

Tin Sensitization and Silver Activation on Indium Tin Oxide Surfaces

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Abstract

Adhesion of electrical contacts on electronic and optoelectronic devices is important for reliable device operation. Sn-sensitization is a widely used process that improves uniformity and adhesion of plated metals to glass and polymer surfaces. Electrically conductive substrates can significantly benefit from improved uniformity, adhesion, and contact resistance to metallic contact layers. In this study, we investigate the process of Sn-sensitization and Ag-activation on indium tin oxide (ITO) surfaces—a dominant transparent conducting oxide used in optoelectronic devices. Our results show that ITO films exposed to Sn-sensitization solutions with HCl concentrations below 10 mM effectively modify the surface termination through the process of Sn-sensitization (Sn-bonding at the surface hydroxide sites) without etching the ITO film. However, the subsequent Ag-activation on an ITO surface does not seem to follow the typical response on a glass substrate, suggesting that Ag-activation of an ITO surface is likely limited by the Ag ion size relative to the area density of surface hydroxide sensitization sites.

Keywords:

Surface modification, sensitization, activation, transparent conducting oxide.

1. Introduction

Transparent conducting oxides (TCO) are widely employed in flat panel displays, smart windows, and thin-film solar cells among numerous other optoelectronic devices [1–4]. Tin doped indium oxide (ITO) is a widely adopted TCO used in such devices due to ease of deposition, high conductivity, carrier concentration, and

transparency [4,5]. Most devices that rely on ITO as a transparent contact require a metallic electrode for effective injection and/or extraction of carriers, and their effectiveness relies on good physical and electrical contact between the ITO and the metal [6–8]. However, adhesion and bonding of metals to oxygen-terminated surfaces is inherently poor due to high chemical stability and thus low reactivity of the metal film surface, resulting in interface uniformity and durability challenges [6,9,10].

The process of sensitization and activation of oxide surfaces has been used for decades to improve uniformity and adhesion of metal coatings, such as Ag, Pt, or Pd to glass [11–13]. Several in-depth studies have thoroughly characterized the mechanisms behind the process of Sn-sensitization and subsequent activation on glass surfaces [11–13]. The mechanism of sensitization and activation processes of Ag or Pd on glass are sometimes assumed to be the same on other surfaces, such as epoxies, and even ITO [14,15]. For industrially relevant solar cell manufacturing, the use of expensive materials such as Pt or Pd is prohibitive. This work is motivated by the use of sensitization and activation on industrially relevant silicon heterojunction solar cells to improve adhesion of silver metallization to the ITO layer. Successful Sn-sensitization followed by Pd-activation on ITO has been reported, however the process of Sn-sensitization followed by Ag-activation on ITO has not yet been reported [6,16].

Notably, however, Sn-sensitization solutions can be problematic for TCO films since they are typically made with a solution of HCl in addition to SnCl₂, and D.I. water. ITO, for example, is significantly etched by HCl even in low concentrations such as the standard molarities reported for most Sn-sensitization solutions (0.1 M HCl, for example) [11,14,17]. Few studies have looked into Sn-sensitization on ITO, and none has examined

the etching damage induced to the surface as a result of HCl concentration in the sensitization solution [1,14]. Herein, we present a study that exposes ITO surfaces to Sn-sensitization solutions of various HCl molarities to examine the effects of the solution on the surface, including etching damage. To our knowledge, standard practices for Sn-sensitization and subsequent activation use concentrations of HCl that would damage ITO [18]. Here, we aim to study Sn-sensitization solutions with low HCl concentrations to prevent etching of the ITO films representative of those used in silicon heterojunction solar cell devices.

It should be emphasized that the mechanisms of Sn-sensitization and Ag-activation on glass surfaces rely on a multistep process, schematically shown on Figure 1. First, a sensitization solution is made by dissolving SnCl₂ in HCl and D.I. water. SnCl₂ readily dissociates in this solution following [19]:



The Sn-sensitization solution is then applied to the surface. Surface hydroxide sites react with SnCl₃⁻ complex ions in solution, leaving Sn²⁺ ions on the surface [11,12].

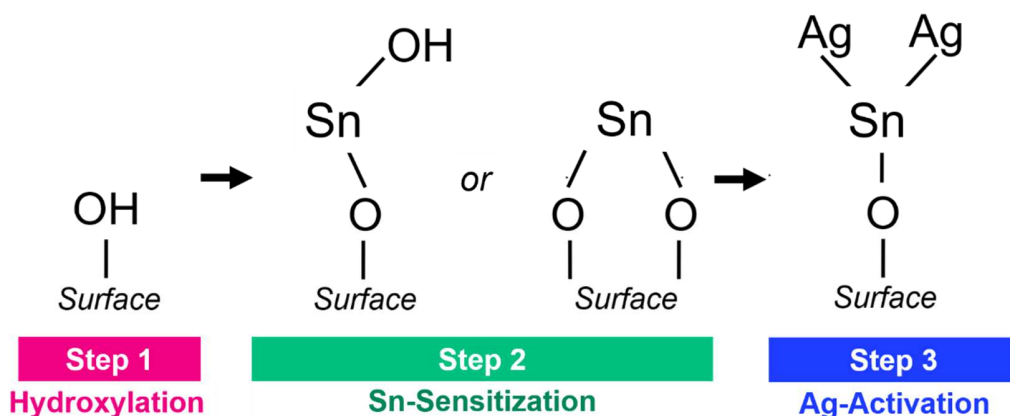


Figure 1. Simplified schematic showing the steps for Sn-sensitization and Ag-activation of a glass or ITO surface.

Thus, the first step—hydroxylation—provides -OH sites that react with SnCl_3^- ions in the sensitization solution.

Next, the surface is rinsed with deionized water to remove any remaining Cl^- or other Cl-containing residues [19,20]. At this point, the sensitized surface sites consist of Sn^{2+} bonded to two O atoms on the surface, or one O atom on the surface and a hydroxide provided by this rinse step [19,20]. Accordingly, the second step (Sn-sensitization in Figure 1) results in an increased Sn concentration at the surface, specifically Sn^{2+} [19–21]. Here, successful bonding of the Sn^{2+} to one or two O atoms on the surface is what is commonly known as “sensitization”.

Next, the Ag-activation solution is applied, and reacts with the Sn^{2+} following the redox reaction [19–21]:



Thus, during the third step for this process (Ag-activation in Figure 1) is 2 Ag^+ ions from solution reduce into metallic Ag and bond to a Sn^{4+} .

Based on the aforementioned steps required for Sn-sensitization and Ag-activation on glass, we evaluate both processes on ITO films, using Sn-sensitization solutions of varying HCl concentrations. We study damage done to the ITO films by the HCl in Sn-sensitization solutions by measuring sheet resistance using a four-point probe and profilometry to measure etch depths. Furthermore, we study the compositional change of ITO surfaces throughout these steps of the Sn-sensitization and Ag-activation process through X-ray Photoelectron Spectroscopy (XPS), and compare the results obtained to the compositional change of glass surfaces with the same Sn-sensitization and Ag-activation process measured by XPS.

2. Experiments

ITO films of ~250 nm-thickness were deposited on 550 μm -thick polished Si substrates. ITO films were prepared by DC magnetron sputtering from a $\text{In}_2\text{O}_3/\text{SnO}_2$ (90/10 wt. %) target at 1kW power, under 3% O_2 flow, with a deposition pressure of 3-4 mTorr.

Sn-sensitization solutions of varying concentrations were prepared by dissolving SnCl_2 in D.I. water and mixing in a vortex mixer for 2 minutes, followed by pipetting HCl in and stirring for an additional 10 s. All Sn-sensitization solutions had HCl molar concentrations twice that of SnCl_2 unless otherwise noted, Ag-activation solutions (1g AgNO_3 in 1 liter 0.1M HNO_3) were prepared following de Minjer *et al.* [20].

Prior to all surface treatments, ITO films were cleaned with an oxygen plasma for 30 s at 60 W. Immediately following plasma treatment, individual samples were rinsed in D.I. water for 1 min. Sn-sensitization solutions were applied by pipetting 2 μL drops on the ITO surface and allowed to sit for 1 min before rinsing again in D.I. water for 1 min. Immediately afterwards, the Ag-activation process was done by submerging the entire sample in Ag-activation solution for 1 min [20]. Lastly, the final rinse was done in D.I. water held between 90- 95 $^\circ\text{C}$ then dried with a nitrogen gun following the procedure reported by de Minjer *et al.* [20].

Sheet resistance was measured using a four-point probe. Film thickness and etch depths were determined using a Dektak XT profilometer. All XPS measurements were carried out using a PHI model 5600 laboratory X-ray photoelectron spectrometer equipped with $\text{AlK}\alpha$ monochromatic source ($h\nu=1486.6$ eV) with 23 eV pass energy and 0.05 eV/step speed with <0.5 eV FWHM for Ag 3d orbital. The detection limit is 0.05 eV in chemical shifts. Surface analyses were taken at a base pressure of 4×10^{-9} Torr.

All spectra binding energies were calibrated to the C 1s peak (at 284.6 eV). XPS data was fitted using CasaXPS software, using Shirley background removal.

3. Results & Discussion

Sn-sensitization solutions classically contain SnCl₂, HCl and D.I. water, with HCl concentrations varying from 0.001 – 9M HCl [11,12,19,20]. The concentration of HCl is typically at least twice that of SnCl₂ in solution to prevent hydrolysis of the SnCl₂ [11]. First, we study the damage done to ITO films as a result of HCl concentration in the Sn-sensitization solution. The sheet resistance of ITO films was measured before and after exposure to HCl in a wide range of concentrations (Figure 2). This was done in order to determine the threshold HCl concentration at which severe etching damage to the ITO surface is observed. HCl solutions were pipetted onto ITO films and allowed to dry fully before measuring changes in sheet resistance. Profilometry (see Figure S1 in supplemental information) was also conducted to measure any related pit depths arising

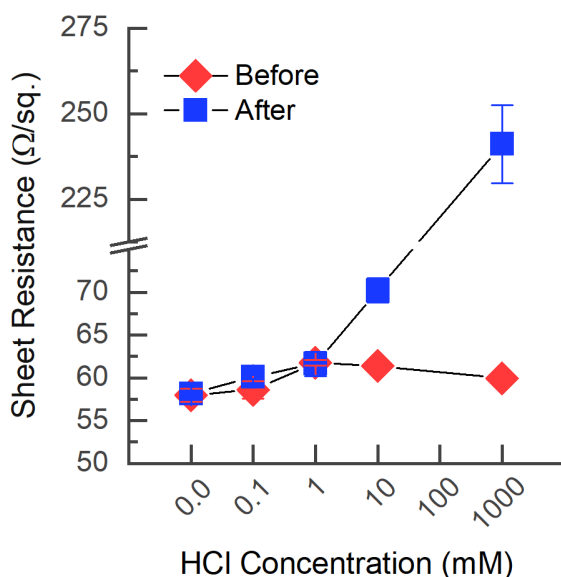


Figure 2. Sheet resistance of ITO films before and after exposure to HCl in varying concentrations, showing damage to ITO films at concentrations above 1 mM HCl.

from etching. The minimum HCl concentration studied was 0.1 mM HCl. This lowest concentration was based on the amount of SnCl₂ in solution necessary to deposit one Sn atom on every -OH site on an ITO surface, while minimizing the HCl molar concentration and avoiding hydrolysis of the SnCl₂ to form an insoluble salt [22,23]. A range of higher concentrations, as shown in Figure 2, was also investigated to represent the various concentrations found in literature [11,12,19,20].

The change in sheet resistance remains unchanged for ITO films treated with 1 mM HCl concentrations and below (Figure 2). However, above 10 mM HCl, the sheet resistance increases, showing that the ITO film is damaged at higher HCl concentrations. Profilometry results confirm these observations, showing no etching for concentrations below 1 mM HCl. At 10 mM HCl the ITO is etched a maximum depth of ~ 40 nm. To our knowledge, the lowest HCl concentration used in a Sn-sensitization solution reported in literature is 10 mM HCl [20], and this concentration avoids fully etching through the ITO films used in this study. Thus, two different Sn-sensitization solutions were prepared for XPS studies; one high-concentration solution—using 10 mM HCl following [20]; and one low-concentration solution—using 0.1 mM HCl. Table 1 shows the combinations of solutions and substrates studied by XPS.

Table 1. ITO and glass samples used for XPS analysis.

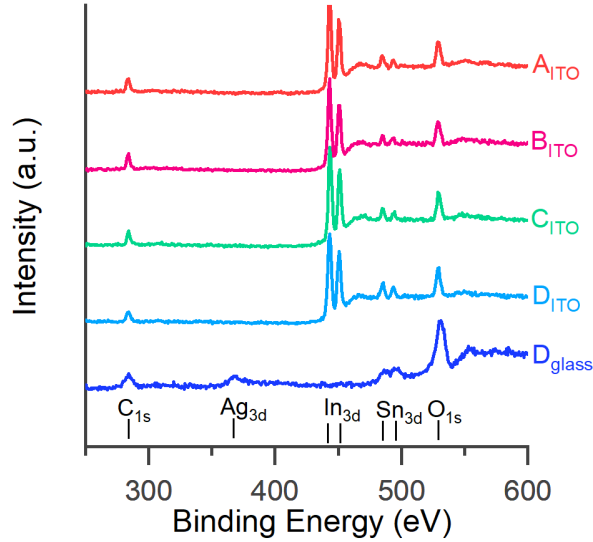


Figure 3. XPS spectra of glass and ITO samples treated with various steps of the Sn-sensitization and Ag-activation process. Binding energies of elements of interest are indicated under the spectra. D_{ITO} and D_{glass} were treated with identical processes, following de Minjer *et al.*, showing that the same process used on glass does not work identically on ITO [18].

Figure 3 shows the XPS spectra of glass and ITO samples treated with various Sn-sensitization and Ag-activation steps (see Table 1). Samples A_{ITO} , and B_{ITO} were not

Processes & Samples	A_{ITO}	B_{ITO}	C_{ITO}	D_{ITO}^*	D_{glass}^*
Clean	•	•	•	•	•
Rinse			•	•	•
Sn-sensitization (Hi/Lo HCl conc.)			• (Lo)	• (Hi)	• (Hi)
Rinse		•	•	•	•
Ag-activation		•	•	•	•
Rinse & Dry	•	•	•	•	•

* Sn-sensitization and Ag-activation solutions prepared following de Minjer *et al.* [20]

subjected to Sn-sensitization and act as controls for “clean” and “Ag-activation-only” ITO surfaces, respectively. To avoid etching the ITO, C_{ITO} was treated with a lower concentration of Sn-sensitization solution (0.1 mM HCl and 0.05 mM SnCl₂), followed by Ag-activation per de Minjer *et al.* [20]. One sample (D_{ITO}) was prepared using the higher-concentration Sn-sensitization solution following the procedure reported by de Minjer *et al.* [20], an identical process was used on a glass sample (D_{glass}) as well.

All ITO film surfaces show the presence of C, In, Sn, and O. The glass sample (D_{glass}) shows the presence of Sn and Ag, which confirms both the successful Sn-sensitization and Ag-activation of the glass surface. The lack of Ag on all ITO samples suggests that no Ag-activation occurs for ITO samples. This demonstrates that the process of Sn-sensitization followed by Ag-activation occur differently on ITO than on glass. To understand the origin of these differences, high resolution XPS measurements were conducted on the ITO samples. Specifically, the occurrence of the three steps depicted in Figure 1 can be evaluated by analyzing the changes in the O1s and Sn 3d_{5/2} peaks across the ITO sample surfaces.

Figure 4 (left column) shows a high resolution XPS spectrum of the O1s peak for the ITO samples, which consists of two peaks. The lower binding energy peak (~530.5 eV) is attributed to the In-O bond in the ITO lattice, and the higher binding energy peak (~532.5 eV) is from surface hydroxides [24,25]. The latter has been reported to also be a convolution of surface hydroxides and hydrocarbons [24,25]. The O 1s peak position, which is attributed to OH, to be at 532.5 eV at slightly higher binding energies than found in Yu *et al.* (532.3 eV), and Lee *et al.* (532.4 eV) [26,27]. However, this difference is within fitting variability. The 1st step (depicted in Figure 1) is the availability of surface -

OH sites that react with SnCl_3^- ions in the sensitization solution. As expected, surface hydroxides are detected on all samples as evident by the presence of the higher binding energy peak, confirming the 1st step of the process.

Sn-sensitization, the 2nd step depicted in Figure 1, can be confirmed through further analysis of the Sn $3d_{5/2}$ peak, which is shown in Figure 4 (right column). Figure 5 (a) shows the change in these atomic ratios for the ITO samples compared to A_{ITO} (“clean” ITO). There is a notable increase in both the Sn/In and O/(In + Sn) atomic ratios for D_{ITO} compared to A_{ITO} .

Lee *et al.* studied the change in surface composition of ITO after HCl etching, finding that HCl-etched ITO surfaces showed a decrease in both Sn/In, and O/(In+Sn) atomic ratios due to O-poor conditions at the surface [2], [24]. In their study, they measured the Sn/In atomic ratios of ITO films as-deposited (clean), and after an HCl solution treatment (HCl concentration unreported). The as-deposited ITO film had a Sn/In atomic ratio of 0.0583, and after the HCl treatment, a Sn/In atomic ratio of 0.0498 (this corresponds to a 14.6% decrease). Comparing our results to those of Lee *et al.*, A_{ITO} (clean ITO) has a Sn/In atomic ratio of 0.083 and samples C_{ITO} and D_{ITO} had Sn/In atomic ratios of 0.081, and 0.158, respectively. Our results show a small (~5%) decrease in Sn/In atomic ratio for C_{ITO} , but a large increase of ~62% for D_{ITO} . It should be noted that this large change in the Sn/In ratio from A_{ITO} (clean ITO) compared to D_{ITO} (high concentration Sn-sensitization solution treatment) could be because 1) the near surface composition of ITO thin films is often different than that of the bulk, and 2) etching of ITO films is often non-uniform etching of the ITO surface, which is also evident in the profilometry data (see supplemental information) [24].

In a related study, we studied change in surface work function of ITO films treated with Sn-sensitization solutions, and with DI water as a control [23]. In that work, we found that compared to the DI water-treated ITO surface, surface work function increased for ITO films treated with Sn-sensitization solutions (HCl concentrations ranging from 0.1mM - 10 mM HCl) [23]. Lee *et al.* demonstrated that following HCl treatment, ITO films exhibited a decrease in surface work function, which is opposite to our observation. This again suggests that the Sn-sensitization solutions modify the C_{ITO} and D_{ITO} surfaces in ways that are not explained by HCl etching alone. The change in the surface of the D_{ITO} is not consistent with HCl etching alone. Although we do not have certainty that the Sn-sensitization process is completed on D_{ITO} , these results suggest that the ITO surface is modified by the Sn-sensitization solution in ways that are not consistent with HCl etching alone.

Figure 5 (b) shows a change in surface Sn atomic composition, specifically a change in the Sn^{2+} and Sn^{4+} component of the Sn $3d_{5/2}$ peak for each ITO sample. The Sn^{4+} is found to be at 486.6 similar to that reported by Yu *et al.* (487.3 eV) [26]. Lee *et al.* reported a splitting of 1.0 eV is found between the Sn^{2+} and Sn^{4+} , in reasonable agreement with our findings of 486.0 eV for Sn^{2+} and 486.8 eV for Sn^{4+} [27]. However, the asymmetry in the Sn $3d_{5/2}$ peak is likely due to relaxation of the final state hole by the free electrons. Essentially the same asymmetry in the In $3d_{5/2}$ spectra is observed (not shown for brevity) in the Sn $3d_{5/2}$ spectra and suggests that a common mechanism contributes to the asymmetry of these peaks. This asymmetry in the In 3d peak was studied by Korber *et al.*, and was suggested to be from Sn doping of In_2O_3 , contributing free electrons to the oxide (improving the conductivity of the oxide)[28]. These electrons

would also contribute to relaxation of the photoemission final state; hence the asymmetry on the low binding energy side of the peak.

Indeed, such asymmetry in photoelectron peaks exist, especially in metals. In such cases an asymmetric Donach Sunjic line shape should be used to fit peak Sn shape. In our analysis, such line shape resulted in a poor fit with large standard deviation. Instead, we used a practical solution offered by Ulrik Gelius which uses a Voigt-like function as the underlying shape modified with an asymmetric parameter in the form: $A(a,b,n)GL(p)$: Gaussian/Lorentzian product formula modified by an asymmetric form [29]. The asymmetric peak shape fits Sn XPS peak well with a residual standard deviation close to 1. However, the same asymmetric peak shape fits the In peak poorly with a residual standard deviation greater than 2, suggesting that the asymmetry in the In and Sn peaks is from different physical effects. Hence, this asymmetry and apparent shift might be addressed by assigning the asymmetric peak shape to an increase in Sn^{+2} as in references [26,27] and this work. Since we are primarily interested in the increase in Sn^{+2} due to adsorption of the sensitizer, the increase in apparent Sn^{+2} is taken as due to adsorption of the sensitizer. We have taken the baseline peaks (before exposure to sensitization solution containing $SnCl_3^-$) as a mixture of Sn^{+2} and Sn^{+4} . We attribute any increase in the apparent Sn^{+2} component to adsorption of sensitizer. These results indicate that Sn-sensitization of the surface has occurred and that preferential etching of In is unlikely, but cannot be fully ruled out without additional studies.

As mentioned above, effective Sn-sensitization results in an increase in Sn concentration at the surface, and furthermore, an increase in the Sn^{2+} component. Both samples that were not treated with Sn-sensitization solutions – A_{ITO} and B_{ITO} –have Sn^{2+}

compositions of ~1.25 at. %. Sn^{2+} composition increases slightly by about 0.25% for the low-concentration Sn-sensitization treated sample, C_{ITO} . Most notably, for D_{ITO} , Sn^{2+} composition increases by ~1.5% compared to A_{ITO} and B_{ITO} , which was treated with the higher-concentration Sn-sensitization solution.

Based on these results, we suggest that D_{ITO} has a Sn-sensitized surface, confirming the 2nd step of the process has taken place. Whereas C_{ITO} shows only a small increase in

Sn^{2+} compared to A_{ITO} and B_{ITO} , suggesting that the sensitization may still be occurring, but is likely limited by the low concentrations of both HCl and SnCl_2 in the solution.

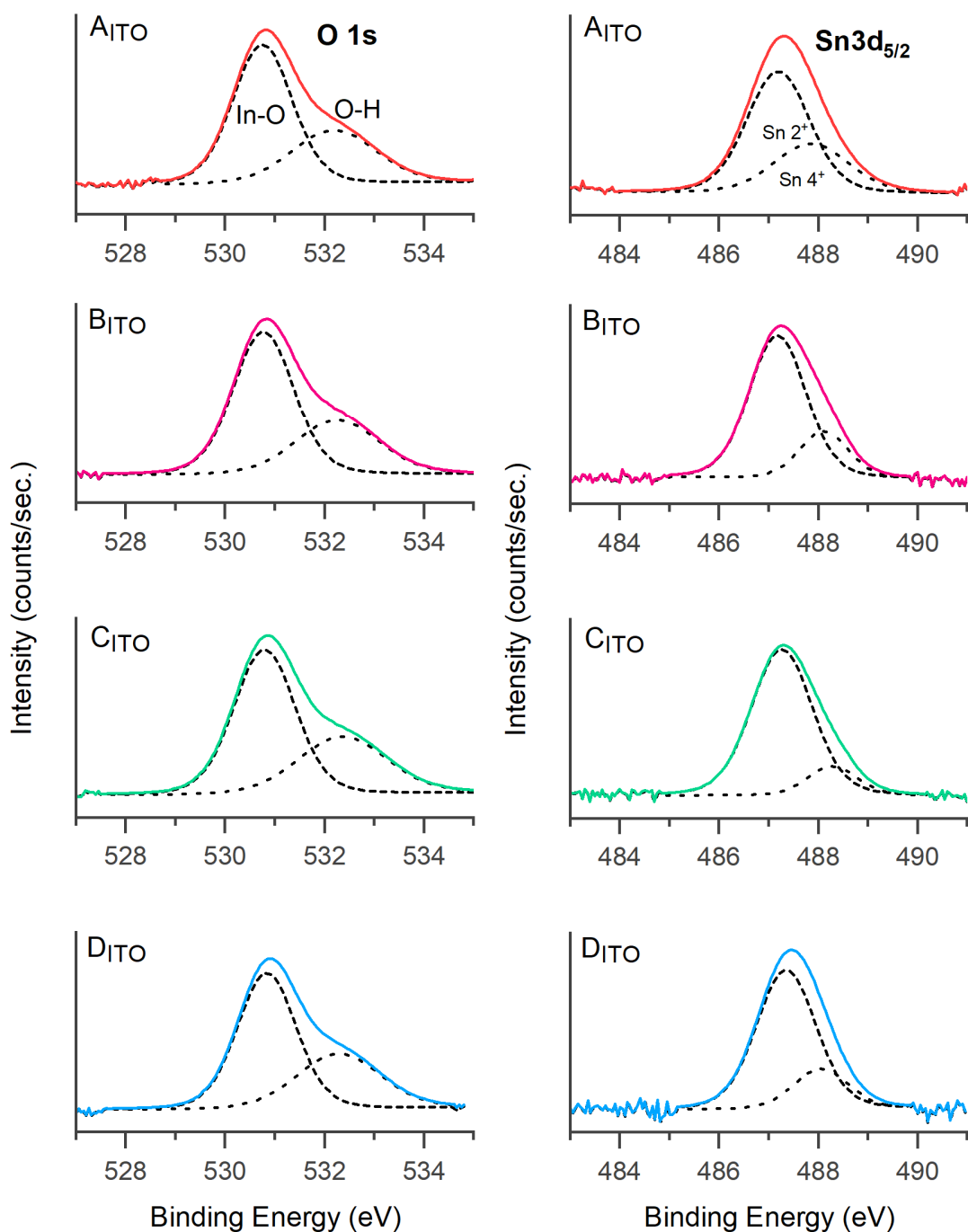


Figure 4. XPS spectra of the O1s peak (left) and Sn 3d_{5/2} peak (right) from ITO samples at various steps in the Sn-sensitization and Ag-activation processes. The O1s peak is fitted with two distinct contributions from In-O and O-H. Likewise, the Sn 3d_{5/2} peak is fitted with two distinct contributions from Sn²⁺ and Sn⁴⁺ bonding states.

Furthermore, since the Sn-sensitization solution for C_{ITO} was optimized to have only roughly one Sn atom for each expected -OH site, it is likely that there still would be less

than one Sn atom per -OH site. That is, it is possible that not all of the Sn in the Sn-sensitization solution droplet travels through the droplet and bonds to the -OH sites before it is rinsed away thoroughly with D.I. water (see procedure in Experiments).

Overall, this means that higher HCl and SnCl₂ concentrations in the sensitization solution, induced more change to the surface composition, but likely at the cost of damaging the ITO surface. This result suggests that regardless of sensitization, some other mechanism governs the Ag-activation of the ITO surface, since no Ag is detected on the ITO surfaces within the detection limits of our experiment.

Furthermore, it is worth a discussion on the point of zero charge (PZC) for ITO and glass surfaces in contact with Sn-sensitization solutions since its vital to understand the surface functionality. Again, the adsorbent for the Sn-sensitization process is the SnCl₃⁻ anion. The pH in both Sn-sensitization solutions are 2 and 3 for the 10 mM HCl and the 1 mM HCl solutions, respectively. First considering the ITO surface, the PZC is between 8.7-9.4 for In₂O₃ [30], and around 6.0 for SnO₂ [31]. When the pH of the solution is

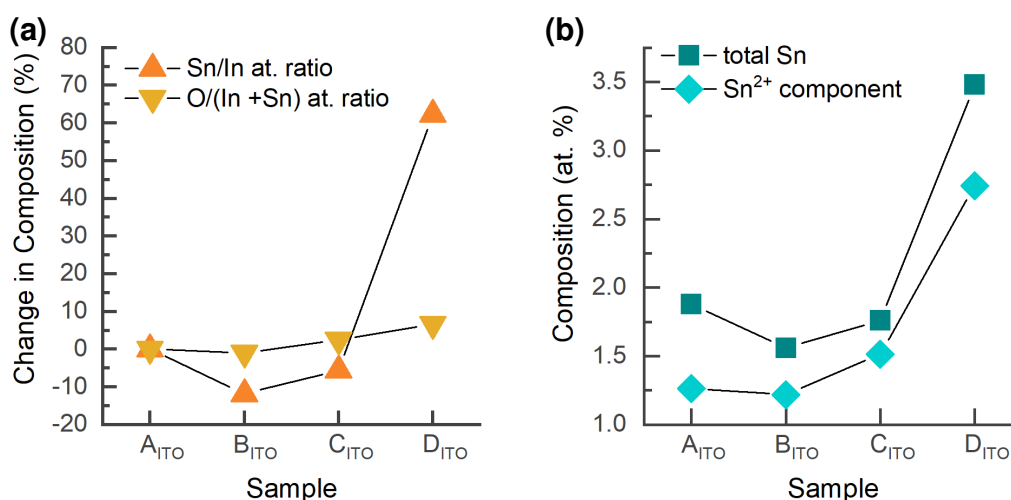


Figure 5. (a) Change in atomic ratio compositions for the ITO samples. (b) Total Sn atomic composition and Sn²⁺ component composition for each ITO sample.

below the PZC of the surface, the surface is positively charged relative to the solution, and readily adsorbs anions. Most oxides are capped by hydroxide groups in water-based solutions, and their surface charge normally comes from the protonation or deprotonation of these -OH groups. Next, considering a glass surface, the PZC is between 1.7-3.5, so for our Sn-sensitization solutions, the SnCl_3^- anions are likely to be adsorbed to sensitize the surface [32].

Interestingly, successful Sn-sensitization and Ag-activation were demonstrated on glass (D_{glass}), yet an identical process used on ITO (D_{ITO}) was not successful. XPS results confirmed that the steps of hydroxylation and Sn-sensitization were met on both D_{glass} and D_{ITO} . However, as mentioned before, the 3rd step of “Ag-activation” is not evident on the D_{ITO} sample. To our knowledge, studies reporting Sn-sensitization on ITO are scarce [1,6]. However, studies by Kim *et al.* report on successful Sn-sensitization followed by Pd-activation for improvements in Cu electroless deposition on ITO surfaces [1,6].

A closer look at these results from Kim *et al.* and our study highlight differences in i) the glass and ITO surface structure, and/or ii) a difference the atomic nature of Pd- and Ag- in their respective activation processes [1,6]. In our study, it appears the Sn-sensitization step is successful on D_{ITO} based on the increased Sn composition, and specifically increased Sn^{2+} composition near the surface compared to the rest of the ITO samples. Thus, we suggest the limiting step in the process is Ag-activation on ITO surfaces.

Again, based on the mechanism of Sn-sensitization on glass, sensitization occurs on -OH sites. To understand the next step of Ag-activation on the ITO surface, we look at

the differences in the atomic nature of the Pd-activation and Ag-activation processes. The step of Ag-activation requires two Ag⁺ ions to react with one Sn²⁺ on the surface following Equation 3. For the case of Pd-activation, only one Pd²⁺ ion is required for activation following Equation 4.



Table 2 lists the availability of -OH sites on glass and ITO, along with cross-sectional area necessary to accommodate one Pd²⁺ ion and 2Ag⁺ ions, given the ionic radii of each species. Glass has approximately one -OH site per 17.6 Å², whereas ITO has a higher density with one -OH site per 10.0 Å². Furthermore, significantly less area is needed to accommodate one Pd²⁺ ion compared to two Ag⁺ ions. Thus, Ag-activation on ITO surfaces has less area to accommodate activation-ions compared to glass, and the larger activation-ions hinder Ag-activation on ITO surfaces compared to Pd-activation. This ionic hinderance effect could account for the differences observed by Kim *et al.* and our study [1,6].

Table 2. Pd and Ag ionic cross-sectional areas and hydroxide site density for ITO and

1× Pd²⁺ area (Å²)	2× Ag⁺ area (Å²)	OH site density (Å²/#)
1.2 – 2.2	6.2 – 21.2	10.0 (<i>ITO surface</i> [33]) 17.6 (<i>glass surface</i> [20])

glass surfaces.

4. Summary

In conclusion, we find that Sn-sensitization solutions modify ITO surfaces, resulting in an increase in surface Sn²⁺ composition. For the higher molar concentration Sn-sensitization solution (with 10 mM HCl), the surface Sn concentration is increased by 1.5

at. %, likely from both Sn-sensitization of surface -OH sites and etching of In-O bonds at the surface by the relatively high molar concentration of HCl. This suggests that Sn-sensitization of ITO surfaces is carried out using low HCl molar concentrations compatible with ITO thin films. However, Ag-activation on ITO surfaces is not evident. We suggest this is due to a high density of surface hydroxide sites on ITO compared to glass, and smaller area to accommodate two Ag⁺ ions, which can be amended by using smaller metal ions such as Pd²⁺ for the activation step, which has been demonstrated by [6,16]. However, Pd activation may be cost prohibitive compared to Ag activation for the purposes of improving adhesion of electrodes to ITO on industrially relevant solar cells.

5. Acknowledgements

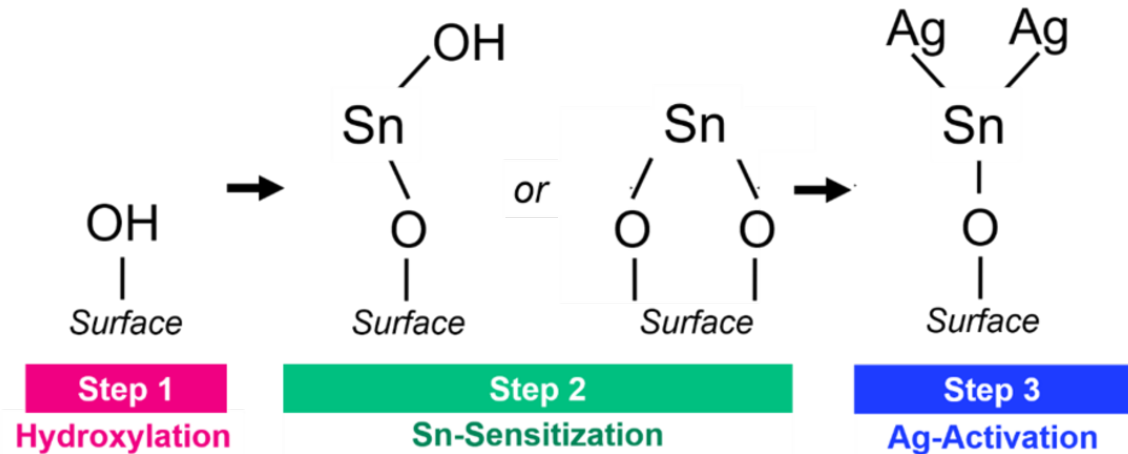
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Glass: ✓
ITO: ✓

