Atomic layer deposition of in In_2O_3

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Atomic Layer Deposition of $\text{In}_2\text{O}_3\text{:H}$ from InCp and $\text{H}_2\text{O}/\text{O}_2$: Microstructure and Isotope Labeling Studies

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Supporting Information

ABSTRACT: The atomic layer deposition (ALD) process of hydrogen-doped indium oxide ($\text{In}_2\text{O}_3\text{:H}$) using indium cyclopentadienyl (InCp) and both O_2 and H_2O as precursors is highly promising for the preparation of transparent conductive oxides. It yields a high growth per cycle (>0.1 nm), is viable at temperatures as low as 100°C , and provides a record optoelectronic quality after postdeposition crystallization of the films (ACS Appl. Mat. Interfaces, 2015, 7, 16723–16729, DOI: 10.1021/acsami.5b04420). Since both the dopant incorporation and the film microstructure play a key role in determining the optoelectronic properties, both the crystal growth and the incorporation of the hydrogen dopant during this ALD process are studied in this work. This has been done using transmission electron microscopy (TEM) and atom probe tomography (APT) in combination with deuterium isotope labeling. TEM studies show that an amorphous-to-crystalline phase transition occurs in the low-temperature regime (100 – 150°C), which is accompanied by a strong decrease in carrier density and an increase in carrier mobility. At higher deposition temperatures ($>200^\circ\text{C}$), enhanced nucleation of crystals and the incorporation of carbon impurities lead to a reduced grain size and even an amorphous phase, respectively, resulting in a strong reduction in carrier mobility. APT studies on films grown with deuterated water show that the incorporated hydrogen mainly originates from the coreactant and not from the InCp precursor. In addition, it was established that the incorporation of hydrogen decreased from ~ 4 atom % for amorphous growth to ~ 2 atom % after the transition to crystalline film growth.

KEYWORDS: transparent conductive oxide, indium oxide, atomic layer deposition, hydrogen isotope doping, morphology, atom probe tomography, transmission electron microscopy

INTRODUCTION

Doped indium oxide (In_2O_3) is a metal oxide that can combine excellent optical transparency with a low electrical resistivity (<1 m Ω cm).¹ As such, this material finds its application as a transparent conductive oxide (TCO) in a multitude of optoelectronic devices such as solar cells,^{2–4} (organic) light-emitting diodes,^{5,6} and flat-panel displays.^{7,8} The most common form of doped In_2O_3 is Sn-doped In_2O_3 (ITO), although in recent years other dopants such as H,^{9,10} Zn,¹¹ Mo,¹² and W¹³ have attracted great attention. Compared to Sn, these novel dopants enable higher electron mobility values exceeding 50 cm²/(V s) at device-relevant carrier densities of $>10^{20}$ cm⁻³, resulting in more transparent and conductive films. Besides requiring excellent optoelectronic properties, many applications impose increasingly stringent requirements in terms of processing: A precise thickness control at the nanometer scale, a high large-area uniformity, and excellent conformality over three-dimensional surface topologies are increasingly often required. In addition, sensitive substrate materials can put restrictions on the available temperature window and the use of

plasma-based deposition techniques due to possible plasma-induced substrate damage. Sputtering¹⁴ and chemical vapor deposition (CVD)¹⁵ are commonly used deposition techniques to prepare In_2O_3 thin films. However, ultimately these methods face limitations with respect to the aforementioned requirements. For example, it is challenging to prepare thin films on three-dimensional surface topologies with a high conformality by sputtering. In addition, the plasma used can lead to substrate damage in OLED¹⁶ and silicon heterojunction¹⁷ devices. However, CVD typically requires higher deposition temperatures. The technique of atomic layer deposition (ALD) enables the deposition of thin films over large-area substrates with superior uniformity, conformality, and subnanometer resolution thickness control.^{18,19} In addition, the absence of a plasma and a considerable thermal budget makes it highly compatible with sensitive substrates.^{20,21}

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Table 1. Growth Properties of Selected ALD Processes for (Doped) In₂O₃ Reported in Literature

precursor	coreactant	dopant precursor	growth per cycle (nm)	substrate temp. (°C)	resistivity (mΩ cm)	ref
InCl ₃	H ₂ O	Sn (SnCl ₄)	0.02–0.03	500	0.24–0.27	22
InCl ₃	H ₂ O ₂	Sn (SnCl ₄)	0.03–0.04	300–500	0.31–0.39	26
InMe ₃	H ₂ O		0.01–0.08	150–320	2.8–5.0	23
InMe ₃	O ₃		0.05	100–200	3–10	27
In(acac) ₃	H ₂ O		0.02–0.03	165–250		24
In(acac) ₃	O ₃		0.01–0.06	165–300		24
In[(ⁱ Pr) ₂ CNMe ₂] ₃	H ₂ O		0.04–0.05	230–300		28
InCA	O ₃		0.08–0.10	50–250	0.22–11.3	25
InEt ₃	O ₃		0.05–0.11	50–250	0.47–2.0	25
DADI	O ₃		0.04–0.08	50–250	0.35–282	25
InCp	O ₃		0.13–0.20	200–450	16	29
InCp	O ₂ /H ₂ O		0.13–0.16	100–250	0.34–1	30
InCp	O ₂ /H ₂ O		0.12	100	0.27	10

In literature, many ALD processes for the preparation of (doped) In₂O₃ can be found. An overview of these processes is presented in Table 1. ALD of In₂O₃ films was first realized using InCl₃ and H₂O as precursor and coreactant, respectively, and SnCl₄ was used for doping.²² Although low resistivity values of 0.24–0.27 mΩ cm could be reached, this process requires high substrate temperatures of around 500 °C and features a fairly low growth per cycle (GPC) of 0.02–0.03 nm. Moreover, it was shown that the deposited In₂O₃ is etched by the InCl₃ precursor. Trimethyl indium (InMe₃) combined with H₂O can be used to prepare In₂O₃ films as well.²³ However, for this process the GPC values obtained at relatively low substrate temperatures (<250 °C) are below 0.04 nm. Meanwhile, the resistivity was observed to be relatively high (2.8–5.0 mΩ cm) due to the low carrier density ($2.7\text{--}7.4 \times 10^{19} \text{ cm}^{-3}$). Indium acetylacetonate (In(acac)₃) can be used to prepare In₂O₃ films with either H₂O or O₃, with a maximum GPC of 0.03 and 0.06 nm, respectively.²⁴ Maeng et al. recently published a comparative study using three liquid In precursors, i.e., diethyl[1,1,1-trimethyl-N-(trimethylsilyl)silanaminato]-indium (INCA), [3-(dimethylamino-kN)propyl-kC]dimethyl-indium (DADI), and triethyl indium (InEt₃), in combination with O₃.²⁵ Using these precursors, ALD growth could be obtained even at temperatures below 100 °C, although the resulting films were highly porous. Nonetheless, at a deposition temperature of 150 °C, very low resistivity values below 0.5 mΩ cm could be obtained, mostly because of a very high carrier density around 10^{21} cm^{-3} .

It has also been reported that In₂O₃ can be prepared at low substrate temperatures and with fairly high GPC values by using cyclopentadienyl indium (InCp) as In-precursor.^{29,30} Together with O₃ as coreactant, GPC values as high as 0.13–0.20 nm were obtained at substrate temperatures ranging from 200 to 450 °C.²⁹ Nonetheless, thermal decomposition of O₃ is catalyzed by the In₂O₃ film surface during the ALD process, resulting in a significant nonuniformity in film thickness, i.e., a lower film thickness is observed at the downstream region of the O₃ injection. Moreover, the films featured a high resistivity well above 1 mΩ cm. In follow-up work, Libera et al. significantly improved the InCp based process by replacing the coreactant O₃ with a combination of both H₂O and O₂.³⁰ With their synergetic growth recipe using InCp, H₂O, and O₂, a high GPC exceeding 0.1 nm at a temperature as low as 100 °C could be realized, while a high uniformity was also obtained.¹³ In addition, resistivity values as low as 0.34 mΩ cm could be obtained at 100 °C. Besides providing good transport

properties at low deposition temperatures, the reaction mechanism of this ALD process employing two separate oxidants is very interesting: From an *in situ* study using a quartz crystal microbalance (QCM) and a quadrupole mass spectrometer (QMS), they revealed that H₂O mainly serves to release the –Cp ligands from the film surface, while O₂ oxidizes the indium atoms from the +1 oxidation state to the +3 oxidation state. Negligible growth was observed when using only H₂O or O₂ as a coreactant. Moreover, the GPC values and film properties were found to be strongly dependent on the order of exposure of the reactant. The highest GPC values and best optoelectronic properties were found for films grown using simultaneous exposure (the so-called “SE-mode”) of H₂O and O₂, followed by H₂O and then O₂ (“WO-mode”), and vice versa (“OW-mode”).¹³ In addition, the carrier density and mobility were found to change drastically within the temperature range of 100–200 °C. These changes were attributed to the change from amorphous to polycrystalline growth as evidenced by X-ray diffraction (XRD). Using the SE-mode, the highest carrier mobility ($111 \text{ cm}^2/(\text{V s})$) was achieved around the amorphous–polycrystalline transition temperature of 140 °C. At the same time the carrier density decreased from 4.5×10^{20} to $0.8 \times 10^{20} \text{ cm}^{-3}$, which was attributed to a reduction of oxygen vacancies. At higher temperatures, the mobility quickly decreased, which was tentatively attributed to an increase in grain density and thereby in grain boundary scattering.

In subsequent publications, we have shown that this InCp + H₂O/O₂ process actually yields H-doped indium oxide (In₂O₃:H) and can be used to grow record-quality In₂O₃:H using a two-step process. The two-step process consists of the deposition of (mostly) amorphous In₂O₃:H at 100 °C, followed by solid-phase crystallization (SPC) by annealing at 150–200 °C in flowing N₂.^{10,31} After crystallization, the 75 nm thick films feature a lateral grain size of ~400 nm and very high mobility ($138 \text{ cm}^2/(\text{V s})$) and low resistivity (0.26 mΩ cm) values. For samples prepared at 100 °C, a H-content of 4.2 atom % was found, which is mostly retained after crystallization at 200 °C. The embedded H was demonstrated to be the main electron donor in the crystallized films rather than the often-mentioned oxygen vacancy (V_{O}^{2+}), as was also predicted by density functional theory.^{31,32} Also the SPC process itself has been studied in detail.³³

For the InCp and H₂O/O₂ process, the inclusion of hydrogen dopants and the crystal structure have proven to be of great influence in determining the optoelectronic properties of the resulting film. Therefore, in this work the crystal growth

and elemental composition have been investigated in detail for this ALD process over an extended temperature window (50–350 °C), and the correlation with the resulting film properties will be reported. More specifically, first our ALD growth process and resulting optoelectronic properties are characterized and compared to the results of Libera et al. From top-view TEM imaging, it is shown that films deposited at 100 °C consist of an amorphous phase with small embedded crystals (as was also observed in previous work³³) and that the grain density increases strongly with deposition temperature. It is shown that at 150 °C the largest grain size is obtained whereas at higher temperatures the grain size decreases and the film even remains partially amorphous. The latter is attributed to the incorporation of a significant amount of carbon impurities at deposition temperatures exceeding 150 °C, with up to 10.0 atom % of C for a film deposited at 350 °C. This decrease in crystal quality and impurity incorporation are thought to be the main reason for the impaired mobility at high deposition temperatures. In addition, it will be shown that the transparency of the films below the band gap of the material is strongly reduced at high deposition temperatures, which is also thought to originate from the significant C contamination. In order to study the incorporation of H in the films, isotope experiments using deuterated water (D₂O) instead of H₂O as coreactant were carried out. Employing both elastic recoil detection (ERD) and atom probe tomography (APT), the incorporation of atomic hydrogen and the distribution thereof have been studied. It is shown that hydrogen in the film mainly originates from the D₂O reactant and that at equal growth temperatures less H is incorporated in the crystalline grains of the films (~2 atom %) than in the amorphous host matrix (~4 atom %).

■ EXPERIMENTAL SECTION

In₂O₃:H films with a thickness of ~40 nm were prepared using an Oxford Instruments OpAL open-load ALD reactor. InCp was used as the indium precursor and was supplied by SAFC Hitech. Unless specified otherwise, deionized water vapor (DI H₂O) and oxygen gas (O₂) were both used as coreactants in the second half-cycle. In specific samples, deionized deuterated water (DI D₂O) was used. DI D₂O (99% purity) was acquired from Merck. InCp held in a stainless-steel bubbler was heated to 40 °C and delivered to the deposition chamber by a 50 sccm flow of Ar carrier gas. H₂O was vapor-drawn, and O₂ was delivered through a mass flow controller at a flow of 50 sccm. The substrate temperature during ALD refers to the temperature of the substrate stage. The chambers walls were heated to the substrate temperature, with a maximum of 180 °C.

Both Si (100) wafers with ~450 nm thermally grown SiO₂ and Si (100) wafers with 1–2 nm native oxide were used as substrates. The 450 nm of SiO₂ serves as an electrical isolation layer in between the TCO and the Si wafer, thereby allowing Hall measurements to be carried out without interference of the conductive Si substrate and also as an optical spacer to enhance the sensitivity of the spectroscopic ellipsometry (SE) measurements. For top-view TEM analysis, films were prepared on TEM windows of SiN_x. In order to exclude differences in growth on SiN_x and SiO₂ surfaces, the TEM windows were coated on both sides with 3–4 nm of ALD SiO₂ prior to deposition of the In₂O₃. The ALD SiO₂ was grown using SAM.24 and O₂ plasma at 200 °C, using the process as reported by Dingemans et al.³⁴

Film growth was monitored by *in situ* spectroscopy ellipsometry (SE). The SE setup used for these measurements is a J. A. Woollam Co. Inc. M-2000D spectrometer with an XLS-100 light source (1.2–6.5 eV of photon energy). After growth, the film thickness and optical constants were verified by *ex situ* SE at room temperature, over a spectral range of 0.75–5.0 eV. The dielectric function of In₂O₃ was

modeled using a combination of a Tauc–Lorentz and a Drude oscillator to account for absorption across the bandgap and free carrier absorption in the infrared, respectively. In addition, a Gaussian oscillator was used to account for subgap absorption, observed at high deposition temperatures. The sheet resistance of the films was measured on wafers with a ~450 nm thermal SiO₂ layer using a Signatone four-point probe (FPP) station, while the Hall mobility and carrier density were measured with a Europa HMS-5300 Hall Effect Measurement System. X-ray photoelectron spectroscopy (XPS) was used to determine the elemental composition of the films (excluding ¹H and ²H). The XPS setup used in this work was a Thermo Scientific K-Alpha KA1066 spectrometer, using monochromatic Al K α ($h\nu$ = 1486.6 eV) X-ray radiation. The XPS sensitivity factors used for oxygen and indium are 2.88 and 37.95, respectively, which were calibrated using a film with known stoichiometry values of O/In as obtained by Rutherford backscattering spectrometry (RBS). The XRD measurements were performed using an X'Pert Pro MRD analyzer, manufactured by Panalytical. ω – 2θ scans were performed on In₂O₃:H films prepared on Si wafers with a native oxide. To avoid a strong Si(400) reflection in the XRD measurements, the symmetry axis was given a 3° offset from the normal of the sample, i.e., $|\omega - \theta| = 3^\circ$. TEM studies were performed using a JEOL JEM-ARM200F transmission electron microscope. The cross-sectional TEM sample was prepared using a standard FIB lift-out procedure.

The areal densities of indium and oxygen atoms were measured by RBS, while the areal densities of hydrogen (¹H) and deuterium (²H) were measured by elastic recoil detection (ERD). The RBS/ERD measurements in this work were performed through Detect99 at the Singletron at AccTec BV in Eindhoven, The Netherlands. The samples were first investigated with ERD and subsequently with RBS using a 1.8 MeV He⁺ beam. The RBS spectra were registered simultaneously by two detectors at scattering angles of 105 and 170°. APT was carried out using a LEAP 4000X-HR from Cameca utilizing picosecond laser pulses with a wavelength of 355 nm. For APT analysis the In₂O₃:H thin films were capped with Cr and prepared into tips using a FEI Nova 600 FIB/SEM Dual beam set up.³⁵ The analyses were carried out at a base temperature of 20 K and with a laser power of 10–25 pJ per pulse. In order to ensure that the contribution to the hydrogen signal from the vacuum background is minimal, measurements were carried out at different laser pulse frequencies (125–250 kHz) and evaporation rates (1.5–3%). No significant changes of the measured hydrogen concentrations were observed over this range.

■ RESULTS AND DISCUSSION

In the work of Libera et al., it was shown that the properties of the In₂O₃ films obtained from the InCp + O₂/H₂O process are heavily dependent on the reactant exposure sequence, with the best properties obtained for a simultaneous exposure (SE). Our ALD tool does however not allow for an exact simultaneous pulse of O₂ and H₂O, due to a time delay of ~5 s for the O₂ to reach the chamber through the purged gas line. Therefore, in order to mimic the SE mode, the O₂ flow was started 5 s prior to the H₂O dose. Our process thus consists of the following steps, as schematically shown in Figure S1: InCp dose–InCp purge–O₂ flow stabilization–O₂/H₂O dose–O₂/H₂O purge.

Saturation curves were made for our process to verify the self-limiting behavior of the process and to determine the required purge and dosing times. These curves are shown in Figure 1. As can be seen, GPC saturates at ~0.12 nm for a 5 s InCp dose, which was therefore chosen as the standard InCp dosing time. The purging time of the InCp does not have any influence on GPC, but this is most likely also related to the subsequent O₂ stabilization step which also acts as a purge step. For the dosing and purging times of the reactants, it was found that 250 ms and ~7 s lead to saturating behavior, respectively. However, because of the slow saturation of the reactant purge

Figure 1. Saturation curves for ALD of $\text{In}_2\text{O}_3\text{:H}$ films using InCp as precursor and $\text{O}_2/\text{H}_2\text{O}$ as coreactants. (a) Precursor dose step, (b) precursor purge step, (c) reactant dose step, and (d) reactant purge step. The substrate temperature was 200°C . Lines serve as a guide to the eye. The optimized recipe consists of 5 s InCp dose–2 s InCp purge–5 s O_2 flow stabilization–0.25 s $\text{O}_2/\text{H}_2\text{O}$ dose–10 s $\text{O}_2/\text{H}_2\text{O}$ purge.

step, a purge time of 10 s was chosen to avoid the possibility of any parasitic CVD.

The ALD temperature window has been investigated for this process, as displayed in Figure 2. As can be seen, high GPC

Figure 2. Growth per cycle (GPC) as a function of substrate temperature for our ALD $\text{In}_2\text{O}_3\text{:H}$ process. For comparison, the GPC values of the SE, OW, and WO mode as obtained by Libera et al. are shown as well.

values exceeding 0.11 nm are obtained over a wide temperature range of $100\text{--}350^\circ\text{C}$. The GPC quickly decreases for lower temperatures, which can likely be attributed to incomplete surface reactions due to insufficient thermal energy supply.¹¹ Figure 2 also shows the GPC values found by Libera et al. for the SE, OW, and WO modes. The GPC values of our process are somewhat lower than the SE mode observed by Libera et al. and coincide more with their WO mode.

The film crystallinity and morphology have been investigated using top-view TEM imaging, selected area electron diffraction (SAED) and XRD, as shown in Figures 3–5. As can be seen from the TEM imaging, the sample deposited at 100°C consists of an amorphous phase with small (~ 50 nm) embedded crystallites. This is in line with results from our earlier work, where a low density ($\sim 6\ \mu\text{m}^{-2}$) of such crystallites was observed in an $\text{In}_2\text{O}_3\text{:H}$ film deposited on Al_2O_3 at 100°C .³³ However, the grain density of the films investigated in this study, which have been deposited on SiO_2 , was found to be consistently higher. Therefore, the nature of the substrate most

likely plays a role in the crystallite nucleation process during growth.

The corresponding XRD pattern of the sample deposited at 100°C shows a dim (222) peak, which is consistent with the partially crystalline nature observed by TEM. Also in the corresponding selected area electron diffraction (SAED) pattern (Figure 4a) both diffuse rings and discrete points are observed, corresponding to the amorphous host matrix and crystals, respectively. At 130°C , the surface of the $\text{In}_2\text{O}_3\text{:H}$ film is observed to be fully crystalline. However, the SAED pattern still consists of both diffuse rings and discrete points, implying that the subsurface of the film is not fully crystalline. For the sample prepared at 130°C an increase in the intensity of the XRD peaks is also observed, with the (222) peak being the strongest. Interestingly, the SPC reference XRD pattern in Figure 5, taken from our earlier work, shows a stronger $\langle 400 \rangle$ texture compared to the samples in this study that are directly grown polycrystalline.

A cross-sectional TEM image of the film prepared at 150°C (Figure 6) shows that the grains have columnar shapes that extend throughout the entire film. Note that the exact lateral size of the grains cannot be extracted unambiguously from this image due to partial overlap of grains within the projected thickness of the TEM sample. Based on the top-view BFTEM images, the SAED pattern, and the cross-sectional image, it is reasonable to believe that the $\text{In}_2\text{O}_3\text{:H}$ films prepared at 150°C are completely crystalline. At temperatures up to 250°C , the grain density increases further, whereas at higher deposition temperatures amorphization of the film is clearly visible in the SAED patterns by the reappearance of diffuse rings. The main reason for this amorphization is thought to be the incorporation of a significant amount of C impurities at high deposition temperatures, as will be discussed later.

The Hall parameters have been investigated, as shown in Figure 7. Again, the values obtained by Libera et al. are shown for comparison.³⁰ In addition, our previous result on postcrystallized $\text{In}_2\text{O}_3\text{:H}$ is shown.^{31,33} Similar to the SE and WO modes of Libera et al., a maximum in mobility of $68\ \text{cm}^2/(\text{V s})$ and a minimum in carrier density of $1.2 \times 10^{20}\ \text{cm}^{-3}$ is found around 150°C . The resistivity increases monotonically with deposition temperature, which is mainly due to a decrease in carrier density up to a deposition temperature of 150°C and a strong reduction of carrier mobility at higher temperatures. This impaired carrier mobility at higher deposition temperatures is thought to originate from the increased grain density and the amorphous fraction in the film as observed by TEM, as well as from a high concentration of incorporated C, as will be discussed later.

The optical constants of the $\text{In}_2\text{O}_3\text{:H}$ films have been determined from SE for the temperature series. In Figure 8, the spectral absorption coefficient α is plotted (see Figure S2 for the n and k values). With increasing substrate temperature, three main trends can be distinguished: (i) The Drude contribution strongly decreases for the samples deposited at $>100^\circ\text{C}$. This is in line with the strongly reduced carrier density when going from amorphous to polycrystalline films, which reduces the plasma frequency. At higher temperatures, the Drude contribution shows some scatter, mainly due to the variation in carrier density. (ii) The transition from amorphous growth to polycrystalline growth is accompanied by an increase in the optical bandgap, as can be seen by the onset of absorption across the bandgap that occurs at lower photon energy for the sample deposited at 100°C . This is similar to the

Figure 3. Top-view bright-field transmission electron microscopy (BFTEM) images of $\text{In}_2\text{O}_3\text{:H}$ films with a thickness of 40 nm as prepared on Si_3N_4 TEM windows covered with 3–4 nm ALD SiO_2 . The $\text{In}_2\text{O}_3\text{:H}$ was deposited at various substrate temperatures: (a) 100 °C, (b) 130 °C, (c) 150 °C, (d) 200 °C, (e) 250 °C, (f) 300 °C, and (g) 350 °C. The corresponding selected area electron diffraction (SAED) patterns are presented in Figure 4.

Figure 4. Selected area electron diffraction (SAED) patterns of $\text{In}_2\text{O}_3\text{:H}$ films with a thickness of 40 nm as prepared on Si_3N_4 TEM windows covered with 3–4 nm ALD SiO_2 . Patterns are given for various substrate temperatures 100–350 °C. Most of the SAED patterns show a combination of diffuse rings (from the amorphous fraction of the film) and sets of (interrupted) more discrete rings (from the crystalline fraction of the film). The interrupted nature of the diffraction rings points to a limited number of grains contributing to the SAED patterns. The contribution of the diffuse rings decreases from (a) to (b), in line with the observed increase in crystallinity in this temperature regime. In (c) and (d), the diffuse rings are absent, indicating a fully crystalline nature of these films. For (e) to (g), a weak diffuse ring can be recognized, in line with the decrease in crystallinity observed by XRD (Figure 5). For all SAED patterns a selected area aperture with a physical diameter of 1.3 μm was used. All patterns can be indexed with the cubic bixbyite structure of In_2O_3 .

increase of the optical gap that was found in earlier work upon postdeposition crystallizing an amorphous $\text{In}_2\text{O}_3\text{:H}$ sample.¹⁰

(iii) With increasing deposition temperature, the subgap absorption strongly increases. This is thought to originate

Figure 5. X-ray diffraction (XRD) $\omega - 2\theta$ spectra for $\text{In}_2\text{O}_3\text{:H}$ films with a thickness of 40 nm prepared on Si(100) wafers at different substrate temperatures. The XRD spectrum of a sample prepared at 100 °C and postcrystallized at 200 °C by SPC is shown for reference.¹⁰ The XRD peak intensities from a standard powder diffraction spectrum of cubic In_2O_3 are given as bar graph (Powder Diffraction File No. 65–3170, Joint Committee on Powder Diffraction Standards, 1955).

Figure 6. Cross-sectional high-resolution transmission electron microscopy (TEM) image of an $\text{In}_2\text{O}_3\text{:H}$ film with a thickness of 40 nm prepared at the substrate temperature of 150 °C on a Si wafer with a native oxide.

Figure 7. (a) Carrier mobility (μ), (b) carrier density (N_c), and (c) Hall resistivity (ρ) as a function of substrate temperature for ~ 40 nm-thick $\text{In}_2\text{O}_3\text{:H}$ films. Solid markers are results obtained in this work. For reference, the results obtained by Libera et al. for the SE, OW, and WO modes are shown in open symbols.³⁰ The star-shaped symbols show results obtained in our earlier work, using the recipe reported in this work to grow 75 nm of $\text{In}_2\text{O}_3\text{:H}$ on Al_2O_3 followed by postdeposition annealing at 200 °C (SPC).^{31,33}

Figure 8. Spectral absorption coefficient α for the $\text{In}_2\text{O}_3\text{:H}$ samples for various deposition temperatures. For reference, the absorption coefficient of the SPC sample from previous work is shown.¹⁰

from the C-impurity incorporation at higher temperatures and not to the crystallinity of the film. The latter statement is supported by the fact that the SPC sample of our previous work, which is shown for reference, does not display this subgap absorption, even though the sample is fully crystalline.¹⁰

The elemental composition of the $\text{In}_2\text{O}_3\text{:H}$ films and the incorporation of the H dopant has been studied using XPS, RBS/ERD, and APT. The resulting compositional properties have been summarized in Table 2, along with the corresponding GPC values and electrical properties.

The incorporation of C impurities has been studied by XPS. C contamination could not be detected by XPS at deposition temperatures up to 150 °C. At higher deposition temperatures the C contamination strongly increases, which is thought to originate from thermal decomposition of the InCp precursor. C levels up to 10 atom % were found for a film prepared at a deposition temperature of 350 °C, as shown in Table 2.

The atomic ratio of oxygen over indium, as determined from XPS, exceeded 1.5 regardless the substrate temperature, indicating that the films are oxygen-rich. The hydrogen content was investigated by ERD for the films prepared at the temperatures of 100, 130, and 150 °C, yielding atomic percentages of around 3–5 atom %. Because the films at low temperatures have a rather high H content and are over-stoichiometric, it is likely that a large part of the H is incorporated as OH-bonds.

In order to study the incorporation of the H dopant and the origin of the H dopant itself, depositions have been carried out using heavy water (D_2O) as coreactant instead of H_2O . This allows us to distinguish between H coming from the coreactant and other possible sources, such as H from the InCp precursor and H_2O in the background of the reactor. For the ERD study, samples deposited at substrate temperatures of 100, 130, and 150 °C were chosen. These films have a low carbon content, i.e., below the detection limits of XPS and RBS, and show relatively low film resistivity values compared to the films prepared at higher temperatures (>150 °C). Moreover, the microstructures of the films prepared at low temperatures are markedly different: The films are mostly amorphous at 100 °C, while fully crystalline films are obtained at 150 °C.

The results of the ERD analysis are listed in Table 3. Even though D_2O was used as coreactant, ^1H was also found in the films. ^1H was however observed to be only present within ~ 10

Table 2. Overview of Growth Per Cycle, Compositional Properties, and Electrical Properties of the In₂O₃:H Films Prepared at Different Substrate Temperatures^a

substrate temp. (°C)	growth per cycle (nm)	compositional properties			electrical properties		
		O/In ratio	carbon (atom %)	hydrogen (atom %)	resistivity (mΩ cm)	carrier density (10 ²⁰ cm ⁻³)	Hall mobility (cm ² /(V s))
100	0.11 ± 0.01	1.56 ± 0.07	0.0	4.9 ± 0.5	0.43 ± 0.02	4.0 ± 0.2	37 ± 2
130	0.12	1.59	0.0	3.3	0.72	1.7	51
150	0.12	1.58	0.0	3.6	0.79	1.2	68
170	0.12	1.57	0.3 ± 0.1	NM	0.85	1.8	40
200	0.12	1.58	0.5	NM	0.91	2.0	35
250	0.12	1.57	3.7	NM	1.3	2.1	23
300	0.13	1.55	6.4	NM	2.14	1.8	16
350	0.12	1.51	10.0	NM	3.93	1.5	10

^aThe films had a thickness of ~40 nm. The growth per cycle was determined from *in situ* spectroscopic ellipsometry measurements. The O/In ratio and the carbon content were measured by X-ray photoelectron spectroscopy. The atomic percentage of hydrogen was calculated by combining the hydrogen content measured by elastic recoil detection with the indium, and oxygen contents were measured by Rutherford backscattering spectrometry. The resistivity, carrier density, and mobility were measured by Hall measurements. The typical experimental errors are shown in the first entry of each column. NM means “not measured”. The hydrogen content in the In₂O₃:H films was only determined for the films deposited at low substrate temperatures as demarcated by the dashed line.

Table 3. Areal Atomic Density of Hydrogen (¹H) and Deuterium (²H) in 40 nm Thick In₂O₃:H Films Prepared by InCp and O₂/D₂O as Measured by Elastic Recoil Detection^a

substrate temperature (°C)	areal atomic density (10 ¹⁵ cm ⁻²)				
	¹ H				² H
	near surface	in the center	near interface	total	total
100	4.0	0	1.1	5.1	8.8
130	2.5	0	1.0	3.5	6.2
150	2.5	0	1.8	4.3	6.2

^a¹H in the In₂O₃:H films is observed to be mainly concentrated within ~10 nm of the surface and within ~10 nm from the substrate. No ¹H is observed in the intermediate center part of the films. ²H was found to be homogeneously distributed throughout the 40 nm film; therefore, only the total ²H areal atomic density is listed. The systematic errors in ¹H and ²H are 7 and 10%, respectively.

nm of the surface and within ~10 nm from the substrate and not in the bulk of the film, as indicated in Table 3. The ¹H residing near the surface of the film most likely originates from interaction with the atmosphere. The ¹H near the interface between the wafer and the In₂O₃:H film may originate from hydroxyl groups and water molecules present on the surface of the substrates before ALD. Another possibility is that residual H₂O has been present in the open-load reactor at the very start of the deposition, which is scavenged during the initial layer growth. The distribution of the ²H atoms is found to be almost homogeneous throughout the entire film within the depth resolution. Such a distribution is consistent with the incorporation of ²H atoms by surface reactions during every ALD cycle, as expected. The total amount of hydrogen in the In₂O₃:H films, including both hydrogen and deuterium, is 4.9 ± 0.5 atom % for the film prepared at 100 °C, as listed in Table 2. Note that this atomic percentage is averaged over the entire film, while the actual distribution of the isotopes is not homogeneous throughout the film. This atomic percentage corresponds to an averaged atomic density of (3.9 ± 0.4) × 10²¹ cm⁻³. The concentration is lower in the films prepared at 150 °C (3.6 atom %, as listed in Table 2).

In order to obtain a three-dimensional image of the distribution of hydrogen, and to investigate the correlation between the crystallinity and hydrogen content, the spatial

distributions of ¹H and ²H in In₂O₃:H films were measured by APT. Two films were selected for the APT study: one prepared at 100 °C and the other at 150 °C. Various APT samples were made for films prepared under these conditions by transferring different areas of the films on the Si substrates to the APT tips using a focused ion beam. Figure 9a,b shows schematic microstructures of the films prepared at 100 and 150 °C, respectively. The reconstructions of the distribution of the elements from three representative areas (two from the 100 °C film and one from the 150 °C film) are shown in Figure 9c–e. Figure 9c is representative for the major part of the film prepared at 100 °C, for which a homogeneous distribution of ²H is observed. Figure 9d represents a distinct area of the same film, for which a region with a relatively low density of ²H can be observed, corresponding to the embedded crystallite. Interestingly, this shows that at equal growth temperatures less ²H is incorporated on crystalline surfaces than that on amorphous surfaces. In previous work we observed an increase in GPC on the embedded crystallites, already pointing to a difference in the growth mechanism on amorphous and crystalline surfaces.³³ Figure 9e is representative for the entire area of the film prepared at 150 °C. At this temperature, ²H is more homogeneously distributed.

To further quantify the distribution of hydrogen, four volumes from the three representative areas were selected to create one-dimensional local depth profiles of ¹H and ²H. The term “local” is used to underline that the profiles are not the projections from the entire three-dimensional data set of the three areas but instead are collected from cylindrical volumes with a diameter of 10 nm. The depth profiles are shown in Figure 10. The locations of the selected volumes are indicated by the red rectangular regions in the schematics included in the figures. The four volumes are chosen to be representative of (a) only an amorphous matrix, (b) a crystallite, (c) a mix of a crystallite and an amorphous matrix in the film prepared at 100 °C, and (d) a crystallite in the film prepared at 150 °C. Note that the atomic percentages of ¹H and ²H obtained by APT are slightly different from the percentages determined by ERD/RBS, which is expected to yield more accurate quantitative results, at least averaged over the full film thickness. An enrichment of ¹H at the interface between the In₂O₃:H film and the Si wafer is observed in all four profiles, which is consistent

Figure 9. (a and b) Schematic representation of the layout of the samples analyzed by atom probe tomography (APT) prepared at 100 and 150 °C. The red rectangles schematically correspond to the areas of the films imaged in (c–e). (c–e) Reconstructions of the three-dimensional atomic distributions of each element in the films. (c) Part of the sample prepared at 100 °C which is completely amorphous and shows a homogeneous deuterium distribution. (d) Part of the sample prepared at 100 °C which contains an embedded crystallite and an inhomogeneous deuterium distribution. (e) Part of the sample prepared at 150 °C. Different elements are color coded as listed on the right side of the figure.

Figure 10. Local one-dimensional depth profiles of hydrogen (^1H) and deuterium (^2H). The embedded schematics represent the microstructure of the $\text{In}_2\text{O}_3\text{:H}$ films and correspond to those in Figure 9a,b. The red rectangular regions indicate the locations of the analyzed volumes, which are cylindrical in shape with a diameter of 10 nm: (a) mix of an amorphous matrix and a crystallite, (b) crystallite, (c) amorphous matrix in the film prepared at 100 °C, and (d) crystallite in the film prepared at 150 °C.

with the ERD data. However, in contrast to the ERD measurements, no enrichment of ^1H is observed at the film surfaces. This might result from the removal of adsorbed hydrogen during the FIB fabrication for the APT samples. Moreover, around 1–2 atom % of ^1H is observed throughout the film, which is not observed by the ERD measurements. Potentially, this hydrogen is present in the background during the APT measurements. In the film prepared at 100 °C, the ^2H

concentration is ~ 4 atom % in the amorphous matrix (Figure 10a) and ~ 2 atom % in the crystallites (Figure 10b). At the location where both an amorphous and a crystalline matrix are measured (Figure 10c), the percentages are ~ 4 and ~ 2 atom % in the amorphous matrix and in the crystallite, respectively. In the fully crystalline film prepared at 150 °C, the atomic percentage of ^2H is ~ 2 atom % (Figure 10d). Summarizing, irrespective of the substrate temperature between 100 and 150

$^{\circ}\text{C}$, the ^2H content is consistently higher in the amorphous phase (~ 4 atom %) than in the crystalline phase (~ 2 atom %). Interestingly, in our previous work, it was observed that the films changed from mostly amorphous to fully crystalline during postannealing, while the hydrogen content only dropped from 4.2 to 3.9 atom %.³¹ This demonstrates that crystalline In_2O_3 can retain a higher H-content than the ~ 2 atom % as found in this study. This also implies that the difference in deuterium content in the amorphous and crystalline regions as found by APT in this study can be attributed to a difference in deuterium incorporation from D_2O during film growth on these surfaces.

CONCLUSIONS

In this work, $\text{In}_2\text{O}_3\text{:H}$ films prepared by ALD using InCp as indium precursor and a combination of $\text{O}_2/\text{H}_2\text{O}$ as coreactant have been investigated over a wide temperature range (100–300 $^{\circ}\text{C}$). Following the earlier report of Libera et al., the ALD recipe was established and it was shown that the process yields a high growth per cycle of ~ 0.12 nm. Consistent with the earlier results, low film resistivities (< 1 m Ω cm) and an increasing degree of crystallinity were also obtained in the temperature range of 100–150 $^{\circ}\text{C}$. The composition and microstructure of the films were studied more extensively in this work and these properties were correlated to the optoelectronic properties. In particular, TEM studies revealed more details about the microstructure of the $\text{In}_2\text{O}_3\text{:H}$ films: Crystallites in an amorphous matrix were observed in the film prepared at 100 $^{\circ}\text{C}$, whereas a columnar grain structure was observed in the fully crystalline film prepared at 150 $^{\circ}\text{C}$. Carbon impurities were present in the films prepared at higher temperatures (> 150 $^{\circ}\text{C}$), which likely explains the reduced crystallinity and carrier mobility for these elevated temperatures when compared to the films prepared at 150 $^{\circ}\text{C}$. Furthermore, since hydrogen plays a crucial role in determining the properties of these films, the origin and distribution of hydrogen in the $\text{In}_2\text{O}_3\text{:H}$ films has been studied by a combination of RBS/ERD and APT. Isotope experiments revealed that the hydrogen in the films mainly originates from the H_2O coreactant, while from the APT study it was concluded that more hydrogen is incorporated in an amorphous region compared to a crystalline region.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acsami.6b13560.

Schematic of the ALD process, optical constants n and k of the ALD $\text{In}_2\text{O}_3\text{:H}$ films and their elemental composition (PDF)

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Notes

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