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Hard x-ray photoelectron spectroscopy study of the buried Si/ZnO thin-film solar cell interface: Direct evidence for the formation of Si–O at the expense of Zn-O bonds

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The chemical structure of the interface between silicon thin films and the transparent conductive oxide ZnO:Al has been investigated by hard x-ray photoelectron spectroscopy. By varying the excitation energy between 2010 and 8040 eV, we were able to probe the Si/ZnO interface buried below 12 nm Si. This allowed for the identification of changes induced by solid phase crystallization (SPC). Based on *in-situ* SPC annealing experiments, we find clear indications that the formation of Si–O bonds takes place at the expense of Zn–O bonds. Hence, the ZnO:Al acts as the oxygen source for the interfacial Si oxidation. © *2011 American Institute of Physics*. [doi:10.1063/1.3644084]

State-of-the-art thin-film solar cells are complex multilayer devices. Hence, their power conversion efficiencies not only depend on the material quality of each deposited film but also on the proper design of the interfaces.[1] By depositing amorphous silicon (a-Si), which is solid-phase crystallized (SPC) during an annealing process at 600–650 °C (Ref. 2) (a-Si → polycrystalline silicon, "poly-Si"), one combines the advantages of a high-quality absorber layer and low-cost processing. One major challenge of this solar cell concept is the implementation of a transparent conductive oxide (TCO) window layer, which would facilitate an easy electric contact and light trapping.[3–5] So far the proposed Al/a-Si:H(p^+)/poly-Si(p)/poly-Si(n^+)/ZnO:Al/glass device structure[3] yields lower efficiencies than the standard device without ZnO:Al. This suggests that either the Si(n^+)/ZnO:Al ("Si/ZnO") interface is not properly designed or/and that its properties deteriorate during subsequent annealing processes. Nevertheless, it was observed that the electrical properties of the ZnO:Al improved due to the heat treatment.[4] First, x-ray spectroscopy experiments[6,7] indeed indicate that the SPC treatment has an impact on the chemical Si/ZnO interface structure, but could not completely clarify the underlying reaction mechanism. In this letter, we employ photoemission and its unique capability in chemical speciation combined with hard x-ray excitation allowing for the study of relevant buried Si/ZnO interfaces i.e., the Si top layer is sufficiently thick to form the same interface structure as present in a *real-world* Si thin-film solar cell layer stack. Note that a Si thin film of sufficient thickness is also a prerequisite to separate surface from interface effects. The combination of our hard x-ray photoelectron spectroscopy (HAXPES) measurements with *in-situ* annealing experiments furthermore aids in the elucidation of the chemical changes induced by SPC.

For our experiments, phosphorous-doped a-Si:H(n+) layers of approximately 12 nm thickness were deposited by plasma-enhanced chemical vapor deposition (PECVD) at 190 °C on 800 nm ZnO:Al, which was previously deposited on Corning Eagle XG® glass substrates by rf-magnetron sputtering. After the deposition, one sample was SPC-treated, i.e., heated in a furnace under continuous N_2 flow for 24 h at 650 °C (annealed "*ex-situ*"). Another sample remained untreated ("as-deposited") to serve as reference for the chemical interface structure before SPC. A third sample was used for our *in-situ* study. Here, the as-deposited layer stack was investigated before and after *in-situ* annealing in the analyzer chamber for 24 h at about 650 °C under ultra-high vacuum (UHV) conditions (base pressure $<3 \times 10^{-9}$ mbar). Hereafter, this sample is referred to as heated "*in-situ*". An oxidized phosphorous-doped single-crystalline Si wafer was investigated as reference. The HAXPES measurements were conducted at the KMC-1 beamline[8] of the BESSY II synchrotron facility using the HIKE endstation.[9] By varying the excitation energy (hν) between 2010 and 8040 eV, the electron inelastic mean free path (IMFP) was varied between 0.7 and 10.6 nm (Ref. 10) enabling the characterization of the buried Si/ZnO interface.

Fig. 1 shows the Si 1s photoemission spectra of the as-deposited and *ex-situ* annealed Si/ZnO samples for different hν. The Si 1s spectra are dominated by two main contributions, which we attribute to Si–Si ("Si $1s^{\text{Si–Si}}$") and Si–O_X ("Si $1s^{\text{Si–Ox}}$") bonds.[11] For an easier comparison, the presented photoemission spectra are normalized to the maximum intensity and aligned to the energetic position of the Si $1s^{\text{Si–Si}}$ feature. After annealing, a slight narrowing of the Si $1s^{\text{Si–Si}}$ signal can be observed. This can be explained by the SPC-induced conversion of a-Si into poly-Si. This is confirmed by the 6030 eV Si 1s spectrum of a single-crystalline Si wafer reference shown in Fig. 1 (blue line). Note that the narrowing can in particular be observed for the measurements in the high-resolution energy range of the

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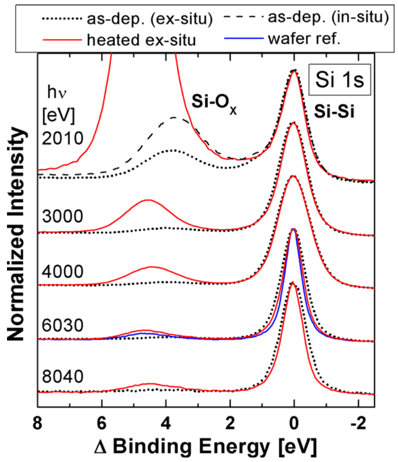

FIG. 1. (Color online) Si 1s photoemission spectra (normalized to maximum intensity) for different excitation energies (hν). The spectra collected for the Si/ZnO stack of the *ex-situ* experiment are shown as dotted black (as-deposited) and solid red (heated) lines. In addition, the 2010 eV "as-deposited" spectrum of the layer stack of the *in-situ* experiment is shown (dashed black line) for comparison. Furthermore, the 6030 eV spectrum of an oxidized Si wafer is presented (solid blue line) for reference. Si–O$_X$ indicates silicon to oxygen bonds.

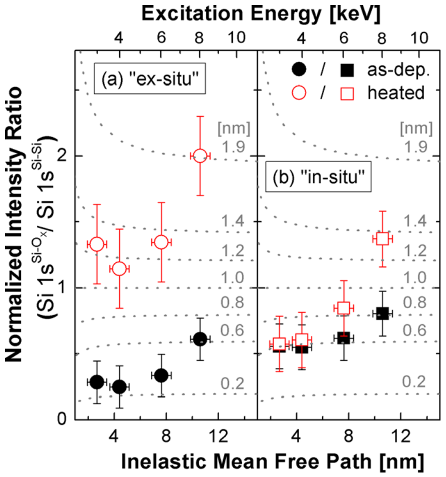

FIG. 2. (Color online) SIRs of the Si/ZnO layer stacks normalized to the respective ratios of an oxidized Si wafer reference. The intensity ratios are shown for the as-deposited samples (black solid symbols) and after annealing (red open symbols) for (a) the *ex-situ* and (b) the *in-situ* experiment as a function of IMFP (the corresponding excitation energies are given at the top). The grey dotted lines indicate the SIR vs. IMFP characteristic as expected for different surface oxide thicknesses given by the grey numbers.

experimental setup.[9] Furthermore, after SPC, the Si 1s^{Si-Ox} signal increases strongly, which clearly indicates that the sample further oxidizes during *ex-situ* SPC. With increasing hν, the Si 1s^{Si-Ox} photoemission signal decreases. This finding suggests that surface oxidation predominates. In order to investigate whether the Si-O$_X$ bond formation exclusively takes place at the sample surface or also at the Si/ZnO interface, the hν–dependent behavior of the Si 1s^{Si-Ox}/Si 1s^{Si-Si} intensity ratio (hereafter referred to as "SIR") of the Si/ZnO layer stack is compared to that of a reference system in which Si–O$_X$ bonds are exclusively present at the surface: an oxidized Si wafer. For details on the quantification procedure, see supplemental material (A).[12] The thickness of the surface oxide layer d_{wafer} was found to be (1.0 ± 0.2) nm [see supplemental material (B)[12]]. In order to evaluate whether the hν–dependent behavior of the Si 1s^{Si-Ox} contribution (and its SPC-induced increase) of the Si/ZnO samples (see Fig. 1) can also be explained by a mere surface oxidation; the SIRs of the Si/ZnO thin-film layer stacks have been normalized to the respective ratios of the oxidized Si wafer reference. The normalized SIRs of the *ex-situ* (a) and *in-situ* (b) experiment before ("as-deposited") and after SPC annealing ("heated") are shown in Fig. 2. A thinner (thicker) surface oxide layer than that found for the oxidized Si wafer reference results in normalized SIRs <1 (>1). The much higher SIR of the *ex-situ* heated Si/ZnO sample (compared to that of the as-deposited sample, see Fig. 2(a)) can thus be interpreted as an SPC-induced increase of surface oxidation. For the *in-situ* heated Si/ZnO samples, no pronounced SPC-induced surface oxidation is observed (Fig. 2(b)). Generally, it can be observed that the normalized SIRs increase with IMFP for all samples. As there is no obscuring additional surface oxidation for the *in-situ* experiment, it can be observed that this increase is more pronounced after heating. The fact that the normalized SIRs agree for low IMFP, but significantly deviate for high IMFP, may indicate a silicon oxidation mechanism that is not covered by the here considered surface oxidation bi-layer model.

In order to investigate the oxidation mechanism further, Eq. (1)—which is based on the suggested bi-layer model—has been used to calculate the expected normalized SIR vs. IMFP characteristic for different surface oxide layer thicknesses "d" shown as grey dotted lines in Fig. 2 for $0.2 \leq d \leq 1.9$ nm.

$$\frac{\left(\frac{I_{Si-Ox}}{I_{Si-Si}}\right)_{sample}}{\left(\frac{I_{Si-Ox}}{I_{Si-Si}}\right)_{wafer}} \propto \frac{\exp\left(\frac{d}{IMFP}\right)-1}{\exp\left(\frac{1.0\ nm}{IMFP}\right)-1} \qquad (1)$$

Direct comparison of the expected with the experimental data reveals a disagreement in all cases. Thus, the hν-dependent behavior of the SIR cannot solely be explained by surface oxidation and thus is indicative for an additional silicon oxidation. The fact that the SIR increases with increasing IMFP points to oxidation at the Si/ZnO interface. Note that the slight increase of the normalized SIR with IMFP for the as-deposited samples may be indicative of a slight interface oxidation already during deposition or is caused by the finite Si layer thickness [see supplemental material (C)[12]]. The much more pronounced SIR increase after SPC, however, clearly indicates a SPC-induced interface oxidation. These findings are in good agreement with results of our earlier studies.[7]

In order to shed more light on the chemical structure of the Si/ZnO interface and how it changes upon SPC annealing, we analyze the Si 1s and O 1s spectra at hν = 6030 eV in more detail (Fig. 3). Comparing the high-binding energy contribution of the 6030 eV Si 1s photoemission line for the Si/ZnO samples of the *ex-situ* and *in-situ* experiment (Fig. 3(a)), it can be observed that after SPC, the signal is shifted to higher binding energies such that it agrees with the position of the high-binding energy contribution of the oxidized Si wafer. Assuming a "complete" oxidation of the Si wafer surface, we attribute the high-binding energy Si 1s contribution as being

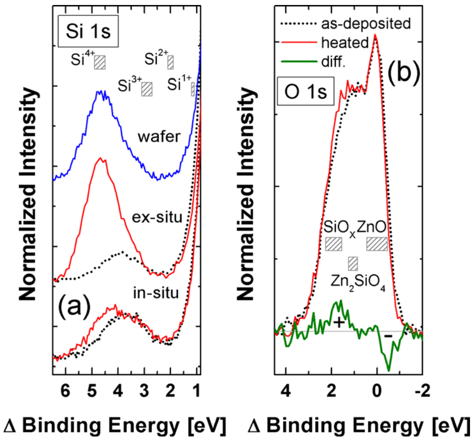

FIG. 3. (Color online) (a) High-binding energy Si 1s contribution (normalized to the Si $1s^{Si–Si}$ contribution) measured at 6030 eV excitation energy of the Si/ZnO samples of the *in-situ* and *ex-situ* experiment as well as of an oxidized Si wafer. Dotted black and solid red lines are before and after heat treatment, respectively. (b) 6030 eV O 1s photoemission spectra (normalized to peak area) shown after background subtraction for the Si/ZnO sample of the *in-situ* experiment. The difference spectrum ("diff" = "heated" − "as-deposited)" is also shown. Hatched boxes indicate binding energy reference values for possibly formed chemical species (see Refs. 11–18).

indicative for SiO_2. Since Si 1s binding energy reference positions for different Si species are scarce in literature, we transferred the respective well-known Si 2p positions of silicon oxides[11] to the Si 1s binding energy region for speciation [see supplemental material (D)[12]]. In Fig. 3(a), the respective reference positions for different Si species are shown as hatched boxes. Comparison of the experimental data with the energetic reference positions reveals that the degree of oxidation is increased as a result of the SPC treatment. Note that the Si 1s binding energy of Zn_2SiO_4 would also agree with the position of the observed high-binding energy Si 1s contribution (in particular of the as-deposited Si/ZnO samples) and hence its presence can also not be excluded.[13,14] Interestingly, this more complete oxidation can also be observed for the *in-situ* annealed samples. In order to identify the source of oxygen, we focus on the O 1s photoemission spectra of the as-deposited and *in-situ* annealed Si/ZnO sample (Fig. 3(b)) in the following analysis. We find that the O 1s signal is a superposition of (at least) two contributions. While the contribution at lower binding energies can be attributed to ZnO, the contribution at higher binding energies is ascribed to Si–O_X bonds. Again Zn_2SiO_4 can also not be excluded. Close inspection reveals that the high-binding energy shoulder becomes more pronounced after heating. The respective difference spectrum ("diff." = "heated" – "as-deposited" in Fig. 3(b)) indicates an SPC-induced increase of Si–O_X bonds ("+") at the expense of Zn–O bonds ("–"). While the first observation agrees with our interpretation of the increase and shift of the high-binding energy Si 1s contribution, the latter may point to a reduction of ZnO by the SPC annealing step. Thus, ZnO may act as an oxygen source for the observed oxidation of Si at the Si/ZnO interface. The extent to which the identified SPC-induced interface oxidation is related to the increase of the charge carrier concentration which is often observed for SPC heated silicon-capped ZnO:Al films[4,19] has to be investigated in more detail in the future. However, we speculate that removing oxygen from the ZnO:Al could very well have an impact on the concentration of intrinsic defects (e.g., oxygen vacancies) or the activation of extrinsic dopants.

In summary, we have employed hard x-rays to be able to probe the chemical structure of relevant buried Si/ZnO interfaces and their change upon SPC annealing using photoemission. Eliminating the obscuring influence of additional surface oxidation by performing *in-situ* experiments and using a sophisticated analysis approach for the HAXPES data, we find evidence for SPC-induced silicon oxidation at the Si/ZnO interface. Furthermore, it is revealed that the increase of Si–O_X bonds takes place at the expense of Zn–O bonds, which points to ZnO:Al as the oxygen source for the interface oxidation. Whenever a ZnO:Al TCO window layer is introduced into a poly-Si thin-film solar cell based on SPC, both findings have to be considered for device optimization.

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