Efficient suboxide sources in oxide molecular beam epitaxy using mixed metal + oxide charges: The examples of SnO and Ga₂O
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ABSTRACT
Sources of suboxides, providing several advantages over metal sources for the molecular beam epitaxy (MBE) of oxides, are conventionally realized by decomposing the corresponding oxide charge at extreme temperatures. By quadrupole mass spectrometry of the direct flux from an effusion cell, we compare this conventional approach to the reaction of a mixed oxide + metal charge as a source for suboxides with the examples of SnO$_2$ + Sn $\rightarrow$ 2 SnO and Ga$_2$O$_3$ + 4 Ga $\rightarrow$ 3 Ga$_2$O. The high decomposition temperatures of the pure oxide charge were found to produce a high parasitic oxygen background. In contrast, the mixed charges reacted at significantly lower temperatures, providing high suboxide fluxes without additional parasitic oxygen. For the SnO source, we found a significant fraction of Sn$_2$O$_2$ in the flux from the mixed charge that was basically absent in the flux from the pure oxide charge. We demonstrate the plasma-assisted MBE growth of SnO using the mixed Sn + SnO$_2$ charge to require less activated oxygen and a significantly lower source temperature than the corresponding growth from a pure Sn charge. Thus, the sublimation of mixed metal + oxide charges provides an efficient suboxide source for the growth of oxides by MBE. Thermodynamic calculations predict this advantage for further oxides as well, e.g., SiO$_2$, GeO$_2$, Al$_2$O$_3$, In$_2$O$_3$, La$_2$O$_3$, and Pr$_2$O$_3$.

I. INTRODUCTION

The desire of mankind for faster and smaller devices has driven Si-based semiconductor technology to be scaled to the verge of its physical limits. Metal oxides (MOs) are promising candidates to overcome these limitations since they not only can compete with Si-based devices but also allow for new device concepts due to the wide tunability of their physical properties. Regarding the fabrication of MOs, molecular beam epitaxy (MBE) is a powerful tool for the growth of single crystalline thin films and their heterostructures.

In MBE, semiconducting oxides (e.g., ZnO, SnO$_2$, In$_2$O$_3$, and Ga$_2$O$_3$) have typically been grown by the reaction of the vapor from a metal charge placed in a heated effusion cell with reactive oxygen (an oxygen plasma or ozone) on the heated substrate in an ultra-high vacuum chamber. This approach comes at the price of (i) a reduced lifetime of filaments in the growth chamber due to their gradual oxidation by the supplied reactive oxygen or the necessity to use expensive, (more) oxidation-resistant parts and (ii) an unintentional oxidation of the elemental source charge and related flux instabilities, observed, e.g., for Si-doping of Ga$_2$O$_3$ using a Si charge.

A potential solution to both problems is the use of oxide source charges to provide metal-oxide molecules instead of metal atoms to the growth surface, thus requiring no or less additionally supplied oxygen, i.e., a lower background oxygen pressure. Early high-temperature vaporization studies of rare-earth oxides and other metal oxides have shown that the main metal-containing constituents of the vapor are suboxide molecules in
many cases, e.g., Ga₂O₃ or SnO from the sublimation of Ga₂O₃ and SnO₂. (The presence of rare-earth suboxides in the source vapor also explains why additionally supplied molecular oxygen is still needed during the growth of rare-earth oxides from sublimed oxide charges.)

Thus, dielectric rare-earth oxides (e.g., Pr₂O₃, Nd₂O₃, La₂O₃, Gd₂O₃, Lu₂O₃) or Ga₂O₃ as dielectric for III–V devices have been typically grown by the sublimation of an oxide charge. Recently, during MBE growth in the presence of additionally supplied reactive oxygen, the sublimation of an SnO₂ charge has been used for Sn-doping of Ga₂O₃ and has become state-of-the-art for growing the complex oxide BaSnO₃. The growth of semiconducting Ga₂O₃-MBE growth of BaSnO₃, SnO₂ and Ga₂O₃ from the oxide charge has been demonstrated to proceed even in the absence of additionally supplied oxygen.

The suboxides Ga₂O₃, SnO₂, and In₂O₃ have also been detected as volatile, desorbing species during plasma-assisted MBE growth of Ga₂O₃, SnO₂, and In₂O₃ from the metal vapor since they are formed as an intermediate product on the surface of the growing oxide films. Thus, besides reducing the required additional oxygen supply, the use of suboxide sources provides simpler growth kinetics by circumventing suboxide formation on the growth surface and it provides suboxide molecules as building blocks for the growth of complex oxides similar to the enabling role of the SnO₂ charge for the growth of high-quality BaSnO₃.

This advantage, however, comes at the price of a significantly higher source temperature (e.g., 1700 °C for Ga₂O₃) often realized by electron–beam evaporation, or ≈1800 °C for Ga₂O₃ requiring the use of an Ir-crucible) compared to that of the corresponding metal charge (e.g., <1000 °C for Ga) required to provide the same (useful) growth rate. Detailed inspection of high-temperature vaporization studies of oxides, however, reveals that the decomposition of heated mixtures of Sn and SnO₂ or Ga and Ga₂O₃ requires significantly lower temperatures than that of SnO₂ or Ga₂O₃ to produce the same suboxide flux. This is in agreement with the observation that Sn, Ga, and In-vapor can rapidly etch SnO₂, Ga₂O₃, and In₂O₃ films in vacuum even at typical growth temperatures (≈600 °C) by the reactions SnO₂ + Sn → 2 SnO, 4 Ga + Ga₂O₃ → 3 Ga₂O₃, and 4 In + In₂O₃ → 3 In₂O₃ followed by desorption of the formed, volatile suboxides.

In this work, we compare the approach of subliming mixtures of metal and oxide to the conventional one of subliming the pure oxide aiming at efficient suboxide sources for oxide MBE with the examples of Sn/SnO₂ and Ga/Ga₂O₃. For this purpose, the temperature-dependent flux of different source charges was investigated by quadrupole mass spectrometry with respect to the contained species and their partial pressure. The experiments were conducted in both vacuum and an oxygen background typical for an oxide MBE growth chamber. The advantages and disadvantages of the investigated approaches will be discussed, concluding with the recommendation of using mixed metal + oxide charges for efficient suboxide sources and the demonstration of SnO₂ growth by plasma-assisted MBE from the mixed Sn + SnO₂ charge. We show that our experimental results largely agree with thermodynamic calculations, which allow us to predict further oxides that can benefit from using the mixed metal + oxide charges as a suboxide source.

II. THERMODYNAMIC PREDICTIONS

To predict the resulting gaseous species and their vapor pressure as a function of temperature for the decomposition of the mixed metal-oxide charges in comparison with that of the pure oxide and the pure metal charges, we calculated the phase diagrams as well as amount and type of reaction products in thermodynamic equilibrium using the FactSage 7.3 software package.

Figures 1(a) and 1(b) show the corresponding phase diagrams. For the mixed charges, the (thick black) lines between the phases “Sn(l) + SnO₂(s)” and “SnO₂(s) + ideal gas” as well as “Ga(l) + Ga₂O₃(s)” and “Ga₂O₃(s) + ideal gas” denote the formation of the gaseous suboxide “SnO” as well as “Ga₂O” from the mixed charges [generally, the “ideal gas” phase refers to gaseous species that are given in Figs. 1(c) and 1(d)]. These lines are, thus, indicating the vapor pressure of the suboxides as a function of source temperatures for the mixed charge. Note, the co-existing solid SnO₂ as well as Ga₂O₃ with the suboxide ideal gas phase is due to the oxide-rich stoichiometry of the source charge chosen in our experiments. At higher temperature, this remaining solid SnO₂ as well as Ga₂O₃ decomposes and sublimes at the boundary to the phase “ideal gas.” This boundary is agreeing well with the decomposition and sublimation of the pure oxides, i.e., the boundary between the phases “SnO₂(s)” and “Ga₂O₃(s)” and “ideal gas” marked by a thick red line.

The comparison of the (thick black) boundaries between the mixed metal-oxide phases and oxide + ideal gas to the (thick red) boundaries between the solid oxides and ideal gas clearly predicts the potential advantage of a lower source temperature required to achieve a certain suboxide vapor pressure when the metal-oxide mixtures are used. In addition, this charge requires even lower source temperatures than the metal charge to achieve the same predicted vapor pressure as comparison to the (thick green) boundary between the liquid and gaseous metals. In our MBE system, a growth rate on the order of 1 Å/s relates to a partial pressure of 1.3×10⁻¹⁰ mbar.

Figure 1(a) suggests that this partial pressure requires source temperatures of ≈760 °C, ≈1050 °C, and ≈920 °C for the mixed SnO₂ + Sn, pure SnO₂, and pure Sn charge, respectively. In comparison, the mixed Ga₂O₃ + Ga, pure Ga₂O₃, and pure Ga charge source temperatures of ≈630 °C, ≈1320 °C, and ≈920 °C, respectively, would be required.

Figures 1(c) and 1(d) shows the composition of the equilibrium reaction products, particularly that of the “ideal gas,” from the mixed metal-oxide source charges as a function of temperature T at a fixed total pressure of P = 10⁻¹³ mbar. The formation of an ideal gas phase that exclusively consists of (SnO₂) and Ga₂O₃ can be seen when T exceeds ≈760 °C and ≈630 °C for the SnO₂ + Sn and Ga₂O₃ + Ga charge, respectively. The remaining solid SnO₂ and Ga₂O₃ decompose at about 1050 and 1250 °C, respectively, by the formation of suboxide and oxygen species. Importantly, at ≈1500 °C and ≈1250 °C, additional gaseous Sn and Ga, respectively, as well as oxygen species are formed coinciding with a reduced formation of suboxide molecules. These results predict pure suboxide fluxes from the mixed charges, an additional oxygen fraction in the fluxes from the pure oxide charges, and another additional Ga fraction in the flux from pure Ga₂O₃ charges.

Figures S1–S6 in the supplementary material show phase diagrams for further mixed metal + oxide charges, i.e., Al₂O₃ + Al,
FIG. 1. (a) and (b) Phase diagrams comparing charges of pure oxide (red), mixed metal-oxide (black), and pure metal (green). Phases denoted “s” are solid, those denoted “l” are liquid. Gas phases are denoted “g” or “ideal gas” in case of gas mixture. The compositions of the “ideal gas” phase of the mixed charges are given in (c, d). (c) and (d) Molar fraction of equilibrium reaction products of the used mixed charges as a function of temperature at a fixed total pressure of $P = 10^{-3}$ mbar that corresponds to a typical pressure inside the effusion cell during oxide MBE. (a) and (c) The case of pure SnO$_2$ compared to 0.6 mol SnO$_2$ + 0.4 mol Sn and pure Sn. (b) and (d) The case of pure Ga$_2$O$_3$ compared to 0.21 mol Ga$_2$O$_3$ + 0.79 mol Ga and pure Ga.

In$_2$O$_3$ + In, SiO$_2$ + Si, GeO$_2$ + Ge, La$_2$O$_3$ + La, and Pr$_2$O$_3$ + Pr, that are predicted to result in suboxide vapors. Similar thermodynamic calculations for Nd$_2$O$_3$ + Nd, Gd$_2$O$_3$ + Gd, and Lu$_2$O$_3$ + Lu resulted in metal vapor instead of suboxide vapor.

III. EXPERIMENTAL

For the present study, a high temperature single filament effusion cell (CreaTec) with a 10 cm$^3$ Al$_2$O$_3$ crucible was mounted opposite to a quadrupole mass spectrometer (QMS; model HALO 201 HidenAnalytical) in a custom-built, tube-shaped vacuum chamber with an approximate volume of 5500 cm$^3$. The electron energy of the ionizer inside the QMS can be tuned in a range from 6 eV to 120 eV. In this setup, schematically shown in the inset of Fig. 2(a), the front end of the effusion cell directly points at that of the QMS with a distance of ~60 cm in between. A shutter between the effusion cell and QMS allowed interrupting the flux to the QMS. The system is connected to a turbo molecular pump (with a pumping capacity for N$_2$ of 400 l/s) that maintained a background pressure in the range of $10^{-8}$ to $10^{-7}$ mbar measured by an ion gauge. To simulate the background pressures in an oxide-MBE system, a variable leak valve allowed molecular oxygen (99.99% purity) to be provided to the system. For the SnO suboxide study, the following charges were investigated: SnO$_2$ powder (4N), SnO powder (3N), Sn slugs (5N), and a mixture of 60 mol.% SnO$_2$ and 40 mol.% Sn. For the Ga$_2$O$_3$ suboxide study, the studied charges were Ga$_2$O$_3$ powder (5N), Ga slugs (7N), and a mixture of 21 mol.% Ga$_2$O$_3$ and 79 mol.% Ga. The molar percentages were chosen in such a way that only oxide will remain in the cell when the charge is used up completely for suboxide formation. After inserting the effusion cell, the vacuum chamber was evacuated and the cell was outgassed. The source materials were heated up to typical sublimation temperatures, and mass spectra of the emitted species were recorded at different cell temperatures.
and background oxygen pressures as follows and also described in Sec. IV.

For the Sn-related system, we monitored only isotopes with the highest natural abundance, i.e., Sn and SnO, at 120 amu and 136 amu with an abundance of 32.6% and Sn2, Sn2O, and Sn2O2 at 238 amu, 254 amu, and 270 amu with an abundance of 17.1%, respectively. Note that for molecules containing two Sn atoms, the probabilities of all isotopic combinations which, i.e., result in 270 amu have been summed up. For Ga, we observed a parasitic background signal at 69 amu. As a consequence, we monitored the peak related to 71Ga, with a natural abundance of 39.9% for Ga, whereas for GaO, the isotope at 85 amu with an abundance of 60.1% was tracked. For Ga2 and Ga2O, we monitored the isotopes with the highest abundance of 48% at 140 amu and 156 amu, respectively. The QMS is calibrated for N2 regarding ionization cross section σ and multiplier efficiency γ measuring the investigated species in terms of partial pressure. In our measurements, no correction was made to account for the different sensitivity of the QMS to the investigated species. As a consequence of this and the fact that we did not measure all isotopes, the partial pressures in our discussion are given in arbitrary units (arb. unit). Nevertheless, partial pressures of the same species can be quantitatively compared among different charges since they all were measured in the same manner. In order to relate the measured fluxes to actual growth rates for the Sn-related system, we conducted deposition experiments on Si substrates mounted at a distance of ≈30 cm away from the source. A discussion of the deposition rates will be given in Secs. IV C and IV D.

Finally, as an initial application test of our mixed SnO source scheme, we mounted a dual filament effusion cell with a mixed Sn + SnO2 charge inside a pyrolytic boron nitride (BN) crucible in a plasma-assisted MBE growth chamber. The BN crucible allowed us to run the hot lip of the cell 150 K hotter than the base to prevent clogging of the source. (Care has to be taken when venting or pumping the growth chamber to prevent the oxide powder from being blown out of the cell.) For comparison to the growth of SnO2 from the pure metallic Sn charge, a single filament effusion cell filled with Sn was also mounted on the growth chamber. Activated oxygen was supplied by a defined flow of molecular oxygen passed through an RF plasma source run at a constant RF power of 300 W. Laser reflectometry (LR) allowed us to measure the growth rate in situ during growth as described in Ref. 7.

A great advantage of the QMS is its sensitivity to the smallest amounts of emitted species from the source charge as well as the ability to distinguish different isotopes, leading to unique fingerprints. In Figs. 2(a) and 2(b), typical QMS spectra are shown. Due to the isotopic distribution of Sn, the Sn and SnO signals in Fig. 2(a) can be clearly identified (black solid lines). Note that no SnO2 was recorded. In Fig. 2(b), the recorded QMS spectra show the presence of Ga2O and Ga2, whereas no Ga2O3 was recorded. Also here, the isotopic distribution allows for a clear identification of the molecules sublimed from the source material Ga2O3.

A frequently observed problem in QMS, however, is cracking of molecules from the direct flux inside the ionizer of the QMS. The resulting cracking products show up as additional species in the mass spectra. Cracking products can be distinguished from parent molecules of the direct flux by determining the minimum electron energy required for their ionization (and thus detection), the so called appearance potentials. The appearance potential of a cracking product A from a species AX should be higher than that of the same species A in the direct flux, as additional energy to that of ionization of A is required for cracking the parent species AX.

An example of this behavior is shown in Fig. 3. The Sn
signal from a Sn charge which we used as a reference for the Sn signal (upper graph) rises from the background at significantly lower electron energy compared to the ones from the SnO$_2$ and SnO + Sn charges (middle and lower graph). Considering the SnO dissociation energy of 5.44 eV$^{37}$ which is similar to the difference of the Sn appearance potentials in Fig. 3, we assume the Sn signal from the SnO$_2$ and SnO$_2$ + Sn charges to be a fragment which is created in the QMS by cracking and ionization processes.

IV. RESULTS AND DISCUSSION

A. Species in the SnO source flux

For all charges, QMS spectra at sufficiently high temperatures were recorded. The detected species of the different charges and their appearance potentials are listed in Table I. In addition, we marked the parent ions and the fragments by p and f, respectively, as discussed above.

The SnO$_2$ + Sn mixture and the SnO charge resulted in the same appearance potentials within their uncertainty. Assuming that SnO decomposes into 50 mol. % SnO$_2$ and 50 mol. % Sn above 400 °C, no difference in the behavior of the SnO$_2$ + Sn charge and the SnO charge in terms of the constituents coming out from the cell can be made. In the following, only the mixture will be discussed since the purity of the components for SnO$_2$ + Sn charge is higher compared to that of SnO, and therefore, is more suitable for oxide MBE. All results are shown in Table I. A comparison of our results to those from other groups in the same table shows a good agreement. As discussed for Fig. 3 and following the argumentation in the literature, 27,29,30 we identified SnO and Sn$_2$O$_2$ to be parent ions for the SnO$_2$ charge and Sn to be a fragment created in the QMS. For the SnO$_2$ + Sn charge, SnO and Sn$_2$O$_2$ were determined to be parent ions, while Sn, Sn$_2$, and Sn$_3$O$_2$ were identified as fragments. Here, the energy gap between the Sn$_2$O$_2$ and the Sn$_3$O$_2$, as well as the gap between SnO$_2$ and Sn$_2$, and the gap between SnO and Sn are in good agreement with the binding energy of the SnO molecule (i.e., 5.44 eV). 29 The presence of Sn$_2$ ions at high electron energies indicates the potential existence of Sn$_2$O$_2$ molecules with Sn–Sn bonds.

From these results, we can confirm the following reactions within the different source charges: 29,30

\[
\text{SnO}_2(s) = \frac{1}{n} (\text{SnO})_n(g) + \frac{1}{2} \text{O}_2(g),
\]

\[
\frac{1}{2} \text{SnO}_2(s) + \frac{1}{2} \text{Sn}(l) = \frac{1}{n} (\text{SnO})_n(g),
\]

with \(n \geq 1, 2\).

For Eq. (2) also, \(n = 4 \) and \(6 \) have been measured by Zimmermann et al. 30

B. Species in the Ga$_2$O source flux

For the Ga$_2$O suboxide sources, we performed the experiments in the same manner as for the SnO suboxide sources and summarize the detected species and appearance potentials for the different charges in Table II. The parent ions and fragments are, again, labeled with p and f, respectively.

From our results and in accordance with the literature, 31–33 we consider Ga$_2$O to be a parent ion for all investigated charges since we did not detect any Ga$_2$O$_3$ as potential parent ion of Ga$_2$O [see Fig. 2(b)]. We also assume Ga$_2$ to be a fragment for all investigated charges due to its high appearance potential that lies ~7 eV above the one of Balducci et al., who investigated vapors of gallium–indium alloys. 33 Our data further indicates that the Ga and GaO signals recorded from the Ga$_2$O$_3$ + Ga mixture are fragments since their appearance potentials lie more than 5 eV above the findings of Burns, who also investigated solid and molten powder of Ga$_2$O$_3$ by electron bombardment (which, in contrast to our findings, also produces GaO parent ions). 31 In addition to that, the Ga$_2$O molecule is considered to have the symmetric structure Ga–O–Ga 32–34 and a GaO bond energy in the range of 5.3–5.4 eV, 34,35 from which we can draw the conclusion of Ga and GaO being created by fragmentation and ionization processes by simply adding up the energy contributions (as we did in the discussion about the SnO charges). We further assume the Ga and GaO signals of the Ga$_2$O$_3$ charge to be parent ions since their appearance potentials are very close to the values of Burns 31 and 4–5 eV below the ones we found for the Ga$_2$O$_3$ + Ga charge. The appearance potentials of the recorded Ga signal confirm

| Charge | Sn | SnO | SnO$_2$ + Sn | SnO$_2$ | SnO$_2$/Sn + SnO$_2$ | SnO + Sn |
|--------|----|-----|-------------|---------|---------------------|---------|
| $T_{\text{Cell}}$ | 1050 °C | 1200 °C | 800 °C | 800 °C | 800 °C | 800 °C |
| Sn | 8.7 ± 0.2 (p) | 15.0 ± 0.7 (f) | 15.6 ± 1.2 (f) | 16.1 ± 0.5 (f) | 7.3 ± 0.2 (p) | 13.0 ± 1.0 (f) | 13.5 ± 1.0 (f) |
| SnO | 11.5 ± 0.4 (p) | 11.1 ± 0.3 (p) | 10.8 ± 0.7 (p) | 10.5 ± 0.5 (p) | 10.7 ± 0.5 (p) |
| Sn$_2$ | 20.3 ± 2.2 (f) | 18.9 ± 2.4 (f) | 13.8 ± 0.5 (f) |
| Sn$_3$O | 14.5 ± 1.3 (f) | 15.1 ± 1.1 (f) | 9.8 ± 0.5 (p) | 9.7 ± 0.5 (p) |
| Sn$_2$O$_2$ | 10.5 ± 0.8 (p) | 9.9 ± 0.4 (p) | 9.9 ± 0.4 (p) | 9.8 ± 0.5 (p) | 9.7 ± 0.5 (p) |
Ga to be a parent ion from the Ga charge in accordance with the values in the literature.\textsuperscript{32,33}

Our results indicate the Ga\textsubscript{2}O\textsubscript{3} charge to produce also Ga and GaO next to Ga\textsubscript{2}O, while the Ga\textsubscript{2}O\textsubscript{3} + Ga mixture produces a pure Ga\textsubscript{2}O flux:

\[
\text{Ga}_2\text{O}_3(g) \rightarrow \frac{1}{2}\text{Ga}_2\text{O}(g) + \frac{1}{2}\text{GaO}(g) + \frac{1}{2}\text{Ga}(g) + \text{O}_2(g),
\]

\[
\text{Ga}_2\text{O}_3(s) + 4\text{Ga}(l) \Rightarrow 3\text{Ga}_2\text{O}(g).
\]

Our findings are also in line with the results of Frosch and Thurmord\textsuperscript{37} who also investigated the Ga\textsubscript{2}O\textsubscript{3} + Ga mixture using a tube oven with the result that Ga\textsubscript{2}O suboxide is formed according to Eq. (4).

### C. Quantitative flux and activation energies of the SnO source

For the temperature dependent measurements, electron energies of 50 eV were used for the detection of the species to maximize the sensitivity. As a result, some of the measured signals might be affected by fragmentation.

After the identification of all parent ions of the SnO and Ga\textsubscript{2}O suboxide sources, we measured the fluxes in terms of partial pressures at different temperatures. The recorded SnO partial pressures of the SnO\textsubscript{2} and SnO\textsubscript{2} + Sn charges are shown as Arrhenius plots in Fig. 4 along with the related activation energies. The activation energies of SnO and SnO\textsubscript{2} from the SnO\textsubscript{2} charge are higher compared to the ones from the SnO\textsubscript{2} + Sn mixture. We observe a small deviation of the SnO flux from the ideal behavior to smaller partial pressures at higher temperatures for the measurements whose origin is unclear at present.

We extrapolated the estimated partial pressures at higher temperatures from the SnO activation energy (shown as red dotted line for the SnO\textsubscript{2} charge). In addition to the SnO suboxide, however, a non-negligible amount of the higher oligomer Sn\textsubscript{x}O\textsubscript{2} is detected in the particle flux from the SnO\textsubscript{2} + Sn in contrast to the pure SnO\textsubscript{2} charge where the amount of Sn\textsubscript{2}O\textsubscript{3} is about two orders of magnitude lower at the same SnO flux assuming similar detection probabilities of the species.\textsuperscript{29} Further oligomers of Sn\textsubscript{x}O\textsubscript{2} with x = 4, 6, outside the mass-range of our QMS, were reported in the literature arising from the heated SnO\textsubscript{2} + Sn mixture.\textsuperscript{29,30} Whether or not these oligomers are detrimental for the growth of SnO related oxides will be discussed later. According to Zimmermann et al.,\textsuperscript{31} the partial pressure of SnO is only 13% of the total flux when using a mixture. In contrast to that, when using a SnO\textsubscript{2} charge, almost 100% of the total flux is given by the SnO. As a consequence of these findings, we added a green dotted line to Fig. 4 in which we multiplied the SnO signal of the mixture by a factor of 7.7 to account for all oligomers which contribute to the SnO deposition. Note that also here for higher temperatures, the values were extrapolated from the activation energy in the same way as for the red dotted line. We carried out deposition experiments to correlate the partial pressures to growth rates when using MBE. Therefore, Si wafers were mounted line of sight with the effusion cell at a distance of ≈30 cm away from the cell. A HF dip was carried out on the wafers to build a smooth surface. The deposition experiments lasted 4–6 h. The thickness of the films was determined by a profilometer and cross sectional SEM.

### TABLE II. Appearance potentials of the different species from Ga\textsubscript{2}O\textsubscript{3} + Ga, Ga\textsubscript{2}O\textsubscript{3}, and Ga charges. For comparison, values derived from Burns\textsuperscript{31,32} (“Burns”) and Balducci et al.\textsuperscript{33} (“Bald.”) are shown.

| Species          | Our measurements | Burns | Bald. |
|------------------|------------------|-------|-------|
|                  | Ga               | Ga\textsubscript{2}O\textsubscript{3} + Ga | Ga\textsubscript{2}O\textsubscript{3} | Ga\textsubscript{2}O\textsubscript{3} + Ga | Ga + In |
| Ga               | 6.6 ± 0.3 (p)    | 11.9 ± 0.4 (f) | 7.5 ± 0.6 (p) | 6.0 ± 0.3 (p) | 6.0 ± 0.5 (p) |
| GaO              | 15.1 ± 1.8 (f)  | 11.4 ± 1.1 (p) |              | 9.4 ± 0.5 (p) |
| Ga\textsubscript{2}O\textsubscript{3} | 16.3 ± 1.4 (f) | 14.9 ± 1.8 (f) |            | 6.2 ± 0.5 (p) |
| Ga\textsubscript{2}O\textsubscript{3} | 9.8 ± 0.5 (p)  | 9.7 ± 1.0 (p)  |            | 8.4 ± 0.6 (p) |

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**FIG. 4.** Arrhenius diagram of the parent ion partial pressures for different SnO source charges listed in the legend. The blue lines denote the linear fit from which the activation energies were calculated. The detection limit is in the range of \(10^{-12}\) arb. units. The red and green stars denote the partial pressure during the deposition experiments at 1200 °C and 800 °C for the SnO\textsubscript{2} charge and the SnO\textsubscript{2} + Sn charge, respectively. The corresponding deposition rates are written below the deposition temperature. The red dotted line marks the extrapolation of the total amount of SnO to 1200 °C for the SnO\textsubscript{2} charge. The green dotted line marks an upper limit for the partial pressure taking all SnO oligomers into account which contribute to the SnO deposition using the SnO\textsubscript{2} + Sn charge.
Source temperature and deposition rates are also added to Fig. 4, and the corresponding partial pressures are marked as stars. We assume the partial pressure of the sum of all \((\text{SnO})_x\), \(x = 1, 2, 4, 6\) oligomers to be in the region between the green dotted line and the green triangles according to the value of the deposition rate. The measurements reveal the advantage of the \(\text{SnO}_2 + \text{Sn}\) mixture since the same \(\text{SnO}\) flux can be reached at cell temperatures \(\approx 400\) K below the ones needed for the \(\text{SnO}_2\) charge, exemplified by the black dashed lines and corresponding deposition rates in Fig. 4. Given the experimental uncertainties, this temperature difference is in fair agreement with the theoretically predicted one of \(\approx 300\) K [cf. Fig. 1(a)]. Growth rates in our MBE chamber from the mixed charge will be discussed in Sec. IV F. For growth rates of \(\text{BaSnO}_3\) on the order of \(0.2\) Å/s, the authors of Refs. 18 and 19 have used an \(\text{SnO}_2\) cell temperature of \(\approx 1100\) °C corresponding to an \(\text{SnO}\) flux of \(8 \times 10^{13}\) cm\(^{-2}\) s\(^{-1}\). According to our theoretical predictions and experimental results in Figs. 1(a) and 4, the same flux can be obtained from mixed \(\text{Sn + SnO}_2\) charge at a \(300–400\) K lower cell temperature.

During sublimation from the \(\text{SnO}_2 + \text{Sn}\) charge as well as from the \(\text{SnO}\) charge, solid \(\text{SnO}\) accumulates at the top of the single-filament cell closing the cell aperture completely. Figure S7 in the supplementary material shows the partially closed cell after sublimation of a quantity of \(\text{SnO}\) at \(850\) °C. The black dashed and dotted lines correspond to growth rates on the order of \(0.5\) Å/s. As shown in Fig. S7, the same growth rate could be achieved by using the \(\text{Ga}_2\text{O}_3 + \text{Ga}\) charge at temperatures that are \(\approx 500\) °C lower than those required for the bare \(\text{Ga}_2\text{O}_3\) charge. [Comparison to the theoretically predicted \(\text{Ga}_2\text{O}_3\) vapor pressures in Fig. 1(b), however, suggests \(1800\) °C or \(1100\) °C to be significantly too high for typical MBE growth rates.] This is likely related to the significantly lower activation energy for the \(\text{Ga}_2\text{O}_3\) formation from the reaction of Ga with \(\text{Ga}_2\text{O}_3\) compared to that for the decomposition of pure \(\text{Ga}_2\text{O}_3\). Moreover, the \(\text{Ga}_2\text{O}_3\) flux from the \(\text{Ga}_2\text{O}_3 + \text{Ga}\) charge does not contain measurable additional Ga in contrast to that from the pure \(\text{Ga}_2\text{O}_3\) charge (see discussion of appearance potentials). Due to these findings, the use of the \(\text{Ga}_2\text{O}_3 + \text{Ga}\) mixture as \(\text{Ga}_2\text{O}_3\) suboxide source seems to be a promising candidate for both highly pure \(\text{Ga}_2\text{O}_3\) suboxide fluxes at adequate cell temperatures using standard cell crucibles and longer lifetimes of inner MBE components.

### D. Quantitative flux and activation energies of the \(\text{Ga}_2\text{O}_3\) source

For the \(\text{Ga}_2\text{O}_3\) suboxide sources, we proceeded in the same manner as for the \(\text{SnO}\) suboxide sources. In Fig. 5, the fluxes of the \(\text{Ga}_2\text{O}_3\) suboxide from \(\text{Ga}_2\text{O}_3\) and \(\text{Ga}_2\text{O}_3 + \text{Ga}\) charges are shown. The authors of Ref. 20 grew \(160\) nm-thick \(\text{Ga}_2\text{O}_3\) layers by MBE from a \(\text{Ga}_2\text{O}_3\) charge heated to \(\approx 1800\) °C. Assuming a typical growth rate on the order of \(0.1\) Å/s, this would correspond to a growth rate on the order of \(0.5\) Å/s. As shown in Fig. 5, the same growth rate could be achieved by using the \(\text{Ga}_2\text{O}_3 + \text{Ga}\) charge at temperatures that are \(\approx 700\) °C lower than those required for the bare \(\text{Ga}_2\text{O}_3\) charge. [Comparison to the theoretically predicted \(\text{Ga}_2\text{O}_3\) vapor pressures in Fig. 1(b), however, suggests \(1800\) °C or \(1100\) °C to be significantly too high for typical MBE growth rates.] This is likely related to the significantly lower activation energy for the \(\text{Ga}_2\text{O}_3\) formation from the reaction of Ga with \(\text{Ga}_2\text{O}_3\) compared to that for the decomposition of pure \(\text{Ga}_2\text{O}_3\). Moreover, the \(\text{Ga}_2\text{O}_3\) flux from the \(\text{Ga}_2\text{O}_3 + \text{Ga}\) charge does not contain measurable additional Ga in contrast to that from the pure \(\text{Ga}_2\text{O}_3\) charge (see discussion of appearance potentials). Due to these findings, the use of the \(\text{Ga}_2\text{O}_3 + \text{Ga}\) mixture as \(\text{Ga}_2\text{O}_3\) suboxide source seems to be a promising candidate for both highly pure \(\text{Ga}_2\text{O}_3\) suboxide fluxes at adequate cell temperatures using standard cell crucibles and longer lifetimes of inner MBE components.

### E. Role of oxygen background

Next, we investigated the quantitative influence of an externally supplied oxygen background on the sublimation of the suboxides from the different charges. This situation mimics typical growth conditions in an oxide MBE growth chamber as some form of oxygen is typically required to oxidize the metal or suboxide vapors toward the “full” oxide on the substrate surface. When the mixtures \(\text{SnO}_2 + \text{Sn}\) or \(\text{Ga}_2\text{O}_3 + \text{Ga}\) are used, no changes of the suboxide flux according to Eqs. (2) and (4) were observed. The same conclusions could be made for the \(\text{SnO}_2\) and \(\text{Ga}_2\text{O}_3\) charges. However, at high oxygen background pressures \(p_{\text{O}_2} = 10^{-6} – 10^{-8}\) mbar, we observed a slight decrease in the suboxide signals by \(\approx 10\%\)–\(30\%\) (see Fig. S8 in the supplementary material) which could be important for cell flux calibration in oxide MBE. The origin of this decrease could be attributed to a reduced mean free of the molecules in the chamber or might be related to a reduced vapor pressure which is caused by the high amount of oxygen.

Furthermore, sublimation of the pure oxide charges coincides with its decomposition.\(^{14,20}\) The consequent oxygen loss can have a non-negligible contribution to the oxygen background pressure in the growth chamber. Indeed, this parasitic oxygen background has even been used for growth of \(\text{Ga}_2\text{O}_3\) from the pure oxide charge.\(^{29}\) Figure 6 shows the oxygen background pressure measured with the QMS during sublimation of the pure oxide charges in comparison to that of the mixed charge in our setup, both in the absence of additionally supplied oxygen. A clear increase in the oxygen partial pressure with temperature of the \(\text{SnO}_2\) and \(\text{Ga}_2\text{O}_3\) charges is observed according to the reaction given in Eqs. (1) and (3), respectively. The trends evidence the creation of a significant oxygen background at cell temperatures required for typical growth rates (e.g., \(1100\) °C for \(\text{SnO}_2\) and \(>1300\) °C for \(\text{Ga}_2\text{O}_3\) charges) with the pure oxide charge. This parasitic oxygen background prevents access to oxygen-poor growth conditions. In contrast, the significantly lower cell...
temperatures required for the same growth rate (or suboxide flux) from the mixed oxide + metal charges prevents the oxide decomposition with oxygen release, supporting the assumption of the reactions given by Eqs. (2) and (4) taking place directly in the crucible. Thus, the use of the mixed charges prevents the formation of a significant parasitic oxygen background as exemplified by the arrows in Fig. 6.

F. Plasma-assisted MBE growth of SnO$_2$ using the mixed Sn + SnO$_2$ charge

As application example, an SnO$_2$ film was grown from the mixed SnO$_2$ source at a substrate temperature of 800 °C, a SnO base temperature of 810 °C (hot lip at 960 °C), and an oxygen flow of 0.5 standard cubic centimeters per minute (sccm). (Note that these growth conditions have not been optimized.) We used an r-plane sapphire substrate that has been shown to lead to the formation of (101)-oriented, single crystalline films by plasma-assisted MBE growth from the metallic source.\textsuperscript{30-41} Figure 7(a) shows the LR trace of the initial growth phase in our experiment where the oxygen flow and plasma had been turned on before time \( t = 0 \) s. The increasing LR signal after opening the SnO shutter indicates film growth. At \( t = 480 \) s, the plasma was turned off, maintaining the molecular oxygen flow. The plateau in the LR signal indicates that growth ceased at this point, demonstrating the need of activated oxygen to oxidize SnO in our MBE environment. Growth continued when the plasma power was turned back on at \( t = 870 \) s as indicated by the further increasing LR signal. Figure 7(b) shows the out-of-plane symmetric 2\( \theta \) – \( \omega \) x-ray diffraction (XRD) scan of the \( \approx 300 \) nm-thick (estimated from oscillations in the LR signal) final layer after a total growth time of \( \approx 100 \) min, confirming growth of an epitaxial SnO$_2$(101) layer using the SnO source and plasma-activated oxygen.

For comparison to growth of SnO$_2$ using an Sn source, we operated the SnO and the Sn source at similar fluxes that correspond to growth rates of 0.95 and 1.2 Å/s, respectively, under conditions of full cation incorporation into the SnO$_2$ film. The corresponding cell temperatures of the Sn and the SnO sources were 1175 °C and 815 °C (hot lip 965 °C), respectively, being in good agreement with the thermodynamic predictions in Fig. 1(a). At a substrate temperature of 700 °C, the growth rate as a function of activated oxygen flow was determined by LR for the growth on c-plane Al$_2$O$_3$ substrates for both sources individually. An oxygen flow of 0.15 sccm enabled a growth rate of 0.99 Å/s for growth from the SnO source. At the same oxygen flow, the growth rate using the Sn source was as low as 0.2 Å/s and an oxygen flow of 0.32 sccm was required to achieve a growth rate of 0.9 Å/s (i.e., almost full Sn incorporation into the film). Our results confirm two advantages of the SnO source using a mixed Sn + SnO$_2$ charge over an Sn source: (1) Less (but activated) oxygen is required for the growth of SnO$_2$, and (2) a significantly lower cell temperature is required to obtain the same growth rate.

V. SUMMARY AND CONCLUSION

In summary, an effusion cell with SnO$_2$ or Ga$_2$O$_3$ charge and mixed Sn + SnO$_2$ or Ga + Ga$_2$O$_3$ charge was investigated as a source of the suboxide SnO$_3$ or Ga$_2$O$_3$, respectively, for the oxide growth by MBE. For this purpose, the direct flux from the cell run at temperatures up to 1280 °C was analyzed by quadrupole mass spectrometry in vacuum without and with an externally supplied oxygen background pressure up to 10$^{-5}$ mbar, the latter one mimicking typical conditions in an oxide MBE growth chamber. These source scenarios were also assessed by thermodynamic calculations that predict the vapor pressure of the resulting species as well as approximate source temperatures for typical MBE growth rates.

The high temperature required for a realistic suboxide flux from the conventionally used oxide charge (SnO$_2$ or Ga$_2$O$_3$) results in an appreciable background of oxygen created by the decomposition of the source material. In addition, metallic Ga was detected in the vapor from the Ga$_2$O$_3$ charge.

FIG. 6. Comparison of the oxygen background created during sublimation of the pure oxide charges and sublimation of the mixed (oxide + metal) charges. Oxygen background pressure \( p_{O_2} \) dependence on the temperature \( T \) of the SnO$_2$, SnO$_2$ + Sn, Ga$_2$O$_3$, and Ga$_2$O$_3$ + Ga charges. The arrows mark the oxygen background pressures created from SnO$_2$ vs SnO$_2$ + Sn and Ga$_2$O$_3$ vs Ga$_2$O$_3$ + Ga charges at the given temperatures that lead to the same suboxide flux (given as horizontal dotted lines in Figs. 4 and 5, respectively). The dotted line denotes the background pressure of 10$^{-7}$ mbar measured by an ion gauge for the SnO$_2$ charge at 1200 °C. (a) Laser reflectometry signal during the beginning of growth showing the temperature dependence on the temperature of the SnO$_2$, SnO$_2$ + Sn, Ga$_2$O$_3$, and Ga$_2$O$_3$ + Ga charges. (b) Laser reflectometry signal showing the temperature dependence on the temperature of the SnO$_2$, SnO$_2$ + Sn, Ga$_2$O$_3$, and Ga$_2$O$_3$ + Ga charges.

FIG. 7. Plasma-assisted MBE growth of SnO$_2$ on r-plane sapphire using the Sn + SnO$_2$ mixed charge. (a) Laser reflectometry signal during the beginning of growth demonstrating no growth without plasma activation. The high-frequency oscillations are an artifact of the substrate rotation. (b) XRD symmetric out-of-plane 2\( \theta \) – \( \omega \) scan of the resulting layer demonstrating single-phase, epitaxial SnO$_2$. The diffraction peaks are labeled.
An efficient alternative is the mixed metal + oxide charge, producing a metal-free suboxide flux at lower activation energy and significantly lower cell temperature without measurable creation and emission of additional oxygen. These lower cell temperatures allow the use of standard effusion cells and crucibles (e.g., PBN, Al2O3) but require the use of a hot-lip effusion cell in the case of SnO to prevent clogging of the cell by solid SnO deposits at the tip of the crucible. The mixed SnO2 + Sn charge creates a significant fraction of higher oligomers (e.g., Sn2O3), which is almost absent in the case of the pure SnO2 charge. We further demonstrated that plasma-assisted MBE of an epitaxial SnO2 film from the mixed SnO source allows for a lower activated oxygen flux and cell temperature than the corresponding growth from an Sn source.

We conclude that mixed metal + oxide charges are a promising, efficient source of suboxides that can outstrip the pure oxide charge. Our results are generally applicable to further oxides (e.g., In2O3, Al2O3, La2O3, Pr2O3, GeO2, SiO2) that possess suboxides (e.g., In2O3, Al2O3, La2O3, Pr2O3, GeO2, SiO2), as well as selenides, sulfides, and tellurides that possess respective subcompounds (e.g., Ga2Se, In2Se, SnSe, In3S, In2Te).

SUPPLEMENTARY MATERIAL

The supplementary material contains phase diagrams similar to Figs. 1(a) and 1(b) of the metal + oxide charges: Al2O3 + Al, In2O3 + In, SiO2 + Si, GeO2 + Ge, La2O3 + La, and Pr2O3 + Pr. It further contains a photograph of the clogged SnO cell and the measured suboxide flux from the mixed charges SnO2 + Sn and Ga2O3 + Ga as a function of externally supplied oxygen.

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