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Atomic layer deposition of amorphous tin-gallium oxide films

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A wide range of applications benefit from transparent semiconducting oxides with tunable electronic properties, for example, electron transport layers in solar cell devices, where the electron affinity is a key parameter. Presently, a few different ternary oxides are used for this purpose, but the attainable electron affinity range is typically limited. In this study, the authors develop a low-temperature atomic layer deposition (ALD) process to grow amorphous $\text{Sn}_{1-x}\text{Ga}_x\text{O}_y$ thin films from dimethylamino-metal complexes and water. This oxide is predicted to provide a wide selection of possible electron affinity values, from around 3 eV for pure Ga_2O_3 to 4.5 eV for pure SnO_2 . The ALD process is evaluated for deposition temperatures in the range of 105–195 °C by *in situ* quartz crystal microbalance and with *ex situ* film characterization. The growth exhibits an ideal-like behavior at 175 °C, where the film composition can be predicted by a simple rule of mixture. Depending on film composition, the growth per cycle varies in the range of 0.6–0.8 Å at this temperature. Furthermore, the film composition for a given process appears insensitive to the deposition temperature. From material characterization, it is shown that the deposited films are highly resistive, fully amorphous, and homogeneous, with moderate levels of impurities (carbon, nitrogen, and hydrogen). By tailoring the metal cation ratio in films grown at 175 °C, the optical bandgap can be varied in the range from 2.7 eV for SnO_2 to above 4.2 eV for Ga_2O_3 . The bandgap also varies significantly as a function of deposition temperature. This control of properties indicates that $\text{Sn}_{1-x}\text{Ga}_x\text{O}_y$ is a promising candidate for an electron transport layer material in a wide electron affinity range. *Published by the AVS.* <https://doi.org/10.1116/1.5092877>

I. INTRODUCTION

Transparent semiconducting oxides of transition metals form a class of materials that is attractive for a wide range of applications, such as fabrication of thin-film transistors (TFTs),¹ gas sensing,² photocatalysis,³ and as electron transport layers (ETLs) in solar cell structures.⁴ The conduction band minimum is often dominated by metal s-orbitals in these oxides, while the valence band maximum mainly consists of oxygen p-orbitals.⁵ This type of electronic structure leads to high electron mobility for many oxide materials, which can in numerous cases be preserved even if the oxide structures become disordered. That is one of the reasons why amorphous In-Ga-Zn-O (a-IGZO) has replaced a-Si as the active layer in TFTs.⁶ The similar electronic structures of the various transition metal oxides make alloys of two or more binary oxides highly adaptable. It is straight forward to vary properties such as electron mobility, electron affinity, and optical bandgap by simply varying the cation composition in the ternary oxide.⁷ This is especially true for amorphous ternary oxides, where the oxides can be freely mixed in most cases, without being restricted by possible structural differences as for crystalline materials.

The electron affinity is a key parameter for ETLs in solar cell applications and can influence the charge carrier

transport and recombination processes in the solar cells.^{8,9} It is, therefore, very attractive to apply ETLs with tunable electron affinities. Several ternary oxides have already been successfully implemented in $\text{Cu}(\text{In,Ga})\text{Se}_2$ solar cells, including Zn-Mg-O and Zn-Sn-O.⁴ Furthermore, the choice of ETL material has also been found to be crucial for the conversion efficiency for perovskite solar cells.⁹ However, most of the ETLs in use today cannot be tuned to the low electron affinity values needed to form a favorable conduction band alignment to wide bandgap solar cell absorbers, by solely varying the composition.

Amorphous tin-gallium oxide (a-SGO) is a compound for which a wide range of possible electron affinity values are expected, depending on cation composition. The estimated range is from 4.5 eV for SnO_2 (Ref. 10) down to around 3 eV for Ga_2O_3 .^{10–12} It should be noted that a relatively large uncertainty in the literature data is present for the SnO_2 – Ga_2O_3 system. For instance, it has been shown that the electron affinity of sputtered a- Ga_2O_3 varies with deposition conditions.¹³ The amorphous structure is required to be able to achieve a homogeneous a-SGO due to the low solubility of the two binary oxides in each other.¹⁴ In addition, gallium substitution in crystalline SnO_2 would possibly lead to charge compensation from aliovalent doping effects, which might not be desired.

To this date, tin-gallium oxide films in a wide composition range have been prepared with various deposition

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techniques, such as magnetron sputtering,^{15–17} sol-gel spin-coating,¹⁸ and chemical vapor deposition.¹⁹

Atomic layer deposition (ALD) offers several advantages for depositing thin transparent semiconducting oxide layers.²⁰ With ALD, it is possible to deposit uniform conformal layers in a sequential self-terminating way, where the films grow in a layer-by-layer fashion. As a result, ALD provides excellent accuracy in both thickness and composition control over large areas. Furthermore, ALD enables coating of sensitive surfaces prone to sputter-induced damage and temperature-sensitive substrates depending on the chosen precursors.

In this study, we develop a ternary ALD process to grow a-SGO by combining existing low-temperature process for SnO_2 and Ga_2O_3 , respectively.^{21,22} The process is characterized by *in situ* quartz crystal microbalance (QCM) to monitor growth characteristics, as well as *ex situ* film characterization in terms of structural properties, morphology, composition, impurity content, and optical absorption.

II. EXPERIMENTAL DETAILS

$\text{Sn}_{1-x}\text{Ga}_x\text{O}_y$ films were deposited in an F-120 laminar-flow ALD system (ASM Microchemistry) at substrate temperatures in the range from 105 to 195 °C. The reactor is equipped with externally heated quartz substrate holders with space for two 25 cm² sized substrates, where one substrate position can be replaced with a QCM sensor head. A flow of 500 sccm highly purified N_2 (99.9999%) ensured a pressure of around 5 mbar in the reactor while providing an inert transport and purge gas. The N_2 gas was additionally purified by using a gas filter at the reactor inlet.

The precursor used for tin was tetrakis(dimethylamino) tin(IV) [DMA_4Sn , $((\text{CH}_3)_2\text{N})_4\text{Sn}$] (Pegasus), where the liquid was evaporated at 40 °C in a bubbler configuration using N_2 as a carrier gas. The gallium precursor used was tris(dimethylamino)gallium(III) [DMA_3Ga , $((\text{CH}_3)_2\text{N})_3\text{Ga}$] (Aldrich, 98%), which was a solid sublimed from an open-boat source at 80 °C. Deionized water was used as coreactant for both metal precursors.

A supercycle approach was used to grow the ternary oxide, where A number of subcycles of SnO_2 and B number of Ga_2O_3 subcycles were repeated in a supercycle with the pulse scheme $(\text{DMA}_4\text{Sn}:\text{N}_2:\text{H}_2\text{O}:\text{N}_2)_A:(\text{DMA}_3\text{Ga}:\text{N}_2:\text{H}_2\text{O}:\text{N}_2)_B$, where A:B or A/(A+B) denotes the subcycle ratio. The pulse time was 1 s for all pulses, which was confirmed to be sufficiently long for saturated growth according to QCM measurements.

The substrates used were made of fused quartz which were ultrasonically cleaned in ethanol prior to ALD processing (if not otherwise specified in the text).

QCM measurements were performed to study film growth characteristics. The crystal frequency was logged by using an SQM-160 monitor (Inficon). Assuming constant temperature and pressure, the deposited mass is proportional to the negative of the measured frequency change.²³ In order to quantify the deposited mass per area, we calibrated the QCM data to SnO_2 and Ga_2O_3 films (grown at 175 °C for 1000 cycles),

where the films thicknesses and densities were determined using x-ray reflectivity (XRR). Furthermore, the incoming gases were preheated at a higher temperature to ensure a constant temperature at the sensor head during pulsing of the precursors.²⁴ All reported numerical values, extracted from the QCM curves, are averaged over at least 30 cycles.

The composition of the deposited films was characterized with x-ray fluorescence (XRF), time-of-flight elastic recoil detection analysis (ToF-ERDA), and Rutherford backscattering spectrometry (RBS). An Epsilon 5 (Panalytical) XRF spectrometer was used to determine the cation ratio in the films. RBS measurements were additionally used to calibrate the XRF relative sensitivity factor for the Ga/Sn signal ratio. ToF-ERDA and RBS were measured using a 5 MV tandem accelerator at the Tandem Laboratory at Uppsala University, Sweden, in order to determine the impurity level and oxygen content in the films. In ToF-ERDA, $^{127}\text{I}^{8+}$ ions with 36 MeV primary energy were used as primary particles, which entered the target at an angle of 67.5° with respect to the target normal. The recoiled particles were detected at a 45° angle by a carbon-foil time of flight detector and by a segmented gas ionization chamber.²⁵ RBS measurements were performed using 2.0 MeV $^4\text{He}^+$ ions incident under 60° with respect to the surface normal of the target. The backscattered ions were detected at a 170° scattering angle by a silicon energy detector.

The film homogeneity, morphology, structure, and density were characterized by scanning transmission electron microscopy (STEM) and XRR. A Titan Themis 200 (FEI) microscope operated at 200 kV was used for the STEM analysis. The microscope was equipped with a high-angle annular dark-field detector (HAADF) and a super-x energy dispersive spectrometer (EDS). The sample lamellae were prepared with a focused gallium-ion beam according to the *in situ* lift-out method,²⁶ in a Strata DB235 focused ion beam system (FEI). XRR was performed with a Philips X'pert MRD system (Panalytical) equipped with an x-ray mirror and parallel plate collimators, using Cu K_α radiation ($\lambda = 1.541 \text{ \AA}$).

The optical properties of the films were characterized with reflectance and transmittance spectrophotometry (R-T), using a Lambda 900 spectrometer (PerkinElmer) equipped with an integrating sphere. The absorption coefficient was extracted by using the method described by Hong.²⁷

III. RESULTS AND DISCUSSION

A. ALD growth characteristics—Subcycle ratio

The growth per cycle (GPC) as a function of the subcycle ratio is shown in Fig. 1, as recorded by QCM for depositions performed at 175 °C. It can be seen that the mass gain per cycle is rather constant around 34–37 ng/cm² at this temperature, with merely a slight dependency on the subcycle ratio. The resulting GPC is not constant due to differences in film density. Moreover, the GPC increases approximately linearly from 0.6 Å for pure SnO_2 to 0.8 Å for pure Ga_2O_3 . The GPC of SnO_2 in our process is in

FIG. 1. GPC (squares) and mass gain per cycle (circles) vs subcycle ratio, determined by QCM for ALD $\text{Sn}_{1-x}\text{Ga}_x\text{O}_y$ grown at 175 °C. The error bars represent the estimated within-run standard deviation.

well agreement with literature values,^{21,28} whereas our Ga_2O_3 GPC is slightly lower than the reported value of 1.0 Å.²²

QCM measurements of ALD growth of SnO_2 , Ga_2O_3 , and $\text{Sn}_{0.4}\text{Ga}_{0.6}\text{O}_y$ (using a 1:1 subcycle ratio) are shown in Fig. 2. From the QCM curves, it is evident that the mass change during the Sn-O and Ga-O subcycles at 175 °C is not significantly influenced by alternation between the two types of subcycles. The mass gain per cycle (Δm) is listed in Table I, as well as the ratio between the mass gain during the metal precursor (m_1) and Δm . If the growth mechanism for a given process is known, the $m_1/\Delta m$ ratio can provide insight into the ligand-exchange reactions that typically occur during ALD growth.²⁹ However, it has been shown that ALD of SnO_2 from $\text{DMA}_4\text{Sn}/\text{H}_2\text{O}$ leads to incomplete ligand-exchange reactions in the temperature region of this study.³⁰ In our case, the exact growth mechanism for the ALD of

Ga_2O_3 is also uncertain. In addition, DMA_3Ga sublimates as dimers,³¹ and it is unknown how this influences the chemisorption of DMA_3Ga on active surface sites. Nevertheless, for the purpose of investigating if the growth mechanism is influenced by the subcycle ratio, it is sufficient to compare the $m_1/\Delta m$ values. As listed in Table I, the $m_1/\Delta m$ ratio for an Sn-O subcycle is essentially the same for a mixed process with a 1:1 subcycle ratio as for a pure SnO_2 process. The same holds for Ga-O. This implies either that the surfaces of growing SnO_2 and Ga_2O_3 at 175 °C are similar in terms of density of active surface sites or that the growth is limited by steric hindrance.

The near-constant mass gain per cycle at 175 °C makes it straightforward to predict and control the film composition. In Fig. 3, the measured metal cation ratio versus subcycle ratio is plotted. RBS-calibrated XRF was used to determine the cation composition for the 62–79 nm thick films deposited on fused quartz substrates with 1000 ALD cycles. In addition, the data displayed in Fig. 3 include values calculated from QCM measurements.

The QCM data provide a measure of the mass gain per each individual subcycle [$\Delta m_{\text{sub},i}$ (ng/cm²), where $i = \text{Sn-O}$ or Ga-O]. This makes it possible to calculate the cation composition ratio according to Eq. (1), assuming that no surface etching processes occur during the precursor pulses. In Eq. (1), n denotes the amount of substance, M denotes molar mass in g/mol, and A and B denote the number of Sn-O and Ga-O subcycles per supercycle, respectively

$$x_{\text{QCM}} = \frac{n_{\text{Ga}}}{n_{\text{Ga}} + n_{\text{Sn}}} = \frac{1}{1 + 0.5 \left(\frac{A}{B} \right) \left(\frac{M_{\text{Ga}_2\text{O}_3}}{M_{\text{SnO}_2}} \right) \left(\frac{\Delta m_{\text{sub-Sn-O}}}{\Delta m_{\text{sub-Ga-O}}} \right)}. \quad (1)$$

Furthermore, the expected composition for each subcycle ratio can be calculated based on a simple rule of mixture concept,³² in which it is assumed that the GPC is linearly dependent on the subcycle ratio. This assumption is valid when each Sn-O or Ga-O subcycle show the same GPC as for the binary

FIG. 2. QCM measurements of ALD growth of (a) SnO_2 , (b) Ga_2O_3 , and (c) $\text{Sn}_{0.4}\text{Ga}_{0.6}\text{O}_y$ deposited using a 1:1 subcycle ratio at a substrate temperature of 175 °C.

TABLE I. Extracted growth parameters from QCM measurements.

Process	Δm (ng/cm ²)	$m_i/\Delta m$
$T_{\text{ALD}} = 175\text{ }^{\circ}\text{C}$		
SnO ₂	36	1.4
Ga ₂ O ₃	36	1.5
1:1 Sn-O subcycle	39	1.3
1:1 Ga-O subcycle	38	1.5
$T_{\text{ALD}} = 105\text{ }^{\circ}\text{C}$		
SnO ₂	55	1.2
Ga ₂ O ₃	37	1.4
1:1 Sn-O subcycle	45	1.2
1:1 Ga-O subcycle	43	1.4

processes for pure SnO₂ and Ga₂O₃, respectively, regardless of subcycle ratio. It follows that the expected composition can be calculated by using the following:

$$x_{\text{Exp.}} = \frac{n_{\text{Ga}}}{n_{\text{Ga}} + n_{\text{Sn}}} = \frac{1}{1 + 0.5 \left(\frac{A}{B} \right) \left(\frac{M_{\text{Ga}_2\text{O}_3}}{M_{\text{SnO}_2}} \right) \left(\frac{\Delta m(\text{SnO}_2)}{\Delta m(\text{Ga}_2\text{O}_3)} \right)}. \quad (2)$$

It is shown in Fig. 3 that the experimental composition values accurately follow the compositions that are expected from the simple mixing rule. This is a strong indication that the growth process at 175 °C is mainly free from nonideal effects, such as growth inhibition by enhanced reaction activation barriers or reduced reaction site density, or surface etching effects by exchange reactions.

B. ALD growth characteristics—Substrate temperature

The growth per cycle and film composition over the temperature range of 105–195 °C were monitored by QCM for

FIG. 3. Cation composition vs subcycle ratio for ALD Sn_{1-x}Ga_xO_y films grown at 175 °C. The composition values were determined by RBS-calibrated XRF on films grown on quartz substrates ($d = 62\text{--}79\text{ nm}$) or calculated from QCM data using Eq. (1). The experimental data fit very well to the expected values from Eq. (2), which assumes a simple mixing rule (solid line).

SnO₂, Ga₂O₃, and a mixed process with a 1:1 subcycle ratio. This is shown in Fig. 4. It is observed that the mass gain per cycle for Ga₂O₃ is relatively unaffected by the deposition temperature in the investigated temperature range, whereas the mass gain per SnO₂ cycle decreases from around 55 ng/cm² at 105 °C to 31 ng/cm² at 195 °C. The substantial increase in mass gain for SnO₂ at lower temperatures has previously been reported.²⁸ A proposed explanation to this is a facilitated growth due to increased density of –OH groups on the surface at lower temperatures (including a possibly increased –OH density due to physisorption of water).³³ The average mass gain per cycle for a 1:1 process is in-between the mass gains for pure SnO₂ and Ga₂O₃, respectively (except a slight deviation for 175 °C). This behavior would be expected from the simple mixing rule. However, the mass gain from the individual subcycles in the 1:1 process differs from the mass gain per cycle for pure SnO₂ and Ga₂O₃, at other temperatures than for 175 °C. For example, as listed in Table I, the mass gain per cycle is around 55 and 37 ng/cm² for pure SnO₂ and Ga₂O₃, respectively, for ALD growth at 105 °C. In the 1:1 process at the same temperature, the mass gain per cycle for the Sn-O subcycle is reduced to around 45 ng/cm², while the mass gain per cycle for the Ga-O subcycle is increased to 43 ng/cm². If the active reaction site density is assumed to limit the GPC, then the observed trends in mass gain can be explained by a varying amount of reaction sites on the different surfaces for the different deposition temperatures, presumably –OH groups in this case. This is plausible since the growth is unlikely to be limited by steric hindrance, due to the variation of mass gain with temperature. If the surface density of –OH groups is higher on the growing SnO₂ surface than on a growing Ga₂O₃ surface, at lower deposition temperatures, an intermediate –OH surface density is possibly obtained in the mixed 1:1 process. In that case, a reduced mass gain would, therefore, be expected for the Sn-O subcycle, and an increased mass gain for the Ga-O subcycle, as compared to the binary processes for SnO₂ and Ga₂O₃.

An important feature is that the composition of an Sn_{1-x}Ga_xO_y film grown with a 1:1 subcycle ratio is constant around $x = 0.6$, regardless of deposition temperature (in the range of 105–195 °C), as shown in Fig. 4(b). This observation suggests that the process is very robust in terms of controlling the cation composition in the films.

C. Structural properties

Film homogeneity and crystallinity were evaluated by STEM, using HAADF imaging and nanobeam diffraction, for an Sn_{0.4}Ga_{0.6}O_y film deposited on soda-lime glass at 175 °C. Figures 5(a) and 5(b) show the HAADF at low magnification and high magnification, respectively. No indications of inhomogeneities in the bulk of the Sn_{0.4}Ga_{0.6}O_y film can be distinguished from the noise level. Therefore, if domains with varying composition exist, they are limited to a few nanometers in size. In addition, an EDS line-scan was performed over the entire the Sn_{0.4}Ga_{0.6}O_y film [see Fig. 5(c)], which does not show any sign of a composition gradient in

FIG. 4. (a) Average mass gain per cycle vs ALD temperature for SnO₂, Ga₂O₃, and a mixed process with a 1:1 subcycle ratio. (b) Cation composition vs ALD temperature for the 1:1 mixed process, determined by RBS-calibrated XRF on films grown on quartz substrates or calculated from QCM data using Eq. (1).

the sample. In the present study, we focus on the bulk properties of the films. The interface to the substrate, which can change for different substrates due to dissimilar process initiation, remains to be studied more in detail.

Furthermore, the inset in Fig. 5(b) displays a nanobeam diffraction pattern taken from the middle of the Sn_{0.4}Ga_{0.6}O_y film. The diffraction pattern shows diffuse rings, which confirms that the film is fully amorphous. This result is in accordance with the high magnification HAADF images in Fig. 5(b), where no nanocrystallites or ordered atomic planes

can be observed. However, the formation of nanocrystallites cannot be completely excluded, due to the limited total volume probed in STEM. Nanobeam diffraction was only performed on one sample. However, x-ray diffraction experiments show that the deposited films are x-ray amorphous over the entire investigated range of compositions and deposition temperatures (diffractograms not shown here).

Figure 6 shows how the Sn_{1-x}Ga_xO_y film density varies with film composition and deposition temperature, as determined by XRR measurements on two series of samples. In the first series, Sn_{1-x}Ga_xO_y films with the varying composition in the range $0 \leq x \leq 1$ were deposited at 175 °C. Then,

FIG. 5. (a) HAADF STEM image of a homogenous Sn_{0.4}Ga_{0.6}O_y film deposited on soda-lime glass (SLG). (b) High-resolution STEM image and electron diffraction pattern (inset) taken from the center of the film. No atomic planes are visible in the Sn_{0.4}Ga_{0.6}O_y layer. (c) Relative intensity from an in-depth EDS line-scan over the entire Sn_{0.4}Ga_{0.6}O_y film.

FIG. 6. Film density vs Sn_{1-x}Ga_xO_y cation composition, determined by XRR and RBS-calibrated XRF, for samples grown at 175 °C (squares), and film density vs ALD temperature for Sn_{0.4}Ga_{0.6}O_y films processed using a 1:1 subcycle ratio (circles).

films with a constant composition of $x=0.6$ were deposited at varying temperatures in the range from 105 °C to 195 °C.

The density is measured to be 5.6 g/cm³ for an SnO₂ film deposited at 175 °C. Here, the density is reduced with increasing Ga content to around 4.4 g/cm³ for pure Ga₂O₃. These values are 20–25% lower than the bulk density values of rutile SnO₂ (6.99 g/cm³) and β -Ga₂O₃ (5.95 g/cm³), respectively.^{34,35} This change in density may be explained by the films amorphous structure, and by residual –OH or other species, originating from the ligands in the metal-organic precursors, in the films.

Furthermore, the density is lower at lower deposition temperatures. The density for an Sn_{0.4}Ga_{0.6}O_y film ranges between 4.2 and 5.3 g/cm³ for deposition temperatures in the range of 105–195 °C. Lower density values for lower ALD temperatures are not uncommon for amorphous oxides and have previously been observed for SnO₂,³⁶ Al₂O₃,³⁷ and SiO₂.³⁸ At the same time, an increased amount of residual –OH groups (and/or other species) are normally observed.

D. Elemental analysis

ToF-ERDA was used to quantify the impurity content in the films. It was found that the films contain moderate amounts of carbon, nitrogen, and hydrogen. In Table II, the concentration of the impurities are listed for Sn_{1-x}Ga_xO_y films with varying cation composition, which were grown at 175 °C with subcycle ratios of 3:1, 1:1, and 1:3. The values are corrected by RBS measurements, to compensate for an inaccurate tin quantification in the ToF-ERDA measurements, caused by overlapping signals between recoiled tin and scattered iodine. The carbon concentration in the films is around 2 at. % and the nitrogen concentration is in the range of 1–2 at. %, independently of the cation composition. Hydrogen is present at slightly higher levels in the range of 4–6 at. %.

Attempts were made to use ToF-ERDA to determine the impurity content in a film grown at 105 °C with a 1:1 process. Comparison of RBS and ToF-ERDA data clearly suggested that this film was prone to highly effective hydrogen release under ion bombardment in ToF-ERDA, already for very short exposure times. Note that the same film was also found to be extremely sensitive to the electron beam in STEM. By using RBS only, we can estimate the order of magnitude of impurities in the film grown at 105 °C, without suffering from any noticeable beam damage.

Figures 7(a)–7(c) show RBS spectra of Sn_{1-x}Ga_xO_y films grown on fused quartz substrates, deposited at 175 °C with different subcycle ratios (3:1, 1:1, and 1:3). Figure 7(d)

shows the RBS spectrum for a film grown at 105 °C with a 1:1 subcycle ratio. From the RBS measurements, it is possible to estimate the impurity concentration by analyzing the total tin gallium and oxygen content in the films. For the films grown at 175 °C, the RBS is in accordance with ToF-ERDA. In contrast, in order to achieve a good fit between the experimental and calculated data for the film grown at 105 °C, a high impurity content must be included in the film (e.g., 35 at. % hydrogen). Due to the sensitive nature of the film, it is difficult to determine the exact ratio between hydrogen, carbon, and nitrogen impurities. However, supplementary measurements using time-resolved nuclear reaction analysis on the same film indicated the presence of high amounts of hydrogen (>20 at. %) that were quickly lost during ion irradiation (resonance energy 6.385 MeV, 6.38–7.00 MeV ¹⁵N⁺ primary ions, data not shown here).

The oxygen-to-metal ratio was determined from the RBS spectra in Fig. 7. For the films grown at 175 °C, the oxygen-to-metal ratios match the theoretical values expected for pure Sn_{1-x}Ga_xO_y films that maintain their charge balance (see Table II). For the film grown at 105 °C, the measured oxygen-to-metal ratio is 2.3, as compared to the expected value 1.7. This high oxygen-to-metal ratio is likely related to the enhanced amount of hydrogen in the film, which presumably is present in the form of residual –OH or water.

E. Optical and electrical properties

The optical absorption in the Sn_{1-x}Ga_xO_y films was extracted from R-T spectrophotometry measurements. The absorption coefficient spectra for different cation compositions are displayed in Fig. 8(a), for films grown at 175 °C. Figure 8(b) shows the corresponding Tauc plots, for amorphous films, which are used to extract the optical bandgap values.⁴⁰ The values are plotted in Fig. 8(c).

The optical bandgap of a-SGO is evidently shifted to higher photon energies when the gallium content is increased. This observation is in line with our expectation that the bandgap and electron affinity can be tuned between the values for SnO₂ and Ga₂O₃, respectively, although a shift in the conduction band minimum through decreased electron affinity remains experimentally unconfirmed. The determined optical bandgap for the SnO₂ film grown at 175 °C is 2.7 eV, which is lower than the bulk value of 3.6 eV for rutile SnO₂ phase,³⁴ but is consistent with previously reported bandgaps for SnO₂ films deposited by ALD from DMA₄Sn and H₂O.²⁸ The optical bandgap of the Ga₂O₃ film grown at 175 °C is at the limit of being determinable with the used optical setup. However, a lower limit is estimated to be 4.2 eV. Nonetheless, the bandgap is certainly lower than the value of 4.9 eV for bulk β -Ga₂O₃. It is known that the optical bandgap of amorphous gallium oxide can be tuned in a relatively wide range (~4–5 eV), which has been proposed to be caused by oxygen deficiency.^{13,41} In our case, we do not expect the films to be oxygen deficient to a significant extent, based on the elemental analysis.

Furthermore, quite large absorption tails are observed. The origin of the tails is unknown for the a-SGO material

TABLE II. Elemental analysis by ToF-ERDA and RBS for films grown at 175 °C.

Sn:Ga subcycle ratio	Ga/(Ga + Sn) (RBS)	Measured				
		O/Me (RBS)	Expected O/Me	at. % C (ERDA)	at. % N (ERDA)	at. % H (ERDA)
3:1	0.33	1.8	1.9	1.8	1.4	3.8
1:1	0.59	1.7	1.7	2.2	1.3	4.8
1:3	0.77	1.7	1.6	1.8	1.5	5.6

FIG. 7. (a)–(c) RBS spectra of $\text{Sn}_{1-x}\text{Ga}_x\text{O}_y$ films, deposited on fused quartz at 175 °C with 1000 cycles with subcycle ratios of 3:1, 1:1, and 1:3, respectively. (d) RBS spectrum of a film grown at 105 °C with a 1:1 subcycle ratio. All spectra were recorded using 2.0 MeV $^4\text{He}^+$ primary ions with an incidence angle of 60°. The simulated spectra were calculated using the SIMNRA software (Ref. 39).

FIG. 8. Optical absorption coefficient of $\text{Sn}_{1-x}\text{Ga}_x\text{O}_y$ films vs composition for films grown at 175 °C (a) and vs ALD temperature for films with $x = 0.6$ (d), with corresponding Tauc plots (b) and (e). The extracted optical band gaps are plotted vs composition (c) and ALD temperature (f).

system. However, it is plausible that the tails are due to localized oxygen p-states above the valence band, which is known to produce absorption tailing in other similar amorphous semiconducting oxides.^{42–44}

Interestingly, the deposition temperature also has a significant effect on the optical bandgap of $\text{Sn}_{1-x}\text{Ga}_x\text{O}_y$ films with a constant composition of $x = 0.6$. The effect of deposition temperature on the optical properties of these films is seen in Figs. 8(d)–8(f), which show the absorption coefficients, Tauc plots, and extracted optical bandgaps, respectively. The measured optical bandgap is 4.1 eV for a $\text{Sn}_{0.4}\text{Ga}_{0.6}\text{O}_y$ film grown at 105 °C as compared to 3.2 eV when grown at 195 °C. The temperature-induced bandgap shift can have different causes. Firstly, the films are homogenous and amorphous layers, which are not likely to exhibit any microstructural features that can produce a bandgap shift (see Sec. III C). Instead, the shift is possibly caused by the enhanced impurity content or due to an overall structural change in the amorphous network, which in turn alters the electronic structure. For instance due to altered average interatomic distances, as evidenced by the observed distinct change in film density (the average Me–Me distance in the films increases by 20–25% when the growth temperature is decreased from 195 to 105 °C according to data from XRF and XRR). In the present study, it is not possible to distinguish between the two possible effects. A more detailed study is required to pinpoint the exact mechanism.

It is clear that the optical (and electronic) properties of a-SGO can be tuned continuously in a controlled way, both by manipulating the cation composition and by varying the deposition temperature. This fulfills a key criterion for using a-SGO as a tunable electron transport layer, in, for instance, solar cell applications.

Two other relevant properties for electron transport layers are the carrier concentration and resistivity. In this study, all deposited a-SGO films are extremely resistive, which is in accordance with the measured stoichiometric metal to oxygen ratios. The resistivity values are larger than $10^4 \Omega\text{cm}$, as measured using a van der Pauw setup,⁴⁵ whereas the resistivity of an SnO_2 film grown at 175 °C was measured to be in the $10^4 \Omega\text{cm}$ range. Due to the high resistivity of a-SGO, it was not practically possible to determine the carrier mobility in this setup. However, assuming mobility values in the range of $1\text{--}100 \text{ cm}^2/(\text{Vs})$, a resistivity value higher than $10^4 \Omega\text{cm}$ corresponds to a carrier concentration value lower than $10^{13}\text{--}10^{15} \text{ cm}^{-3}$.

F. Note on precursor purity

High precursor quality is essential for a well-functioning ALD process. We have noticed that it can occur that commercial DMA_3Ga precursors contain relatively high amounts of chlorine, which presumably originate from the synthesis process. An established route to synthesize DMA_3Ga is through a one-pot salt synthesis route using GaCl_3 and $\text{LiN}(\text{CH}_3)_2$.⁴⁶

The chlorine contamination has two direct consequences. Firstly, the deposited Ga_2O_3 (or a-SGO) films also contain the chlorine contaminant. For instance, we have measured around 7 at. % Cl concentration in Ga_2O_3 films using

different DMA_3Ga suppliers, which roughly corresponds to a Ga/Cl ratio of 5. If it is assumed that the Ga/Cl ratio in the precursor is maintained during deposition, which is likely due to the inability of the adsorbed $-\text{Cl}$ species to react with water at the low deposition temperatures in this study, a Ga/Cl ratio of 5 corresponds to approximately 0.8 at. % Cl in the precursor. If incautious, this may falsely appear to be a low concentration of contamination.

Secondly, the ALD growth is severely affected as well. The growth mechanism (and GPC) is modified, where the QCM curves indicate the presence of two chemisorption processes (not shown here).

It should be noted that for the films in this present paper, no chlorine could be detected by x-ray photoelectron spectroscopy, RBS, or ToF-ERDA.

IV. CONCLUSIONS

A low-temperature process was successfully developed for the fabrication of high resistivity a-SGO thin films by ALD from dimethylamino-metal complexes and water.

QCM studies revealed that the growth exhibits an ideal-like behavior at 175 °C, where the composition can be predicted by a simple rule of mixture. Depending on film composition, GPC varies in the range of 0.6–0.8 Å, at this temperature. At lower temperatures, the growth per individual subcycle (Sn–O or Ga–O) differs from the corresponding GPC values in pure SnO_2 or Ga_2O_3 processes and therefore deviates from the rule of mixture. Despite this, the composition of $\text{Sn}_{x-1}\text{Ga}_x\text{O}_y$ films fabricated using a 1:1 subcycle ratio was constant at $x = 0.6$ over the entire studied ALD temperature range ($T = 105\text{--}195 \text{ °C}$). This contributes to an overall good process stability.

Detailed characterization of deposited films showed that the films are fully amorphous and homogenous. It was also discovered that the film density changes not only with composition but also with ALD temperature to a large degree (a 20% density reduction was observed when the growth temperature decreased from 195 to 105 °C for an $\text{Sn}_{0.4}\text{Ga}_{0.6}\text{O}_y$ film). This distinct density change indicates an extensive modification of the amorphous network. In addition, the density reduction is associated with elevated impurity levels for lower deposition temperatures, notably by a higher hydrogen content.

Optical characterization confirmed that the optical bandgap shifts continuously from 2.7 eV for SnO_2 to above 4.2 eV for Ga_2O_3 (for films grown at 175 °C). This is in line with the expectation that one should be able to shift the optical bandgap and electron affinity from the values for pure SnO_2 to those of Ga_2O_3 , by mixing of the two amorphous materials. However, it was also found that the optical bandgap is strongly influenced by the ALD temperature as well, where the optical bandgap increases from 3.2 to 4.1 eV, when the ALD temperature is decreased from 195 to 105 °C for an $\text{Sn}_{0.4}\text{Ga}_{0.6}\text{O}_y$ film.

Since the optical and electronic properties can be accurately controlled in a continuous manner, ALD grown a-SGO films are believed to have a large potential for many applications, such as the implementation as a tunable

electron transport layer in solar cell devices and other applications.

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