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### Title

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### Publication Date

2010-08-17

### DOI

10.1063/1.3462316

Peer reviewed

# Impact of solid-phase crystallization of amorphous silicon on the chemical structure of the buried Si/ZnO thin film solar cell interface

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The chemical interface structure between phosphorus-doped hydrogenated amorphous silicon and aluminum-doped zinc oxide thin films is investigated with soft x-ray emission spectroscopy (XES) before and after solid-phase crystallization (SPC) at 600 °C. In addition to the expected SPC-induced phase transition from amorphous to polycrystalline silicon, our XES data indicates a pronounced chemical interaction at the buried Si/ZnO interface. In particular, we find an SPC-enhanced formation of Si–O bonds and the accumulation of Zn in close proximity to the interface. For an assumed closed and homogeneous SiO<sub>2</sub> interlayer, an effective thickness of (5 ± 2) nm after SPC could be estimated.

□

Polycrystalline silicon (poly-Si) is a promising absorber material candidate for low-cost, high efficiency thin film solar cells. An attractive approach to obtain poly-Si at relatively low process temperatures is solid-phase crystallization (SPC) of hydrogenated amorphous silicon (a-Si:H).<sup>1</sup> Solar cell mini modules (94 cm<sup>2</sup>) based on poly-Si prepared by the SPC process have already demonstrated efficiencies of up to 10.4% by utilizing a complex point contact design.<sup>2</sup> If this contact structure could be replaced by a transparent conducting oxide (TCO), the manufacturing process would be greatly simplified and an easy series interconnection scheme using laser scribing would become possible; both would aid large-scale mass production needed for commercialization. In addition, by texturing the TCO, one could easily improve light trapping. For these reasons, an Al/a-Si:H(p<sup>+</sup>)/poly-Si(p)/poly-Si(n<sup>+</sup>)/ZnO:Al/glass device structure was recently suggested.<sup>3</sup> This design, however, involves a high-temperature annealing step (SPC at 600 °C), which leads to significantly higher electron mobilities in the capped ZnO:Al layer<sup>4</sup> but could also induce chemical interaction/diffusion processes at/across the Si/ZnO interface. Hence, this letter presents a soft x-ray emission spectroscopy (XES) investigation of the buried Si/ZnO interface before and after SPC.

For our experiments we used Borofloat<sup>®</sup> borosilicate glass covered with an approximately 80 nm thick Si<sub>3</sub>N<sub>4</sub> layer (as diffusion barrier) as the substrate. As TCO a 900 nm ZnO:Al layer rf-sputtered onto the substrate was used [sample (i)]. Subsequently, 50 nm thin films of phosphorus-doped a-Si:H(n<sup>+</sup>) were deposited by plasma-enhanced chemical vapor deposition (PECVD) at approx. 200 °C [sample (ii)]. For more details about sample preparation see

Ref. 2. After a-Si:H(n<sup>+</sup>) deposition, some samples underwent SPC at 600 °C for 24 or 72 h in a tube furnace under N<sub>2</sub>-flow [samples (iii<sub>24</sub>) and (iii<sub>72</sub>)]. A schematic presentation of the investigated samples is shown in Fig. 1. To identify and eliminate spectral contributions of native silicon oxides at the Si thin film surfaces, XES measurements were performed before and after sample etching in hydrofluoric (HF) acid (30 s in 5% aqueous HF-solution). Reference materials (single crystalline Si as well as SiO<sub>2</sub> and ZnO powders) were characterized for comparison. XES measurements at the Si L<sub>2,3</sub> and O K edge were conducted at the ALS using the soft x-ray fluorescence spectrometer of Beamline 8.0.1. The Si L<sub>2,3</sub> (O K) spectra were calibrated with Si and SiO<sub>2</sub> reference spectra (SiO<sub>2</sub> reference spectra and the Zn L<sub>2,3</sub> emission

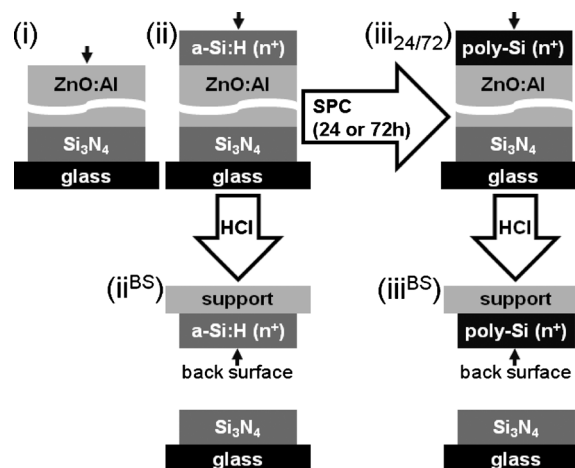


FIG. 1. Schematic presentation of the investigated samples: (i) bare ZnO:Al substrate, (ii) a-Si thin film (before SPC), (iii<sub>24</sub>) or (iii<sub>72</sub>) poly-Si layer (after 24 and 72 h SPC), and respective Si back surfaces (ii<sup>BS</sup>) and (iii<sup>BS</sup>) (after ZnO:Al dissolution in HCl). The small black arrows indicate the probing direction.

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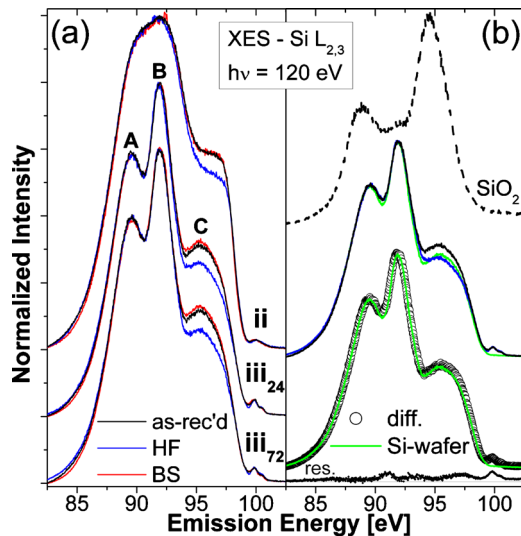


FIG. 2. (Color online) (a) Normalized Si  $L_{2,3}$  emission of *as-received* (“*as-rec’d*”), *HF-etched* (“*HF*”), and *back surface* (“*BS*”) samples (ii), (iii)<sub>24</sub> and (iii)<sub>72</sub>. (b) Direct comparison of the spectra of the *as-received* and *HF-etched* sample (iii)<sub>72</sub> with those of SiO<sub>2</sub> (top) and Si-wafer (center and bottom) references. A computed difference spectrum [“*diff.*” = “*as-rec’d*(iii)<sub>72</sub>” – 0.07 × “*SiO<sub>2</sub>*”, open circles] and its residuum (“*res.*” = “*diff.*” – “*Si wafer*”) are also shown at the bottom.

of ZnO detected in second order).<sup>5–7</sup> The effective attenuation lengths ( $\lambda^*$ ) for the Si  $L_{2,3}$  and O  $K$  emission roughly correspond to 0.5 and four times the Si layer thickness, respectively.<sup>8</sup> Hence, the Si  $L_{2,3}$  spectra are dominated by the *near-surface* material properties of the Si layer and the O  $K$  measurements primarily probe the chemical structure of the TCO *bulk*. In order to increase the sensitivity of our XES measurements in the Si/ZnO interface region, two different approaches were followed. (1) For the Si  $L_{2,3}$  measurements, the ZnO:Al TCO was dissolved in concentrated (37%) HCl to expose the Si thin film back surface (BS). The Scotch<sup>®</sup> tape-stabilized BS samples [schemes (ii)<sup>BS</sup> and (iii)<sup>BS</sup> in Fig. 1] were thoroughly rinsed in several rinsing baths to prevent redeposition of Zn due to dissolved ZnO residues in the used etch/rinsing solutions. For these BS samples, Zn  $L_{2,3}$  XES spectra were also measured. (2) The O  $K$  emission measurements were conducted at “grazing” (10°) incidence, resulting in a reduced information depth.

In Fig. 2(a), Si  $L_{2,3}$  XES spectra of samples (ii), (iii)<sub>24</sub>, and (iii)<sub>72</sub> are compared. XES spectra of *as-received*, *HF-etched*, and BS samples are presented in black, blue, and red, respectively. According to previous XES studies,<sup>9,10</sup> the different Si  $L_{2,3}$  emission spectra in Fig. 2 indicate the expected phase transition from amorphous Si before SPC [spectra (ii)], to poly-Si after SPC [spectra (iii)]. Following Rubensson *et al.*,<sup>5</sup> the three Si  $L_{2,3}$  main features A–C observed for spectra (iii) are ascribed to electrons from Si 3s (A), hybridized *s-p* (B), and 3*p*-derived states (C) decaying into the Si 2*p* core holes. The difference in the Si  $L_{2,3}$  spectra (i) can be explained by the broadening of these contributions due to the amorphous nature of the material. The origin of the small features at approx. 100 eV has been vividly discussed<sup>10</sup> but is still widely unknown to date. A conclusive clarification is the aim of ongoing research and will be the topic of a later publication.

An intensity decrease at 95–98 eV can be observed after HF-etching for all samples. To investigate this in more detail, the spectra of the *as-received* and *HF-etched* sample (iii)<sub>72</sub>

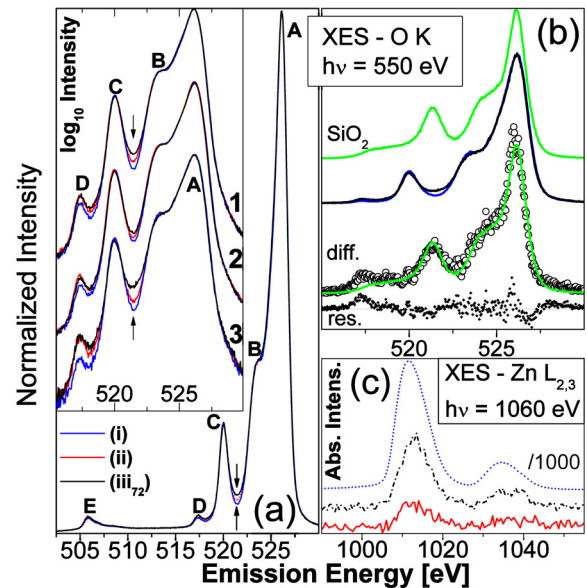


FIG. 3. (Color online) (a) O  $K$  XES spectra of sample (i) and *as-received* samples (ii) and (iii)<sub>72</sub>. Inset: O  $K$  spectra of *as-received* [spectra (1)] and *HF-etched* Si thin film samples measured under regular [spectra (2)] and grazing incidence conditions [spectra (3)], on a logarithmic scale. (b) Comparison of the (grazing incidence) O  $K$  spectra of sample (i) and the *HF-etched* sample (iii)<sub>72</sub> with a SiO<sub>2</sub> reference. In addition, a weighted difference spectrum [“*diff.*” = “*sample*(iii)<sub>72</sub>” – 0.86 × “*sample*(i)”, open circles] and the residuum (“*res.*” = “*diff.*” – “*SiO<sub>2</sub>*”) are shown. (c) Comparison of the Zn  $L_{2,3}$  XES spectrum of sample (i) (dotted line, divided by 1000) with back surface samples (ii)<sup>BS</sup> and (iii)<sup>BS</sup> (solid and dashed/dotted line, respectively).

are directly compared with a clean Si wafer (green spectrum) in Fig. 2(b), center. The spectrum of the *HF-etched* sample (iii)<sub>72</sub> agrees very well with that of the Si-wafer. A comparison with the Si  $L_{2,3}$  emission of a SiO<sub>2</sub> reference (dashed spectrum, top) reveals that the intensity difference between the spectra of the *as-received* and *HF-etched* sample is in the same spectral range as the maximum of the SiO<sub>2</sub> Si  $L_{2,3}$  emission. In order to test whether a SiO<sub>2</sub> contribution is the explanation for the observed intensity difference, a suitably weighted Si  $L_{2,3}$  difference spectrum [“*as-received*” (iii)<sub>72</sub> – 0.07 × “*SiO<sub>2</sub>*”] was computed. The direct comparison with the Si-wafer [Fig. 2(b), bottom] indicates an excellent agreement with low residuum (“*diff.*” – “*Si wafer*”). Hence, the observed variations in the Si  $L_{2,3}$  intensity at 94–98 eV are an indicator for (varying degrees of) Si–O bond formation. As a result, we interpret the higher intensity in that spectral region observed for the *as-received* samples as the well-known formation of SiO<sub>2</sub> on Si surfaces exposed to ambient air. Interestingly, a small but significant intensity increase in that energy range can also be observed in the BS spectra of the *as-received* samples which underwent SPC [spectra (iii)<sub>24</sub> and (iii)<sub>72</sub>, Fig. 2(a)], while no significant difference can be observed for the Si  $L_{2,3}$  emission of the *as-received* and BS sample before SPC [spectra (1)]. This might be a first indication of an SPC-induced formation of Si–O bonds at the Si/ZnO interface.

To test the Si–O interface bond formation hypothesis, the corresponding O  $K$  XES spectra (Fig. 3) are discussed next [for brevity, we will focus on the 72 h SPC sample (iii)<sub>72</sub> only]. Figure 3(a) shows the O  $K$  emission for sample (i) and the *as-received* samples (ii), (iii)<sub>72</sub> as blue, red, and black spectra, respectively. The spectra are dominated by five dis-

tinct features A–E. A, B, and C are ascribed to electrons from hybridized O  $2p$ –Zn  $4p$ , Zn  $4s$ , and Zn  $3d$  states, respectively, decaying into the O  $1s$  core hole.<sup>11</sup> Features D and E, in contrast, are attributed to Zn  $L_{2,3}$  emission (detected in second order of the spectrometer, see also Ref. 12). All three spectra are very similar and resemble quite well that of a ZnO reference.<sup>13</sup> Only a direct comparison reveals a small but significant intensity difference in the energy region between feature B and C at approximately 521.5 eV [indicated by arrows in Fig. 3(a)]. The O  $K$  spectra of the *as-received* samples plotted on a logarithmic scale in the inset of Fig. 3(a) [spectra (1)] show very clearly that the dip at 521.5 eV becomes less pronounced in the following sample order: (i)  $\rightarrow$  (ii)  $\rightarrow$  (iii<sub>72</sub>). The same comparison after HF-etching of samples (ii) and (iii<sub>72</sub>) [spectra (2)] confirms this order, yet the differences are less pronounced. Under grazing incidence conditions [spectra (3)], the most pronounced intensity difference in the dip region is observed. Note that the higher intensity of feature D for samples (ii) and (iii<sub>72</sub>) is due to the larger attenuation length of the Zn  $L_2$  emission,<sup>8</sup> which results in a less pronounced attenuation and hence in an intensity increase relative to features A, B, and C upon capping sample (i) with the Si thin films. Since grazing incidence conditions decrease the information depth,<sup>8</sup> this effect is even more pronounced in spectra (3).

To understand the intensity variations in the dip at 521.5 eV, the grazing incidence O  $K$  emission of sample (i) and (iii<sub>72</sub>) is directly compared to that of a SiO<sub>2</sub> reference (green spectrum) in Fig. 3(b). The dip energetically coincides with a local intensity maximum of the O  $K$  emission of SiO<sub>2</sub>, which is ascribed to hybridized O  $2p$ –Si  $3p$  states. As for the Si  $L_{2,3}$  emission, we compute a difference spectrum [“sample(iii<sub>72</sub>)”–0.86 $\times$  “sample(i)”] to test whether the observed spectral variations in the dip could be explained by a SiO<sub>2</sub> contribution. The excellent agreement of the derived difference with the SiO<sub>2</sub> O  $K$  XES reference spectrum affirms this hypothesis. Note that the statistically most pronounced feature in the residuum is due to the Zn  $L_2$  attenuation effect discussed above.

Thus, we interpret the intensity variation observed at 521.5 eV for spectra (1) in the inset of Fig. 3(a) as indicative of surface oxidation of the *as-received* samples. This oxidation is removed by HF-etching, minimizing the intensity variation in spectra (2). The most pronounced intensity variation found for the grazing incidence measurements [spectra (3)] then gives further evidence for the formation of Si–O bonds at the Si/ZnO interface. Even for sample (ii) a higher intensity can be observed in the considered spectral range, which suggests a formation of interfacial Si–O bonds already during silicon deposition. This agrees well with other a-Si:H/ZnO interface studies.<sup>13</sup>

Assuming that a closed, homogeneous SiO<sub>2</sub> interfacial layer is formed between the deposited (SPC treated) Si thin films and the ZnO:Al layer, an effective thickness  $d$  can be estimated.<sup>8</sup> We find the SiO<sub>2</sub> interface layer thickness to be  $(1 \pm 1)$  nm before and  $(5 \pm 2)$  nm after SPC. This is similar to thickness values of interfacial SiO<sub>2</sub> layers identified in ZnO/Si-wafer structures.<sup>14</sup>

In addition to the discussed Si  $L_{2,3}$  and O  $K$  XES spectra, Zn  $L_{2,3}$  XES spectra of the BS samples were also recorded. Figure 3(c) shows the corresponding spectra for BS samples

(ii<sup>BS</sup>) and (iii<sup>BS</sup>) in comparison to sample (i) (divided by 1000). Zn  $L_{2,3}$  emission signals can be identified on both silicon BS samples, most strongly for sample (iii<sup>BS</sup>). Apart from a potential presence of ZnO:Al residues, this could be interpreted as an (SPC-enhanced) accumulation of Zn close to the Si/ZnO interface. Since metallic Zn is well soluble in HCl (just like ZnO), Zn is either incorporated into the Si or has formed an HCl resistant compound. Considering our findings on the enhanced Si–O bond formation at the interface, this might suggest a (SPC-enhanced) formation of a Zn<sub>2</sub>SiO<sub>4</sub> interface species (as discussed for ZnO/Si-wafer structures<sup>15</sup>).

In summary, we have used soft XES to investigate the chemical structure of the buried Si/ZnO interface before and after SPC. With a combination of different sample treatments and measurement geometries, as well as selected XES lines of different information depths, the (SPC-enhanced) formation of Si–O bonds and the accumulation of Zn in the proximity of the Si/ZnO interface were revealed. The potential presence of Zn-incorporated silicon (with significantly altered electronic properties) and/or a wide-gap interlayer (e.g., SiO<sub>2</sub> or Zn<sub>2</sub>SiO<sub>4</sub>) in the solar cell structure could have significant consequences for the photovoltaic performance and needs to be considered in next optimization steps.

The authors thank Forschungszentrum Jülich and CSG Solar for providing the ZnO:Al/Si<sub>3</sub>N<sub>4</sub>/glass substrates. This work (the ALS) was supported by the Federal Ministry for the Environment, Nature Conservation and Nuclear Safety under Contract No. 0327693H (the Department of Energy, Basic Energy Sciences, Contract No. DE-AC02-05CH11231).

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