Growth and Doping of $\alpha - (Al_xGa_{1-x})_2O_3$ using Suboxide Molecular-Beam Epitaxy

Kira Martin [1], Jacob Steele [2], and Darrel G. Schlom [2,3,4,5]

[1]Department of Material Science and Engineering, University of Illinois at Urbana-Champaign, Urbana, Illinois 61801
[2] Department of Material Science and Engineering, Cornell University, Ithaca, New York 14853
[3] School of Applied Physics and Engineering Physics, Cornell University, Ithaca, New York 14853
[4] Kavli Institute at Cornell for Nanoscale Science, Ithaca, New York 14853
[5]Leibniz-Institut für Kristallzüchtung, Max-Born-Str. 2, Berlin, Germany 12489

Abstract: $\alpha - (Al_xGa_{1-x})_2O_3$ 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, $\alpha - (Al_xGa_{1-x})_2O_3$ must be doped. This work attempted to dope $\alpha - (Al_xGa_{1-x})_2O_3$ 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 $\alpha - (Al_xGa_{1-x})_2O_3$ 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_2O_3 has increased due to its ultra-wide bandgap and high breakdown field. The β phase is the most widely studied as it is thermodynamically stable under standard conditions and has an ultrawide-bandgap of 4.6-4.9 eV as well as a breakdown field of 8.0 MV/cm. [1] This gives Ga_2O_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_2O_3 with Al_2O_3 to extend the bandgap and breakdown field of the material even further.

$(Al_xGa_{1-x})_2O_3$ has two main phases: rhombohedral (α) and monoclinic (β) . The $\beta - (Al_xGa_{1-x})_2O_3$ is limited to Al compositions of $x < 0.6$. Phase segregation begins to occur at high Al compositions because Al_2O_3 is stable in the α phase. This limits the bandgap of $\beta - (Al_xGa_{1-x})_2O_3$ to 4.6-6.0 eV. The $\alpha - (Al_xGa_{1-x})_2O_3$ is preferred 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_2O_3 films but at slower growth rates than other epitaxial methods. [3] In conventional MBE three reactions take place.

$$2Ga + O \rightarrow Ga_2O \quad (1)$$

$$Ga_2O + 2O \rightarrow Ga_2O_3 \quad (2)$$

$$4Ga + Ga_2O_3 \rightarrow 3Ga_2O \quad (3)$$

The first reaction forms gallium suboxide (Ga_2O), 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_2O is extremely volatile at the temperatures required for growth. Suboxide molecular-beam epitaxy (*S*-MBE) significantly increases the growth rate of Ga_2O_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. $(Al_xGa_{1-x})_2O_3$ is an insulator and must be doped to be conductive. Previous computational work has predicated the Al composition at which dopants transition from shallow to deep donors in $\alpha - (Al_xGa_{1-x})_2O_3$. [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 $\alpha - (Al_xGa_{1-x})_2O_3$ films up to $x = 0.3$ using other growth methods, while tin has only resulted in conductive films at $x = 0$. [7,8] Germanium has successfully doped conductive $\beta - Ga_2O_3$ films. [9] Si is predicted to remain a shallow donor up to $x = 0.72$, but previous attempts to dope $\alpha - (Al_xGa_{1-x})_2O_3$ with Si during *S*-MBE growth resulted in insulating films. Successfully doping $\alpha - (Al_xGa_{1-x})_2O_3$ 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 $\alpha-(Al_xGa_{1-x})_2O_3$ 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: ~20 nm and ≥100 nm. The ≥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°C. All ≥100 nm samples were grown at a substrate temperature of 630°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_2source 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_2O_3. Besides the increased growth rate, other benefits of MOCATAXY may include: improved surface morphology, enhanced crystalline quality, and stabilization of energetically unfavorable phases. [10] 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 α-Ga_2O_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_2O_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 1. A change in growth rate was observed during growths with the SnO_2source due to MOCATAXY

SnO_2 Temperature (°C)	Ga Flux (10^{14} cm^{-2}s^{-1})	Growth Rate (μm/hr)
0	7.01	0.312
881	6.97	0.546
938	7.98	0.894

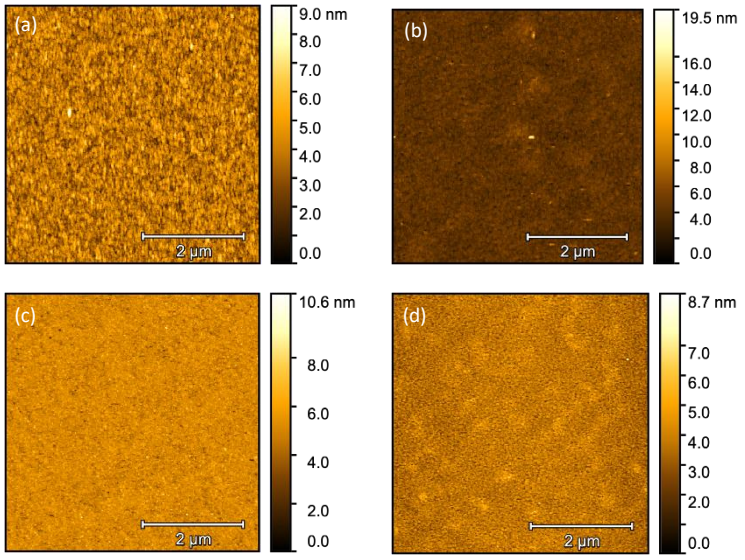

FIG. 1. AFM of the growth surface of films grown with SnO_2 source**. (a)** rms roughness = 0.860 nm; film thickness = 116 nm; $x = 0.2$ **(b)** rms roughness = 0.702 nm; film thickness = 108 nm; $x = 0$ **(c)** rms roughness = 0.533 nm; film thickness = 18.1 nm; $x = 0$ **(d)** rms roughness = 0.577 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 $\alpha-(Al_xGa_{1-x})_2O_3$ 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 $\alpha-(Al_xGa_{1-x})_2O_3$ 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 insulting and how to successfully grow conductive $\alpha-(Al_xGa_{1-x})_2O_3$ films using *S*-MBE.

Acknowledgments

I would like to thank my mentor Jacob Steele and Professor Darrell G. Schlom for their support and guidance in this project. This research was funded by the National Science Foundation (NSF) Platform for the Accelerated Realization, analysis, and Discovery of Interface Materials (PARADIM) under Cooperative Agreement No. DMR-2039380 as well as the NSF REU Site: Summer Research Program at PARADIM under Cooperative Agreement No. DMR-2150446.

References

[1] Pearton et al. 2018, Appl. Phys. Rev. 5, 011301
[2] Jinno et al. 2021, Sci Adv. 7, eabd5891
[3] McCandless et al. 2021, Appl. Phys. Lett. 119, 062102
[4] Vogt et al. 2021, APL Mater. 121, 031101
[5] Azize et al. 2023, APL Mater. 11, 041102
[6] Wickramaratne et al. 2022, Appl. Phys. Lett. 121, 042110
[7] Dang et al. 2020, AIP Advances 10, 115019
[8] Chikoidze et al. 2016, J. Appl. Phys. 120, 025109
[9] Alema et al. 2021, APL Mater. 9, 091102
[10] McCandless et al. 2023, Jpn. J. Appl. Phys. 62, SF1013

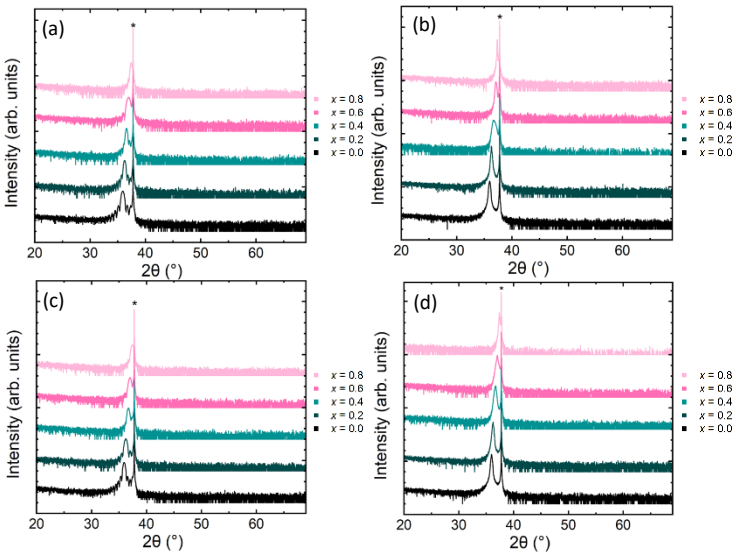

FIG. 2. ω-2Θ XRD scans of the samples over the 2Θ range of 20°-70°, offset on the vertical axis for clarity. The scans show the films are single phase. The 110 peak for the α-Al_2O_3 substrate is marked by a *. The film peaks shift over 2Θ as the Al composition changes. **(a)** Low doping, 20 nm samples **(b)** Low doping, >100 nm samples **(c)** High doping**,** 20 nm samples **(d)** High doping, >100 nm samples