Atomic Layer Deposition of In$_2$O$_3$ Using Cyclopentadienyl Indium: A New Synthetic Route to Transparent Conducting Oxide Films

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Received March 30, 2006. Revised Manuscript Received May 24, 2006

Indium oxide (In$_2$O$_3$) forms the basis for an important class of transparent conducting oxides that see wide use in optoelectronic devices, flat-panel displays, and photovoltaics. Here we present a new method for depositing In$_2$O$_3$ thin films by atomic layer deposition (ALD) using alternating exposures to cyclopentadienyl indium and ozone. Using a precursor vaporization temperature of 40 °C and deposition temperatures of 200–450 °C, we measure growth rates of 1.3–2.0 Å/cycle. A significant advantage of this synthesis route over previous techniques is the ability to conformally coat porous materials such as anodic aluminum oxide membranes. The deposited films are nanocrystalline, cubic phase In$_2$O$_3$, and are highly transparent and conducting. In situ quadrupole mass spectrometry and quartz crystal microbalance measurements elucidate the details of the In$_2$O$_3$ growth mechanism.

1. Introduction

In$_2$O$_3$ thin films have applications as transparent conducting oxides (TCOs),† gas sensors,‡§ and catalysts.¶ For optimum performance, all of these applications require precise control over film thickness and composition, and some require the ability to coat high aspect ratio or porous materials. In$_2$O$_3$ thin films can be deposited using a variety of methods including sputtering, 10,11 chemical vapor deposition,12–15 and atomic layer deposition (ALD).16–20 Of these techniques, ALD shows significant promise as this method affords excellent control over both the thickness and the composition of the deposited film.21 Most importantly, ALD offers unmatched conformality that enables the coating of porous materials with aspect ratios in excess of 1000.22–24

Previously, In$_2$O$_3$ ALD has been accomplished using InCl$_3$ with either H$_2$O15 or H$_2$O$_2$16 as the oxygen source. Although useful for coating planar surfaces, this method suffers from several limitations. First, the InCl$_3$ chemistry requires high growth temperatures of ∼300–500 °C and yields a low growth rate of only 0.25–0.40 Å/cycle. In addition, the InCl$_3$ has a very low vapor pressure and must be heated to 285 °C just to saturate a planar surface. Furthermore, the corrosive HCl byproduct can damage the deposition equipment. But the greatest limitation of the InCl$_3$/H$_2$O method, especially for coating nanoporous materials, is that InCl$_3$ can etch the deposited In$_2$O$_3$.16 Nanoporous materials require very long precursor exposures that are likely to completely remove the In$_2$O$_3$ from the outer portions of the nanoporous substrate.

The primary goal of this study was to develop an improved ALD process for In$_2$O$_3$ that allows the coating of nanoporous materials. A number of alternate precursors have been investigated previously including β diketonates20 (In(hfac)$_3$ (hfac = hexafluoropropionate), In(thd)$_3$ (thd = 2,2,6,6-tetramethyl-3-cyclohexene-1-carboxaldehyde). The choice of the ALD precursor has a significant influence on the deposition efficiency and the composition of the deposited film. Stofko et al.25 investigated the use of an InCl$_3$/H$_2$O$_2$ bath to form In$_2$O$_3$ thin films. They observed that InCl$_3$ etches In$_2$O$_3$; however, they found that the InCl$_3$/H$_2$O$_2$ bath could be used to form In$_2$O$_3$ thin films by alternating with the H$_2$O$_2$ bath. They also observed that the InCl$_3$/H$_2$O$_2$ bath could be used to form In$_2$O$_3$ thin films by alternating with the H$_2$O$_2$ bath.

In summary, the InCl$_3$/H$_2$O$_2$ bath can be used to form In$_2$O$_3$ thin films by alternating with the H$_2$O$_2$ bath. They also observed that the InCl$_3$/H$_2$O$_2$ bath could be used to form In$_2$O$_3$ thin films by alternating with the H$_2$O$_2$ bath.

tetramethyl-3,5-heptanedionate), and In(acac)3 (acac = 2,4-pentanedionate) and trimethyl indium. Unfortunately, these efforts were unsuccessful. No growth was observed using β-diketonates with water or hydrogen peroxide, while trimethyl indium did not yield self-limiting growth. In this paper we describe a new method for In2O3 ALD using cyclopentadienyl indium(I) (InCp) and ozone. A related compound, pentamethylcyclopentadienyl indium(I), has been used previously for InP chemical vapor deposition. We utilize in situ quadrupole mass spectrometer (QMS) and quartz crystal microbalance (QCM) measurements to understand the growth mechanism. Next, we deposit In2O3 films on Si(100) and glass substrates and analyze the films using spectroscopic ellipsometry, X-ray powder diffraction (XRD), four-point probe resistivity, atomic force microscopy (AFM), UV-visible absorption spectroscopy, and scanning electron microscopy (SEM). These analyses reveal that cubic phase, nanocrystalline In2O3 is deposited at a growth rate of 2.0 Å/cycle. Finally, we apply this technique to conformally coat nanoporous anodic aluminum oxide (AAO) membranes.

2. Experimental Section

The ALD films were deposited in a custom viscous flow reactor similar in design to those that have been described previously. Briefly, a stainless steel flow tube with an inside diameter of 5 cm houses substrates for film growth as well as the QCM. Ultrahigh purity nitrogen carrier gas continuously passes through the flow tube at a mass flow rate of 360 sccm and a pressure of 1 Torr. A constant reactor temperature is maintained by four separate temperature controllers connected to resistive heating elements attached to the outside of the reactor. The four heating zones create a uniform temperature profile along the length of the flow tube to reduce the influence of temperature transients on the QCM measurements.

In2O3 ALD was performed using alternating exposures to cyclopentadienyl indium(I) (InCp, Strem, electronic grade 99.999+% In) and ozone. The InCp is held in a stainless steel bubbler maintained at 40 °C, and the tubing connecting the bubbler to the ALD reactor is maintained at 200 °C to prevent the deposition of InCp on the reactor walls. Ultrahigh purity nitrogen (99.999%) at a mass flow rate of 60 sccm was sent through the bubbler during the InCp exposures and was diverted to bypass the bubbler following the InCp exposures. The ozone was produced using a commercial ozone generator (Ozone Engineering L11) using a feed of ultrahigh purity oxygen at a flow rate of 400 sccm to produce ~10% ozone in oxygen. We also attempted In3O5 ALD using β-diketone precursors with ozone. The β-diketone precursors used were In(hfac)3 (Gelest) and In(acac)3 (Gelest). Additional oxygen sources evaluated for In3O5 ALD included deionized water (18 MΩ cm), hydrogen peroxide (30% solution in water, Aldrich), ultrahigh purity oxygen, and nitrous oxide (Aldrich, 99%).

The ALD timing sequences can be expressed as t1−t2−t3−t4, where t1 is the exposure time for the first precursor, t2 is the purge time following the first exposure, t3 is the exposure time for the second precursor, t4 is the purge time following the exposure to the second precursor, and all units are given in seconds (s). The timing sequence for In3O5 ALD was typically 2−4−2−2 s.

A QCM was installed in the ALD reactor in place of substrates enabling in situ measurements during the In2O3 growth. These measurements utilized a Maxtek BSH-150 bakeable sensor and AT-cut quartz sensor crystals with a polished front surface obtained from the Colorado Crystal Corp., part no. CCA185K-1007-000. The QCM measurements were made using a Maxtek TM400 film thickness monitor interfaced to a personal computer. In addition, the ALD reactor was equipped with a QMS (Stanford Research Systems RGA300) located downstream of the QCM in a differentially pumped chamber separated from the reactor tube by a 35 μm orifice and evacuated using a 50 L/s turbomolecular pump.

In2O3 ALD films were deposited on 1 cm × 2 cm Si(100) and glass substrates. Prior to loading, the substrates were ultrasonically cleaned in acetone and then 2-propanol and blown dry using nitrogen. After loading, the substrates were allowed to outgas in the ALD reactor for 10 min at the deposition temperature (typically 250 °C) in 1 Torr of flowing ultrahigh purity nitrogen. Next, the substrates were cleaned in situ using a 60 s exposure to 10% ozone in oxygen at a pressure of 2 Torr and a mass flow rate of 400 sccm. We observed a reactor conditioning effect in which the thicknesses of the In2O3 films deposited immediately following Al2O3 growth were thinner than expected. To compensate for this effect, we always deposited an In2O3 buffer layer on the inside of the reactor using ~100 InCp/O3 cycles following deposition of a different material.

SEM images were acquired using a Hitachi S4700 scanning electron microscope with a field emission gun electron beam source, secondary electron and backscattered electron detectors, and an energy dispersive analysis of X-rays (EDAX) detector for elemental analysis. AFM measurements were performed on a Digital Instruments Dimension 3000 with a NanoScope IIIa controller operated in tapping mode. XRD measurements were taken on a Rigaku Miniflex Plus diffractometer. Ellipsometric measurements of the In2O3 films deposited on Si(100) surfaces were performed using a J. A. Woolam Co. M2000 variable angle spectroscopic ellipsometer using a table of refractive indexes for In2O3 supplied with the instrument. Optical absorption spectra were acquired from ALD In3O5 films deposited on glass using the M2000 operated in transmission mode and were fit to a model using the same In3O5 optical constants. AAO membranes (Whatman Anodisc 13) with pore diameters of 200 nm and a membrane thickness of 70 μm were also coated by In2O3. Prior to SEM analysis, cleaved cross sections of the membranes were embedded in conducting epoxy and polished with progressively finer diamond polishing compound ending with 0.25 μm.

3. Results and Discussion

A) Initial Studies Using β-Diketonates. A previous study measured virtually no InO3 growth using indium β-diketones (In(acac)3, In(hfac)3, and In(thd)3) with either water or hydrogen peroxide as the oxygen source. The lack of growth was attributed to the very low reactivity of these β-diketone precursors to the In2O3 surface; however, ALD with ozone was not tested in this previous study. Ozone is often successful in ALD with β-diketonates, so we
initially tried using In(acac)$_3$ and In(hfac)$_3$ with O$_3$. In situ QCM experiments performed at 150–300 °C on a previously deposited ALD Al$_2$O$_3$ surface consistently yielded 0.3–1.0 Å of In$_2$O$_3$ during the first ALD cycle but little or no growth afterward. This suggests that the reactivity of the indium β-diketonates is relatively high on Al$_2$O$_3$ but too low on the In$_2$O$_3$ to support growth even using O$_3$. We attempted to deposit In$_2$O$_3$ films on Si(100) and glass substrates using In(hfac)$_3$/O$_3$ at a higher temperature of 350–500 °C. When an In(hfac)$_3$ bubbler temperature of 160 °C was used, the growth rate increased sharply with temperature from 0.03 Å/cycle at 350 °C to 0.51 Å/cycle at 500 °C, but the results were erratic. These difficulties may result from thermal decomposition of the In(hfac)$_3$ inside the reactor tube or in the bubbler or possibly sintering of the solid indium compound.

After our lack of success with In(acac)$_3$ and In(hfac)$_3$, we shifted our attention to InCp. Our initial measurements were encouraging as we discovered that we could deposit In$_2$O$_3$ films using InCp/O$_3$. Preliminary experiments were performed to determine the appropriate InCp bubbler temperature. In$_2$O$_3$ films were deposited using the timing sequence 2–2–1–2 on Si(100) substrates at 250 °C for 100 cycles while varying the InCp bubbler temperature between 30 and 60 °C. These measurements demonstrated that the InCp growth rate was nearly constant using bubbler temperatures above 40 °C. Using the Baratron pressure gauge, we measured a vapor pressure for InCp of 0.1 Torr at 40 °C. We tried using InCp with other oxygen sources, but the growth rates were substantially lower as shown in Table 1. We looked for the cyclopentadiene (C$_5$H$_6$). We also explained why no O$_3$ exposure precedes the InCp exposure, the sharp spike at the leading edge followed by a smaller plateau that persists as long as the InCp dosing valve is held open as illustrated by the first two ALD cycles in the figure. However, if no O$_3$ exposure precedes the InCp exposure, the sharp spike in the m = 66 peak is absent as shown by the final two ALD cycles in Figure 1a. From these observations we conclude that the sharp feature represents a gas-phase product of reaction 1, while the smaller plateau is simply decomposition of the InCp precursor in the QMS.

Similarly, we see a sharp spike in the m = 44 signal coincident with the O$_3$ exposures that are preceded by InCp exposures (Figure 1b); however, this spike is not seen when the InCp exposures are absent. Consequently, we conclude that m = 44 is a gas-phase product of reaction 2. The small peak in the m = 44 data coincident with the InCp exposures is present whether or not the InCp exposure is preceded by an O$_3$ exposure, and therefore this is a crack of InCp rather than a reaction product. The large, slow transient feature in the m = 44 signal that appears during the purge cycle of each O$_3$ exposure results from a CO$_2$ impurity in the ultrahigh purity oxygen which is pumped slowly by our system.

By collecting QMS data over the mass range 12–115 amu, we discovered that m = 44 (CO$_2$) is the only product of the O$_3$ reaction, while the InCp reaction yields the following products (and relative abundances): m = 66 (100), 65 (67), 39 (53), and 40 (33). This mass pattern matches closely the fragmentation pattern for cyclpentadiene (C$_5$H$_6$)$_3$. We also looked for the cyclpentadienyl dimer at m = 132, but we found none. It is surprising that we do not observe water during the O$_3$ half-reaction. One explanation is that the hydrogen from the Cp ligands in reaction 2 remains on the surface as hydroxyl (OH) groups that subsequently react with InCp to form HCP (cyclpentadiene, m = 66). This would explain why no m = 18 is observed in reaction 2, while the main product from reaction 1 is m = 66 rather than m = 65.

The ratio of gas-phase products measured during the InCp and O$_3$ half-reactions can be used to calculate x in eqs 1 and 2. By integrating the product mass peaks observed during the InCp exposures and correcting for variations in electron multiplier gain, quadrupole transmission, and ionization efficiency, we calculate that the amount of Cp released during the purging half-reaction is (in arbitrary units) 1 – x = 15. Similarly, after correcting for the relative effusion rate of CO$_2$ versus

| Table 1. Growth Rate for In$_2$O$_3$ Films Deposited on Si(100) Substrates Using 100 Cycles of InCp and Different Oxygen Sources at 250–275 °C |
|-----------------|------------------|
| oxygen source   | In$_2$O$_3$ growth rate (Å/cycle) |
| ozone           | 1.3              |
| oxygen          | 0.16             |
| water           | 0.068            |
| hydrogen peroxide | 0.039         |
| nitrous oxide   | 0.065            |

In these reactions, the surface species are designated with an asterisk and x is the fraction of Cp ligands remaining on the surface following each InCp exposure. The gas-phase products, the initial reactive sites, and the oxidant are all left unspecified but will be determined from the in situ measurements.

QMS measurements were performed to determine the gas-phase products of the InCp and ozone half-reactions. Representative QMS data recorded during the InCp and O$_3$ half-reactions are shown in Figure 1a,b, respectively. As shown in Figure 1a, a peak at m = 66 appears during the InCp half-reaction, but not during the O$_3$ half-reaction. When the InCp exposure follows an O$_3$ exposure, the m = 66 peak has a sharp spike at the leading edge followed by a smaller plateau that persists as long as the InCp dosing valve is held open as illustrated by the first two ALD cycles in the figure. However, if no O$_3$ exposure precedes the InCp exposure, the sharp spike in the m = 66 peak is absent as shown by the final two ALD cycles in Figure 1a. From these observations we conclude that the sharp feature represents a gas-phase product of reaction 1, while the smaller plateau is simply decomposition of the InCp precursor in the QMS.

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cyclopentadiene, the amount of CO$_2$ released during eq 2 is $5x = 13.8$, where the quantity $5x$ accounts for the fact that five CO$_2$ molecules are released from each Cp ligand. Combining these expressions, $(1 - x)/(5x) = 1.09$ so that $x = 0.15$.

Figure 2a shows the QCM data recorded simultaneously with the QMS measurements demonstrating that alternating InCp/O$_3$ exposures results in a linear mass increase versus time. The slope of the data in Figure 2a yields a net mass change of 55 ng/cm$^2$/cycle. Assuming a bulk density for In$_2$O$_3$ of 7.19 g/cm$^2$, this corresponds to a growth rate of 0.76 Å/cycle. As described in the next section, this growth rate is lower than the 1.3–2.0 Å/cycle measured on Si(100) substrates. This difference arises because the QCM is located ~33 cm downstream from the substrates where the O$_3$ concentration is lower.

Figure 2b shows an expanded view of the QCM data for two ALD cycles. There is an abrupt mass increase during each InCp exposure and a transient mass decrease coincident with each O$_3$ exposure followed by a slow increase such that the net mass change produced by the O$_3$ exposures is almost zero. We attribute the apparent mass decrease during the O$_3$ exposures to a transient heating of the QCM produced by the thermal decomposition of O$_3$ or the oxidation of the Cp ligands. The mass changes produced by the individual half-reactions can predict the fraction of Cp ligands remaining on the surface after the InCp exposures. Using the relationship $R = \Delta m / \Delta m_2$, where $\Delta m$ is the mass change from one complete cycle and $\Delta m_2$ is the mass change during reaction 1, we calculate from eqs 1 and 2 and the atomic masses that $\Delta m(\text{InO}_1) = 139$ and $\Delta m_2[\text{In} + (x)\text{Cp}] = 115 + 65x$ so that $R = 139/(115 + 65x)$. From Figure 1a, $R = 1.0$ so that $x = 0.37$ which implies that, on average, 37% of the Cp ligands remain on the surface after reaction 1. This value is somewhat higher than the value $x = 0.15$ calculated from the QMS data. This difference probably arises from uncertainties in the QMS parameters used to calculate the cyclopentadiene and CO$_2$ concentrations or from inaccuracies.
atomic layer deposition of in$_2$o$_3$

in the QCM data caused by the temperature-induced transient feature during the $O_3$ exposures. Nevertheless, the primary conclusion from the QCM data is the same as from the QMS data: a majority of the $Cp$ ligands are lost during the InCp exposures, and the small fraction remaining is subsequently removed during the following $O_3$ exposure.

One additional finding from the in situ measurements is that the reactive oxygen species during the In$_2$O$_3$ ALD is most probably oxygen radicals formed by the thermal decomposition of ozone ($O_3 \rightarrow O_2 + O$). This process occurs primarily on the In$_2$O$_3$ surface but also to a lesser degree on other surfaces (e.g., Al$_2$O$_3$) or possibly in the gas phase. The In$_2$O$_3$ growth rate drops off abruptly at 200 °C to nearly zero (Figure 7) suggesting that we must exceed a threshold temperature for ozone decomposition to enable In$_2$O$_3$ growth. This interpretation is supported by the observation that the $m = 48$ QMS signal from ozone is $\sim 10\times$ larger at temperatures below 200 °C. Furthermore, In$_2$O$_3$ appears to catalyze $O_3$ decomposition more efficiently than Al$_2$O$_3$ or gas-phase decomposition. Figure 3 demonstrates that when we first execute InCp/O$_3$ cycles following Al$_2$O$_3$ growth, the $m = 48$ signal is initially high but decreases nearly to zero following 40–50 In$_2$O$_3$ cycles. Moreover, in situ QCM measurements reveal that the In$_2$O$_3$ growth is initially inhibited following Al$_2$O$_3$ growth. Taken together, these results suggest that ozone decomposes on the growing surface to form a more active oxidizing species. This species is most likely a surface-bound oxygen radical or possibly a surface peroxide.$^{35}$

To summarize the in situ measurements, we can rewrite eqs 1 and 2 with the unknown surface species, gaseous products, and oxidant filled in:

$$5OH* + O* + 6InCp \rightarrow 5O-In* + O-In(Cp)* + 5C_5H_6$$

(3)

$$5O-In* + O-In(Cp)* + 19O* \rightarrow 5O-In(O)_{1.5}^- + OH* + O-In(O)_{1.5}^- + 5CO_2$$

(4)

In reaction 3, the initial reactive sites are five OH groups and one surface oxygen species. Six InCp molecules react with the surface liberating five cyclopentadiene molecules and leaving one Cp ligand on the surface. In reaction 4, surface-bound oxygen species formed by the decomposition of $O_3$ release the carbon from the remaining Cp ligand as five CO$_2$, but the hydrogen atoms remain to reform five new hydroxyl groups. Consequently, reaction 4 regenerates the initial surface and forms In$_2$O$_3$ with the proper stoichiometry, In/O = 1:1.5. Equations 3 and 4 yield $x = 1/6 = 0.17$, which is in the range of $x = 0.15–0.37$ determined from the in situ measurements. Although somewhat speculative, this mechanism has the appeal that the single remaining Cp ligand will exactly balance the five OH groups so that no hydrogen-containing products are released during the $O_3$ reaction. Although the indium oxidation state is not explicit in eqs 3 and 4, the conversion from In$^{3+}$ to In$^{5+}$ probably occurs mostly during the ozone step. In situ measurements using infrared absorption spectroscopy$^{36}$ could verify the existence of OH groups following the $O_3$ exposures. If oxygen radicals are indeed the active oxidizing species in this process, then substituting an oxygen plasma$^{37}$ in place of the $O_3$ may allow In$_2$O$_3$ growth below 200 °C.

(C) Growth of In$_2$O$_3$ Films. Following the in situ measurements, we proceeded with In$_2$O$_3$ deposition on Si-(100) and glass substrates to study the In$_2$O$_3$ growth. Figure 4a shows the results of uptake measurements made while varying the exposure time to InCp using the timing sequence $x - 2 - 2 - 2$. This figure demonstrates self-limiting behavior for InCp for exposure times of $\sim 2$ s. Figure 4b shows a similar graph exploring the effect of increasing ozone exposures using the timing sequence $2 - 2 - x - 2$ and demonstrates self-limiting In$_2$O$_3$ growth for ozone exposure times beyond $\sim 2$ s. Increasing the InCp and $O_3$ purge times did not affect the In$_2$O$_3$ growth rates, indicating that purge times $\geq 2$ s are sufficient to avoid mixing the precursors. For the remainder of the measurements, a timing sequence of $2 - 4 - 2 - 2$ was used unless otherwise noted.

Figure 5 reveals nearly linear In$_2$O$_3$ growth over the range of 50–1000 InCp/O$_3$ cycles at an average growth rate of 2.0 Å/cycle. Figure 6 demonstrates that the In$_2$O$_3$ growth rate actually increases somewhat with the number of cycles from 1.3 to 2.0 Å/cycle over the range of 50–2000 ALD cycles. This increase probably results from an increase in surface area with the evolution and growth of the In$_2$O$_3$ nanocrystals. Gradual changes in ALD growth rates have been observed previously for nanocrystalline materials in which the morphology or crystal size evolves with film

The effect of deposition temperature on the \( \text{In}_2\text{O}_3 \) growth is shown in Figure 7. Surprisingly, the \( \text{In}_2\text{O}_3 \) growth rate drops precipitously below 200 \( ^\circ \text{C} \). We believe that 200 \( ^\circ \text{C} \) is the threshold temperature below which ozone no longer decomposes to form oxygen radicals necessary for \( \text{In}_2\text{O}_3 \) growth. Between 200 and 450 \( ^\circ \text{C} \), the \( \text{In}_2\text{O}_3 \) growth rate is nearly constant at 1.2–1.4 Å/cycle. At 500 \( ^\circ \text{C} \), it was difficult to control the film thickness because most of the \( \text{InCp} \) decomposed at the leading edge of the sample holder in the reactor.

We also examined the variation in \( \text{In}_2\text{O}_3 \) film thickness along the flow direction of the reactor. Using the 2–4–2–2 timing sequence, the film thickness was constant for the first \( \sim \)15 cm of the reactor, after which the film thickness dropped off by 53% over 22 cm. The film uniformity improved using 15 s of \( \text{O}_3 \) exposure times so that the thickness decreased by only 33% over 22 cm, but the thickness variation was unaffected using longer \( \text{InCp} \) exposure times. We attribute this behavior to the depletion of ozone along the flow direction of the reactor.

The results of the film growth studies are summarized in Table 2 where we compare the \( \text{InCp}/\text{O}_3 \) process with the existing \( \text{In}_2\text{O}_3 \) ALD process using \( \text{InCl}_3/\text{H}_2\text{O}_2 \).

(D) Properties of \( \text{In}_2\text{O}_3 \) Films. Figure 8 shows an XRD measurement for a 176 nm film deposited on glass at 275 \( ^\circ \text{C} \). The peaks in Figure 8 match closely cubic, polycrystalline \( \text{In}_2\text{O}_3 \) (PDF number 00-006-0416) as illustrated by the Miller indices in the figure. In agreement with the XRD, the AFM image in Figure 9 reveals a relatively rough,
nanocrystalline topography for a 100 nm In$_2$O$_3$ film deposited on Si(100). This image has a $z$ range of 30 nm and yields a root-mean-squared (RMS) roughness of $R = 3.96$ nm for the $1 \times 1 \mu$m scan. The RMS roughness increases somewhat to $R = 4.9$ and 5.8 nm for scan sizes of $2 \times 2$ and $10 \times 10$

\[ \text{nanocrystals with a lateral dimension of 50–100 nm are evident in the plan view SEM image for the 100 nm In$_2$O$_3$ sample on Si(100) shown in Figure 10.} \]

Table 2. Comparison of InCl$_3$ and InCp Precursors for In$_2$O$_3$ ALD

<table>
<thead>
<tr>
<th>Indium precursor</th>
<th>InCl$_3$</th>
<th>InCp</th>
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<tbody>
<tr>
<td>Oxygen source</td>
<td>H$_2$O</td>
<td>O$_3$</td>
</tr>
<tr>
<td>ALD temperature window (°C)</td>
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<td>Precursor temperature (°C)</td>
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<td>Growth rate (Å/cycle)</td>
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<tr>
<td>Reference</td>
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<td>this work</td>
</tr>
</tbody>
</table>

Figure 7. In$_2$O$_3$ growth rate versus deposition temperature measured by ellipsometry for films deposited on Si(100) using 100 In$_2$O$_3$ ALD cycles with the timing sequence 2–4–2–2.

Figure 8. X-ray diffractogram recorded from 173 nm ALD In$_2$O$_3$ film deposited on glass using the timing sequence 2–4–2–4 at 275 °C.

Figure 9. Tapping-mode AFM image recorded from 100 nm ALD In$_2$O$_3$ film deposited on Si(100) using the timing sequence 2–4–2–4 at 275 °C. The contrast scale for this image is 30 nm, and the RMS roughness is 3.96 nm.

Figure 10. Plan view SEM image of 100 nm ALD In$_2$O$_3$ film deposited on Si(100) using the timing sequence 2–4–2–4 at 275 °C.

Figure 11. Optical transmission spectrum for 173 nm ALD In$_2$O$_3$ film deposited on glass using the timing sequence 2–4–2–4 at 275 °C referenced to uncoated glass.
Cross-sectional SEM images (not shown) demonstrate that the In$_2$O$_3$ films are dense and free of voids, pinholes, or cracks.

Figure 11 shows the optical transmission spectrum of a 173 nm thick In$_2$O$_3$ film deposited on glass referenced to the uncoated glass. The average transmission of the In$_2$O$_3$ film over the wavelength range 400–1000 nm is $T = 90.0\%$ and is comparable to ALD In$_2$O$_3$ films deposited previously using InCl$_3$/H$_2$O. This film had a resistivity of $16 \times 10^{-3}$ Ω cm which is somewhat higher than the value of $(3-6) \times 10^{-3}$ Ω cm obtained using InCl$_3$/H$_2$O, suggesting that the O$_3$ used in our process produces a more perfect In$_2$O$_3$ stoichiometry with fewer oxygen vacancies resulting in increased resistivity.

(E) In$_2$O$_3$ ALD in AAO Membranes. Next, we coated AAO membranes with In$_2$O$_3$ using 80 InCp/O$_3$ cycles at 250 °C. The AAO had an initial pore diameter $d = 200$ nm and thickness $L = 70$ μm such that the aspect ratio is $L/d = 350$. To allow gaseous diffusion of the precursors into the high aspect ratio pores, relatively long ALD cycle times of 60–15–60–15 were used. Figure 12a shows a backscattered electron image recorded from the middle of a cleaved cross section of the AAO membrane. The white lines visible on the edges of the AAO nanopores are the In$_2$O$_3$ coating and appear brighter than the surrounding Al$_2$O$_3$ because the higher-Z indium backscatters electrons more efficiently. Because this sample was polished prior to imaging, the white lines are not likely caused by edge contrast. In fact, the pore structure was practically invisible in secondary electron images (not shown). Figure 12b shows an EDAX spectrum recorded from the same location at the center of the AAO membrane, and the prominent In L$_\alpha$ peak at 3.29 keV demonstrates that the ALD In$_2$O$_3$ completely infiltrates the high aspect ratio AAO membrane. The intensity of the In L$_\alpha$ peak decreases by only 20% between the edge and the middle of the membrane, indicating very high conformality of the ALD In$_2$O$_3$ coating. We also coated much higher aspect ratio AAO membranes ($L/d = 2300$) using an identical treatment, but the coating was less conformal and the In L$_\alpha$ signal decreased by ~90% between the edge and the middle of the membrane. This is most likely due to a decrease in concentration of the O$_3$ or oxygen radicals along the very high aspect ratio pores.

4. Conclusions

We have presented a method for preparing In$_2$O$_3$ films by ALD using alternating exposures to cyclopentadienyl indium(I) and ozone. This method yields a growth rate of 1.3–2.0 Å/cycle over the temperature range 200–450 °C using a precursor evaporation temperature of only 40 °C. In situ measurements reveal a mechanism in which approximately one in six of the initial Cp ligands remain on the surface following each InCp exposure, and the remaining Cp ligand is burned off during the subsequent O$_3$ exposure to form CO$_2$. The reactive sites for InCp adsorption are likely to be OH groups formed during the preceding oxidation step, and the active oxidizing species is believed to be oxygen radicals formed by O$_3$ thermal decomposition on the growing surface. The resulting films are nanocrystalline, cubic In$_2$O$_3$ that is highly transparent and conducting. Using this method, we demonstrate for the first time the conformal coating of very high aspect ratio porous membranes with ALD In$_2$O$_3$. This technique will enable the functionalization of porous materials with In-based TCO films for the fabrication of novel photovoltaic devices.

Acknowledgment. The work at Argonne is supported by the U.S. Department of Energy, BES-Materials Sciences, under Contract No. W-31-109-ENG-38. The work at Northwestern University is supported by the U.S. Department of Energy, Basic Energy Sciences Program, under Grant DE-FG02-87ER13808, and by the Link Foundation (graduate Fellowship for A.B.F.M.).