Initial stages of ITO/Si interface formation: In situ x-ray photoelectron spectroscopy measurements upon magnetron sputtering and atomistic modelling using density functional theory

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Initial stages of ITO/Si interface formation: \textit{In situ} x-ray photoelectron spectroscopy measurements upon magnetron sputtering and atomistic modelling using density functional theory

O. M. Løvvik, S. Diplas, A. Romanyuk, and A. Ulyashin

SINTEF Materials and Chemistry, Forskningsveien 1, NO-0314 Oslo, Norway
University of Basel, Kingelbergstr. 82, CH-4056 Basel, Switzerland

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Initial stages of indium tin oxide (ITO) growth on a polished Si substrate upon magnetron sputtering were studied experimentally using \textit{in situ} x-ray photoelectron spectroscopy measurements. The presence of pure indium and tin, as well as Si bonded to oxygen at the ITO/Si interface were observed. The experimental observations were compared with several atomistic models of ITO/Si interfaces. A periodic model of the ITO/Si interface was constructed, giving detailed information about the local environment at the interface. Molecular dynamics based on density functional theory was performed, showing how metal-oxygen bonds are broken on behalf of silicon-oxygen bonds. These theoretical results support and provide an explanation for the present as well as previous \textit{ex situ} and \textit{in situ} experimental observations pointing to the creation of metallic In and Sn along with the growth of SiO\textsubscript{x} at the ITO/Si interface. © 2014 AIP Publishing LLC.

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I. INTRODUCTION

A. TCO-Si heterojunctions

It is well established that indium tin oxide (ITO), deposited under appropriate conditions, is a degenerate n-type semiconductor with low resistivity and high transmission in the visible range of the solar spectrum. In general, transparent conducting oxides (TCO) such as ITO and ZnO:Al are widely used for different types of solar cells, both as antireflection coatings and transparent conducting electrodes due to their attractive combination of electrical and optical properties. TCO thin films deposited on any p-type semiconductor material like Si, copper indium gallium selenide, etc., form heterojunctions, which can be used for fabricating efficient solar cells. In most of these applications, the quality of interfaces limits the performance of solar cells and other electronic devices in which transport of electrical current through TCO/Si interfaces is required. As was noticed in Ref. 2, the use of two chemically different semiconductors, which is the characteristic feature of heterojunction solar cells, introduces a new set of problems not encountered in homojunction cells, such as: (i) chemical compatibility and stability, (ii) reproducibility of the chemical and physical interface, and, in the case of crystalline and polycrystalline materials, (iii) lattice compatibility at the metallurgical junction. Thus, interfaces play an important role in photovoltaic systems based on heterojunctions containing ITO, since a significant and increasing part of charge carrier losses is due to defects at the interfaces. It is interesting to note that already long time ago it was reported that efficient ITO/Si solar cells can be made when ITO is deposited on both n- and p-type Si substrates.\textsuperscript{3,5}

Previous research on TCO (ITO, SnO\textsubscript{2})/Si solar cells indicated that the junction between two semiconductors can be considered as a metal-insulator-semiconductor (MIS) (Schottky-barrier) device, since it is expected that a thin SiO\textsubscript{x} layer formed at the TCO/Si interface during processing of such type of solar cell structures can determine their properties.\textsuperscript{3} Indeed, TCO/SiO\textsubscript{x}/n-Si solar cell structures in which thin SiO\textsubscript{x} layers were purposely formed by heating the Si wafers at temperatures below 600 °C or by immersing them in a chemical solution have been intensively investigated in the past.\textsuperscript{6-8} Remarkable progress for TCO/n-Si solar cells has been demonstrated by SANYO using an ultra thin (few nm) p+ a-Si:H buffer layer between the TCO top electrode and the n-type Si substrate.\textsuperscript{9,10} It has to be noticed that in the latter case, formation of a thin oxide layer at the interface between ITO and a-Si:H occurs. Thus, no single mechanism can explain so far the performance of several ITO/Si based solar cell structures. It is most probable that a number of mechanisms (including heterojunctions and Schottky barriers) are responsible for the efficiency of all types of TCO/Si based solar cells with different types of buffer layers. It is necessary to note that the conversion efficiency of TCO/Si based solar cells depends crucially on the properties of these buffer layers as well as interfaces, which can be strongly influenced and regulated by chemical pre-treatment of Si substrates, deposition conditions, as well as prior- and post-deposition heat treatments of Si substrates and processed solar cell structures.\textsuperscript{11-19}

B. ITO-Si interfaces

The properties of the interfaces depend strongly on the properties of the TCO layers grown. It is known that ITO forms upon substitution of In for Sn at the In sub-lattice in the In\textsubscript{2}O\textsubscript{3} structure up to a tin content of approximately 10%. This implies the presence of Sn\textsuperscript{3+} and thus an excess of negative fixed charge. At higher tin content, a network of stoichiometric In\textsubscript{4}Sn\textsubscript{3}O\textsubscript{12} starts to form; this time with Sn being
present as Sn\(^{4+}\). The latter compound does not have the desired properties, and its formation should thus be avoided. Nevertheless, detailed knowledge about the electronic and geometric structure of this compound is essential, since its accidental formation may affect the properties and the subsequent performance of the TCO film.

Rhombohedral In\(_2\)Sn\(_3\)O\(_{12}\) can be formed by, e.g., electron-beam evaporation,\(^{20}\) magnetron sputtering,\(^{21}\) or isothermal annealing of In\(_2\)O\(_3\) and SnO\(_2\) nanopowders.\(^{20,22}\) The band gap of single-crystalline In\(_2\)O\(_3\) was for a long time a source of controversy,\(^{23,24}\) but has recently been determined to be 2.93 \(\pm\) 0.15 and 3.02 \(\pm\) 0.15 eV for the cubic bixbyite and rhombohedral polymorphs, respectively.\(^{25,26}\) The band gap of ITO is about 3.5 eV\(^{27,28}\) and depends on the composition and deposition conditions.\(^{29}\)

A (222) preferential orientation of ITO was seen in thin films grown by thermal evaporation in vacuum.\(^{30}\) However, the texture of ITO films depends on the deposition method and processing conditions. For example, magnetron sputtered and electron beam deposited ITO films on amorphous and crystalline Si substrates are usually amorphous in the as-deposited state with the substrate being at room temperature (RT) during deposition, whilst they crystallize upon heat treatment and/or upon deposition at higher substrate temperatures. The crystalline films have in this case no preferred orientation.\(^{31,32}\) It is furthermore known that Sn segregates to the surface of Sn-doped In\(_2\)O\(_3\),\(^{33}\) and that metallic Sn-In in ITO can be formed after heat treatment,\(^{34}\) as well as upon electron beam evaporation.\(^{31,35,36}\) In the case of e-beam deposition, the amount of metallic In present in the amorphous as-deposited film decreases with increasing the incident angle of the ITO vapour to the Si substrate, with increasing the deposition temperature and/or the post deposition annealing temperature, as well as with reducing the deposition rate.\(^{35,36}\)

In a number of studies, the Si-ITO interface has been studied experimentally; see Refs. 31, 32, 37–42 and references therein. Early studies (e.g., Ref. 40) have attributed the thermal degradation of ITO/p-Si solar cell structures, which were fabricated by ion beam sputtering of an ITO target on both polycrystalline and single crystal Si substrates, to the formation of a SiO\(_2\) interfacial oxide. The formation of this oxide was connected to inwards oxygen diffusion through the ITO layer towards the Si substrate. However, no direct interfacial characterisation methods were employed to support these claims. The presence of a non-stoichiometric Si oxide at the interface has been reported for ITO deposited on HF-etched Si substrate by x-ray photoelectron spectroscopy (XPS) and depth profiling with Ar\(^{+}\) sputtering.\(^{39}\) Recent studies employing a combination of transmission electron microscopy (TEM) and XPS on thin and ultra-thin ITO films deposited on Si have shown the formation of a mixed In-Si oxide along the ITO-Si interface where Si does not participate in its formal stoichiometry (i.e., SiO\(_2\)).\(^{31}\) Ex-situ XPS and TEM studies\(^{41}\) on ITO films deposited on p-Si (100) substrates by dc magnetron sputtering revealed the presence of amorphous In clusters at the interface associated with oxygen deficiency in the ITO film. A recent in-situ XPS study\(^{42}\) (similar to the one presented in this paper) of ITO grown on p-Si showed the presence of elemental In and Sn as well as Si sub-oxides.

C. Ab initio modelling

There have been a few previous first-principles modelling studies of ITO. Sn-doped In\(_2\)O\(_3\) was studied with density functional theory (DFT) for Sn contents of 12.5% by Odaka \textit{et al.},\(^{43}\) 6.25% by Mryasov and Freeman,\(^{44}\) between 3% and 37.5% by Brewer and Franzen\(^{45}\) while Tripathi \textit{et al.} used 6.25% Sn in their DFT calculations on ITO.\(^{46}\) Agoston \textit{et al.} used hybrid DFT-Hartree Fock potentials to calculate the solubility of Sn in In\(_2\)O\(_3\),\(^{47}\) which was in good correspondence with the experimental solubility of around 6%. Inerbaev \textit{et al.} studied defect clusters in ITO by DFT calculations,\(^{48}\) and a recent study by Bai \textit{et al.} investigated several different doping sites of Sn in In\(_2\)O\(_3\) and concluded that the preferable site is substituting for In.\(^{49}\) Some studies have also focused at the atomistic properties of Si-oxide interfaces. The Si-SiO\(_2\) interface was the first one to be studied by DFT.\(^{50,51}\) Examples of similar studies include descriptions of band alignment and defect levels in the Si-HfO\(_2\) interface studied with DFT,\(^{52}\) and band offsets in different Si-oxide interfaces calculated with hybrid DFT-HF calculations.\(^{53}\) To our knowledge, less activity has been devoted to the atomistic modelling of the ITO-Si interface.

In this work, in order to investigate the initial stages of ITO growth on crystalline Si, we performed in-situ XPS measurements upon magnetron sputtering of such layers on polished crystalline Si. DFT modelling has been used to support experimentally observed facts concerning the formation of ITO/Si interfaces.

II. EXPERIMENTAL

ITO ultra thin layers with different thicknesses were deposited onto a polished mono-crystalline p-type Si (100) oriented surface. Prior to deposition, 2% HF dip has been applied to remove the native oxide. The substrate was rinsed in deionized water and blown dry with nitrogen. Afterwards, the substrate was transferred quickly into a magnetron sputtering chamber, which was integrated with a VG ESCALAB 210 spectrometer. The spectrometer was equipped with a monochromatized Al K\(\alpha\) (1486.6 eV) radiation source. The energy positions of the spectra were calibrated with reference to the Au 4f\(_{7/2}\) level of a clean gold sample positioned at 84.0 eV binding energy.

ITO layers with thicknesses of 0.5, 1.5, and 3 nm were deposited by RF magnetron sputtering at nominally RT. XPS analysis was performed in-situ after deposition to each of the above thicknesses. The in-situ measurements allowed us to study the ITO film and the ITO-Si interfacial growth avoiding the complications present in ex-situ measurements due to sample contamination or Ar sputtering effects. The thickness of the deposited layers was controlled by a quartz microbalance system, which was calibrated by ellipsometry and TEM measurements of the deposited ITO layers. An ITO sintered target with In\(_2\)O\(_3\) and SnO\(_2\) in a weight proportion of 9:1 was used. The base pressure in the sputter system was about 1.33 mPa (10\(^{-5}\) Torr). The total pressure of sputtering
gas mixture was adjusted to 0.399 Pa (3 mTorr) during the film preparation. Only pure Ar gas was used upon the sputtering. The RF plasma power was about 50 W.

III. MODELLING: METHODOLOGY AND APPROACHES

DFT calculations were performed using the Vienna \textit{ab initio} Simulation Package (VASP).\textsuperscript{54,55} The generalized gradient approximation (GGA) was employed, using the PBE potential.\textsuperscript{56} It is well-known that this level of theory often significantly under-estimates band gaps, and it is possible to remedy this by using more expensive hybrid calculations including Hartree-Fock exchange or by self-energy \textit{GW} calculations.\textsuperscript{57} However, the primary output from this work is based on molecular dynamics (MD), geometric structures, and relative energies, none of which depend on the band gap. Band gaps beyond GGA are thus beyond the scope of this work. The valence electron configuration of the potentials was $5s^2 5p^1$ (In), $5s^2 5p^2$ (Sn), $2s^2 2p^4$ (O), and $3s^2 3p^2$ (Si). The criterion for self-consistency was a difference of less than $10^{-5}$ eV of the calculated total electronic energy $E_{tot}$ between two consecutive electronic iterations. A \textit{k}-point distance of $0.20 \text{Å}^{-1}$ was sufficient to achieve numeric convergence of $E_{tot}$ within 1 meV. A similar convergence was obtained for a plane-wave cut-off energy of 800 eV; this value was only used for single point high-accuracy calculations. A cut-off energy of 400 eV was used for all relaxations and molecular dynamics calculations. This was found to be sufficient for numeric convergence of forces within 0.05 eV/Å; the criterion for structural relaxation was similarly that all calculated forces should be below 0.05 eV/Å. A quasi-Newton formalism was used for the force relaxation, using the residual minimization method direct inversion in iterative subspace (RMM-DIIS) technique. When the number of electrons was even, the calculations were spin-restricted, since no magnetic material was included. Some of the Sn-doped In$_2$O$_3$ (ITO) models were exceptions; then it was necessary to allow for spin polarization to accommodate the odd number of electrons. In these models, a background charge was also added, to compensate for the extra electrons added to the system by Sn. DFT-based MD calculations were performed on an interface model using the following temperature profile: heating for 2.5 ps at a temperature $T = 1000 \text{K}$ followed by quenching from $T = 1000 \text{K}$ to 100 K during 90 ps and then relaxed. The time step was 2.5 fs.

IV. RESULTS AND DISCUSSION

A. \textit{In situ} XPS measurements for initial stages of ITO on Si growth

Fig. 1 displays high resolution Si 2p, In 3d, and Sn 3d spectra acquired during deposition of ITO on polished p-type crystalline Si. The absence or limited amount of Si oxide is seen prior to deposition (lowest Si 2p spectrum on the left). In the early stages of deposition (0.5 nm), SiO$_x$ starts forming accompanied with formation of metallic In and Sn as seen by the low binding energy shoulders of the In and Sn 3d peaks. It should be noted that the energy separation between the Si 2p main peak and the oxide component is $\sim 3.0 \text{eV}$ which is less than that corresponding to SiO$_2$. This should be attributed to the small interfacial oxide thickness\textsuperscript{58} and/or to an oxidation state less than $4^+$. There is an enhanced presence of metallic In and Sn in the early stages of deposition (0.5 nm). The presence of metallic In and Sn indicates that at the early stages of deposition the deposited oxidized In and Sn species from the ITO target are reduced upon deposition on the Si substrate. The Gibbs free energies $\Delta G^0$ for the formation of In$_2$O$_3$, SnO$_2$, and SiO$_2$ are $-827$, $-516$, and $-855 \text{kJ/mol}$, respectively.\textsuperscript{59} There is thus a thermodynamic driving force to oxidize Si on behalf of Sn and to a less extent In. Therefore, from a thermodynamic point of view, an oxide free Si substrate could take up oxygen and reduce the above species by forming SiO$_x$ when in contact with ITO. However, kinetic factors influenced by deposition parameters such as the deposition (substrate) temperature and the angle of incidence (Refs. \textsuperscript{35} and \textsuperscript{36}) are expected to play a significant role.
a significant role. As an example, surface diffusion would determine the time available for reduction of In and for Sn depositing species and subsequent oxidation of Si substrate as well as influencing clustering of the atoms of the reduced species. The energy separation between Si 2p and Si oxide upon deposition and after a film thickness 1.5 nm remains at about 3.3 eV which is smaller than those reported for thin SiO₂ films on Si. We attribute this low value to the mixed nature of the interfacial oxide where the contribution of the trivalent In is significant. The presence of a mixed interfacial oxide or the presence of SiOₓ (x < 2) has been also reported in previous studies.³¹,⁴²

To clarify the mechanism of SiOₓ and pure metallic In and Sn species formation at the ITO/Si interface, several atomistic models were thus made in correspondence with previous studies.³¹,⁴² The experimental crystal structure of ITO is in the cubic Ia 3 space group (No. 206),⁶⁰ and most of the sites are partially filled. Even the average number of atoms in each unit cell (UC) differs from whole numbers, as can be seen in Table I. This means that we have to choose whole numbers as closely as possible to the average number of atoms when creating supercell models of ITO. In practice, this means that we choose the number of atoms according to the rightmost column of Table I. We substitute, e.g., one of the In₁ and one of the In₂ atoms with Sn to create a 6.25% Sn filled model. Also, we neglect the partially filled O₂ position in our calculations, which may serve to compensate the charge carried by tin substitutions under oxidizing conditions. We thus create three such models, with 1–3 Sn atoms substituting for In. We first substitute on the Sn₂ site, then Sn₁, and finally on Sn₁. The Sn atoms are placed by maximizing the Sn-Sn distance, assuming effective repulsive interaction between Sn atoms in the lattice, according to test calculations not presented here. The atomistic model with 6.25% Sn is shown in Fig. 2.

### TABLE I. Atomic positions in ITO with 6.25% Sn.⁶⁰

<table>
<thead>
<tr>
<th>Type</th>
<th>Wyckoff position</th>
<th>Occupancy</th>
<th>Number of atoms in exp. UC</th>
<th>Number of atoms in model UC</th>
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</thead>
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<tr>
<td>In₁</td>
<td>8b</td>
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<td>7.2</td>
<td>7</td>
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<tr>
<td>Sn₁</td>
<td>8b</td>
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<td>0.8</td>
<td>1</td>
</tr>
<tr>
<td>In₂</td>
<td>24d</td>
<td>0.95</td>
<td>22.8</td>
<td>23</td>
</tr>
<tr>
<td>Sn₂</td>
<td>24d</td>
<td>0.05</td>
<td>1.2</td>
<td>1</td>
</tr>
<tr>
<td>O₁</td>
<td>48e</td>
<td>1</td>
<td>48</td>
<td>48</td>
</tr>
<tr>
<td>O₂</td>
<td>16c</td>
<td>0.032</td>
<td>0.5</td>
<td>0</td>
</tr>
</tbody>
</table>

### B. Tin-doped In₂O₃ (ITO)

We first need to establish models of tin-doped indium oxide (ITO) in order to create Si/ITO surfaces in the next section. The focus of this was to achieve an appropriate geometric structure, without regarding electronic band properties beyond what is relevant for the geometry. The atomistic models were thus made in correspondence with previous first-principles studies on ITO.⁴³–⁴⁹ The experimental crystal structure of ITO is in the cubic Ia 3 space group (No. 206),⁶⁰ and most of the sites are partially filled. Even the average number of atoms in each unit cell (UC) differs from whole numbers, as can be seen in Table I. This means that we have to choose whole numbers as closely as possible to the average number of atoms when creating supercell models of ITO. In practice, this means that we choose the number of atoms according to the rightmost column of Table I. We substitute, e.g., one of the In₁ and one of the In₂ atoms with Sn to create a 6.25% Sn filled model. Also, we neglect the partially filled O₂ position in our calculations, which may serve to compensate the charge carried by tin substitutions under oxidizing conditions. We thus create three such models, with 1–3 Sn atoms substituting for In. We first substitute on the Sn₂ site, then Sn₁, and finally on Sn₁. The Sn atoms are placed by maximizing the Sn-Sn distance, assuming effective repulsive interaction between Sn atoms in the lattice, according to test calculations not presented here. The atomistic model with 6.25% Sn is shown in Fig. 2.

Relaxation of the ITO models is relatively straightforward, since cubic symmetry is maintained even when all lattice parameters are allowed to relax without any restrictions (the maximal deviation from cubic symmetry is 0.03% of the lattice constants and 0.08° of the angles). The structures are thus fully relaxed; the results of those relaxations are shown in Table II.

We see from Table II that both the total electronic energy and the average lattice constant vary almost linearly with the Sn content. This is expected due to the difference in binding energy between Sn-O and In-O and due to the larger size of the Sn atom.

### C. Interface between ITO and Si

We then create an atomistic model of the ITO/Si interface using the ITO models discussed above as the starting point for the oxide. There is always a challenge to find matching lattice constants when two crystalline surfaces are to be joined at an interface. A very good fit was found between the hexagonal (111) surface of Si and a sublattice of the hexagonal (111) surface of cubic ITO. In order to fit the number of atoms, a part of the (111) surface unit cell was chosen, containing seven In atoms and one Sn atom. Three such layers were added, with one Sn atom in each layer. Six Si layers were attached to this, giving a unit cell with 108 atoms and orthorhombic symmetry. No vacuum was added between any layers, so this actually represents a repeating structure with two interfaces defined by 8 and 9 Å thick ITO and Si slabs, respectively, as shown in Fig. 3. The Sn content

![FIG. 2. The ITO model with 6.25% Sn, that is with two Sn atoms per unit cell. In and Sn atoms are shown as large grey and yellow balls, while O atoms are shown as small red balls.](image-url)
is 12.5%, which is slightly higher than the models discussed in the previous section. The O content is similar to that of undoped In$_2$O$_3$.

This model is then used as input to molecular dynamics calculations. Molecular dynamic calculations can be used to probe and predict interfacial changes occurring upon, e.g., thermal treatments such as deposition at elevated temperatures, post deposition air annealing, etc., of ITO-Si structures. Figure 3 shows the model before and after a molecular dynamics calculation consisting of heat treatment followed by quenching and relaxation (see Sec. III for details). The calculations were performed spin restricted without extra background charge, since it was found that this did not influence the calculated forces significantly. It is seen that significant changes in the geometric structure occurred during the simulations, particularly at the lower interface in Fig. 3. Several Si-O bonds were created, and some oxygen atoms even moved into the Si slab; the number of Si-O bonds (with distance \( <1.8 \text{ Å} \)) is increased from 6 to 18 during the MD simulation. This was accompanied by a reduction of the nearby metal atoms, of which several oxygen bonds were broken. The number of In-O bonds (with distance \( <2.8 \text{ Å} \)) was reduced from 5.2 per atom to 4.2 per atom; this means that 21 bonds between In and O were broken, primarily at the interface. The number of Sn-O bonds (with distance \( <2.8 \text{ Å} \)) was already 5.0 per atom and was not reduced any further during MD simulation. (The number of metal-oxygen bonds is 6 per atom in bulk ITO.) While there is not yet metallic In or Sn in the model after 90 ps, there is a clear tendency towards reduction of the metal oxides, particularly the In oxide. This is consistent with the experimental findings, where a similar tendency is found—in that case reduction of both oxidised Sn and In is seen, only more pronounced for In.

This result is apparently not consistent with the relative stability of the oxide phases cited above (tin oxide being the least stable and SiO\(_2\) only slightly more stable than In\(_2\)O\(_3\)). One could speculate that this is due to kinetics: if the kinetics of Sn diffusion is slower than that of In, this could explain the difference. Since the atomic radius of metallic Sn is smaller than that of metallic In, it cannot be explained by diffusion of metal atoms forming clusters. The remaining option is that Sn-O clusters diffuse faster than In-O clusters towards the Si surface when arriving onto the Si substrate, so that the reduction rate of Sn oxide is slower than that of In oxide.

Another possible explanation is associated with the thermodynamics of the ternary and quaternary systems which may be drastically different from that of the binary oxides; this may lead to the simplified arguments based on the stability of binary oxides not being valid anymore. Finally, there may be hydrogen atoms present in the experiments, which can change the thermodynamics or kinetics of this system significantly. The Si substrate has been subjected to HF treatment and H has passivated dangling bonds. One possible effect is that H preferentially reduces oxidised In and to a lesser extent Sn. However, even if H plays such a role this is not applicable in the simulations as H was not taken into account. All the explanations above remain speculative, since there is no experimental or theoretical support for anyone.

We should furthermore keep in mind that the DFT-MD models in this study do not exactly simulate the growth of the interface upon impingement of oxidised species on Si substrates. It rather simulates the changes of an initially formed ITO-Si interface upon temperature variations. The presence of metallic In and Sn is associated with nanoclusters (as has been shown, e.g., in Ref. 41) which form most probably mainly by surface diffusion. The DFT-MD model in the present study refers to bulk rather than surface diffusion. This may explain why we do not see formation of metallic bonds (clustering) within the duration of the simulation as bulk diffusion is slower than surface. Moreover, the MD calculations were only performed for a few picoseconds, so many effects on a larger timescale may have been left out by the calculations.

In any case, it is interesting that the experiments and calculations consistently demonstrate that the stability of binary oxides is not sufficient information to predict the qualitative behaviour of complicated systems like the present ones. In addition, the experiments and calculations in the present study clearly show that there is a tendency to form SiO\(_2\) at the interface, which is also consistent with previously reported work. \textsuperscript{31,35,36,42,61}

V. CONCLUDING REMARKS

Initial stages of ITO growth on a polished Si substrate upon magnetron sputtering were studied experimentally using \textit{in-situ} XPS measurements. The presence of pure indium and tin as well as Si bonded to oxygen related peaks at the ITO/Si interface was detected confirming previous results from \textit{ex-situ} and a recent \textit{in-situ} study. Several atomistic models of ITO as well as an ITO/Si interface were constructed in order to interpret the experimental findings.

Atomistic models of ITO were created by substituting Sn at the In sublattice, using the cubic In$_2$O$_3$ structure as starting point. It was found that the predicted lattice constant

![FIG. 3. The atomistic interface model between Si and ITO before (left) and after (right) a molecular dynamics simulation. The temperature profile of the simulation is described in Sec. III. The vertical axis corresponds to the (111) axis of both Si and ITO. The Si, In, Sn, and O atoms are represented as light blue, grey, orange, red balls, respectively.](image-url)
changed almost linearly with the Sn content, and that cubic symmetry was preserved. These models were used to construct an atomistic model of the Si/Ito interface. The Sn content in this model was 12.5% to ensure a homogeneous distribution of Sn atoms, and the model contained 108 atoms. Molecular dynamics calculations on this structure revealed that oxygen from ITO was attracted to the Si phase, initiating formation of SiO₂. Similarly, the first stage of metallic In and Sn formation was indicated via several metal-O bonds being broken in the MD models.

It is important to note that processes at the ITO/c-Si interface discussed and simulated above should not depend on the type of conductivity of the Si substrate. Formation of a thin SiO₂ layer at the ITO/c-Si interface produces a MIS nanostructure. It should be noted that formation of a thin SiO₂ layer, as well as pure In at the ITO/Si interface upon in-situ ITO deposition has been reported very recently in Ref. 42. Formation of a MIS structure provides an explanation for the long time ago experimentally established fact that degenerate n-type semiconductor ITO being deposited on n-type Si can be used for fabrication of high-efficiency ITO/n-Si heterojunction solar cells. These phenomena can be extremely useful for current activities, related to processing of Si nanowire based solar cells, in which an ultrathin emitter is an important issue.57,62,63 In particular, processing technology of such cells can be essentially simplified, if instead of a-Si:H based ultrathin emitter, which has been used in Refs. 57, 62, and 63, only an ITO layer will be deposited at special conditions, as discussed in Ref. 4.

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