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Synthesis of High Surface Area—Group 13—Metal Oxides via Atomic Layer Deposition on Mesoporous Silica

Robert Baumgarten 1, Piyush Ingale 1, Kristian Knemeyer 1, Raoul Naumann d’Alnoncourt 1,∗, Matthias Driess 1,2 and Frank Rosowski 1,3

1 BasCat—UniCat BASF JointLab, Technische Universität Berlin, Hardenberstraße 36, 10623 Berlin, Germany; r.baumgarten@bascat.tu-berlin.de (R.B.); p.ingale@bascat.tu-berlin.de (P.I.); k.knemeyer@bascat.tu-berlin.de (K.K.); matthias.driess@tu-berlin.de (M.D.); frank.rosowski@basf.com (F.R.)
2 Institut für Chemie: Metalloganik und Anorganische Materialien, Technische Universität Berlin, Straße des 17. Juni 135, 10623 Berlin, Germany
3 Process Research and Chemical Engineering, BASF SE, Carl-Bosch-Straße 38, 67056 Ludwigshafen, Germany
∗ Correspondence: r.naumann@bascat.tu-berlin.de; Tel.: +49-30-314-73683

Abstract: The atomic layer deposition of gallium and indium oxide was investigated on mesoporous silica powder and compared to the related aluminum oxide process. The respective oxide (GaOₓ, InOₓ) was deposited using sequential dosing of trimethylgallium or trimethylindium and water at 150 °C. In-situ thermogravimetry provided direct insight into the growth rates and deposition behavior. The highly amorphous and well-dispersed nature of the oxides was shown by XRD and STEM EDX-mappings. N₂ sorption analysis revealed that both ALD processes resulted in high specific surface areas while maintaining the pore structure. The stoichiometry of GaOₓ and InOₓ was suggested by thermogravimetry and confirmed by XPS. FTIR and solid-state NMR were conducted to investigate the ligand deposition behavior and thermogravimetric data helped estimate the layer thicknesses. Finally, this study provides a deeper understanding of ALD on powder substrates and enables the precise synthesis of high surface area metal oxides for catalytic applications.

Keywords: atomic layer deposition; thermogravimetry; metal oxides; Ga₂O₃; In₂O₃; trimethylgallium; trimethylindium; high surface area; mesoporous silica

1. Introduction

Group 13 metal oxides (e.g., Al₂O₃, Ga₂O₃, and In₂O₃) possess key properties for a broad range of applications such as semiconductors, optoelectronics, and catalysts. Aluminum oxide is used as an insulator in gate transistors [1], as inert fillers [2], and as ceramics due to its firmness [3]. Gallium oxide can be applied as oxygen-gas sensors [4], as surface passivation of solar cells [5], and in electroluminescent devices [6]. Because of its high optical transparency and electric properties, indium oxide is used in numerous optoelectronic applications such as photovoltaics [7], light-emitting diodes [8], and modern displays [9].

In addition to electronic applications, group 13 metal oxides are crucial components of heterogeneous catalysts. Al₂O₃ acts as a typical catalyst support, for example in Pt-Sn/Al₂O₃ which is employed industrially for the dehydrogenation of propane [10]. Ga₂O₃ has been studied for the dehydrogenation of light alkanes such as propane. Moreover, In₂O₃-based catalysts have received tremendous attention due to their ability to convert CO₂-rich syngas into methanol [11,12]. Especially in heterogeneous catalysis, most of the reactions take place at active sites on the material’s surface. Therefore, a high surface area and homogeneous dispersion of deposited interfaces (e.g., metal oxides) are vital for enhanced activity [13].

The native bulk oxides of gallium and indium exhibit specific surface areas below 120 m²/g [12,14,15]. In order to increase the surface areas for catalytic applications, the
oxides can be deposited on a carrier material such as porous silica, alumina, and carbon with up to 600 m²/g [16,17]. One well-established tool for the deposition of uniform, nanoscale films is atomic layer deposition (ALD). This technique follows sequential reactions of a gaseous precursor and a reactant with the terminal groups of a material’s surface, growing one sub-monolayer per cycle (ca. 1 Å) [18]. One of the most commonly studied materials grown by ALD is Al₂O₃, using trimethylaluminum (TMA) and water as a precursor-reactant combination [19]. Alumina can be deposited on substrates with various topographies such as flat silicon wafers for passivation [20], electrodes for enhanced cyclability [21], and even polymers [22].

Since ALD is applicable to materials with different topographies, it progressively gained recognition in heterogeneous catalysis [23,24]. It was also investigated as a synthesis tool for the precise deposition of active metals [25,26] or metal oxides [27–29]. For instance, alumina overcoating on a Pt/Al₂O₃ catalyst was shown to prevent the sintering of Pt during propane dehydrogenation (PDH) [30]. Additionally, an alucone layer on Ni/SiO₂ prevented unwanted carbon formation under dry reforming conditions [31]. Further, ZnO ALD was applied to synthesize PDH-active Pt₁Zn₁ nano-alloys [32]. Thereby, SiO₂ was used as a carrier material for the ZnO ALD layer to increase the specific surface area up to 400 m²/g. Although Al₂O₃ ALD is widely applied in catalyst research, synthesis strategies employing ALD of the other group 13 oxides (e.g., GaOₓ and InOₓ) are seldom investigated.

Yet, there are some examples such as the usage of GaOₓ ALD to introduce acid sites on zeolites [28] or the application of InOₓ ALD to grow an In₂O₃ layer over Pt/Al₂O₃ as an efficient PDH catalyst [29].

To date, published studies on the deposition behavior of GaOₓ or InOₓ ALD on powder substrates are limited, especially with regard to higher surface area and porous structure [33]. On flat substrates, however, different precursor-reactant combinations were studied for the deposition of GaOₓ such as GaMe₃/O₂-plasma [34–37], GaEt₃/O₂-plasma [38,39], Ga(OPr)₃/H₂O [40], Ga(CpMe₃)/O₂ + H₂O [41], and [Ga(NMe₂)₃]₂/O₂-plasma [42]. Yet, all of them aimed for coatings of Si-wafer, fused silica, or SiO₂ terminated Si, focusing for example on electronic applications such as thin-film transistors [43]. The same accounts for InOₓ ALD investigations on flat substrates which comprise the usage of numerous combinations such as InCl₃/H₂O [44], InMe₃/(H₂O or O₂-plasma) [45–48], InEt₃/O₂-plasma [39], InCp/O₂ + H₂O [49,50], and others [46,51–58].

The consensus of the studies collected above is that water as an oxygen source, especially in combination with GaMe₃, leads to low growth rates due to the insufficient removal of methyl ligands [35]. Similar conclusions were made for the combination of InMe₃ and water [47]. Nevertheless, Kim et al. [45] found that a longer Langmuir exposure of H₂O (ca. 2 Torr·s) enabled the complete exchange of methyl groups, yielding In₂O₃ with linear growth per cycle (gpc). These findings can be rationalized by high activation barriers to remove the methyl group through water (Eₐ(Ga-CH₃) = 151.0 and (In-CH₃) = 169.8 kJ/mol), calculated by Shong et al. [59]. Insufficient ligand removal can be overcome by the usage of reactants with higher oxidation potential such as O₂-plasma [47]. However, plasma has the drawback of swift recombination on larger steel set-ups [60,61] and might lead to unwanted changes in the surface morphology of the substrate [62]. In addition to ALD, metal organic chemical vapor deposition (MOCVD) was used to synthesize defined layers of indium oxides. For example, Kakanakova-Georgieva et al. managed to stabilize two-dimensional (2D) layers of InO between graphene and Si/C via MOCVD of InMe₃ [63]. Hereby, DFT calculations were applied to investigate bonding and structure particularities, revealing a sequence of O-In-In-O for the 2D InO quadruple layer [64]. However, on amorphous silica, the formation of highly ordered oxides is unlikely as the surface structure is far more complex than ordered Si/C.

In order to use the full potential of ALD for the modification of porous substrates, deeper knowledge about the deposition mechanisms on powders is essential. Additionally, ALD on powders demands different process parameters which are less relevant for the coating of flat substrates [65,66]. For instance, diffusion limitations in the pores and
high surface areas (100–500 m$^2$/g) require different reactor geometries and longer dosing times [66,67]. Fixed- or fluidized-bed reactors were shown to be convenient, however, they cannot accommodate spectroscopic ellipsometry or a quartz crystal microbalance (QCM) for in-situ monitoring. Therefore, ALD processes on powders such as AlO$_x$/SiO$_2$ [68], ZnO/SiO$_2$ [67], and PO$_x$/V$_2$O$_5$ [69] were studied using a magnetic suspension balance for in-situ thermogravimetric analysis [70]. In the current study, we progressed with detailed investigations of the ALD growth behavior of gallium and indium oxides on mesoporous silica powder as a model system. The respective oxide was deposited with up to three cycles by the sequential dosing of trimethylgallium (TMG)/H$_2$O and trimethylindium (TMI)/H$_2$O at 150 °C.

2. Materials and Methods

2.1. Materials
Silica powder (SiO$_2$ amorphous, ≥99%, high-purity grade (Davisil Grade 636), average pore size 60 Å, particle size 250–500 µm, specific surface area 505 m$^2$/g, Sigma-Aldrich, St. Louis, MO, UAS) was used as a substrate for atomic layer deposition. Trimethylaluminium (Al(CH$_3$)$_3$, TMA, elec. grade (99.999%—Al)), Trimethylgallium (Ga(CH$_3$)$_3$, TMG, elec. grade (99.999%—Ga)), and Trimethylindium (In(CH$_3$)$_3$, TMI, elec. grade (99.999%—In)) (Strem Chemicals Europe, Bischheim, France) were employed as atomic layer deposition precursors. Water (H$_2$O, CHROMASOLV®, for HPLC, Riedel-de Haën/Honeywell Specialty Chemicals Seelze GmbH, Seelze, Germany) served as a reactant and was used without further purification. High purity argon (Ar, 99.999%) was used as a carrier and purging gas.

2.2. Atomic Layer Deposition of GaO$_x$ and InO$_x$ on SiO$_2$
Initially, the deposition behavior was examined in a magnetic suspension balance (MSB) for in-situ monitoring of mass changes (marked with MSB or in-situ). Afterward, the developed processes were scaled up in a quartz tube fixed bed reactor, producing up to 20 mL of ALD-modified material for ex-situ analysis. Both self-build setups possess fixed bed geometry operating at atmospheric pressure with top-to-bottom flow, as further described elsewhere [70]. In the MSB, GaO$_x$ and InO$_x$ ALD was carried out under a constant flow of 50 mL/min containing precursor or reactant diluted in argon. For each cycle, reactants were dosed until no further mass change was detected to ensure saturation. The same procedure accounted for intermediate purging steps to ensure the removal of gaseous precursors. For the larger fixed bed reactor (FB), a continuous flow of 100 mL/min was applied and saturation of the precursor was determined by an online quadrupole mass spectrometer (Pfeiffer Vacuum, Asslar, Germany). The point of saturation is reached once a constant ion current of unreacted precursor ions is measured in the MS shortly after the signal breakthrough (TMG: 69 m/z for Ga* and TMI: 115 m/z for In*), similar to previously described [67]. The precursor chamber of TMG was kept at RT and TMI at 80 °C while the reactors were maintained at 150 °C. For both oxides, three cycles were performed employing an ALD-sequence (cycle) of TMX/Ar-purge/H$_2$O/Ar-purge on dried silica powder.

2.3. Characterization of the Materials
Nitrogen physisorption measurements were performed at liquid N$_2$ temperature (77 K) using a Quadrasorb SI (Quantachrome GmbH & Co. KG, Odelzhausen, Germany). Prior to measurements, the samples were degassed at 150 °C for 2 h. The specific surface areas were determined applying the B.E.T. method (Brunauer–Emmett–Teller) and the corresponding pore size distribution was calculated from the desorption branches using the B.J.H. method (Barrett–Joyner–Halenda). Powder X-ray diffraction (XRD) patterns were acquired with an XPERT Pro (PANalytical, Malvern, UK) equipped with a scintillation detector, using Cu Ka1 radiation (λ = 0.154 nm). Inductively coupled plasma optical emission spectrometry (ICP-OES) was employed to determine In and Ga contents and
measured on a Varian 720-ES (Varian Inc., Palo Alto, CA, USA). Solutions from the powder were prepared via acidic leaching. Respective metals were detached from silica in a sealed container using saturated hydrochloric acid (35%) at 120 °C. The spectroscope was three-point calibrated with a commercially available, diluted standard for In and Ga. Mass fractions of carbon, hydrogen, nitrogen, and sulfur were determined by combustion analysis (CHN), executed on a EuroEA Elemental Analyzer (HEKAtech GmbH, Wegberg, Germany). FT-IR spectroscopy was measured in transmission (4000–400 cm⁻¹) on a Bruker ALPHA FT-IR spectrometer inside a glove box. Samples were diluted with KBr, ground in a mortar, and pressed into pellets. Prior to preparation, samples were dried at 130 °C for 3 h and transferred into the glovebox. Spectra were collected as data point tables by the usage of OPUS (Bruker, Billerica, MA, USA). Solid-state (SS) nuclear magnetic resonance (NMR) spectra were recorded with a Bruker Avance 400 MHz spectrometer operating at 100.56 MHz for ¹³C and 79.44 MHz for ²⁹Si. High-power decoupled (HPDEC) ¹³C and ²⁹Si cross-polarization magic angle spinning (CP/MAS) NMR experiments were carried out at a MAS rate of 10 kHz, contact time of 2.0 ms, and a recycle delay of 2 s, using a 4 mm MAS HX double-resonance probe. Spectra are referenced to those of external tetramethylsilane (TMS) at 0 ppm for ¹³C and ²⁹Si, using adamantane and tetrakis(trimethylsilyl)silane (TKS) as secondary references, respectively. X-ray photoelectron spectroscopy (XPS) was carried out on a K-Alpha™ + X-ray Photoelectron Spectrometer System (Thermo Fisher Scientific, Waltham, MA, USA), equipped with a Hemispheric 180° dual-focus analyzer connected to a 128-channel detector. The as-prepared samples were loaded directly on the sample holder for measurement. Data were collected with an X-ray spot size of 200 µm, 20 scans for the survey, and 50 scans for regions. Binding energy surveys were calibrated according to the C1s orbital fixed at 284.8 eV. Scanning transmission electron microscopy (STEM) was performed on an FEI Talos F200X (Thermo Fisher Scientific, Waltham, MA, USA) with an XFEG field emission gun and acceleration voltage of 200 kV. Energy-dispersive X-ray (EDX) mappings were recorded with a SuperX system of four SDD EDX detectors (Analysis software: Velox 2.9.0 by Thermo Fisher Scientific, Waltham MA, USA). The surface density of OH groups was determined via a Grignard titration method described in detail elsewhere [71]. A j-young NMR tube was loaded with ca. 20 mg of SiO₂ (dried at 150 °C), ferrocene, and self-synthesized Mg(CH₂Ph)₂·2(THF) as Grignard reagent (mass-ratio ca. 3:1:5) inside a glovebox. The solid mixture was suspended in benzen-d₆ and the NMR tube was sealed and shaken to let the reagents react with the OH-groups of SiO₂. ¹H NMR spectra were measured on a Bruker Avance II 200 MHz spectrometer (Bruker BioSpin MRI GmbH, Ettlingen, Germany). The total number of OH-sites was determined by calculating the number of moles of toluene produced (based on its methyl group peak integral at 2.1 ppm) using ferrocene as an internal standard.

3. Results
3.1. In-Situ Thermogravimetric Analysis
Deposition of GaOₓ and InOₓ was carried out on mesoporous SiO₂ using the ALD processes of TMG/H₂O and TMI/H₂O at 150 °C. The mass change during ALD was monitored using an in-situ magnetic suspension balance (MSB, Figure 1). Both ALD processes showed self-limitation for all first half-cycles when the precursor is dosed as well as during the ligand removal steps in the second half-cycles, representing ALD growth behavior. In the case of GaOₓ ALD, self-limitation of precursor chemisorption was reached within minutes, as for InOₓ, the first half-cycles extended over two hours. This can be rationalized by the three times higher vapor pressure of the gallium precursor under our conditions (TMG₃₀₀K = 327 mbar [72] and TMI₃₅₃K = 107 mbar [73]). Subsequently, the slight increase in mass during the second half-cycles relates to the exchange of the methyl group (15 g/mol) by the heavier OH-groups (17 g/mol) introduced by water.
in mass during the second half-cycles relates to the exchange of methyl groups (15 g/mol) introduced by water. Observation was made by Kim et al. for the deposition of InOx on a SiO2 terminated silicon flat substrate [45]. Our in-situ gravimetric studies also indicated lower GaOx uptakes (~33%) after the first ALD cycles. However, the use of H2O as a reactant did not hinder distinct growth during subsequent cycles. Moreover, a fourth cycle was conducted (Figure S1), resulting in uptakes of 13.4 wt% GaOx being of the same order of magnitude as the third cycle (14.2 wt%). Therefore, incomplete ligand removal does not necessarily translate to full inhibition of further growth.

In contrast, the InOx ALD led to a mass-uptake of 38.7 wt% in the first cycle and increased to 44.3 and 45.8 wt% in the following cycles. Increased uptake at higher cycle numbers hints at higher reactivity between the precursor and deposited oxides or a higher abundance of OH-groups compared to SiO2. Elam et al. demonstrated poor nucleation employing TMG/H2O in a quartz crystal microbalance and therefore proposed using O2 plasma [47]. Nevertheless, our study clearly demonstrates the constant growth of InOx on SiO2, indicating the suitability of H2O as a reactant. A similar observation was made by Kim et al. for the deposition of InOx on a SiO2 terminated silicon flat substrate [45].

Interestingly, Elam et al. observed a declining ALD growth of GaOx due to insufficient removal of methyl ligands using TMG/water above 200 °C [35]. Our in-situ gravimetric studies also indicated lower GaOx uptakes (~33%) after the first ALD cycles. However, the use of H2O as a reactant did not hinder distinct growth during subsequent cycles. Moreover, a fourth cycle was conducted (Figure S1), resulting in uptakes of 13.4 wt% GaOx being of the same order of magnitude as the third cycle (14.2 wt%). Therefore, incomplete ligand removal does not necessarily translate to full inhibition of further growth.

In the following, the trend of growth is discussed based on the in-situ mass-uptake, defined as the mass deposited by ALD divided by the initial mass of the support (Table 1). In the first full cycle, the GaOx ALD led to a mass-uptake of 24.3 wt% while the uptake declined within the second and third cycles to 16.3 and 14.2 wt%. This indicates either a substrate enhanced growth or incomplete ligand removal in the second half-cycles, as further discussed in the following section.

Table 1. Mass uptakes, molar uptakes, and total mass fractions of AlOx, GaOx, and InOx on SiO2 during three cycles of ALD using TMX (X = A, G, I) and H2O at 150 °C (GaOx, InOx) or 200 °C (AlOx). Mass-uptake = Δm/m0; molar-uptake = est.-Mol(M2O3)/m0; mass-fraction (frac.) = Δm/(m0 + Δm).

| ALD Cycles | AlOx/SiO2 [%] | Molar Up./% | Molar Up./mmol g⁻¹ | Mass Frac./% | GaOx/SiO2 [%] | Molar Up./% | Molar Up./mmol g⁻¹ | Mass Frac./% | InOx/SiO2 [%] | Molar Up./% | Molar Up./mmol g⁻¹ | Mass Frac./% |
|------------|---------------|-------------|---------------------|--------------|---------------|-------------|---------------------|--------------|---------------|-------------|---------------------|--------------|
| 1          | +11.9         | +1.0        | 10.6                | +1.0         | 19.6          | +38.7      | +1.0                | 27.9         |               |             |                     |              |
| 2          | +11.4         | +1.0        | 18.9                | +16.3        | 28.9          | +44.3      | +1.1                | 45.4         |               |             |                     |              |
| 3          | +13.4         | +1.2        | 26.9                | +14.2        | 35.4          | +45.8      | +1.1                | 56.3         |               |             |                     |              |
| Sum        | +36.7         | +3.2        | 26.9                | +54.8        | 35.4          | +128.8     | +3.2                | 56.3         |               |             |                     |              |

Interestingly, Elam et al. observed a declining ALD growth of GaOx due to insufficient removal of methyl ligands using TMG/water above 200 °C [35]. Our in-situ gravimetric studies also indicated lower GaOx uptakes (~33%) after the first ALD cycles. However, the use of H2O as a reactant did not hinder distinct growth during subsequent cycles. Moreover, a fourth cycle was conducted (Figure S1), resulting in uptakes of 13.4 wt% GaOx being of the same order of magnitude as the third cycle (14.2 wt%). Therefore, incomplete ligand removal does not necessarily translate to full inhibition of further growth.

In contrast, the InOx ALD led to a mass-uptake of 38.7 wt% in the first cycle and increased to 44.3 and 45.8 wt% in the following cycles. Increased uptake at higher cycle numbers hints at higher reactivity between the precursor and deposited oxides or a higher abundance of OH-groups compared to SiO2. Elam et al. demonstrated poor nucleation employing TMG/H2O in a quartz crystal microbalance and therefore proposed using O2 plasma [47]. Nevertheless, our study clearly demonstrates the constant growth of InOx on SiO2, indicating the suitability of H2O as a reactant. A similar observation was made by Kim et al. for the deposition of InOx on a SiO2 terminated silicon flat substrate [45].

Under the rough assumption, that the deposited oxides have a stoichiometry of M2O3 (M = Al, Ga or In), the molar uptakes per cycle were calculated based on the thermogravimetric data (Table 1). For each oxide and ALD cycle, the deposited moles of M2O3 per gram
SiO$_2$ are around 1 mmol/g. This indicates similar deposition behavior for each oxide and the deposited mass is a function of the molar mass (Table S1 in Supplementary Materials). Additionally, assuming a stoichiometry of M$_2$O$_3$ (M = Ga or In), the estimated metal contents were 14.5 wt% (Ga) and 23.1 wt% (In) after the first ALD cycle in the magnetic suspension balance (Table 2). The contents determined by ICP-OES were 14.6 wt% (Ga) and 21.1 wt% (In) which points to a stoichiometry of M$_2$O$_3$ for Ga$_2$O$_3$. Therefore, condensation of Ga(OH)$_x$ species might already occur in the first cycle. However, the mass fraction of indium is overestimated for the first cycle, indicating that the actual deposited species has a lower mass fraction of indium than in In$_2$O$_3$.

Table 2. Mass fractions of GaO$_x$ and InO$_x$ on SiO$_2$ within three cycles of ALD using TMX (X = G, I) and water at 150 °C. Values are calculated from thermogravimetric data (MSB) and compared to ICP-OES data. Mass-fraction (frac.) = $\Delta m/(m_0 + \Delta m)$.

| Sample       | Mass Frac.%  | $^1$M$_2$O$_3$ Frac.% | $^2$M(OH)$_2$ Frac.% | Mass Frac.% (ICP-OES) |
|--------------|--------------|------------------------|-----------------------|------------------------|
| 1c GaO$_x$   | 19.6 (Ga$_x$)| 14.5 (Ga)              | 13.1 (Ga)             | 14.6 (Ga)              |
| 3c GaO$_x$   | 35.4 (Ga$_x$)| 26.3 (Ga)              | 23.8 (Ga)             | 26.0 (Ga)              |
| 1c InO$_x$   | 27.9 (In$_x$)| 23.1 (In)              | 21.5 (In)             | 21.1 (In)              |
| 3c InO$_x$   | 56.3 (In$_x$)| 46.6 (In)              | 43.4 (In)             | 48.5 (In)              |

$^1$ calculated from in-situ mass-fraction, assuming M$_2$O$_3$ species being deposited. $^2$ assuming M(OH)$_2$ species being deposited on a single OH-group each.

Considering chemisorbed In(OH)$_2$ instead delivered an estimated indium content of 21.5 wt% which matches the measured content of 21.1 wt% (In). For subsequent cycles, the estimated indium contents have a better fit to ICP-OES when In$_2$O$_3$ is assumed. Hence, chemisorbed In(OH)$_2$ might resist condensation and do not collapse towards oxidic species in the first cycle. In subsequent cycles, the formation of In$_2$O$_3$ is favored during the reaction with TMI and water.

3.2. Effect of ALD on Surface Area and Pore Size

N$_2$ physisorption measurements were conducted to analyze ALD-induced changes to the surface area and pore structure of silica. The resulting isotherms are shown in Figure 2 and the differential pore size distributions are displayed in the supplementary material. All samples led to a type IV(a) isotherm with a mixture of type H1 and H2(b) hysteresis loop, characteristic of capillary condensation in materials with larger mesopores (>4 nm).

![Figure 2](image_url)  

**Figure 2.** N$_2$ physisorption isotherms of SiO$_2$ coated with (a) 1–3 cycles GaO$_x$ ALD and (b) 1-3 cycles InO$_x$ ALD, using TMX (X = G or I) and water at 150 °C substrate temperature.

The contribution of the H1 mode derives from equilibrium (liquid-vapor) transitions at cylindrical pores, indicated by mostly parallel adsorption and desorption branches. The
addition of the H2(b) mode is associated with delayed phase transition at more complex structures, such as ink-bottle-shaped pores with a wide distribution of neck sizes [74,75]. For all samples, the overall shape of the hysteresis is not affected by ALD indicating maintained pore character and conformal coating with GaOₓ and InOₓ [76].

The volume of adsorbed N₂ decreased as a function of the ALD cycle number which translates to the loss of specific surface area. The related values, calculated from the N₂ isotherm using the BET method, are shown in Table 3. A stepwise decrease in specific surface area from 505 to 259 m²/g was observed within three ALD cycles of GaOₓ. At the same time, the total pore volume was approximately halved from 0.79 to 0.39 cm³/g. Furthermore, the InOₓ ALD showed an even more pronounced effect as the specific surface area decreased to 142 m²/g and the pore volume to 0.23 cm³/g after three cycles.

Table 3. Specific surface areas (SA, calculated via BET) and total pore volume (PV) after ALD on SiO₂ using TMX (X = A, G, I) and water at 200 °C (AlOₓ) or 150 °C (GaOₓ, InOₓ).

| ALD Cycles | AlOₓ/SiO₂ [68] SA/m²·g⁻¹ PV/cm³·g⁻¹ | GaOₓ/SiO₂ SA/m²·g⁻¹ PV/cm³·g⁻¹ | InOₓ/SiO₂ SA/m²·g⁻¹ PV/cm³·g⁻¹ |
|------------|-----------------------------------|--------------------------------|--------------------------------|
| 0          | 505 0.79                           | 505 0.79                      | 505 0.79                      |
| 1          | 435 0.66                           | 336 0.57                      | 277 0.55                      |
| 2          | 383 0.55                           | 296 0.46                      | 216 0.34                      |
| 3          | 337 0.47                           | 259 0.39                      | 142 0.23                      |

However, the drastic decline of the specific surface area can be rationalized by the significant change in density induced by ALD. With a rising mass fraction of the deposited oxide, the sample exhibits less volume and surface area per gram. For instance, a given quantity of silica reaches 1.83 times its initial mass after two cycles of InOₓ ALD (Table 1). Consequently, the mass-related (specific) surface area would decrease from initially 505 to 276 m²/g, assuming no change in the exposed surface area. The estimated value is in good agreement with the measured value of 216 m²/g. Similar findings were made for the AlOₓ process on porous silica [68]. In fact, the observed changes are in a reasonable range as demonstrated in detail in the supplementary materials (Tables S2–S4 and Schemes S1–S3).

Additionally, the pore size distributions were calculated using the BJH method based on the rough assumption of having only regular and cylindrical pores (Figures S2 and S3 in Supplementary Materials). In both cases, ALD led to an even shift to smaller pore diameters with increasing cycle numbers. At the same time, the absolute desorption volume decreased, as it is also normalized to the mass of the sample. Both phenomena indicate that the pores of all diameters are decorated and accessible by the precursors. However, the calculated distribution has to be treated with reservation as the silica substrate featured an irregular and unknown system of different pore types [74,75].

3.3. Investigation of the Formed Phase and Its Dispersion

Powder X-ray diffraction (XRD) was employed to rule out the formation of crystalline agglomerates greater than the typical detection limit of around 2 nm [77,78]. The X-ray diffractograms of the as-deposited GaOₓ show no crystalline phase after three ALD cycles, thus being XRD amorphous (Figure 3). Moreover, the broad reflection at 21.8° (2θ), which accounts for amorphous SiO₂, and the diffractograms provide no defined intensity features.
Figure 3. X-ray diffractograms of (a) 1–3 cycle GaOx ALD and (b) InOx ALD on SiO2 (500 °C) indicate calcination at 500 °C in 20% O₂ for 3 h. Ga₂O₃ (19 wt%)/SiO₂ and In₂O₃ (27 wt%)/SiO₂ were synthesized via incipient wetness impregnation (IWI).

X-ray amorphous GaOx films were also deposited by Biyikli et al. [36] until 500 cycles of TMG/O₂-plasma. In their case, the transition to crystalline Ga₂O₃ only occurred under annealing in N₂. However, calcination of the three-cycle sample at 500 °C (20% O₂) did not result in the formation of detectable crystallites. This underlines the stability and dispersion of the layer despite a mass-fraction of 35 wt% GaOx. As a reference, 19 wt% Ga₂O₃ was supported on silica using the incipient wetness impregnation method with gallium nitrate (Ga₂O₃/SiO₂) (SI). After calcination at 500 °C, the impregnated sample exhibited broad signals characteristic of α- or β-Ga₂O₃ [79].

In the case of InOx ALD, the x-ray diffractograms exhibited no distinct reflections, being also XRD amorphous (Figure 3). On the contrary, an additional phase centered around 31.6° (2θ) emerged in the diffractogram of the three-cycle sample after calcination. It lies close to the reflection of the (222) plane of cubic In₂O₃ typically located around 30.6° (2θ) [80]. It might also be an indication for the (200) facet of In(OH)₃ lying between 31 and 32° [81]. However, the new phase might still be nanocrystalline and only the starting point for the formation of In(OH)₃ or In₂O₃ crystallites.

These findings agree with the literature, as Elam et al. showed that defined reflections of the (222) plane of In₂O₃ only appear upon 800 cycles after annealing or at higher deposition temperatures [47]. For comparison, 27 wt% In₂O₃ was supported on silica via incipient wetness impregnation and calcined at 500 °C (In₂O₃/SiO₂). The impregnated sample showed sharp reflections characteristic of cubic In₂O₃. Therefore, the impregnated In₂O₃ was clearly agglomerated and crystallized, while ALD provided a more dispersed InOx species.

STEM and EDX-mapping revealed agglomeration of the impregnated In₂O₃ sample with particle sizes between 20 and 100 nm (Figure 4). The calculated crystal diameter based on the 35.5° (2θ) reflection was approximately 21 nm, applying the Debye–Scherrer equation (FWHM = 0.82° (2θ)). Consequently, the atomic ratios between Si and In varied significantly between 25:1 and 2:1 within the mapping. EDX-mappings of the ALD samples of InOx and GaOx on SiO₂ demonstrate the opposite, without changes in morphology compared to the underlying support material. In the case of GaOx, the atomic ratio of Si and Ga varied between 6:1 to 8:1 in selected areas after one cycle (Figure 4).
Decreasing contribution of the O2s signal might be the result of the increased degree of coverage of substrate oxygen (SiO2) [82,83]. With increasing GaO2-related peak (Ga3d) in relation to the O2s peak. Decreasing contribution of the O2s signal might be the result of the increased degree of coverage of substrate oxygen (SiO2) by gallium oxide species. An alteration of hydroxylated Ga content was not observed (typ. around 19.6 eV) [84].

Increased loading of the three-cycle sample led to lower Si:Ga ratios (5:2) while being contained over the whole sample which indicates high dispersion. The same was found for the InOx ALD samples while the In:Si ratios were 8:1 in the one cycle and 2:1 in the three-cycle sample.

X-ray photoelectron spectroscopy (XPS) was conducted to determine the oxidic species of as-deposited InOx and GaOx on SiO2. The photoemission spectra of the Ga3d region showed two overlapping peaks (Figure 5a). One can be assigned to Ga, bound with oxygen as in Ga2O3, located at 20.8 eV. The second derives from the O2s orbital, around 24.8 eV [82,83]. With increasing GaOx cycle number, the intensity of the Ga2O3-related peak (Ga3d) increases in relation to the O2s peak. Decreasing contribution of the O2s signal might be the result of the increased degree of coverage of substrate oxygen (SiO2) by gallium oxide species. An alteration of hydroxylated Ga content was not observed (typ. around 19.6 eV) [84].
The peaks associated with the electron binding energies (BE) of the spin-orbit-coupled In3d orbitals (J = 3/2 and 5/2) are shifted to the lower BE with increasing cycle number (Figure 5b). After one ALD cycle of InOx, the In3d3/2 signal appeared at BE of 445.1 eV which can be assigned to In(OH)3 (445.2 eV [85]). After two cycles, the peak was located at 444.9 eV and after three cycles at 444.8 eV, while the latter is matching the binding energy as in In2O3 (444.7 eV [85]). Therefore, the deposited InOx species might transition from In(OH)x to In2O3 species with increasing cycle number. Additionally, increasing content of In2O3 could be observed within the O1s region (Figure 5c). The related signal was fitted into two peaks at about 532.2 eV and 530.2 eV after the third cycle. The former can be assigned to the oxygen of silica (O-Si) [86] and the second corresponds to oxygen as in In2O3 (O-In) [81,87,88]. Thereby, the ratio between Si and In2O3-related oxygen increased from 20:1 after the first cycle to 3:1 after the third cycle (see also Table S5 in Supplementary Materials).

3.4. Determination of Ligand Implementation

The InOx ALD process led to negligible carbon contamination. CHN analysis revealed carbon contents of 0.08, 0.16, and 0.14 wt% after the first, second, and third ALD cycles. The number of moles of deposited indium equating with the moles of incorporated precursors can be determined from the indium content. The ratio between moles of methyl groups of used precursor and moles of carbon provides information about the number of methyl groups still being attached after the dosing of water. As a result, approximately 1 out of 105 methyl groups of the deposited precursor remained, on average, after each cycle.

Ultimately, the question arises where the carbon species is deposited and of which nature it is. In addition to the typical absorption bands of SiO2, the FTIR spectra of InOx/SiO2 showed no features in the C-H stretching regions (Figure 6). The silanol band around 3740 cm⁻¹ and 977 cm⁻¹ decreased in intensity with higher cycle numbers as TMI chemisorbed on Si-OH. Still, the silanol-related bands persisted as weak shoulders after the third cycle. This indicates unreacted Si-OH groups that might be sterically blocked or in the bulk. For further evaluation of carbon species solid-state (SS), NMR analysis is necessary. Yet, the amount of carbon was not sufficient to induce changes in the silicon environment visible in the Tn zone (−50 to 80 ppm) of the 29Si SS-NMR spectrum or signals in the 13C SS-NMR spectra (Figure 7).

Figure 6. FTIR spectra (4000–400 cm⁻¹) of 1-3 cycle (a) GaOx and (b) InOx ALD on silica using TMX (X = G, I) and water at 150 °C.
Conversely, the GaOₓ ALD process provided carbon contents of 1.84 (1c), 2.56 (2c), and 2.70 wt% (3c) measured via CHN analysis. The amount of carbon after the first cycle was therefore in the same order of magnitude as for our AlOₓ/SiO₂ process (1.52, 1.59, and 1.33 wt% C [68]). Since the carbon content did not further increase after the second cycle of AlOₓ, the favored methylation of underlying SiO₂ might be the reason for carbon contamination. Conducting the same calculation as for InOₓ suggests that 1 out of 8 methyl groups persist during the re-hydroxylation of the first cycle and 1 out of 19 persist within three cycles of AlOₓ. In the case of GaOₓ, the carbon content increased further for subsequent cycles indicating different carbon deposition behavior. Hereby, one out of five methyl groups remained on the substrate after the first cycle and one out of six within three cycles. A constant proportion of un-removed carbon in each cycle hints at methylated gallium as the contact of TMG to underlying silica becomes less likely with a higher cycle number.

The FTIR spectra of GaOₓ/SiO₂ (Figure 6) held two sharp absorption bands in the C–H stretching region at 2980 and 2921 cm⁻¹ which can be attributed to [₁₅₁₅₁₅C-H] and [₁₃₁₃₁₃C-H] of methyl species [89–91]. Hereby, Si-CH₃ is formed through the dissociative chemisorption of TMG on Si-O-Si, and methoxy species were not found [92,93]. The band at 2980 cm⁻¹ is essentially shifted to a higher wavenumber and therefore attributed to methylated gallium as reported by Ring et al. [93]. Additionally, new features emerge in the fingerprint region at 742, 596, and 562 cm⁻¹. The band at 742 cm⁻¹ is assigned to the CH₃ rocking mode, while 596 and 562 cm⁻¹ are related to [₁₅₁₃Ga-C₂] and [₁₃₁₃Ga-C₂]. This underlines the formation of resilient, di-methylated gallium [81]. These findings are in line with the results of Elam et al. as they also detected CH₃ species via FTIR which were not fully removed upon exposure to water [35]. At the same time, the bands corresponding to silanol at around 3740 and 977 cm⁻¹ disappeared after the third cycle, indicating nearly full coverage of Si-OH between the second and third cycles.

In the present case, methylation was also observed in the ¹³C SS-NMR spectra as broad signals with maxima positioned around −8.6 and −15.5 ppm chemical shift (Figure 7). The peak closest to 0 ppm can be assigned to mono-methylated silicon (O₃–Si–CH₃) and the signal more up-field might derive from methylated gallium (O-Ga-CH₃ or O-Ga-(CH₃)₂) [94,95]. The formation of methoxy species or longer alkyl chains can be ruled out as they typically appear down-field at around 50 or 22 ppm [89,96,97]. Methylation of gallium indeed explains inhibition of uptake as full recreation of hydroxyl termination is impossible. Nevertheless, OH-groups and bridging oxygens were sufficiently available on the outer layer of GaOₓ which resulted in distinct growth in all cycles.

The presence of alkyl species in the vicinity of Si was also observed in the ²⁹Si SS-NMR spectrum of GaOₓ/SiO₂ (Figure 7). The broad signal reaching from −50 to −70 ppm agrees with the classic Tₖ zone of alkylated SiO₂ [98]. Within the Tₖ zone, the maxima found
between −55 and −59 ppm can be assigned to T2 (HO-Si-CH3) being attached to two bridging oxygen of the silica bulk. The maxima in the T3 region, located between −62 and −65 ppm, are related to Si-CH3 being connected to three bridging oxygen [94,99–101]. This essentially proves the methylation of silicon during the GaOx ALD process. Methylation of silicon mostly originates from the dissociation of precursors on oxygen-bridged silicon. Therefore, the TMG precursor might favor the dissociation reaction more than TMI. Finally, the distorted peak positioned between −85 and −120 ppm is clearly assignable to silanol groups and bridged silicon of Q3+4 (O3-Si-OH, O4-Si) [100,102].

3.5. Decryption of the Growth Mechanism

Combining in-situ thermogravimetric data with ICP-OES facilitates the determination of a tendency of the ligand exchange mechanism during the first cycle of the GaOx and InOx ALD. The carbon content is neglected for convenience and multiple dissociation steps are excluded as repeated dissociation does not lead to further change in mass. In the first cycle, the precursor TMX (X = Ga or In) can either react with Si-OH groups in a ligand exchange mechanism or with bridging oxygen of Si-O-Si (Figure 8). In the case of ligand exchange, the mass-uptake per mol of precursor depends on the number of ligands being replaced by silanol groups. The dissociative chemisorption of TMX on bridging oxygen results in the highest molar mass-uptake because all methyl groups are chemisorbed [93]. Subsequently, the methyl groups are exchanged by OH groups through a reaction with water. Thereby, methane is released as the only byproduct detected by the mass spectrometer.

Dividing the mass fraction of metal oxide (in-situ) by the moles of metal in the sample (ICP-OES) yields the average molar mass of chemisorbed precursor (in g/molprec). As a result, the GaOx ALD process led to mass gains of 93.3 g/molTMG after the first, 95.4 g/molTMG after the second, and 94.9 g/molTMG after the third cycle. This indicates the single (+102.7 g/molTMG) and double (+84.7 g/molTMG) ligand exchange mechanism

![Figure 8. Possible reaction pathways during the ALD of trimethyl gallium or indium (TMG, TMI) and water on silica. Calculated mass changes per mol of used precursor are displayed as g/mol. Multiple dissociation steps do not lead to further mass change and are therefore excluded. The abbreviation hc implies an ALD half-cycle.](image-url)
to occur as also estimated for AlOₓ ALD [68]. However, the contribution of dissociative chemisorption cannot be neglected as methylated silica was found by NMR.

The number of surface OH-groups of silica was determined as 3 OH/nm² via Grignard titration. Considering the specific surface area of GaOₓ/SiO₂ and the mass fraction of gallium, the number of Ga atoms is calculated to be 3.75 Ga/nm² after the first cycle. Therefore, dissociative chemisorption of TMG is necessary to reach the number of deposited gallium atoms. Any ratio of the ligand exchange reactions using the maximum number of 3 OH-groups/nm² filled up with dissociative reactions to obtain 3.75 Ga/nm² leads to around a 106 g/mol TMG uptake. As the first cycle only led to 93.3 g/mol TMG, condensation of Ga(OH)ₓ might already happen within the first cycle, resulting in lower uptakes and M₂O₃ stoichiometry.

In the case of the InOₓ ALD process, 151.8 g/mol TMI is added in the first cycle. As the uptake is higher than the theoretical maximum by ligand exchange (147.8 g/mol TMI), dissociation clearly has a contribution. The mass fraction of indium suggests 4 In/nm² being deposited in the first cycle. Any combination of ligand exchange reactions and dissociation, leading to 4 In/nm² and consumption of 3 OH/nm² (silica), would yield an uptake of 152.3 g/mol TMI. This value is close to the observed mass gain of 151.8 g/mol TMI which proves the dissociative reaction occurs.

In the second and third cycles, the average molar mass of the chemisorbed precursor is 135.9 g/mol TMI and 133.2 g/mol TMI which are between a single (+147.8 g/mol TMI) and double (+129.8 g/mol TMI) ligand exchange mechanism (Figure 8). Therefore, chemisorption of TMI on In(OH)ₓ might favor the ligand exchange mechanism, whereas dissociative chemisorption has a higher contribution when reacting with SiO₂. This phenomenon is accompanied by increased OH-group densities of 5–6 OH/nm² after InOₓ deposition, which allows more ligand exchange reactions. Moreover, less uptake per mole of used precursor might also be the result of condensation reactions between In-OH after the first cycle. Condensation leads to more intra-molecular In-O-In bonds which result in M₂O₃ character in higher cycles as suggested by XPS.

### 3.6. Estimated ALD Oxide Layer Thickness

The layers’ thickness is of special interest as it is comparable to literature values for flat substrates. It also serves as an approximate indicator for the formation of a closed monolayer as previously reported for AlOₓ on powder [68]. Within the first cycles, the grown oxide follows the nature of the substrate’s surface, enforcing an amorphous structure with less density than the crystalline bulk oxide [103]. With further cycles, the layer eventually transforms into more crystalline material, yet the structure can only be estimated roughly.

In order to estimate the thickness of the InOₓ layers, a density of 6.75 g/cm³ is assumed, which was determined by Chung et al. for amorphous, ALD-grown In₂O₃ [104]. Considering the respective mass fraction and surface area, InOₓ grows 1.5 Å per cycle on average (gpc), generating a 4.6 Å thick oxide layer after three cycles (Table 4). The gpc is in the upper range of values reported for flat substrates which vary from 0.3 Å to around 2 Å [48,51–53]. Moreover, the growth increases with cycle number, which might be due to the favored formation of In(OH)ₓ in the first cycle [104].

### Table 4. Calculated layer thicknesses of the respective metal oxide on mesoporous silica after 1–3 cycles ALD using TMX (X = A, G, I) and water at 150 °C (gpc = average growth per cycle).

| Sample [68] | Thickness/Å | Sample | Thickness/Å | Sample | Thickness/Å |
|-------------|-------------|--------|-------------|--------|-------------|
| 1c AlOₓ     | 0.8         | 1c GaOₓ | 0.9         | 1c InOₓ | 1.1         |
| 2c AlOₓ     | 1.6         | 2c GaOₓ | 1.6         | 2c InOₓ | 2.8         |
| 3c AlOₓ     | 2.5         | 3c GaOₓ | 2.2         | 3c InOₓ | 4.6         |
| gpc         | 0.8         | gpc    | 0.7         | gpc    | 1.5         |
For the amorphous GaO\(_x\) film, a reduced density of 5.5 g/cm\(^3\) is considered, calculated by Elam et al. [35]. As a result, the estimated gpc is 0.7 Å, leading to a layer thickness of 2.2 Å after the third cycle (Table 4). This is in agreement with values reported for flat substrates which are in the range of 0.5–1.5 Å [35,42]. As a comparison, TMA/H\(_2\)O on the silica powder led to similar gpc of around 0.8 Å [68].

In cubic In\(_2\)O\(_3\), the indium atoms are octahedrally coordinated with two different O–O distances depending on the Miller plane orientation. Along the (110) plane, the average oxygen layer distance is approximately 2.5 Å and along the (111) plane, In\(_2\)O\(_3\) grows less dense with a distance of 3.5 Å [105,106]. The calculated thickness for the second cycle (2.8 Å) indicates a defined monolayer being formed after the second and latest within the third cycle (4.6 Å). In β-Ga\(_2\)O\(_3\), the gallium atoms are either octahedral or tetrahedral coordinated by oxygen with average distances of 2.8 and 3.0 Å [107,108]. Therefore, a monolayer is not considered to be formed within three cycles, as the estimated layer thickness reaches 2.2 Å after three cycles of GaO\(_x\) ALD. This is in line with findings for the AlO\(_x\) ALD on silica powder, as we estimated a monolayer to be formed around the third cycle [68].

4. Conclusions

The ALD processes for the deposition of gallium and indium oxide on mesoporous silica powder using trimethylgallium or trimethylindium and water were investigated. In-situ thermogravimetry confirmed self-limitation of the precursor-chemisorption and water was shown to be effective for the ligand removal. CHN analysis revealed carbon amounts below 0.2 wt% after InO\(_x\) ALD and the deposited carbon species in the case of GaO\(_x\) ALD were determined as methylated Si and Ga by FTIR and SS-NMR. Both processes showed distinct growth in every cycle, leading to mass fractions of 20–35 wt% GaO\(_x\) and 28–56 wt% InO\(_x\) within three ALD cycles. Thermogravimetric and ICP-OES data suggested a stoichiometry of Ga\(_2\)O\(_3\) being present already after the first cycle. In the case of InO\(_x\) ALD, the transition from In(OH)\(_x\) to In\(_2\)O\(_3\) with increasing cycle number was observed by XPS and confirmed by calculations based on thermogravimetric data and ICP-OES.

Despite their high mass fractions, the oxides were found to be highly dispersed and amorphous by STEM EDX-mappings and XRD. Additionally, the ALD processes led to specific surface areas of 260–340 m\(^2\)/g for GaO\(_x\) and 140–280 m\(^2\)/g for InO\(_x\) determined by N\(_2\) physisorption analysis. The layer thicknesses were estimated based on thermogravimetric data which revealed a gpc of 0.7 Å for GaO\(_x\) and 1.5 Å for InO\(_x\). In conclusion, the study provides new insights into the ALD of GaO\(_x\) and InO\(_x\) on mesoporous supports with high surface area. Both processes can potentially be applied for catalyst synthesis while the oxide loading is tunable by the cycle number. Supported ALD catalysts might be further investigated for application in hydrogenation and dehydrogenation catalysis.

Supplementary Materials: The following supporting information can be downloaded at: [https://www.mdpi.com/article/10.3390/nano12091458/s1](https://www.mdpi.com/article/10.3390/nano12091458/s1), Figure S1: In-situ gravimetric monitoring of 4 ALD cycles GaO\(_x\) on SiO\(_2\) powder, Figure S2: Differential pore size distributions of GaO\(_x\) ALD modified SiO\(_2\), Figure S3: Differential pore size distributions of InO\(_x\) ALD modified SiO\(_2\), Figure S4: STEM-HAADF image and EDX-mappings of (a) 1 ALD cycle GaO\(_x\) on mesoporous SiO\(_2\), Figure S5: STEM-HAADF image and EDX-mappings of (b) 3 ALD cycle GaO\(_x\) on mesoporous SiO\(_2\), Figure S6: STEM-HAADF image and EDX-mappings of (c) 1 ALD cycle InO\(_x\) on mesoporous SiO\(_2\), Figure S7: STEM-HAADF image and EDX-mappings of (d) 3 ALD cycle InO\(_x\) on mesoporous SiO\(_2\), Figure S8: STEM-HAADF image and EDX-mappings of (e) impregnated In\(_2\)O\(_3\) (22 wt% In) on mesoporous SiO\(_2\), Table S1: Metal-uptakes of Al, Ga and In on SiO\(_2\) within 3 cycles of ALD using TMX (X = A, G, I) and water, Table S2: Estimated (blue) specific surface areas (ESA) and total pore volumes (EPV) of ALD-modified SiO\(_2\) based on model 1, Table S3: Estimated (blue) specific surface area (ESA) and mass-uptake (EUp) of ALD-modified SiO\(_2\) based on model 2, Table S4: Estimated (blue) surface area (ESA) and pore volume (EPV) of ALD-modified SiO\(_2\) based on model 3, Table S5: Fit parameters for the XPS scans of the Ga3d, In3d and O1s regions after GaO\(_x\) and InO\(_x\) ALD on SiO\(_2\), Scheme S1: Schematic description of model 1, based on two ALD cycles of InO\(_x\) on SiO\(_2\), Scheme S2: Schematic
description of model 2 (Core-shell), based on two ALD cycles of InO\textsubscript{x} on SiO\textsubscript{2}, Scheme S3: Schematic description of model 3 (volumetric), based on two ALD cycles of InO\textsubscript{x} on SiO\textsubscript{2}.

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