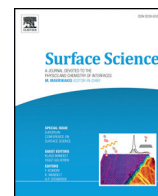




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# The oxidation and surface speciation of indium and indium oxides exposed to atmospheric oxidants

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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  $\text{In}_2\text{O}_3$  and  $\text{In}(\text{OH})_3$  were examined with XPS to provide standard spectra. Indium was exposed to  $\text{O}_2$  and  $\text{H}_2\text{O}$ , and the ratio of  $\text{O}^{2-}$  to  $\text{OH}^-$  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  $\text{In}_2\text{O}_3$  forms at higher temperatures. Initially,  $\text{OH}^-$  is the major species at the surface. Pure  $\text{In}_2\text{O}_3$  is also  $\text{OH}^-$  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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## 1. 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 is not as well documented as more abundant and more widely used structural metals.

Due to its wide use in electronics, ITO, unlike  $\text{In}^0$  and  $\text{In}_2\text{O}_3$ , 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].  $\text{SnO}_2$  nanoparticles have even been used as humidity sensors, showing significant conductivity perturbation in the presence of varying water vapor pressures [7]. Little attention has been placed on the role of  $\text{In}_2\text{O}_3$ –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  $\text{CO}_2$  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  $\text{CO}_2$  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  $\text{In}^0$  with  $\text{O}_2$ ,  $\text{H}_2\text{O}$ ,  $\text{CO}$ , and  $\text{CO}_2$ , finding that an In oxide layer developed on exposure to all of the oxygen containing species, but in the case of  $\text{CO}$  and  $\text{CO}_2$ , oxidation may have been due to trace  $\text{O}_2$  and  $\text{H}_2\text{O}$  contamination [12]. The oxidation of polycrystalline  $\text{In}^0$  with  $\text{O}_2$  was investigated with XPS and secondary ion mass spectrometry (SIMS) by Hewitt et al., who observed that  $\text{O}_2$  continues to oxidize  $\text{In}^0$  after thousands of Langmuirs (L) of  $\text{O}_2$  exposure, forming an  $\text{In}_2\text{O}_3$  film [13]. Concurrently, Sen et al. showed the formation of an  $\text{In}_2\text{O}_3$  film on  $\text{O}_2$  exposure to  $\text{In}^0$ , using AES. They noted the loss of  $\text{In}^0$  signal after  $10^6$  L of  $\text{O}_2$  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].

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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  $\text{In}^0$  and  $\text{In}_2\text{O}_3$  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  $\text{H}_2\text{O}$ ,  $\text{O}_2$ , and  $\text{CO}_2$  was systematically probed here.

## 2. 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.

### 2.1. 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 ~0.3 mm thickness and allowed to oxidize in atmosphere overnight before being introduced into vacuum. Powder samples of  $\text{In}_2\text{O}_3$  (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  $\text{Ar}^+$  beam at 2 keV and 10 mA emission current, delivering 4–6  $\mu\text{A}$  to the sample for 1 h.

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

### 2.2. 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.  $\text{H}_2\text{O}$ ,  $\text{O}_2$ , and  $\text{CO}_2$  dosing experiments were performed on an  $\text{Ar}^+$  sputtered indium metal substrate in the ESCALab 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  $\text{O}_2$  and  $\text{CO}_2$  were obtained from AirGas Inc. and leaked into the chamber through a mechanically pumped manifold via a bakeable sapphire sealed leak valve.  $\text{H}_2\text{O}$  was obtained from a Millipore MilliQ system with a resistance of 18.2 M $\Omega$ /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.

### 2.3. Speciation at high $\text{H}_2\text{O}$ 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  $\text{In}^0$  sample was prepared from metallic indium shot, then  $\text{Ar}^+$  sputtered at 2 keV and ~6  $\mu\text{A}$  for 1.5 h, and an  $\text{In}_2\text{O}_3$  sample was prepared by drop-casting isopropanol suspended powder onto a 1 micron film of Au on a 1  $\text{cm}^2$  Si wafer and then baking at 250 °C for 1 h. Ultra-high purity  $\text{CO}_2$  (AirGas) and water from a Millipore MilliQ water system at 18.2 M $\Omega$ /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.

### 2.4. 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  $1.2 \times 10^{-10}$  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  $\text{N}_2$  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  $5 \times 10^{-6}$  Torr and sputtering at 2 keV and ~6  $\mu\text{A}$  for 1 h at an  $\text{Ar}^+$  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 ~3 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 in. of the ionizing filament of the RGA. Programmed desorption was performed at a rate of 1 K/6 s.

## 3. Results and discussion

### 3.1. Authentic control samples

XPS of  $\text{Ar}^+$  sputtered indium metal shows that sputtering removes almost all detectable O 1s and C 1s XPS signal after 1 h at 2 keV and 6  $\mu\text{A}$  current to the sample. As seen in Fig. 1a, as the metallic In 3d<sub>5/2</sub> 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<sub>5/2</sub> and In 3d<sub>3/2</sub> peaks are considerably less than the fwhm of the In 3d peaks of  $\text{In}_2\text{O}_3$  (In 3d<sub>5/2</sub> at 444.7 eV) and  $\text{In}(\text{OH})_3$  (In 3d<sub>5/2</sub> at 445.1 eV), as seen in Fig. 1b and c, 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<sub>5/2</sub> 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  $\text{In}_2\text{O}_3$  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,

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