenomenon of chemically-assisted diffusion seems to be responsible for the excessively high sodium and phosphorous concentrations. The high P and Na concentrations point to a strong probability of the formation of compounds such as sodium phosphates and hydro-phosphates. The high concentrations of precipitated impurities have resulted in complete delamination. The origin of the phosphorous surface concentrations was in the n-type doped Si layer. The sodium concentration arose from soda-lime glass superstrate. PV-module durability could be improved if precautionary measures are taken to control the sources of impurities into the structure of PV modules as well as if the diffusion of inadvertent impurities is limited.

It is recommended that excessive phosphorous concentration in doped n-type layer should be avoided; attempts should be made to obtain glass with lower sodium content; and attention should be paid to the overall diminution of the adhesional strength after accelerated-testing or field-deployment rather than focusing only on cases of delamination.

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