Bottom-Up Design of a Supercycle Recipe for Atomic Layer Deposition of Tunable Indium Gallium Zinc Oxide Thin Films

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ABSTRACT: We present a successful bottom-up approach to design a generic plasma-enhanced atomic layer deposition (PEALD) supercycle recipe to grow high-quality indium gallium zinc oxide (IGZO) thin films with tunable composition at a relatively low temperature of 150 °C. In situ real-time ellipsometric characterization in combination with ex situ complementary techniques has been used to optimize the deposition process and quality of the films by identifying and solving growth challenges such as degree of oxidation, nucleation delays, or elemental composition. The developed supercycle approach enables facile control of the target composition by adapting the subcycle ratios



within the supercycle process. Compared to other low-temperature deposition techniques resulting in amorphous films, our PEALD-IGZO process at 150 °C results in nearly amorphous, nanocrystalline films. The preparation of IGZO films at low temperature by a supercycle PEALD approach allows controlling the thickness, composition, and electrical properties while preventing thermally induced segregation.

KEYWORDS: IGZO, PEALD, supercycle, XPS depth profiling, current density

1. INTRODUCTION

In recent years, the quaternary oxide semiconductor indiumgallium-zinc oxide (IGZO) has attracted particular attention due to its high optical transparency and electron mobility^{1,2} as well as low fabrication costs.³ These properties make IGZO a promising candidate for thin-film transistors (TFTs) in the next generation of ultrahigh-resolution organic light-emitting diode displays and flexible electronic devices.⁴⁻⁷ To date, several techniques have been used to deposit IGZO films, including pulsed laser deposition (PLD),⁴ radio frequency (RF) magnetron sputtering,⁸ solution processing,⁹ and atomic layer deposition (ALD),^{10–14} where the film quality and thus its optoelectronic properties are highly dependent on the growth method employed. Besides, multiple applications in compatible metal-oxide semiconductor technology require precise control of thickness and conformability of ultrathin deposits on complex 3D structures, significantly hindering the use of physical methods (e.g., PLD and RF magnetron sputtering) for the IGZO film growth as the atoms or molecules are directionally deposited. In addition, the use of high-energy plasma species could damage the films and lead to interfacial defects during deposition, whereas inexpensive production methods based on solution processing are challenging to upscale and perform in such a way that they offer precisely tunable film properties.

In this context, the ALD technique has gained relevance in materials and surface science as it can overcome the abovementioned challenges in depositing binary oxides, providing high uniformity over large 3D-complex areas and precise control of film composition and thickness,¹⁵⁻¹⁷ notably important for, e.g., TFTs. In particular, plasma-enhanced ALD (PEALD) provides higher growth rates at lower temperatures by increasing the chemical reactivity at the surface and reducing the potential interlayer diffusion compared with conventional thermal ALD (TALD).¹⁸ Although the deposition of more complex compounds with desired optical and electrical properties has proven difficult, some successful attempts to grow IGZO films at relatively low temperatures of 200 °C $\leq T \leq$ 250 °C by different strategies (*i.e.*, precursor coinjection or supercycle procedures) have been reported.10,13,14

Despite the advantages presented by ALD, the low mobility of charge carriers is a matter of concern, particularly in the TFT performance. Due to structural defects, the mobility of

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Figure 1. (a) Scheme of a supercycle consisting of three subsequent single-component steps, each composed of (a, b, and c) subcycles, where the composition of the IGZO layer can be controlled by adjusting the individual subcycle ratio (a:b:c). (b) Sublayer sequence of the IGZO supercycle; (c) ALD temperature windows for the individual InO_{xy} GaO_{xy} and ZnO_x growth to define the common IGZO process temperature (indicated by the vertical straight bar).

IGZO films deposited by ALD is usually found in the lower range of 3.5 to 14.8 cm²/(V s),^{10,12} whereas increasing the indium content results in a significantly higher mobility of 48.3 $\text{cm}^2/(\text{V s})$ as reported by Cho *et al.*¹⁹ Besides, Sheng *et al.*¹¹ have achieved mobilities comparable to IGZO single crystals $[74 \text{ cm}^2/(\text{V s})]^{20}$ by increasing the thickness of the indium sublayer. As these two works exemplify, compositional In/Ga/ Zn variation has proven to be a promising route to overcome the issue of relatively low mobilities. However, the ALD process temperature used in previous works is relatively high $(T \ge 200 \text{ °C})$, which might be a limiting factor as it could induce thermally activated processes that lead to the segregation of binary oxide phases or film crystallization, as well as preventing its use in flexible electronic devices. Notably, the ALD mechanism for growing multicomponent oxide semiconductors such as IGZO is inherently more complex than for binary oxides, for which slight changes in the growth parameters can already significantly impact the film properties and hence their suitability for applications.²¹⁻²³ Therefore, studies focused on developing industrially scalable ALD methods and recipes capable of reproducing IGZO thin films of the desired composition, with a high degree of intermixing and structural amorphity, are relevant.

In this work, we have followed a bottom-up approach to design a generic PEALD supercycle recipe (*i.e.*, a well-adjusted sequence of ALD subcycles of the individual binary oxides to achieve the desired composition of the quaternary oxide, see Experimental Section) to grow high-quality IGZO films of targeted composition at lower temperatures compared to other ALD approaches. Particularly, real-time monitoring (RTM) of the ALD processes by in situ ellipsometry enables a detailed characterization and optimization of the ALD processes,²¹ detecting possible issues related to precursor and coreactant doses and purging times, as well as initial growth deviations related to nucleation delays when switching between precursors in subsequent subcycles. Therefore, by initially investigating the PEALD of the individual binary indium²³ (InO_x) , gallium²² (GaO_x), and zinc (ZnO_x) oxides using the organometallic precursors trimethylindium (TMIn), trimethylgallium (TMGa), and diethylzinc (DEZn) together with oxygen plasma (O2 plasma), we determine the lowest temperature possible to deposit the IGZO films, 150 °C. Furthermore, to illustrate the ALD supercycle designing process, we compare and discuss the deposition of the ZnO_x

sublayer by TALD and PEALD paths, showing that in situ realtime characterization²¹ in combination with ex situ complementary techniques can help to identify and solve growth challenges such as nucleation delays or metal oxidation degree in complex multicomponent compounds. After establishing the generic PEALD supercycle recipe, we discuss its impact on the elemental composition and electrical properties by considering different sequences during the growth. This approach enables facile control of the target composition by suitably selecting the number of repetitions of the individual subcycles within the supercycle process. Our results reveal that preparing IGZO films by PEALD via a supercycle at relatively low temperature allows controlling the thickness, composition, and electrical properties, potentially representing an important step toward a feasible process for manufacturing highly efficient oxide semiconductor TFTs and flexible electronic devices.

2. EXPERIMENTAL SECTION

2.1. Thin Film Deposition. Our complex IGZO supercycle recipe was developed following a bottom-up approach, i.e., the ALD parameters (substrate temperature, pulse durations, and reactor pressure) and the resulting growth characteristics [nucleation delay, growth per cycle (GPC), chemical composition, and metal oxidation state] were first determined and optimized for each binary oxide and subsequently combined to deposit a multicomponent film at the most favorable temperature matching the ALD windows of all three binary oxides. Figure 1a shows the scheme of a generic supercycle: Each ALD supercycle consists of subcycles for the individual binary oxides A, B, and C, which are carried out a, b, and c times, respectively; then, the supercycle is repeated n times to achieve the desired thickness. Figure 1b displays the order of the ALD supercycle in our particular case: $[(InO_x)_a/(GaO_x)_b/(ZnO_x)_c]_n$, deposited on top of 4-in. n-type Si(100) wafers with a native oxide (SiO_x) layer. The IGZO deposition initially starts with InO_x on Si; this process has been extensively described elsewhere.²³

The ALD growth was carried out in a SI PEALD reactor configured with a capacitively coupled plasma source (SENTECH Instruments GmbH)²⁴ and equipped with an ellipsometer for *in situ* ALD RTM (SENTECH, AL Real Time Monitor, AL-RTM).²¹ The IGZO films were prepared using the commercially available organometallic precursors TMIn, TMGa, and DEZn. In all cases, PEALD was performed except for the ZnO_x sublayer, where TALD was also applied for comparison (see Section 3.1). The subcycles for indium, gallium, and zinc oxide were composed of the sequences [0.04s TMIn/4s N₂/5s O₂ plasma/1s N₂], [0.01s TMGa/2s N₂/5s O₂ plasma/1s N₂], respectively. High-purity N₂ (99.9999%) was used as the carrier and

purging gas, with a flow rate of 100, 90, and 120 sccm, correspondingly, while a flow rate of 150 sccm was selected for purging after the O2 plasma step. Oxygen in quality of 99.998% was used. For both the N₂ and O₂ feedstock, a gas purifier was placed before entering the ALD equipment. In the case of TALD of the ZnO_x sublayer, DEZn and ultrapure H₂O were fed in a sequence of [0.04s DEZn/5s N₂/0.08s H₂O/5s N₂]. Again, N₂ was used as the carrier and purging gas, adjusted to 60 and 80 sccm for DEZn and water, respectively. The growth parameters were set according to the optimization of each binary oxide, so that the dose and purging times were reduced as much as possible, as reported elsewhere for the GaO_x^{22} and InO_x^{23} cases. Figure S1 in the Supporting Information provides the saturation curve for the ZnO_x PEALD process. In the case of the GaO_x subcycle, a longer purge time (40 s) is required after the last TMGa dose to ensure a complete purging of the carrier gas tubing, which is shared with the other organometallic precursors via one unique mass flow controller. More details are provided elsewhere.²² Furthermore, after comparing the ALD windows determined for all of the individual binary oxides, as illustrated in Figure 1c, the IGZO thin films were deposited at 150 °C (substrate temperature). All films contain 12 supercycles (n = 12), resulting in a final layer thickness between 7 and 9 nm depending on the final PEALD supercycle sequence. Table 1 summarizes the growth

Table 1. Deposition Parameters for the PEALD (InO_x, GaO_x) and ZnO_x and ZnO_x and $TALD (ZnO_x)$ Subcycles of the IGZO Layers^a

		PEALD		TALD
process parameters	InO _x	GaO_x	ZnO_x	ZnO_x
precursor	TMIn	TMGa	DEZ	DEZ
coreactant	O ₂	O ₂	O ₂	H_2O
$P_{\rm p}$ (W)	200	200	200	
$T_{\rm s}$ (°C)	150	150	150	150
$t_{\rm p}$ (s)	0.04	0.01	0.04	0.04
$t_{\rm c}$ (s)	5	5	5	0.08
t _{purge} (s)	4, 1	2, 1	4, 1	5, 5
$P_{\rm t}$ (Pa)	10	20	20	9
N ₂ -prec (sccm)	100	90	120	60

^aThe parameters are plasma power (P_p), substrate temperature (T_s), precursor pulse duration (t_p), coreactant pulse duration (t_c), purge time (t_{purge}), total pressure (P_t), and N₂ flow rate used with the precursor dose (N₂-prec).

parameters for the PEALD (InO_{x}, GaO_{x}) and $ZnO_{x})$ and TALD (ZnO_{x}) recipes used for each binary oxide subcycle. More information regarding the individual deposition of GaO_{x} and InO_{x} can be found elsewhere.^{22,23}

2.2. Characterization. The *in situ* ALD RTM enables direct monitoring of the ALD process during IGZO film growth and provides a high-resolution thickness control thanks to the high temporal resolution (20 ms) and the very high signal-to-noise ratio ($\delta \Delta = 0.01^{\circ}$, where Δ is the ellipsometric angle) at a single wavelength of 632.8 nm with an incident angle of 70°.²¹

The IGZO films were studied *ex situ* by chemical, structural, optical, and electrical characterization techniques. Their elemental composition and oxidation states were characterized by *ex situ* XPS measurements performed with a hemispherical energy analyzer (PHOIBOS has3500, SPECS) and nonmonochromatic Mg K α and Al K α radiation. The Mg and Al anodes were alternatively used to avoid overlapping the photoelectron and Auger peaks. The XPS survey and individual core-level spectra were collected at a takeoff angle of 90° with pass energies of 50 and 20 eV and energy steps of 0.5 and 0.1 eV, respectively. At a pass energy of 20 eV, the overall spectrometer resolution is 1.0 and 0.9 eV for the Al and Mg anode, respectively. The energy scale was calibrated using the carbon C 1s peak at 284.8 eV.²⁵ The XPS spectra were taken before and after gentle surface cleaning by Ar⁺ sputtering (cold cathode ion source ISE

5, Scienta Omicron), with an accelerating voltage of 500 eV at a pressure of 4×10^{-6} mbar. The same sputtering parameters were also used to generate composition depth profiles with an estimated sputter rate of around 0.3 nm/min. The atomic concentrations were estimated by considering the raw areas of the respective core levels after background removal and weighting by the corresponding atomic sensitivity factor. The XPS core-level spectra were fitted using symmetric pseudo-Voigt functions after subtracting a Tougaard background.²⁶ The full width at half-maximum (fwhm) of each component was set equal for all spectra of the same region, whereas the energy positions were allowed to vary only within a narrow energy range. XPS analysis was performed using CasaXPS software (version 2.3.20rev1.1e, CASA Software Ltd.).

The crystallographic and structural properties of the PEALD–IGZO films were investigated by *ex situ* grazing-incidence X-ray diffraction (GIXRD, Rigaku Model SmartLab, Rigaku Corporation) using monochromatized Cu K α radiation provided by a rotating anode (9 kW, line-focus). A 5° Soller slit and a parallel beam setup were chosen to obtain a sufficient signal intensity. The sample was aligned with respect to the surface, while the incidence angle α was fixed to 0.5°, with a 2 θ scan range from 20 to 70°. The signal was collected by a scintillation counter.

The surface morphology of the prepared IGZO samples was examined by using field-emission scanning electron microscopy (FE-SEM, Tescan Mira 3). This system is equipped with an energy-dispersive X-ray (EDX) spectrometer (Bruker XFlash 6/10) to determine the local elemental composition and sample homogeneity. For these measurements, the working distance was fixed at 15 mm, and the accelerating voltage was set to a low value of 7 kV to reduce charging effects and enhance the surface sensitivity.

Current–voltage (*I*–*V*) measurements were carried out on metal/ insulator/semiconductor (MIS) stacks to investigate the impact of the IGZO layer composition on the electrical properties using a combination of a power supply (Agilent E3649A), a voltmeter (HP34401), and an ampere meter (PREMA4001).²⁷ The MIS stacks were created by coating the IGZO/SiO_x/Si samples with circular aluminum electrodes thermally evaporated (Edwards Auto 306) through shadow masks (variable diameter between 300 and 800 μ m) on top of the IGZO layers. The *I*–*V* measurements were carried out under dark conditions and at room temperature.

3. RESULTS AND DISCUSSION

3.1. Bottom-Up Approach to Design an ALD IGZO Recipe. Our IGZO films were prepared at a substrate temperature of 150 °C, the lowest possible, in all three individual ALD windows (Figure 1). Precise control of the layer composition required an accurate adjustment of the number of ALD subcycles of each binary oxide, for which the GPC and possible nucleation delays on a given surface must be well-known beforehand.

To illustrate how the bottom-up approach can potentially solve the issue of designing the complete IGZO supercycle, we focus in more detail on the growth optimization of the ZnO_r sublayer using two ALD methods: TALD and PEALD. We initially investigated the deposition of ZnO_x by TALD on GaO_x and InO_x surfaces to evaluate how the underlying layer affects the nucleation behavior, observing by in situ ALD-RTM measurements a higher nucleation delay for the ZnO_x deposition on InO_x (about 22 cycles until linear growth starts) in comparison to its deposition on GaO_x (about 13) cycles until linear growth starts, see also Figure 2). Therefore, ZnO_x growth has always been performed on GaO_x . Importantly, we found that the type of ALD process critically determines the occurrence of nucleation delay. Figure 2 shows the growth behavior of ZnO_x (on a PEALD-GaO_x film) by TALD and PEALD. Notably, no nucleation delay is present in the plasma-enhanced approach, resulting in an almost constant



Figure 2. In situ ellipsometric real-time thickness monitoring for ZnO_x TALD (blue) and PEALD (red) growth on an underlying GaO_x PEALD layer. The vertical dashed line indicates the start of ZnO_x deposition.

GPC from the first cycle. Likewise, the PEALD growth of the GaO_x (on InO_x) and InO_x (on ZnO_x) sublayers showed no nucleation delay (not shown here).

To precisely control the layer composition of the IGZO films *via* the ratios of the individual subcycles, we subsequently determined the GPCs of the respective sublayers on the associated underlying sublayer (see Figure 3). GPCs of 0.72, 0.61, and 0.92 Å/cycle were achieved for the PEALD growth of InO_x on ZnO_x , GaO_x on InO_x , and ZnO_x on GaO_x , respectively. Based on these data, different target ratios can be achieved by setting the number of iterations for each subcycle, thus adjusting the composition of the IGZO films. Table 2 shows four IGZO compositions targeted by the PEALD approach (In/Ga/Zn): 1/1/1, 1/1/2, 2/1/1, and 1/2/1. Besides, a 1/1/1 film using TALD for the ZnO_x subcycle was grown for comparison.

Figure 3b shows how the *in situ* RTM allows precise thickness monitoring in every single subcycle [an example of complete growth from the PEALD (1/1/1) film is presented in the Supporting Information, Figure S2]. If a nucleation delay

occurs, as in the case of TALD-ZnO_x (see Figure 2), more cycles in the corresponding sublayer deposition are required to compensate for this delay. For example, to achieve the same target composition of 1/1/1, 12 TALD subcycles instead of 2 PEALD subcycles would be necessary to account for the nucleation delay within the ZnO_x sublayer deposition (see Table 2). From an applied perspective, this issue would directly translate into a waste of the organometallic precursors and higher production times, increasing the production costs. Furthermore, the final film thickness is more difficult to control in processes with a nucleation delay [e.g., when using the same number of supercycles (here 12), the final thickness of the T(1/1/1) sample was about 11 nm compared to 7 nm of the PE(1/1/1) sample]. Instead, when using the full PEALD approach, the total thickness evolution nicely follows the sum of the individual GPCs of the subcycles (cf. Supporting Information, Figure S2). Moreover, the choice of a complete PEALD approach, which, in addition, uses only a single oxidant $(O_2 \text{ plasma})$, simplifies the overall process control by eliminating the need for shutters to switch between the different process types (PEALD and TALD), thereby shortening the processing time and facilitating standardization for industrial film processing.

In addition to the growth parameters, the chemical properties of the deposited sublayers, such as composition, degree of oxidation, and impurity level, need to be examined to adjust the desired properties of the mixed IGZO layer. Importantly, ZnO_x sublayers also show differences in the Zn cation oxidation state depending on whether they were produced via TALD or PEALD. Figure 4 displays the Zn LMM Auger spectra of T(1/1/1) and PE(1/1/1) after gentle surface cleaning (35 s of sputtering). In the case of the TALD sample [T(1/1/1)], a complete oxidation of the ZnO_x sublayer is observed, while this is not the case in the PEALD process [sample PE(1/1/1)], where a tiny (<5%) component of metallic zinc (kinetic energy of ~ 995.2 eV) is found.^{28,29} These differences suggest that the O₂ plasma does not fully oxidize the DEZn precursor in the PEALD process compared to the thermal route using H₂O. These oxidation state differences could also be related to the total number of ZnO_x subcycles used in each case (12 and 2 for TALD and PEALD, respectively), in the sense that the decreased



Figure 3. (a) GPC of the respective binary oxides on the associated underlying oxides, as applied in the supercycle; (b) *in situ* ALD RTM of the thickness evolution within two PEALD–IGZO supercycles comprising 3 InO_{xy} 3 GaO_{xy} and 2 ZnO_x subcycles, which corresponds to a target In/Ga/Zn composition of 1/1/1.

Table 2. From Left to Right, ALD-Type Process, Sample Names, Target In/Ga/Zn Composition, Subcycle Ratio within One Supercycle, Compositional Ratio of the Layers Estimated from EDX Measurements, and the Compositional Ratio of the Surface-Cleaned Samples Estimated from XPS Measurements by Analyzing the In 4d, Ga 3d, and Zn 3d Core Levels

			subcycle ratio (InO _x /GaO _x /ZnO _x) within the supercycle	actual metal ratio (In/Ga/Zn)	
process	sample name (In/Ga/Zn)	target metal ratio (In/Ga/Zn)		EDX	XPS
PEALD	PE(1/1/1)	1/1/1	3/3/2	1.1/1.0/1.3	1.0/1.0/1.1
	PE(1/1/2)	1/1/2	3/3/4	1.0/1.0/2.8	0.9/1.0/2.2
	PE(2/1/1)	2/1/1	6/3/2	2.1/1.0/1.5	1.7/1.0/1.2
	PE(1/2/1)	1/2/1	3/6/2	1.0/2.0/1.2	1.0/2.2/1.2
PEALD/TALD	T(1/1/1)	1/1/1	3/3/12	1.0/1.1/3.1	1.0/1.0/2.4



Figure 4. Zn LMM Auger spectra of the IGZO samples T(1/1/1) (bottom) and PE(1/1/1) (top). Measurements were taken using Al K_{α} radiation.

deposition rate of DEZ leads to more, *i.e.*, longer, oxidizing conditions during the TALD subprocess.

3.2. Chemical and Structural Characterization of IGZO Films. This section focuses on the chemical and structural characterizations of our PEALD-IGZO samples. The XPS survey spectra of the films with different target elemental ratios (see Supporting Information, Figure S3) confirm the presence of indium, gallium, zinc, and oxygen. Traces of carbon were also found, which are related to surface contamination by adventitious carbon caused by the ex situ nature of the XPS measurement (*i.e.*, the samples were exposed to the atmosphere at room temperature between preparation and characterization) and by residual carbon left from the ALD process, which usually accumulates on the surface due to incomplete oxidation of the organometallic precursors.³⁰ From the XPS data of the as-introduced samples, we estimate an initial carbon atomic concentration of around 10% at the surface of the IGZO layers. After a gentle surface cleaning (sputtering for 35 s), the amount of carbon was reduced to only 2-4%, while further cleaning led to the complete removal of carbon, demonstrating the carbon-free nature of the interior of the IGZO layers (no carbon signal within the XPS detection limit, see Supporting Information, Figure S4).

The metal composition depth profiles of the PEALD-IGZO samples expressed in normalized concentration are given in Figure 5a-d, where sequential sputtering steps followed by subsequent XPS measurements were performed for a total time of 20 min, i.e., up to about a 6 nm depth. The depth profiles of the relative atomic concentrations, including oxygen (O 1s) and carbon (C 1s), can be found in the Supporting Information, Figure S4. They show a partial reduction of the IGZO films, which is to some extent due to the preferential sputtering of lighter atoms, i.e., oxygen, despite the gentle sputtering conditions. However, this preferential sputtering should not affect the ratio between the metallic cations shown in Figure 5. To minimize systematic errors in the calculation of the concentrations introduced by using photoelectron peaks with a significant difference in binding energy, and thus critically differing by a factor up to three on their inelastic mean free paths (IMFP), we have used the Ga 3d, In 4d, and Zn 3d core levels.³¹ These core levels are present in a very narrow yet very low binding energy range (<15 eV), *i.e.*, at high photoelectron kinetic energies, thereby increasing the total probe depth of the XPS measurement in line with the applied compositional model that assumes a homogeneous solid. The depth profiles reveal a nearly constant atomic concentration of the metallic elements within the films beyond the topmost surface region, with only slight deviations at the film/substrate interface, similar to previous reports on the interfaces of atomic layer-deposited films.^{32,33} A closer look reveals that the Zn-rich PE(1/1/2) and In-rich PE(2/1/1) samples exhibit a very homogeneous distribution of the elements within the bulk of the films, whereas the PE(1/1/1) and Ga-rich PE(1/2/1)samples show a slight increase in the Ga content with increasing sputtering time, especially close to the interface. EDX mapping measurements show excellent spatial composition homogeneity and the absence of any excess of Ga, giving very close In/Ga/Zn ratios to those obtained by XPS after 35 s of sputtering (the EDX spectra and related Tables S1-S5 with raw elemental composition for all PEALD samples are shown in Supporting Information, Figure S5a, while the calculated metal ratios are given in Table 2). As the in situ RTM measurements show unchanged growth behavior within the Ga subcycles throughout the entire growth (see Supporting Information, Figure S2, refer also to Figure 3b), the influence of a lower sputtering yield for Ga compared to In and Zn on the depth profiles cannot be fully discarded.³⁴



Figure 5. XPS-normalized metal concentration depth profiles of the PEALD–IGZO layers with different In/Ga/Zn target ratios evaluated by subsequent sputtering and XPS measurements using In 4d, Ga 3d, and Zn 3d core levels; (a) PE(1/1/1), (b) PE(2/1/1), (c) PE(1/1/2), and (d) PE(1/2/1) samples.

Thus, the In/Ga/Zn ratios estimated by EDX and XPS show the excellent controllability of the IGZO layer composition by changing the ALD supercycle sequence, as shown in Figure 6 (see also Table 2). The PEALD approach at 150 °C potentially enables tuning the material properties for many promising applications by controlling the In/Ga/Zn ratio, an approach already shown to be successful using alternative deposition methods.^{35,36} In contrast, we observed higher deviations



Figure 6. Comparison between target In/Ga and Ga/Zn ratios and determined values obtained from EDX (solid symbols) and XPS (open symbols) for PEALD–IGZO samples. In the XPS case, In 4d, Ga 3d, and Zn3 d components have been chosen for In/Ga and Ga/Zn ratios (open symbols). The Ga/Zn ratio using Ga 2p and Zn 2p is shown for comparison purposes (crossed open squares). XPS analysis was done after gentle sputtering of 35 s for surface carbon removal. The dashed line shows the 1/1 ideal ratio.

between the target and achieved values in the elemental composition of the T(1/1/1) sample (see Table 2), indicating that the controllability of the mixed PEALD/TALD process is challenging due to the nucleation delay in the TALD of ZnO_x.

We note that the composition estimated by bulk-sensitive EDX measurements is equal to or very similar to the target values, whereas the XPS quantification strongly depends on the selected element-specific core levels under study. As briefly pointed out, using energy levels with very similar binding energies (In 4d, Ga 3d, and Zn 3d), i.e., virtually identical IMFPs, leads to almost identical results as EDX. Considering that the IMFP of this trio is ~ 20 Å,³¹ the close results between surface-sensitive XPS (open symbols) and bulk-sensitive EDX (full symbols) show that the samples are homogeneous with a high degree of elemental intermixing despite the multilayer structure of the PEALD supercycle deposition strategy. In contrast, using the typical, more intense peaks In 3d, Ga 2p, and Zn 2p leads to poor results in elemental quantification (cross open symbols for Ga 2p/Zn 2p in Figure 6), as the IMFP for In 3d is about 3 and about 2 times longer than for Ga 2p and Zn 2p, respectively. Hence, in this case, systematic deviations in the calculated concentrations could partially result from different probing depths for each metallic element as the measured XPS signal intensity decreases exponentially with a decreasing IMFP and increasing sampling depth; furthermore, the simplified assumption of a perfectly homogeneous layer in our composition model may not generally be valid due to the multilayer structure of the deposition. Thus, special care must be taken when performing XPS depth profiling, especially when assuming naive compositional models based on perfectly homogeneous films: the IMFP should be at least larger than the resulting total thickness of one supercycle when estimating film concentrations from surface measurements (i.e., as received or surface-cleaned samples).

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Figure 7. XPS data of (a) Zn 2p, (b) In 3d, and (c) Ga 2p regions of the surface-cleaned PEALD–IGZO films for the as-given target compositions (indicated within each plot). Mg K α radiation was used as the excitation source for Zn 2p and In 3d, and Al K α for Ga 2p.

The peak decomposition of the Zn 2p, In 3d, and Ga 2p XPS spectra taken after gentle surface cleaning reveals a high degree of similarity within the four PEALD samples. The most intense peaks Zn $2p_{3/2}$ (Figure 7a), In $3d_{5/2}$ (Figure 7b), and Ga $2p_{3/2}$ (Figure 7c) are found at 1022.1, 29,37,38 444.4, 11,23,37,38 and 1118.0 eV, 22,37,38 respectively, corresponding to binding energies previously reported for IGZO quaternary metal oxides and individual binary oxides. The Zn $2p_{1/2}$ and Zn $2p_{3/2}$ doublet spectra (Figure 7a) contain two tiny components representative of metallic zinc (\leq 3%) located at 1043.0 and 1019.5 ± 0.1 eV, respectively, due to an incomplete oxidation of the DEZn precursor during the PEALD process, consistent with the Auger Zn LMM findings in Figure 4. Similarly, the In 3d spectra (Figure 7b) show spin-orbit doublet peaks (In $3d_{5/2}$ and $3d_{3/2}$) with weak shoulders at the higher binding energy side, which are attributed to OH groups and defect states.²³ Moving toward gallium in Figure 7c, as for Zn 2p and In 3d, minor contributions at higher and lower binding energy of the main oxide components (Ga $2p_{1/2}$ and Ga $2p_{3/2}$) could be assigned to OH species and defect states (metallic Ga), respectively.³⁹ The presence and variations of these defects, measured for the In, Ga, and Zn core levels, might significantly impact the ALD film properties, and, hence, the performance of related devices.

The structural properties of the PEALD–IGZO films were investigated by GIXRD measurements. The GIXRD patterns shown in Figure 8 present no sharp features but a broad peak in the 2θ range of $30-36^{\circ}$, characteristic of nearly amorphous, nanocrystallized IGZO films.^{14,40} Nevertheless, this peak presents a complex structure that slightly changes, depending on the elemental composition of each PEALD–IGZO film. For example, it is more pronounced in the In-rich PE(2/1/1) film, in line with Sheng *et al.*,³⁷ who reported the increase and widening of an already broad peak at 32° when the thickness of the indium oxide sublayer in PEALD–IGZO films was increased from 0.3 to 1.8 nm. In the case of Ga-rich films



Figure 8. GIXRD patterns of PEALD–IGZO films. The sample names are indicated at each diffractogram. Inset: FE-SEM image showcasing the flat, pinhole-free surface morphology of the PE(1/1/1) sample.

[PE(1/2/1)], we also see the appearance of an extra shoulder at around 29.5° compared with the PE(1/1/1) diffractogram. Although the low thickness of our IGZO films prevents a better signal-to-noise ratio in the diffraction patterns, the qualitative changes that we observed could indicate incomplete elemental intermixing, with the appearance of small portions of segregated binary phases. This would be the case of In- and Ga-rich films, which show similarities to those previously reported using PEALD and varying film composition.^{14,37} However, the direct comparison with the diffractograms of the binary oxide thin layers deposited by ALD under the same



Figure 9. (a) J-E data of the MIS stacks containing the IGZO layers PE(1/1/1), PE(1/1/2), PE(2/1/1), PE(1/2/1), and T(1/1/1). The contact pad diameter was 800 μ m. (b) Statistics of the current density at a fixed electric field of 1 MV/cm for these samples. The statistics represent measurements at different contacts (*i.e.*, different contact area and at different positions of the samples) and the I-V loops in forward and reverse direction. The boxes delimit the first to third quartiles; the interquartile range of 1.5, the median, and the mean values are also indicated.

conditions (see Supporting Information, Figure S6) indicates that, even if the reported shoulders match with the position of the binary oxide peaks, this segregation might be quite limited. These results align with the XPS data discussed above, which showed a small presence of defects within the film. At first glance, our results appear to be in some contrast with those obtained by T. Hong *et al.*,¹⁴ where when applying PEALD at 200 °C, Ga-rich films were amorphous, while In- and Zn-rich ones presented some segregation of ZnO_x and In₂O₃ phases. This discrepancy could be related to our rather moderate variation of the In/Ga/Zn ratios and the lower temperature compared to their work, preventing further segregation.

Finally, the surface morphology of the PEALD–IGZO films was investigated by FE-SEM (inset of Figure 8), revealing a featureless and pinhole-free film surface resulting from a high-quality layer-by-layer growth mechanism derived from the ALD process. The present results recall those from amorphous, high-density ALD–IGZO films deposited at higher temperatures.³⁷ The good morphological film quality achieved by the PEALD–IGZO process compared to other deposition techniques that result in porous films could translate into better device performance and increase their applicability.⁴¹

3.3. Electrical Properties. Exemplary current-voltage measurements on MIS stacks containing the IGZO layers as the (semi)insulating layer are shown in Figure 9a. Here, all PEALD samples are compared to those of the T(1/1/1)sample. The data are depicted as current density versus electric field (J-E) in the positive branch of the I-V loop, assuming that the accumulation of charge carriers of the silicon semiconductor substrate occurs at the interface between the substrate and the IGZO layer and consequently, the applied voltage is dropping mostly across the IGZO layer. This fact was proven by reference capacitance–voltage (C-V) measurements (Supporting Information, Figure S7), which showed a typical MIS C-V behavior with neither flat-band voltage shifts nor hysteresis for the PEALD samples. In addition, the accumulation capacitance of the PEALD samples was not at a constant level, hinting at high leakage currents.

As demonstrated by the J-E characteristics in Figure 9a, high current densities are observed for all PEALD samples. Interestingly, the In-rich PE(2/1/1) shows conductivity slightly lower than that of the other PEALD samples. The high conductivity of all PEALD samples might be related to a combination of oxygen deficiency (Supporting Information, Figure S4) and defects observed in XPS (*cf.* Figure 7), which contribute as active centers to the charge transport through the IGZO layers. This way, all IGZO layers showed similar contributions of defects based on the XPS peak decomposition, resulting in similar conductivities of all investigated PEALD films. The slightly smaller current density of the PE(2/1/1) sample might be related to the most noticeable intensity increase of the first diffraction peak in the XRD data of that sample (*cf.* Figure 8), implying a slightly higher degree of crystallinity and hence a lower defect density.

The I-V measurements were repeated at different contact pad sizes as well as in forward and reverse directions, yielding statistics as depicted in Figure 9b, which displays the variation in current density at a fixed electric field (1 MV/cm). This statistic substantiates the findings described above for a singleshot comparison of the J-E data (Figure 9a). More importantly, it shows that the T(1/1/1) sample differs distinctly from the samples prepared only by PEALD, exhibiting current densities 1.5 to 2 orders of magnitude lower than the latter. For IGZO films grown by magnetron sputtering, Haeberle et al.⁴¹ proposed that a configuration interaction between $d^{10}s^0$ and $d^9\bar{s}^1$ states would induce gap states caused by the opening of the d-shell accompanied by a charge transfer from O 2p to metal 4s/5s states, leading to extended as well as strongly localized in-gap states. The sp hybridization would be weaker for crystalline systems with band-like s states, whereas amorphous films would present a stronger sp hybridization disabling a band-like transport, thus strongly influencing the transport properties of the IGZO layers depending on their atomic structure. Following this model, on the one hand, the combined TALD/PEALD process might result in the synthesis of a material exhibiting a stronger sp hybridization and thus a higher localization of states within the gap, in turn resulting in reduced band-like transport and decreased conductivity compared to the full PEALD process. On the other hand, based on our XPS and XRD data, we argue that our nearly amorphous, nanocrystalline PEALD-IGZO films contain a higher degree of these configuration interaction-induced gap states, presenting a certain degree of band-like extension of the in-gap states that leads to a higher conductivity in comparison to the TALD(1/1/1) sample.

Hence, the nucleation delay of the TALD-ZnO_x process strongly influences the controllability of the ALD process itself and the electrical properties of the deposited IGZO layers. Notably, the differences in the Zn LMM Auger spectra (Figure 4), where metallic-like states were observed for the PE(1/1/1) sample in comparison to the T(1/1/1) sample, are consistent with the I-V data and the previous discussion. Moreover, the C-V behavior of the T(1/1/1) sample differs from that of the PEALD samples (see Supporting Information, Figure S7), where we observed a (negative) flat-band voltage shift as well as a (counterclockwise) hysteresis loop in the former, supporting the fact that strongly localized defect states are present in this layer.^{22,23}

As shown in Figure 9, the selected variations in the target concentrations of the PEALD-IGZO layers do not strongly affect the electrical properties, as expected based on the work of Kamiya and Hosono.⁵ However, mainly amorphous layers were reported in that work. As we have pointed out above, our PEALD layers have some degree of nanocrystalline nature that could lead to this difference. Interestingly, and in contrast to the full PEALD process but more consistent with the work of Kamiya and Hosono,⁵ in the PEALD/TALD sample set, we observed a stronger influence of the target composition on the *I–E* characteristics (see Supporting Information, Figure S8). Particularly, we found higher current densities for the In- and Zn-rich samples. Hence, this combined PEALD/TALD process seems to support the creation of the aforementioned defect states and particularly their degree of localization (i.e., strength of sp hybridization and related variation/limitation in band-like transport), whereas in the full PEALD process, their abundance and degree of localization are almost constant in the investigated target composition matrix.

Indeed, further studies are needed to address the two main questions arising from this interpretation. First, we determined whether further fine-tuning of the electrical properties is possible in the full PEALD process by choosing target compositions different from those used in this work. Here, a detailed comparison to the recent work of Hong and coworkers¹⁴ is of particular interest, as they relate compositional variation and mobility for IGZO films deposited by PEALD at 200 °C. In particular, their TFT devices with composition ranges of In (0.56-0.63), (Ga 0.13-0.17), and Zn (0.17-0.34) exhibited remarkable electrical properties such as a high field effect mobility >40 $\text{cm}^2/(\text{V s})$, low subthreshold swings (~0.25 V/decade), and only slight threshold voltage shifts under bias temperature stress. Considering that we are able to achieve the desired composition with our optimized supercycle recipe (see Figure 6 comparing EDX and XPS elemental ratios), we argue that our PEALD process can produce such IGZO films with similar properties as in those reported by Hong et al.¹⁴ However, testing TFT properties of our IGZO films is beyond the scope of the present work, which mainly aimed to develop a purely PEALD-based supercycle process for the IGZO thin films to demonstrate the controlled tunability of its composition and showcase the emergent materials properties. The second question refers to the full understanding of the target composition, structure, and defects in the electrical properties, which requires more spectroscopic investigations of PEALD/TALD samples (such as those shown in the current work on the full PEALD samples).

Summarizing the electrical data, in Figure 10, we show a collection of current density data at a fixed electric field (0.5 MV/cm) for the binary oxides investigated previously^{22,23} and of the PE(1/1/1) and T(1/1/1) samples of this work. Regarding the binary oxides, PEALD was used for the GaO_x and InO_x layers, whereas for the ZnO_x film, TALD was applied. Combining these processes to a supercycle ("mixed PE/T-ALD") leads to an intermediate value of the current density of



Figure 10. Statistics of the current density at a fixed electric field of 0.5 MV/cm for the binary oxides InO_x [PE(1/0/0)], GaO_x [PE(0/1/0)], and ZnO_x [T(0/0/1)] and the IGZO samples PE(1/1/1) and T(1/1/1). The statistics are shown in the same way as described in the caption of Figure 9b. Please note that the currents had to be compared at lower electric field strengths (than previously shown in Figure 9b) because the binary oxides had a higher film thickness (30 nm) than the IGZO layers (\leq 11 nm).

the IGZO film in comparison to the binary oxides. The change to a "full PEALD" supercycle increased the current density by 1.5 to 2 orders of magnitude.

4. SUMMARY AND CONCLUSIONS

We have successfully developed a bottom-up approach to design a generic PEALD supercycle recipe to grow high-quality IGZO thin films with tunable composition at relatively low temperature (150 °C). In situ real-time ellipsometric characterization in combination with ex situ complementary techniques was used to optimize the deposition process and the quality of the films. In particular, we have compared the use of TALD and PEALD processes for the ZnO_x subcycle to exemplify the complexity arising from the combination of individual ALD recipes, identifying and solving growth issues such as elemental composition, nucleation delays, or degree of metal oxidation. The developed supercycle approach enables the growth of homogeneous and pinhole-free films, with direct control of the target composition by selecting the ratios between subcycles within the supercycle process. The full PEALD supercycle approach results in films with a current density 1.5 to 2 orders of magnitude higher than obtained for mixed PEALD/TALD deposits, which yield an intermediate current density value compared to the corresponding binary metal oxides. Besides, the low-temperature PEALD films exhibit traces of nanocrystalline order and defect states that might increase the electrical conductivity, probably due to a partial band-like electronic structure within the band gap.

From a conceptual perspective, the bottom-up approach guarantees a detailed characterization of not only the individual oxides but also the existing interactions between them, enabling different recipes and devising a minimum number of supercycles to deposit a sufficiently thick IGZO film where intermixing of elements occurs and that is representative of a bulk-like (thick) layer. Finally, as the preparation of IGZO films by a supercycle PEALD approach at low temperature allows a reasonable control of the thickness, composition, and

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electrical properties in a straightforward manner, it may likely represent an essential ingredient of a feasible, scalable process for manufacturing highly efficient oxide semiconductor TFTs and flexible electronic devices.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acsaelm.4c00730.

Experimental details including optimization of individual PEALD binary oxides and IGZO film characterization, including *in situ* RTM, XPS, EDX, XRD, and electrical measurements (PDF)

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work but has been unreachable since and did not participate in the peer review of this manuscript.

Notes

The authors declare no competing financial interest.

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