Growth and Doping of $\alpha - (\text{Al}_x\text{Ga}_{1-x})_2\text{O}_3$ using Suboxide Molecular-Beam Epitaxy

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Abstract: $\alpha - (\text{Al}_x\text{Ga}_{1-x})_2\text{O}_3$ has the potential to be the largest bandgap and largest breakdown field semiconductor making it a useful material for high power and ultra high frequency devices. In order to be conductive and useful, $\alpha - (\text{Al}_x\text{Ga}_{1-x})_2\text{O}_3$ must be doped. This work attempted to dope $\alpha - (\text{Al}_x\text{Ga}_{1-x})_2\text{O}_3$ with Sn during suboxide molecular-beam epitaxy (S-MBE). During growth it was observed the growth rate increased when the SnO$_2$ source was used due to metal-oxide catalyzed epitaxy (MOCATAXY). High quality single-phase $\alpha - (\text{Al}_x\text{Ga}_{1-x})_2\text{O}_3$ thin films were grown by S-MBE at different Al compositions, doping levels, and thicknesses. However, the Sn doping resulted in insulating films at all tested conditions and it is unclear if the Sn is being incorporated into the films during growth.

Introduction

Research interest in Ga$_2$O$_3$ has increased due to its ultra-wide bandgap and high breakdown field. The $\beta$ phase is the most widely studied as it is thermodynamically stable under standard conditions and has an ultra-wide-bandgap of 4.6-4.9 eV as well as a breakdown field of 8.0 MV/cm. $^1$ This gives Ga$_2$O$_3$ a large Baliga’s figure of merit, making it a useful material for high power devices that can operate at high temperatures and high voltages. We can improve these properties by alloying Ga$_2$O$_3$ with Al$_2$O$_3$ to extend the bandgap and breakdown field of the material even further.

$(\text{Al}_x\text{Ga}_{1-x})_2\text{O}_3$ has two main phases: rhombohedral ($\alpha$) and monoclinic ($\beta$). The $\beta - (\text{Al}_x\text{Ga}_{1-x})_2\text{O}_3$ is limited to Al compositions of $x < 0.6$. Phase segregation begins to occur at high Al compositions because Al$_2$O$_3$ is stable in the $\alpha$ phase. This limits the bandgap of $\beta - (\text{Al}_x\text{Ga}_{1-x})_2\text{O}_3$ to 4.6-6.0 eV. The $\alpha - (\text{Al}_x\text{Ga}_{1-x})_2\text{O}_3$ is preferred because it has been alloyed over the entire compositional range, has a bandgap ranging from 5.4-8.6 eV, and can be grown on sapphire substrates. $^2$

Molecular-beam epitaxy (MBE) has grown the highest structural quality Ga$_2$O$_3$ films but at slower growth rates than other epitaxial methods. $^3$ In conventional MBE three reactions take place.

$$2\text{Ga} + \text{O} \rightarrow \text{Ga}_2\text{O} \quad (1)$$
$$\text{Ga}_2\text{O} + 2\text{O} \rightarrow \text{Ga}_2\text{O}_3 \quad (2)$$
$$4\text{Ga} + 3\text{Ga}_2\text{O}_3 \rightarrow 3\text{Ga}_2\text{O}_5 \quad (3)$$

The first reaction forms gallium suboxide (Ga$_2$O), which is further oxidized into gallium oxide in the second reaction. The third reaction may occur when there is an excess of Ga and causes desorption of Ga and O from the growth surface.

The first and third reaction limit the overall growth rate of gallium oxide as Ga$_2$O is extremely volatile at the temperatures required for growth. Suboxide molecular-beam epitaxy (S-MBE) significantly increases the growth rate of Ga$_2$O$_3$ by simplifying the reactions that take place. $^4$ S-MBE utilizes a gallium suboxide source in place of the conventional elemental gallium source. This bypasses the first and third reaction, resulting in a single-step reaction. Other benefits of S-MBE include linear composition control and increased absorption controlled growth regimes. S-MBE has also been shown to be able to grow over the whole Al composition range. $^4$

For ultra-wide bandgap materials to be used in devices, they need to be conductive. $(\text{Al}_x\text{Ga}_{1-x})_2\text{O}_3$ is an insulator and must be doped to be conductive. Previous computational work has predicted the Al composition at which dopants transition from shallow to deep donors in $\alpha - (\text{Al}_x\text{Ga}_{1-x})_2\text{O}_3$. $^6$ Once the critical Al composition is surpassed, the dopants are not expected to contribute to the conductivity of the material. Silicon has been shown to be able to create conductive $\alpha - (\text{Al}_x\text{Ga}_{1-x})_2\text{O}_3$ films up to $x = 0.3$ using other growth methods, while tin has only resulted in conductive films at $x = 0.7$. Germanium has successfully doped conductive $\beta - \text{Ga}_2\text{O}_3$ films. $^9$ Si is predicted to remain a shallow donor up to $x = 0.72$, but previous attempts to dope $\alpha - (\text{Al}_x\text{Ga}_{1-x})_2\text{O}_3$ with Si during S-MBE growth resulted in insulating films. Successfully doping $\alpha - (\text{Al}_x\text{Ga}_{1-x})_2\text{O}_3$ would make it the largest bandgap and largest breakdown field semiconductor.

Methods

A growth series was developed to grow a wide array of doped films. Four different variables were varied between growths: dopant, film composition, doping level, and film thickness. The three dopants used were silicon, tin,
and geranium. Each dopant was incorporated into $\alpha-Al_{x}Ga_{1-x}O_{3}$ films ranging in composition from $x = 0$ to $x = 0.8$ in steps of 0.2. This composition range will capture the shallow to deep donor transition for each dopant allowing us to experimentally validate the computational work. For each film composition and dopant, two different doping levels $10^{19}$ and $10^{20}$ cm$^{-3}$ were tested to make sure the donors are not being compensated. Finally, two different film thicknesses were used: $\sim 20$ nm and $\geq 100$ nm. The $\geq 100$ nm films are expected to be more conductive as the lower surface to volume ratio will result in less scattering. The $20$ nm film is expected to be higher quality and can be used to determine the growth rate.

For this project all films were grown by $S$-MBE on A-plane sapphire substrates. All $20$ nm samples were grown at a substrate temperature of $625^\circ C$. All $\geq 100$ nm samples were grown at a substrate temperature of $630^\circ C$ to help films remain smooth and stabilize the thicker films. After growth, x-ray reflectivity (XRR) was used to measure the film thickness. Then x-ray diffraction (XRD) was used to confirm the Al composition and phase purity. The two-point resistance of each sample was measured using a multimeter.

### Results and Discussion

During growth, it was observed the growth rate increased when the SnO$_2$ source was used. Table 1 summarizes the growth rate at different SnO$_2$ source temperatures for the $x = 0$ films. The Ga flux between each growth remained relatively constant and the main change is the SnO$_2$ source temperature. This increased growth rate is due to metal-oxide-catalyzed epitaxy (MOCATAXY). MOCATAXY utilizes a catalytic element that increases the growth rate through metal-exchange catalysis. Sn acts as a catalyst for the growth of Ga$_2$O$_3$. Besides the increased growth rate, other benefits of MOCATAXY may include: improved surface morphology, enhanced crystalline quality, and stabilization of energetically unfavorable phases. Atomic Force Microscopy (AFM) was used to measure the root mean square (rms) roughness of films grown with the Sn source. As shown in Figure 1, the average rms roughness of films is $0.555$ nm for the $20$ nm films and $0.781$ nm for the $>100$ nm films. They all have sub-nanometer roughness, which has not previously been achieved for $100^+$ nm thick $\alpha$-Ga$_2$O$_3$ films. More AFM can be done to directly compare the rms roughness between films grown for the doping series with and without the SnO$_2$ source. A disadvantage of MOCATAXY is that the composition was no longer linearly controlled. As the Sn and Ga fluxes changed, the Ga$_2$O$_3$ growth rate also changed. This made it more difficult to determine the correct fluxes to grow a film with a specific Al composition.

Even with this difficulty, all $20$ films from the Sn doping series were successfully grown. The Sn concentration in the high doping level, $x = 0.6$, $20$ nm film is believed to be an order of magnitude too large ($10^{21}$ cm$^{-3}$) due to calculation errors. Figure 2 shows the XRD scans of the Sn doped samples. The XRD confirms the films are all single phase and are of high structural quality. The films in Figure 2a and 2c have growth fringes which suggest high structural quality and sharp interfaces in thin films. However, all the films were found to be insulating. The multimeter was unable to give a resistance measurement as the films were not conductive enough. One possibility for the lack of conductivity is that the dopants are not being incorporated into the film during growth. It is currently unclear if the dopants are successfully incorporated into the films. As the Sn is only attempted to be added at doping concentrations, XRD scans cannot be used confirm the incorporation of Sn in the films. SIMS analysis can be used to confirm if the dopants are being successfully incorporated into the films.

<table>
<thead>
<tr>
<th>SnO$_2$ Temperature (°C)</th>
<th>Ga Flux (10$^{14}$ cm$^{-2}$s$^{-1}$)</th>
<th>Growth Rate (µm/hr)</th>
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<tbody>
<tr>
<td>0</td>
<td>7.01</td>
<td>0.312</td>
</tr>
<tr>
<td>881</td>
<td>6.97</td>
<td>0.546</td>
</tr>
<tr>
<td>938</td>
<td>7.98</td>
<td>0.894</td>
</tr>
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</table>

![AFM images](image1.png) ![AFM images](image2.png)

**FIG. 1.** AFM of the growth surface of films grown with SnO$_2$ source. (a) rms roughness = 0.860 nm; film thickness = 116 nm; $x = 0.2$ (b) rms roughness = 0.702 nm; film thickness = 108 nm; $x = 0$ (c) rms roughness = 0.533 nm; film thickness = 18.1 nm; $x = 0$ (d) rms roughness = 0.577 nm; film thickness = 22.4 nm; $x = 0$

### Future Work and Conclusions

The Sn doping series resulted in insulating films at all tested conditions. Rocking curves can be measured to confirm that structural quality of the films is not a concern.
Further work is necessary to understand and achieve the doping of $\alpha-(\text{Al}_x\text{Ga}_{1-x})_2\text{O}_3$ films by S-MBE. Next steps include completing the Si and Ge doping series and more characterization. SIMS analysis can be used to confirm the dopants are being incorporated into the films. Undoped samples at each Al composition were also grown for ion implantation. Ion implantation is a confirmed way to incorporate dopants into the films. These films can be used to characterize how dopants will behave in $\alpha-(\text{Al}_x\text{Ga}_{1-x})_2\text{O}_3$ films. Hall measurements can be used to characterize electronic properties of the films such as the carrier mobility and sheet resistance. High temperature Hall measurements can be done on the insulating films to determine how difficult it is to activate the donors. This work will allow us to have a clearer understanding of why the Sn doped films are insulating and how to successfully grow conductive $\alpha-(\text{Al}_x\text{Ga}_{1-x})_2\text{O}_3$ films using S-MBE.

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References

[9] Alema et al. 2021, APL Mater. 9, 091102

FIG. 2. $\omega$-2$\theta$ XRD scans of the samples over the $2\theta$ range of 20°-70°, offset on the vertical axis for clarity. The scans show the films are single phase. The 110 peak for the $\alpha$-$\text{Al}_2\text{O}_3$ substrate is marked by a *. The film peaks shift over 2$\theta$ as the Al composition changes. (a) Low doping, 20 nm samples (b) Low doping, >100 nm samples (c) High doping, 20 nm samples (d) High doping, >100 nm samples