The oxidation and surface speciation of indium and indium oxides exposed to atmospheric oxidants.

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Abstract

Metallic Indium and its oxides are useful in electronics applications in transparent conducting electrodes, as well as in electrocatalytic applications. In order to understand more fully the speciation of the indium and oxygen composition of the indium surface exposed to atmospheric oxidants, XPS, HREELS, and TPD were used to study the indium surface exposed to water, oxygen, and carbon dioxide. Clean In and authentic samples of In_2O_3 and $\text{In}(\text{OH})_3$ were examined with XPS to provide standard spectra. Indium was exposed to O_2 and H_2O , and the ratio of O^{2-} to OH^- in the O1s XPS region was used to monitor oxidation and speciation of the surface. HREELS and TPD indicate that water dissociates on the indium surface even at low temperature, and that In_2O_3 forms at higher temperatures. Initially, OH^- is the major species at the surface. Pure In_2O_3 is also OH^- terminated following water exposure. Ambient pressure XPS studies of water exposure to these surfaces suggest that high water pressures tend to passivate the surface, inhibiting extensive oxide formation.

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Introduction

Indium in its pure elemental form is used in a few applications, such as a gasket seal in vacuum systems, as a heat conductor in electronic cooling and cryogenic applications, and as a reducing agent in chemical reactions.¹⁻³ More commonly, indium is either alloyed with other metals to modify their properties (for instance, as a component in eutectics like gallium-indium, gallium-indium-tin, and bismuth-indium-tin), combined with group V elements to make III-V semiconductors, or employed as a transparent conductor as indium oxide or, most often, indium tin oxide (ITO).¹ In spite of these important uses, the ambient corrosion of indium metal and its oxides are not as well documented as more abundant and more widely used structural metals.

Due to its wide use in electronics, ITO, unlike In^0 and In_2O_3 , has been characterized extensively using UHV techniques, but the attribution of oxide and hydroxide species (which are extremely important for performance and reproducibility) to Sn or In in ITO species is difficult and often ambiguous.⁴ The work function of ITO can be altered by the method and parameters of preparation and a major contributor to this variation in properties is likely humidity.^{5, 6} SnO_2 nanoparticles have even been used as humidity sensors, showing significant conductivity perturbation in the presence of varying water vapor pressure.⁷ Little attention has been placed on the role of In_2O_3 -water interactions and essentially no studies have been done to discern the impact of atmospheric water on the speciation at the indium solid-gas interface. Elucidating the behavior of water at the gas-solid interface of indium is critical for future applications of indium metal and indium oxide, in addition to various indium containing mixed metal compounds. To determine the role of the indium oxidation state in aqueous electrochemical CO_2

reduction to formate, a deeper understanding of the interfacial speciation at the electrode surface was necessary. Recently the role of these specific oxides has been implicated in electrocatalytic CO₂ reduction at the oxidized indium electrode.⁸

The study of metal and metal oxide interactions with small molecules is a well-developed field with many tools and techniques available. The study of oxygen and water corrosion of various structural metals is extensive, as is the case with the corrosion of iron, for example.^{9, 10} Some corrosion studies of indium metal have previously been performed. Lin *et. al.* studied indium metal and indium (III) oxide using x-ray photoelectron spectroscopy (XPS) and Auger electron spectroscopy (AES).¹¹ Rossnagel *et. al.* employed AES to monitor the oxidation of In⁰ with O₂, H₂O, CO, and CO₂, finding that an In oxide layer developed on exposure to all of the oxygen containing species, but in the case of CO and CO₂, oxidation may have been due to trace O₂ and H₂O contamination.¹² The oxidation of polycrystalline In⁰ with O₂ was investigated with XPS and secondary ion mass spectrometry (SIMS) by Hewitt *et. al.*, who observed that O₂ continues to oxidize In⁰ after thousands of Langmuirs (L) of O₂ exposure, forming an In₂O₃ film.¹³ Concurrently, Sen *et. al.* showed the formation of an In₂O₃ film on O₂ exposure to In⁰, using AES. They noted the loss of In⁰ signal after 10⁶ L of O₂ exposure.¹⁴ More recently, Jeong *et. al.* studied the conductivity of indium oxide thin films as a function of deposition parameters including substrate temperature, deposition rate, and oxygen partial pressure, among others, and demonstrated the importance of the In/O ratio for the conductivity of the oxide film.¹⁵

It is important to note that these experiments on the detailed origin of oxygen and indium species were performed on UHV prepared samples, which qualitatively

demonstrate significant differences from indium oxide species that are present after exposure to atmospheric conditions. Most notably, the identification of the high binding energy O 1s species observed in XPS measurements in all these experiments is conflicting. Here we attempt to address this shortcoming in the literature through a series of XPS, high-resolution electron energy loss spectroscopy (HREELS) and temperature programmed desorption (TPD) experiments. The explicit interactions of water with In^0 and In_2O_3 have not been characterized in terms of adsorption and dissociation, and the actual species formed at the solid-gas interface upon adsorption have been addressed only sparingly. Due to the lack of adequate information about these interactions and the role that indium speciation can play in the electronic properties of indium containing materials, the oxidation of indium upon exposure to H_2O , O_2 , and CO_2 was systematically probed here.

Experimental

In order to probe the fundamental interactions of small molecule oxidants with the most common oxidation states of indium (metallic and trivalent), experiments were performed under both UHV and ambient pressure conditions. First, standards were measured as points of reference for the subsequent exposure studies.

Standard Indium Sample Analysis

XPS control and dosing studies were performed using a VG Scientific Mk II ESCALab with a magnesium x-ray source and hemispherical electron analyzer set at 20 eV pass energy. Spectra were calibrated to the adventitious C 1s peak at 285 eV, or, when absent, the O 1s peak at 530 eV binding energy. Indium metal shot (Alfa Aesar 99.99% metals basis) was pounded into a flat circle of ~1.5 cm diameter and ~0.3mm

thickness and allowed to oxidize in atmosphere overnight before being introduced into vacuum. Powder samples of In_2O_3 (Aldrich 99.99% metals basis) and $\text{In}(\text{OH})_3$ (Aldrich 99.99% metals basis) were liberally pressed onto carbon tape and introduced into vacuum as received. Clean metallic indium spectra were obtained by sputtering the native oxide sample with a differentially pumped Ar^+ beam at 2 keV and 10 mA emission current, delivering 4-6 μA to the sample for 1 hour.

All XPS spectra were deconvoluted using CasaXPS peak fitting software with Shirley background subtractions and Gaussian-Lorentzian peak distributions.

Adsorption experiments studied via XPS

After obtaining the reference speciation peak information from standard samples, the progress of oxidation as a function of oxidant exposure was observed. H_2O , O_2 , and CO_2 dosing experiments were performed on an Ar^+ sputtered indium metal substrate in the ESCA lab described above. The substrate was exposed by controllably leaking in the respective oxidants from between 0.5 L and 10^5 L at pressures from 10^{-9} to 10^{-5} Torr and recording In 3d, In Auger, O 1s, C 1s and survey XPS and Auger spectra after each exposure.

Ultra-high purity O_2 and CO_2 were obtained from AirGas Inc. and leaked into the chamber through a mechanically pumped manifold via a bakeable sapphire sealed leak valve. H_2O was obtained from a Millipore MilliQ system with a resistance of 18.2 $\text{M}\Omega/\text{cm}$ and placed in a glass bulb attached to the manifold and degassed by directly pumping on the volume of water. Gas doses were monitored with a Stanford Research Systems RGA-200 residual gas analyzer with a channeltron electron multiplier.

Speciation at high H₂O pressures studied by AP-XPS experiments at ALS

In order to help extrapolate the UHV information to atmospheric conditions, higher pressure experiments were performed using an ambient pressure XPS (AP-XPS) system to dose metallic and oxidized indium species with water. AP-XPS measurements were obtained at the Advanced Light Source at LBNL beamline 9.3.2. An In⁰ sample was prepared from metallic indium shot, then Ar⁺ sputtered at 2 keV and ~6 μ A for 1.5 hours, and an In₂O₃ sample was prepared by drop-casting isopropanol suspended powder onto a 1 micron film of Au on a 1 cm² Si wafer and then baking at 250 °C for 1 hour. Ultra-high purity CO₂ (AirGas) and water from a Millipore MilliQ water system at 18.2 M Ω /cm was used after evacuating atmospheric gases with a mechanical pump. Gas pressures were monitored with a Stanford Research Systems RGA-100 residual gas analyzer in the electron analyzer chamber.

HREELS and TPD chamber and preparation

In an attempt to gather further information about the mechanism of indium oxidation and surface speciation distributions at oxidized indium surfaces, HREELS and TPD spectra were collected under UHV conditions from a flat, polycrystalline indium sample treated as described below. A custom chamber with a base pressure of 1.2X10⁻¹⁰ Torr was used to perform these HREELS and TPD measurements on an indium foil from Alfa Aesar (99.99% metals basis) mounted to a custom tantalum foil stage capable of being resistively heated and liquid N₂ cooled. The indium foil was brought to a mirror finish by pressing into a glass slide. An ELS 3000 HREELS system was used to obtain HREELS spectra and a Stanford Research Systems RGA-200 residual gas analyzer was used to record system pressure during TPD analysis. The sample was sputtered clean by

backfilling the chamber with Ar to a pressure of 5×10^{-6} Torr and sputtering at 2 keV and $\sim 6 \mu\text{A}$ for 1 hour at an Ar^+ beam incidence angle of 20° .

HREELS spectra were obtained at the specular angle with a beam energy of 5 eV and direct transmission fwhm of $\sim 3\text{meV}$, and incident beam angle of 60° .

TPD was performed with the sample 35° off normal from the RGA in an attempt to obtain a normalized desorption profile for various species. The stage was brought within 3 inches of the ionizing filament of the RGA. Programmed desorption was performed at a rate of 1 K/ 6 seconds.

Results and Discussion

Authentic Control Samples

XPS of Ar^+ sputtered indium metal shows that sputtering removes almost all detectable O 1s and C 1s XPS signal after 1 hour at 2 keV and 10 mA emission current. As seen in Figure 1a, as the metallic In $3d_{5/2}$ peak at 443.7 eV is exposed, a significant plasmon loss feature grows in at 11.7 eV higher binding energy than its parent peak, in accordance with previous studies.^{11, 13} In addition, the full width half max (fwhm) of the In $3d_{5/2}$ and In $3d_{3/2}$ peaks are considerably less than the fwhm of the In 3d peaks of In_2O_3 (In $3d_{5/2}$ at 444.7 eV) and $\text{In}(\text{OH})_3$ (In $3d_{5/2}$ at 445.1 eV), as seen in Figure 1b and Figure 1c, respectively. Even after sputtering at length, there is still a small O 1s signal from the indium substrate at 529.9 eV, which coincides with a small shoulder in the In 3d region with an In $3d_{5/2}$ peak at 444.8 eV. This O 1s signal likely is due to residual oxygen contamination in the chamber, which reacts before spectra can be obtained, or is from oxide already present in the indium sample.

As is common for the O 1s region previously reported for bulk In_2O_3 samples, there are two significant peaks present at 530.4 eV and 532.3 eV, generally attributed to bulk oxygen and surface adsorbed oxygen, respectively.^{11, 13} However, this assignment makes little sense when the peaks are of equal size, as is the case here. More likely, the higher binding energy peak is actually a hydroxyl species.^{16, 17} The only other features seen in the In 3d region are due to $\text{K}\alpha_3$ and $\text{K}\alpha_4$ lines from the un-monochromated x-ray source, observed as satellites of large peaks at ~8.4 eV lower binding energy in collected XPS spectra.

The O 1s region of the $\text{In}(\text{OH})_3$ sample demonstrates oxygen species which are similarly spaced as the In_2O_3 species, but shifted to slightly lower binding energy (529.3 eV and 531.7 eV, respectively). The shift in the In $3d_{5/2}$ peak to higher binding energy and shift in O 1s peaks to lower binding energy indicates that the In atom has lower electron density in $\text{In}(\text{OH})_3$ than in In_2O_3 , which is normally the case for metal hydroxides compared to their equivalent oxidation state metal oxide.

It is important to note that although the oxidized indium species are not metallic, In_2O_3 has a band gap of 2.3 eV and is commonly used with tin oxide as a transparent conducting film in electronics, and no significant charging was observed. $\text{In}(\text{OH})_3$ on the other hand, displayed significant charging (up to 5 eV) and emitted a visible blue glow under x-ray illumination, understood to originate from oxygen vacancies in the crystal structure of the hydroxide.¹⁸

Figure 1. XPS spectra of the In 3d and O 1s regions of (a) sputtered In metal, (b) In_2O_3 , and (c) $\text{In}(\text{OH})_3$.

Oxidation of Indium with Gases (O_2 , H_2O and CO_2) Monitored by XPS

After collecting peak information from the authentic samples, it was possible to begin measuring the change of indium surfaces during exposure to the small molecule oxidants of interest. As mentioned above, the presence of two oxygen species in In_2O_3 has been previously noted, but the assignment of the species that generates the higher binding energy O 1s peak at ~532 eV is not widely agreed upon, some assigning it to adsorbed oxygen and others attributing it to hydroxide. Those that attribute this O 1s species to adsorbed oxygen do so because they have only exposed the indium to oxygen in UHV conditions in order to monitor oxide growth, so that any oxygen signal was assumed to originate from O_2 .^{11, 13} Those who attribute the higher binding energy peak to a hydroxyl species do so in analogy to what has previously been reported for oxygen

speciation at other metal oxide interfaces.^{17, 19} For this reason, the oxidation study performed by Rossnagel *et. al.* at indium metal with gaseous oxidants was repeated, but with a focus on the O 1s speciation.

Figure 2a again shows the Ar⁺ sputtered indium substrate, which is essentially oxide free, demonstrated by the flat O 1s region. The In 3d region shows that there is a dominant In 3d_{5/2} peak at 443.7 eV with a strong 11.7 eV plasmon loss feature. The In LMM Auger region shows very sharp transitions, indicative of the metallic species, which is now dominant at the exposed interface. Figure 2b shows the sputtered indium surface after it has been exposed to around 100,000 L of O₂. The O 1s region shows a large gain in O 1s signal, with a significant peak at 530 eV and a small shoulder around 531.8 eV. The In 3d region now distinctly shows two In 3d_{5/2} species, the metallic species at 443.7 and an oxidized species at 444.8 eV that matches closely with In₂O₃, but is not distinguishable, within the resolution of the spectrometer, from an In(OH)₃ In 3d_{5/2} signal. After oxygen exposure the In Auger region has significantly different, broadened features, with residual sharp peaks from the metallic species. XPS after exposing an equal amount of H₂O to the sputtered substrate is shown in Figure 2c. The O 1s region demonstrates a significantly larger amount of the high binding energy oxygen species. In addition, the In 3d region shows a smaller amount of oxidation, which is also seen in the Auger region, where the metallic peaks are more pronounced in the region between the two indium species.

Figure 2. XPS spectra of (a) an Ar⁺ sputtered indium foil that has subsequently been exposed to (b) 100,000 L of O₂ or (c) 100,000 L of H₂O.

The oxidation of indium can be followed as a function of O₂ or H₂O exposure in order to determine sticking coefficients of the oxygen containing species and their oxidation rates of the bulk sample. Figure 3 shows the In³⁺/In⁰ ratio, determined by comparing the peak areas for the two In 3d_{5/2} species at 444.8 eV and 443.7 eV, respectively. It is important to note that even though the sputtering has managed to dramatically rid the surface of oxidized indium, there is still a reasonable amount of oxidized indium peak area that cannot be removed. The ratios for indium speciation demonstrate similar behavior to that seen by Rossnagel *et. al.*, who reported the oxygen coverage as a function of O₂ and H₂O exposure.¹²

For clarity in the following discussions, the main peaks of interest are summarized in Table 1. The In^{3+} peak is attributed to a mixed oxide state, including both indium oxide and indium hydroxide species. These two species cannot be resolved in the In 3d peak region with the photoelectron spectrometer used in this study. The O 1s peaks however, can be strongly attributed to the oxide speciation present. These peak positions allow subsequent observations to be easily discussed and exposures will be presented in this context.

	In 3d		O 1s	
	In^{3+}	In^0	O^{2-}	OH^-
Peak Binding Energy (eV)	444.8	443.7	530	532

Table 1. Binding peak energies for the main indium 3d and oxygen 1s species highlighted in the following discussions.

The $\text{In}^{3+}/\text{In}^0$ ratio for an O_2 exposed indium surface shows significant increase after about 20 L of oxygen exposure to the substrate. This ratio quickly increases over the next 1,000 L of O_2 exposure, plateauing at around 5,000 L. In contrast, the $\text{In}^{3+}/\text{In}^0$ ratio does not demonstrate significant oxidation until after 1000 L of H_2O exposure, and begins to plateau at around 100,000 L.

Figure 3. $\text{In}^{3+}(444.8 \text{ eV})/\text{In}^0(443.7 \text{ eV})$ ratios plotted as a function of oxidant exposure by comparing the peak areas of the $\text{In } 3d_{5/2}$ peaks at each exposure point.

The most striking contrast between O_2 and H_2O oxidation of sputtered metallic indium foil in UHV is displayed in Figure 4. By taking the ratio of $\text{O}^{2-}/\text{OH}^-$ and plotting it against exposure for each oxidant, it becomes clear that the indium surface terminates differently in each case. The O^{2-} signal in the case of O_2 exposure is very large in the initial stages of oxidation and remains the dominant feature as exposure increases. The $\text{O}^{2-}/\text{OH}^-$ ratio decreases logarithmically with O_2 exposure. The $\text{O}^{2-}/\text{OH}^-$ ratio for H_2O oxidation of indium shows a much lower value at low water exposure values, and stays nearly constant until very high exposures.

Figure 4. The ratio of the low binding energy O 1s peak, associated with O²⁻, and the high binding energy O 1s peak, associated with OH⁻, plotted against the exposure of O₂ (black squares) and H₂O (gray triangles).

This data suggests that O₂ is the better oxidant for indium and adsorbs dissociatively. Dissociation is likely driven by the oxidation of In⁰ to In³⁺, which starts to form an In₂O₃ layer. As more oxygen dissociatively adsorbs, O²⁻ is free to migrate to the oxide/metal interface growing a thin In₂O₃ film. As exposure increases, the O²⁻/OH⁻ ratio decreases, suggesting that, slowly, due to trace H₂O or H₂ found in the chamber, OH⁻ is beginning to significantly coat the oxide film by water adsorption, potentially dissociating directly at an O²⁻ site into two OH⁻ in an acid-base equilibrium. The O²⁻/OH⁻ ratio continues to decrease as both O²⁻ migration into the metallic phase slows, and trace H₂O and H₂ increasingly impinge or react on the surface.

Oxidation of In by H₂O takes place by a significantly different mechanism than O₂ oxidation, but yields a very similar oxide film. H₂O first adsorbs dissociatively, making surface hydroxide and hydride. Bulk oxidation occurs as surface hydroxide loses a proton to recombine with hydride, producing H₂, which desorbs, as observed and discussed in the TPD experiments below. The O²⁻ is then mobile enough to move to the In⁰ interface below the exposed surface, creating an In₂O₃ under layer between the hydroxylated surface and the metallic bulk. It appears that the rate of oxidation slows as this oxide film grows. In the case of H₂O oxidation, the O²⁻/OH⁻ ratio stays relatively constant as the oxidation occurs since there is an excess of OH⁻ at the surface that is constantly being replenished by incident water. As the oxide layer reaches saturation thickness for the P_{O_2} of the system, the OH⁻ signal becomes more intense as the driving force for incorporation of O²⁻ into the substrate decreases. The growth of oxide in both the H₂O and O₂ environments is in accord with the growth of an n-type semiconducting oxide, which agrees with previous reports on In₂O₃.

As was observed by Rossnagel *et. al.*, the present work does show slight oxidation of indium with CO₂ exposures. However, the exposures were so high and took so long that it is likely that trace O₂ and H₂O in the system may have been responsible for the oxidation.¹² The almost identical oxygen species observed for CO₂ exposure as for oxygen and water exposure supports the oxidation via trace O₂ and H₂O contamination. Small carbonate or potentially formate species were observed in the C 1s region at ~298 eV in all samples after significant exposure. This suggests that the sequestration of carbon as a carbonate or formate species is favorable, but highly surface localized. Due to the weak carbon peak intensity and the observation of this peak in samples not exposed

directly to CO₂, it is difficult to confidently assign the origin of the carbon species as CO₂ or trace CO in the system.

Oxidation of Indium with H₂O at Ambient Pressures

After having demonstrated that a significant exposure of oxidant causes the indium surface to reach a relatively constant oxide/hydroxide speciation, a stronger correlation to atmospherically exposed samples was desired. In order to obtain this link, the speciation of indium foil and indium oxide was observed with XPS at relatively high H₂O pressures. **Figure 5a** shows the In 3d region of sputtered clean indium metal foil as acquired from a monochromatic x-ray source at the Lawrence Berkeley National Laboratory (LBNL) Advanced Light Source (ALS) Beamline 9.3.2 at 640 eV beam energy. The metallic In 3d_{5/2} peak at 443.7 eV is the main species, with a small, oxidized In 3d_{5/2} shoulder at a binding energy of 444.8 eV, in addition to corresponding In 3d_{3/2} peaks and plasmons at higher binding energies. **Figure 5b** shows the Ar⁺ sputtered foil at an ambient P_{H_2O} of 50 mTorr. The 444.8 eV peak becomes the dominant species under these conditions, and although the plasmon peak is no longer apparent, there is a distinct amount of metallic species still detectable. The In 3d region of an In₂O₃ powder, seen in **Figure 5c**, did not change significantly between UHV and 50 mTorr P_{H_2O} conditions.

The ratio of In³⁺/In⁰ is 14.2 for the H₂O exposed foil, which is much higher than the In³⁺/In⁰ ratio observed in either O₂ or H₂O exposures of 100,000 L carried out at 10⁻⁵ Torr. This indicates that the observed plateaus of the In³⁺/In⁰ ratio in the O₂ and H₂O exposures under UHV/HV conditions were due to the limited extent of indium oxidation at low oxidant pressures.

Figure 5. AP-XPS spectra in the In 3d region for (a) an Ar^+ sputtered indium foil in UHV, (b) an Ar^+ sputtered indium foil while at a $P_{\text{H}_2\text{O}}$ of 50 mTorr, and (c) In_2O_3 powder in UHV.

As with the previous O_2 and H_2O exposures, more detail about surface speciation can be gleaned from the O 1s region of the spectrum. Figure 6a shows the O 1s region of the Ar^+ sputtered indium foil, where there are small peaks that can be assigned to the O^{2-} and OH^- species. When the $P_{\text{H}_2\text{O}}$ in the chamber is raised to 50 mTorr, both oxygen peaks increase in intensity dramatically, as seen in Figure 6b, in unison with the In^{3+} peak seen Figure 5b. The $\text{O}^{2-}/\text{OH}^-$ ratio at 50 mTorr pressure of H_2O is 0.80, lower than previously observed in the UHV/HV exposures. Interestingly, as shown in Figure 6c, the

O^{2-}/OH^- ratio *increases* on evacuation of the H_2O to 0.82. This shows that the O^{2-}/OH^- ratio is dependent on the P_{H_2O} in the system, indicating that an equilibrium exists between the oxidized indium layer and $H_2O_{(g)}$.

Figure 6d shows the O 1s region of an In_2O_3 powder, corresponding to the In 3d region shown in Figure 5c. Both O 1s species are present with an O^{2-}/OH^- ratio of 1.32. Again, at a P_{H_2O} of 50 mTorr, the O^{2-}/OH^- ratio drops significantly to 0.74 as seen in Figure 6e. The highest binding energy peak seen in Figure 6b at 536 eV, and Figure 6e at 535 eV is due to water in the vapor phase. It does not fall at the same binding energy in the two experiments because the sample of In_2O_3 charged significantly under the intense light source, and had to be calibrated according to the C 1s region. In both of these cases

Figure 6. AP-XPS spectra in the O 1s region for (a) an Ar^+ sputtered indium foil in UHV, (b) an Ar^+ sputtered indium foil while at a P_{H_2O} of 50 mTorr, (c) the foil after exposure at a P_{H_2O} of 50 mTorr after pumping back down to UHV pressure, (d) In_2O_3 powder in UHV and (e) while at a P_{H_2O} of 50 mTorr.

there is also a peak around 533.5 eV that can be attributed to physisorbed H₂O.

These combined UHV and ambient pressure XPS data demonstrate that the order and extent of indium oxidation is dictated by the distribution and pressure of oxidants present in the oxidizing atmosphere. The terminal hydroxylation of the indium substrate appears to depend on the level of water in this oxidizing atmosphere.

HREELS at Metallic Indium and Oxidized Indium with H₂O Exposure

In order to probe the mechanism of adsorption and the potential implications on oxide growth and stability, HREELS was performed under UHV conditions to study the initial steps of metallic oxidation with O₂ and H₂O. HREELS spectra were obtained from an Ar⁺ sputtered indium metal foil at 135K, and are shown in **Figure 7a**. Only after exposing to 40 L of H₂O were any H₂O vibrational modes observed. These modes were seen at 720 cm⁻¹, 1640 cm⁻¹, and 3660 cm⁻¹, which correspond to a frustrated rotation mode, a scissoring mode, and an O-H stretching mode of H₂O, respectively.²⁰ In addition to the H₂O vibrational modes, there also appears to be a mode at 450 cm⁻¹. This mode is likely an In-O mode of In hydroxide, as seen in previous work.²¹ Additionally there are small hydrocarbon contamination modes seen at 1450 cm⁻¹ and 2920 cm⁻¹. Exposing this surface to another 60 L of H₂O, (total of 100 L) shows an increase in the water modes and the In-O mode, indicating both water ice and In hydroxide formation on the surface. If the sample is then annealed to 350 K (77 °C), the vibrational spectrum changes significantly, displaying a large peak at 530 cm⁻¹ and a small OH stretch at 3620 cm⁻¹. The large peak around 530 cm⁻¹ is most likely due to the formation of In oxide, and the small OH peak around 3600 cm⁻¹ is due to small amounts of surface hydroxide formation

by residual H₂O. Additionally, after annealing there is no detectable signal from molecular water vibrational modes.

The differences between water adsorption on indium oxide and metallic indium were observed by pre-oxidizing the metallic indium surface with oxygen and subsequently exposing water. **Figure 7b** shows the Ar⁺ sputtered surface after exposure to 50 L of O₂ at room temperature. The metal oxide mode seen after annealing the H₂O exposed metallic sample is seen again at 530 cm⁻¹. After exposing to a total of 2000 L of O₂, there is a very large peak at 560 cm⁻¹, and significant OH stretch mode 3610 cm⁻¹. There is, once again, hydrocarbon contamination present at 1450 and 2940 cm⁻¹. After collecting the 2000 L O₂ exposed HREELS spectrum, the sample was cooled to 135 K and then exposed to 10 L of H₂O. In this spectrum there were very strong H₂O vibrational modes observed at 1620 cm⁻¹ and at 3580 cm⁻¹. Low energy water modes are obscured by a strong 560 cm⁻¹ signal. This difference in OH stretch and bend frequency indicates formation of a more ordered ice film at the oxidized indium surface than at the metallic surface, perhaps due to the improved wetting of H₂O on the oxide surface compared to the metallic surface. Signal strength may also imply that there is more H₂O adsorbed on the oxide surface after 10 L of H₂O exposure than adsorbed to the metallic surface after 100 L of H₂O exposure. This could be explained by the formation of In hydroxide during the 100 L H₂O exposure.

Figure 7. HREELS spectra of (a) an Ar^+ sputtered metallic indium foil at ~ 135 K exposed to 40 L and 100 L of H_2O before annealing to 350 K, and (b) an Ar^+ sputtered metallic indium foil exposed to 50 L then 2000 L of O_2 at room temperature, before being cooled to ~ 135 K and then exposed to 10 L of H_2O .

The HREELS data strongly indicate that even at low temperatures, H_2O can dissociatively adsorb, but the formation of indium oxide is suppressed until higher temperatures. This may be due to the barrier to O^{2-} diffusion to the metallic interface through a growing oxide lattice thin film. From XPS and HREELS data, an indium

surface appears to oxidize through the dissociative adsorption of O_2 or H_2O , followed by the diffusion of O^{2-} to the metal/oxide interface, forming a subsurface oxide film. The depth of this oxide and the speciation of the exposed surface is governed by the adjacent atmosphere composition.

TPD from Metallic Indium and Oxidized Indium in UHV After H_2O Exposure

In order to further understand how H_2O adsorbs on indium metal and indium oxide differently and to observe what reaction products are present, water was exposed to the two substrates independently and then temperature programmed desorption spectra were obtained for varying surface exposures.

Figure 8a demonstrates the desorption spectra following the exposure of 0.5 L, 1 L, 2 L, and 10 L of H_2O to an Ar^+ sputtered indium surface. At 0.5 L of exposure, there are two distinct peaks at 158 K and 169 K, with a broad feature centered around 197 K. The TPD spectrum for 1 L of H_2O exposure shows similar peaks, but the peak positions shift to higher temperatures, 164 K, 176 K, and 212 K, respectively. H_2O exposure of 2 L shifts the peaks to even higher temperatures, 166 K, 181 K, and 216 K, respectively. Lastly, at 10 L of H_2O exposure on metallic indium, the desorption peaks shift to temperatures of 173 K, 191 K, and 230 K, respectively, with the broad peak at around 230 K distinctly displaying multiple features.

Figure 8b shows the TPD spectra for the same H_2O exposures on an Ar^+ sputtered indium metal substrate that was exposed to ~ 2000 L of O_2 at room temperature to generate an oxidized surface. The 0.5 L H_2O exposure shows a distinctly different shape for the oxidized species, with two overlapping peaks. The primary peak is found at 163 K, with the shoulder centered at approximately 169 K, and a broad feature centered around

200 K. At 1 L H₂O exposure the primary peak area increases, but is centered at the same temperature as 0.5 L H₂O exposure: 163 K. The shoulder peak shifts to ~172 K, and the broad feature shifts to 208 K. After 2 L H₂O exposure the primary peak is still found at 163 K, with the shoulder shifted to ~175 K. The broad feature also appears to shift to higher temperature. Upon exposure to 10 L of H₂O, the primary peak shifts substantially to 171 K. The shoulder distinctly separates with a peak at 190 K, and the broad feature, similar to 10 L H₂O exposure on clean metallic indium, shows multiple desorption peaks centered at 233 K.

Figure 8. TPD spectra on a logarithmic pressure scale of (a) sputtered indium and (b) indium exposed to 2,000 L of O₂ at room temperature, each after being exposed to (black) 0.5 L, (red) 1 L, (green) 2 L, and (blue) 10 L of H₂O at ~135 K.

Figure 9 shows the TPD for the low H₂O exposures from Figure 8 on a linear scale instead of a logarithmic scale. Here the increase in peak area is more pronounced and the peak position shifts are emphasized. The behavior of the primary peak in Figure 9a is indicative of a zeroth order process, which is typical of molecular water adsorption to form ice. This indicates that the adsorbed water at this temperature is more strongly interacting with itself than with the metallic substrate.²² The dramatic change in peak shape and position to higher temperatures in the primary peak for the oxidized indium, seen in Figure 9b, is indicative of a change in desorption to first order.²³ The higher desorption temperature observed for low H₂O exposure indicates greater adsorption strength between H₂O and the oxidized substrate than between H₂O and the metallic substrate. The change to first order reaction is indicative of a non-dissociative adsorption of H₂O on the oxidized substrate.²⁴

In addition to monitoring H₂O (18 M/Z) during programmed desorption, O₂ (32 M/Z), H₂ (2 M/Z), N₂ (28 and 14 M/Z), CO (28 and 12 M/Z) and Ar (40 M/Z) were also recorded. Of these, only H₂ showed significant desorption over the observed temperature range. The single H₂ peak corresponded closely to desorption of the primary H₂O peak for both metallic indium and oxidized indium, and sat on a higher baseline than the other monitored gases. Overlaid H₂ and H₂O TPD spectra for 1 L of H₂O exposure on metallic indium, Figure 10a, and oxidized indium, Figure 10b, show similar relative H₂/H₂O peak ratios. Interestingly, the H₂ peak and H₂O peak from the oxidized indium sample appear at the same temperature, 163 K. This is not the case for H₂ and H₂O desorption from metallic indium, where H₂O peaks at 164 K, while H₂ peaks slightly later, at 166 K, which corresponds to a delay of ~15 seconds at this heating rate. This offset in H₂ peak

from the H₂O primary peak is observed at 2 L H₂O exposure to metallic indium as well, while H₂ and H₂O peaks for the 2 L H₂O exposure on oxidized indium again demonstrate coincidence.

Figure 9. TPD spectra on a linear pressure scale of (a) sputtered indium and (b) indium exposed to 2,000 L of O₂ at room temperature, each after being exposed to (black) 0.5 L, (red) 1 L, and (green) 2 L of H₂O at ~ 135 K. The inset for each spectrum shows the primary peak region in greater detail.

The TPD spectra suggest that H₂O adsorbs more strongly on the oxidized surface, where the adsorption of H₂O to the metal surface at these temperatures is a weaker interaction. Further, the metallic indium demonstrates a slightly higher temperature release of H₂, suggesting that as the substrate desorbs water, at some small coverage, the

metallic substrate is oxidized. This is supported by the change in HREELS spectrum after annealing the substrate above the desorption peak temperature, as seen in **Figure 7**, showing the presence of metal-oxide after water is desorbed.

Figure 10. TPD spectra on a linear pressure scale of (red) H₂O and (black) H₂ desorption from (a) Ar⁺ sputtered metallic indium, and (b) 2000 L O₂ oxidized indium.

Conclusions

From the data discussed above, it is evident that the major species exposed at a native indium metal surface under atmospheric conditions is a hydroxide species. O₂ and H₂O exposure demonstrates that after or during terminal hydroxylation, an In₂O₃ layer is formed. The hydroxyl termination of this native oxide is also observed in pure In₂O₃ samples, attesting to the basicity of the metal oxide, which forms OH groups from oxide and H₂O. There is a strong possibility that the equilibrium that favors hydroxyl formation at high H₂O pressures acts to passivate the metal from further oxidation in a manner similar to other group XIII elements.²⁵ The data demonstrate how a humid atmosphere can directly affect the order of oxidation and the potential for processing conditions to significantly impact the conductivity of the final oxide due to incorporation

of hydroxide doping. This understanding is useful for the development of further indium-derived products. This work also has potential implications for the mechanistic pathways of indium surface catalyzed reactions currently being performed in various settings. It is thus important that the active environment be considered in indium catalysis and indium materials synthesis, since the surface speciation is a sensitive function of the composition of the oxidizing atmosphere.

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Graphical Abstract