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Characterization of Ultrathin Layers in Perovskite/TOPCon Tandem Cells With Photoelectron Spectroscopy Utilizing Advanced Data Evaluation Methods

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Abstract. Next generation solar cells like tunnel oxide passivated contacts (TOPCon) or perovskite/TOPCon tandem solar cells require efficient interface passivation by ultrathin organic or inorganic layers to uncover their true efficiency potential. Especially the microstructure and the Si suboxide content of the tunnel oxide in poly-Si(O_x)/SiO_2/c-Si TOPCon stacks have been shown to have a tremendous influence on macroscopic device properties. Similarly, perovskite/ITO interface modification by a self-assembled monolayer (SAM) molecule is necessary to achieve high power conversion efficiencies of the perovskite sub cell. However, the characterization of such thin film structures and the interfacial composition is challenging. In this contribution, we present characterization results of ultrathin passivation layers using angle-resolved X-ray photoelectron spectroscopy (XPS) and advanced data evaluation routines, including maximum entropy methods and analyses of inelastically-scattered electron background data. In particular, the interfaces in the stacks (1) partially oxidized a-Si/SiO_2/c-Si and (2) 2PACz/ITO after different thermal treatment were investigated. It could be shown that already a ~5 nm thin SiN_x layer prevents unwanted oxidation from ambient during cooldown of TOPCon-like stacks and that annealing above 100 °C can convert a 2PACz multilayer to a 2PACz monolayer on an ITO substrate.

Keywords: Perovskite/Silicon Tandem, Passivation Layer, Photoelectron Spectroscopy

1. Introduction

Next generation solar cells like tunnel oxide passivated contacts (TOPCon) or perovskite/TOPCon tandem solar cells require efficient interface passivation by ultrathin organic or inorganic layers to uncover their true efficiency potential [1]. Especially the microstructure and the Si suboxide content of the tunnel oxide in poly-Si/SiO2/c-Si TOPCon stacks have been shown to have a tremendous influence on macroscopic device properties [2], [3]. Another crucial interface is that of a self-assembled monolayer (SAM) to the indium-tin oxide (ITO) used as recombination layer [4]. However, the characterization of such thin film structures like their thickness, substrate coverage and the interfacial composition is challenging. In this contribution, we present characterization results of ultrathin passivation layers using angle-resolved X-ray photoelectron spectroscopy (ARXPS) and advanced data evaluation routines. In particular, the interfaces in the stacks

(1) SiO_2 and partially oxidized amorphous silicon (O:aSi) deposited onto polished crystalline silicon substrates (c-Si) by plasma-enhanced chemical vapor deposition (PECVD).
(2) 2PACz deposited onto ITO-coated glass substrates by spin-coating with ex-situ or in-situ annealing.

were investigated. It will be shown how non-destructive chemical depth profiles with sub-nm resolution can be reconstructed using maximum entropy methods (MEM) and how thickness and coverage of those ultrathin layers can be determined independently by investigation of the inelastically-scattered photoelectron background signal. The methods are employed to investigate the influence of a specific ambient during cooldown of TOPCon-like stacks and to study the effects of annealing with temperatures exceeding 100 °C on 2PACz film formation on ITO substrates.

2. Experimental

SiO_2 and O:aSi were deposited onto polished c-Si substrates by PECVD. Afterwards, the samples were subjected to a predetermined cooling-rate in a not further specified ambient. Details about process parameters, maximum temperature and cooling speed cannot be disclosed.

2PACz was deposited onto commercial ITO-coated glass substrates by static spin-coating (100 µL of a 4 mmol solution in ethanol at 3000 rpm) and ex-situ annealed in air in a temperature range between 100 °C and 150 °C. Additionally, after the initial measurement, the 100 °C ex-situ annealed sample was heated in-situ within the vacuum chamber of the XPS up to temperatures of 500 °C to investigate if there is a difference between ex-situ and in-situ annealing.

XPS was performed in either a Kratos Axis Ultra DLD photoelectron spectrometer or in a Thermo Fischer Nexsa G2 in an angular range of 0° - 70° between surface normal and analyzer axis. XPS intensities and backgrounds were simulated analytically and compared to measured data using the Avantage ARProcess & Tougaard QUASES software packages. Values of inelastic mean free paths for spectral simulation were taken from the NIST Electron Effective Attenuation Length Database or calculated by the TPP-2M formula. Simulation of background shape and magnitude has been accomplished by combining the inelastic scattering cross-section of generic polymers (representing the SAM) with the universal cross-section of metals and oxides (representing ITO) by a suitable relative weighting. Relative errors in quantification of thicknesses are estimated to be below ~30%. Further results on the simulation and fitting routine will be given in a separate publication. (Scanning) transmission electron microscopy ((S)TEM) was performed with an image-corrected TEM/STEM FEI TITAN3 G2 60-300 operating at 300 kV and fitted with a 2k × 2k Ultrascan charge-coupled device camera (Gatan Inc.) for imaging in TEM mode.

3. Methodology

Two data evaluation methods have been employed for this study, that inherently use different information types one can obtain from a usual XPS spectrum, as explained below.

3.1 Method 1: ARXPS + Maximum Entropy Method (MEM)

Fig. 1 shows the principal methodology for data evaluation using MEM [5].

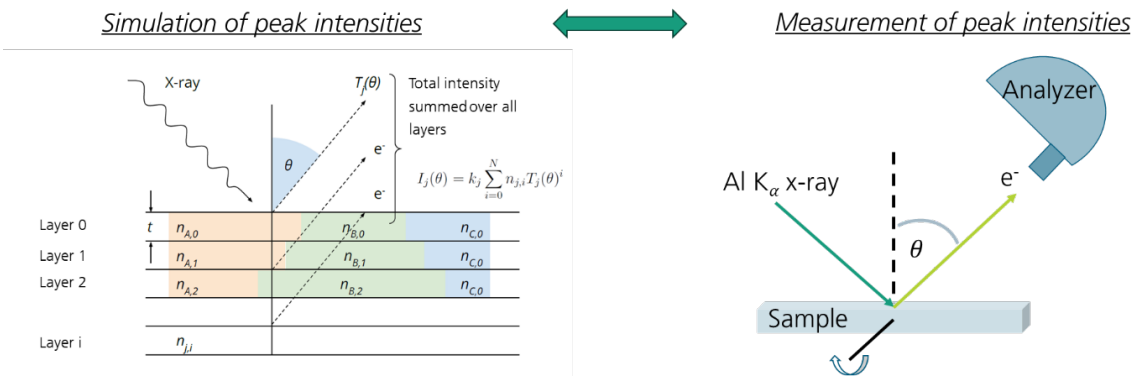

Figure 1. *Principle of data evaluation using MEM. The angle-dependence of XPS peak intensities is simulated and compared to measured intensities.*

In this kind of analyses, one is only concerned with photoelectrons that underwent elastic scattering processes before they have left the sample surface, i. e. the element- and chemical bonding specific characteristics XPS peaks that dominate the spectrum. A model is set up that approximates a sample with arbitrary depth-inhomogeneity in its composition of *j* chemical elements by a stack of *i* slices with thickness *t*, whereas the molar fractions are denoted as n_{ji} as shown in Fig. 1. The total intensity of a XPS peak from element *j* is then the sum of signals originating from all slices and is dependent on the angle θ between sample surface normal and photoelectron analyzer axis through the transmission function $T_j(\theta)$. The simulated dependence of peak intensities to electron emission angle is then compared to the measured intensities and the model is refined until a best and most probable match to the experimental data is achieved.

3.2 Method 2: XPS + Inelastic Background Analysis

Fig. 2 shows the principal methodology for data evaluation using the inelastic background.

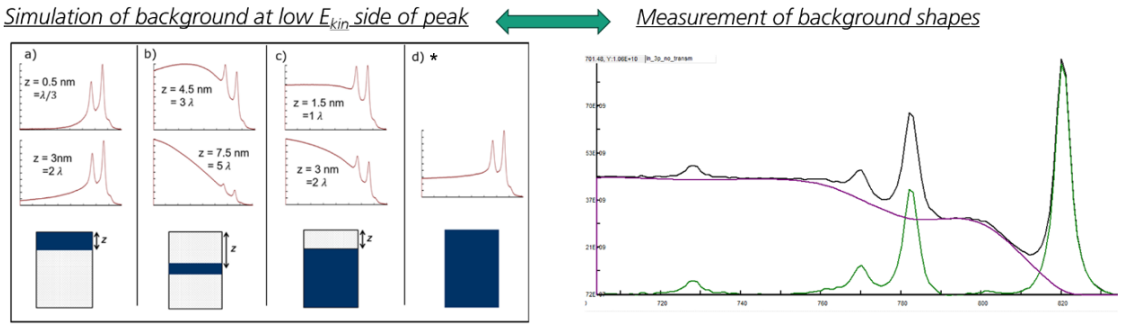

Figure 2. *Principle of data evaluation using inelastically-scattered photoelectron backgrounds. The background shape of the low kinetic energy side of a XPS peak for a specific surface nanostructure is simulated and compared to measured background shapes.*
**[6]*

Contrary to MEM-based data evaluation, one is not concerned with peak intensities, but rather with the background shape at the low kinetic energy side of XPS peaks that originates from inelastic scattering processes of photoelectrons after their excitation and during the way to the sample surface. As illustrated in Fig. 2, the background shape and magnitude are dependent on the sample nanostructure (conformal overlayer, buried layer, coated substrate, homogeneous material or e. g. nanoparticles on a substrate) and the material itself (through the inelastic mean free path λ and the inelastic scattering cross-section). Notably, different surface nanostructures can lead to same elastic peak intensities, and a differentiation is then only possible due to vastly different background signals. For the data evaluation, a nanostruc-

tural sample model is set up, the background signal is simulated and compared to the measured background shape. The model is iteratively refined until the best fit to the measured data is obtained.

4. Results

4.1 Application Case 1: SiO_2/c-Si Interface in TOPCon Bottom Cell

The objective here was to investigate the impact of a specific ambient during sample cooldown after deposition of SiO_2 and O:aSi onto a c-Si substrate and to evaluate the effectiveness of a thin SiN_x barrier layer.

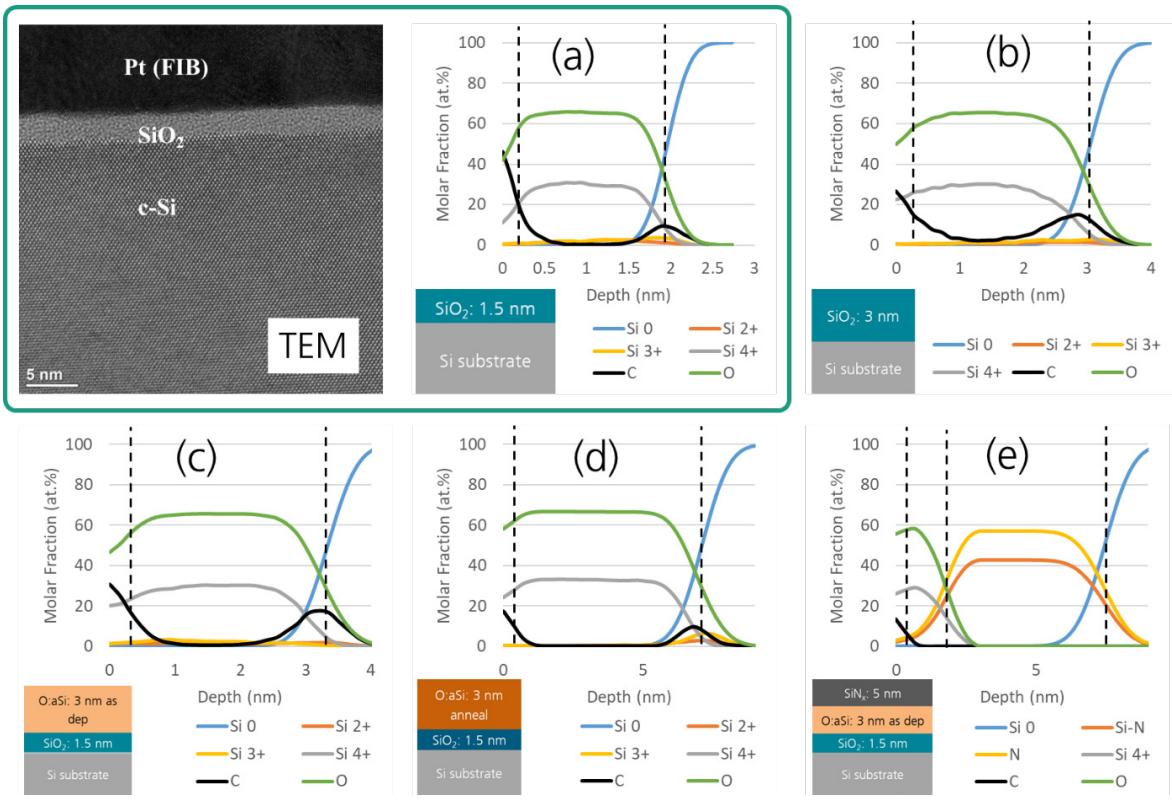

Figure 3. *Reconstructed depth profiles from ARXPS measurements of different (nominal) sample types as depicted in the lower left of each graph. The thickness of the SiO_2 layer of sample (a) was also measured with TEM (left image) as benchmark method. Samples (d) and (e) experienced a thermal cooldown in a specific ambient. Dashed vertical lines indicate interfaces between layers as well as surficial contamination.*

Fig. 3 visualizes MEM-reconstructed depth profiles of different samples in terms of chemical bonding types. In (a), a high-resolution TEM (HR-TEM) micrograph of nominally 1.5 nm SiO_2 on c-Si is shown. The amorphous SiO_2 can be distinguished from the c-Si and the Pt protection layer by the different mass-thickness-contrast. It is continuous and a thickness of 1.95±0.18 nm can be deduced. (a) also depicts the corresponding non-destructive chemical depth profile. From that, additionally to the TEM image, one can differentiate between chemical states of the overlayer: it consists of an adsorbate layer of ~0.24 nm thickness and the stoichiometric SiO_2 layer of 1.57 nm thickness, together yielding a total overlayer thickness of 1.81 nm. The thickness determined from TEM and ARXPS agree within 0.2 nm. As deposited O:aSi (c) is almost fully oxidized (compare to the nominally 3 nm thick oxide in (b)). Low amounts of suboxide species (Si in oxidation state +1, +2, +3) are present within the layer. The cooldown phase oxidizes the O:aSi and c-Si further (d). During that, the suboxide species and C content within O:aSi are removed. As shown in (e), a SiN_x layer of already 5 nm thickness prevents

unwanted oxidation of O:aSi and c-Si from the ambient, whereas the SiN_x surface itself became partially oxidized.

Note that the ARXPS information limit is approximately 6-7 nm in that material system and the Si^0 signal of sample (e) (here originating from O:a-Si) is already almost at the limit of detection and hence prone to a larger error. At this stage, the methodology has to be combined with destructive depth profiling techniques.

4.2 Application Case 2: 2PACz/ITO Interface in Perovskite Top Cell

In literature, the SAM layers often receive an annealing treatment of 100 °C [7], [8]. However, little is known about what influence a higher temperature can have on the 2PACz properties. The objective of this study was to investigate the impact of annealing with temperatures $T \geq 100$ °C on 2PACz thickness and coverage after wet-chemical deposition.

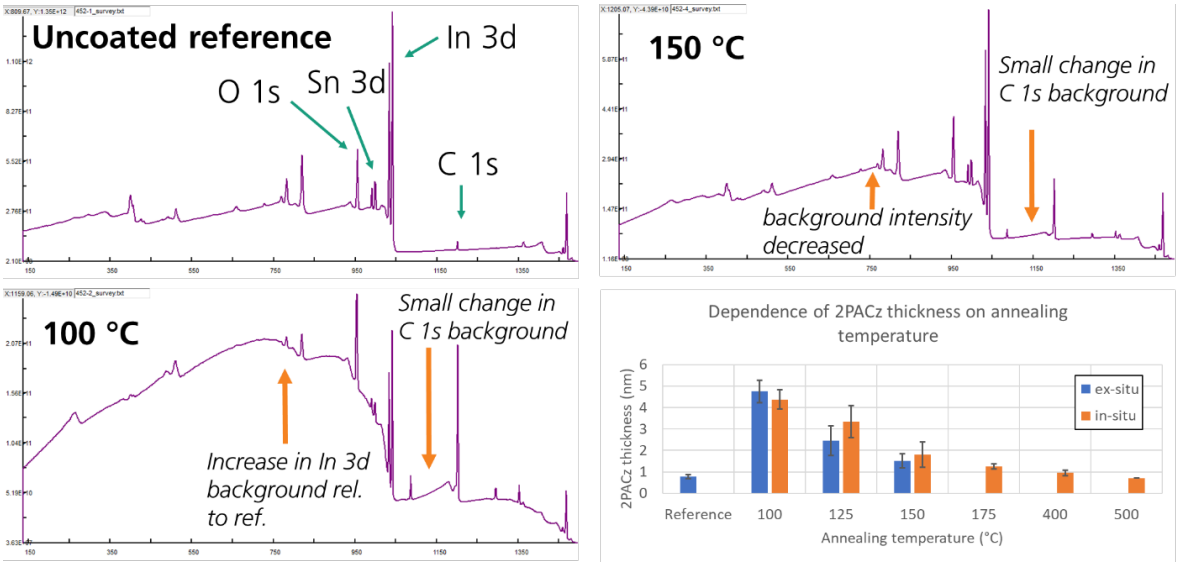

Figure 4. *XPS survey spectra of uncoated ITO substrate reference (top left) and 2PACz/ITO samples after annealing at 100 °C (bottom left) and 150 °C (top right), respectively. The effect of annealing temperature on 2PACz thickness is given in the bottom right diagram.*

As one can see for the uncoated ITO reference sample (Fig. 4, top left), the XPS survey spectrum consists of O, In, Sn peaks related to ITO. Furthermore, there is a small C 1s peak that is attributed to adventitious carbon from the atmospheric handling of the samples. The inelastically-scattered background left of the In 3d peak is relatively flat. For the 2PACz coated ITO sample after annealing at 100 °C (Fig. 4, bottom left), there is a pronounced C 1s peak with fading background, but the background of the In 3d peak increased significantly in intensity compared to the reference, forming a hill-like structure. For annealing temperatures greater than 100 °C, the background shape of In 3d gradually declines until almost the same background shape as that of the uncoated reference is reached at 150 °C (Fig. 4, top right), although a prominent C 1s peak is still present. The experiment was repeated by in-situ heating the 100 °C (ex-situ) annealed sample again at 100 °C and then successively at higher temperatures. Qualitatively, the same results as for full ex-situ annealing were obtained.

The surface nanostructure has been modelled and compared with the experimental results as described in section 3.2. It has been found that the best fits of the simulated and measured background shape of the In 3d peak are obtained for layer coverages in the range of 90 – 100 %. The quantified layer thicknesses depending on the annealing temperature are shown in Fig. 4, bottom right. At around 100 °C annealing temperature, the 2PACz thickness lies in the range 4 – 5 nm and is reduced with T. Our hypothesis is that at 100 °C 2PACz is not

present as monolayer, but rather as a multilayer stack. Increasing the temperature then removes loosely bound molecules. At 150 – 175 °C and above, the determined 2PACz thickness is in good accordance with the thickness of ~ 1 nm one would expect for a 2PACz monolayer. Also note the good agreement in quantified thicknesses from ex-situ and in-situ annealing.

5. Conclusion

ARXPS coupled with MEM and QUASES inelastic background analyses are powerful tools to study ultrathin passivation layers in modern and emerging solar cell technologies. Both methodologies deliver non-invasive quantifiable chemical depth information. However, ARXPS is only feasible to be applied to (ideally atomically) flat samples. This requirement was met by the SiO_2/c-Si-related layer stack that we studied. We could show how a certain post-deposition treatment led to unwanted oxidation of O:aSi and thickening of the SiO_2 tunnel oxide, and that a ~5 nm thin SiN_x is a good barrier preventing unwanted oxidation. However, single-crystal photoelectron diffraction effects can modulate measured intensities in this material system, making the data evaluation more difficult and uncertain. Another drawback of the method is that one usually needs to assume either a certain layer coverage or a certain layer thickness – both parameters cannot be determined independently from such a measurement/analysis. That is different for QUASES inelastic background analyses, that has been applied successfully to 2PACz/ITO model stacks. The method enables to independently quantify thickness and coverage of such an organic overlayer by use of suitable bulk reference samples. Also rough surfaces are not as critical as with ARXPS and the information depth is greater, since inelastically-scattered electrons originate from deeper into the sample. Using the QUASES method, we were able to measure the 2PACz thickness on ITO in dependence of the annealing temperature for $T \geq 100$ °C by ex-situ as well as in-situ heating. At 100 °C we determined 2PACz thicknesses well above that of a monolayer, gradually decreasing for higher temperatures and reaching monolayer values at around 150 – 175 °C.

Author contributions

Stefan Lange: Writing – review & editing, Writing – original draft, Visualization, Methodology, Investigation, Formal analysis, Conceptualization. **Carl Eric Hartwig:** Writing – review & editing, Writing – original draft, Visualization, Methodology, Investigation, Formal analysis, Conceptualization. **Oussama Er-Raji:** Writing – review & editing, Writing – original draft, Visualization, Methodology, Investigation, Formal analysis, Conceptualization. **Patricia S.C. Schulze:** Writing – review & editing, Project administration, Funding acquisition. **Marko Turek:** Writing – review & editing. **Juliane Borchert:** Writing – review & editing, Project administration, Funding acquisition.

Competing interests

The authors declare that they have no competing interests.

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