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LDRD PROJECT NUMBER: 191190

LDRD PROJECT TITLE: Fundamental Science of Doping and Defects in Ga_2O_3 for Next Generation Power Semiconductors

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ABSTRACT: The aim and scope of this project was the development of a capability to prepare high-quality, epitaxial beta gallium oxide films by oxide reactive molecular-beam epitaxy. The purpose was to demonstrate that beta gallium oxide could be grown by such a method using Sandia's existing oxide molecular-beam epitaxy instrument. The key activity in this project was the installation of a gallium oxide capability on the Sandia instrument. This required the acquisition of several custom items for the instrument, including: a gallium effusion cell, appropriate cell power supplies and temperature controllers, a shutter to block beam flux, installation of an existing ozone generator with a directed gas nozzle and controlled leak valve, and re-routing the chilled water system to accommodate the cell. In addition, beta gallium oxide single crystals were acquired and their surfaces characterized by reflection high energy electron diffraction.

INTRODUCTION: The purpose of this project was to investigate the growth of beta gallium oxide by reactive molecular-beam epitaxy with an ultimate goal of establishing its suitability as a power semiconductor. Recently, beta gallium oxide has been identified as a potential generation-after-next power semiconductor. Based upon its high breakdown strength and reasonable electron mobility, it is expected to have a Baliga power semiconductor figure of merit that is 10X better than SiC and 3X better than GaN. While there are other materials with even higher figures of merit, such as (Al,Ga)N, AlN, and diamond, each of these also has potential drawbacks. For example, by alloying GaN with AlN to make (Al,Ga)N there is an alloy scattering effect that effects both phonons and electrons. This results in reductions in thermal conductivity and electron mobility for intermediate compositions. Performance gains in terms of the power semiconductor figure of merit are not recovered until high AlN-containing compositions are achieved. Additionally, by moving to such high AlN compositions, the bandgap increases substantially and the ability to dope the material becomes challenging. The same is true for diamond, where it is very difficult to dope, much less grow. Beta gallium oxide has attributes that make it a promising material system. For example; large single-crystal wafers are now commercially available, which is not true for either AlN, (Al,Ga)N, or diamond; it has been demonstrated that it can be doped with several different elements that have shallow, but unknown doping energy levels; it has a very high breakdown strength that makes it appropriate for power switching applications; and, while the thermal conductivity is modest, it doesn't need to be alloyed to achieve a high bandgap and therefore may have a higher thermal conductivity and electron mobility than (Al,Ga)N alloys.

While there are many promising attributes to beta gallium oxide, there are many fundamental material properties that are not known. Energy levels of different dopants and defects are not presently known. The defect chemistry, while known, is underappreciated. For example, while it is an oxide material and many would expect that best doping results would be had for growing and processing the material in oxygen-rich environments, oxygen may actually be detrimental to doping efficacy. This is common for *n*-type doped oxides. It would be best to actually grow and process the material in slightly reducing conditions to stabilize an electronic compensation mechanism for the doping elements. Further, there has been limited research into the best dopants for gallium oxide. Most research focuses on using tin, zirconium, or silicon as *n*-type dopants. While these have been shown to be effective, if one analyzes the size of these ions in the gallium oxide lattice with respect to gallium ions, it can be seen that these will impart a great deal of strain. It was our hypothesis in this work that tantalum or niobium would be better *n*-type dopants and that magnesium would be a good *p*-type dopant, based on ion size.

Even though several groups have demonstrated growth of gallium oxide by oxide molecular-beam epitaxy, this was seen as a risk and this project was funded to minimize that risk prior to considering a larger program. The goal therefore was to develop and demonstrate a capability for epitaxial gallium oxide growth at Sandia.

DETAILED DESCRIPTION OF EXPERIMENT/METHOD: The experimental method for growth of beta gallium oxide is reactive molecular-beam epitaxy. Molecular-beam epitaxy is a film growth technique that was pioneered in the 1960s for growth of gallium arsenide. Molecular-beam epitaxy instruments are essentially well-controlled ultra-high vacuum evaporation systems. The general design is a means to heat an element (or chemical) to achieve the desired vapor pressure of that species. In a typical evaporator, this takes the form of a pseudo-point-source where a roughly equivalent flux of species is present over a hemispherical geometry. In molecular-beam epitaxy, the flux is confined to a narrow beam directed at the substrate or substrate platen. This flux beam can be achieved multiple ways. The most conventional is the use of an effusion cell to heat the desired element. An effusion cell is a small furnace with one open end. A conical or cylindrical crucible partially filled with the desired element is loaded within the crucible and the effusion cell is installed into the vacuum system such that it directs a beam of vapor flux at the substrate. The other means of forming a directed flux beam, which is common in molecular-beam epitaxy instruments that use electron beam evaporators, is to form an orifice over the crucible to block most of the flux and form a narrow beam. Since ultra-high vacuum conditions are used in molecular-beam epitaxy, a line-of-sight directed flux beam can be expected. If the system pressure is too high, the beam would become scattered and diffuse and loss of flux control would result. In addition to a directed element flux beam, molecular-beam epitaxy instruments also have heated substrates to provide for increased adatom mobility to enable epitaxial growth. Further, these instruments typically have shutters located between the source and the substrate to modulate pulses of the element flux toward the substrate surface.

In oxide molecular-beam epitaxy, there are some additional considerations for growth. In this case, it is not common for the flux beam to be an oxide. That is, it is uncommon for a user to evaporate an oxide and use it to condense as an oxide film on the substrate surface. Rather, it is much more common to produce a metallic vapor that is directed toward the substrate and then to

react that vapor with an oxygen species at the substrate surface. This can be achieved one of several ways. For most metal oxides that have low free energies of formation, introduction of molecular oxygen is sufficient to drive oxidation of the metal species at the elevated growth temperatures. Some metal oxides, however, have higher free energies of formation and are less easily oxidized. This is the case for metals such as copper, lead, bismuth, nickel, and gallium. While high enough oxygen pressures within the molecular-beam epitaxy instrument could enable oxidation of these species, the requisite high pressures may interfere with the flux beam and also any electron beam diagnostics. In this case, it is beneficial to provide a higher activity source of oxygen such as ozone or atomic oxygen. This can be achieved with either an external ozone source or an oxygen plasma source. Further, using a directed gas nozzle toward the substrate can enable locally higher oxygen pressures that can aid in oxidation. Oxide molecular-beam epitaxy is typically a harsh environment for heating elements and other hot filaments. Care must be taken to select materials for heating elements that can withstand the harsh conditions.

In situ diagnostics provide a means to monitor film growth. The typical molecular-beam epitaxy instrument is configured with a reflection high-energy electron diffraction (RHEED) system to provide this diagnostic. The basic principal is that a high energy electron beam (similar to that used in an electron microscope) is formed and is directed at the substrate surface, but at a glancing angle (typically less than five degrees). The beam diffracts off of the surface reciprocal space rods and the diffracted beams impinge upon a phosphorescent screen where the image is captured (usually with a digital camera) and the growth mode can be interpreted. This technique provides information on film growth mode that are difficult to monitor in other growth techniques and is enabled by the ultra-high vacuum environment of the molecular-beam epitaxy tool.

Efforts in this work focused on upgrading the existing Sandia oxide molecular-beam epitaxy tool for growth of gallium oxide. The steps taken to establish this capability are discussed in detail in the results section.

RESULTS: Gallium is a common molecular-beam epitaxy element owing to its importance in a wide variety of conventional III-V semiconductors, such as GaAs, GaP, GaSb, and GaN, and many other quaternary compounds. Gallium oxide growth is much less common, however. The primary goal of this project was to establish a gallium oxide growth capability and then demonstrate that high-quality nominally undoped films could be grown. The first step was the development of a gallium oxide growth capability. The existing Sandia oxide molecular-beam epitaxy instrument was first constructed in ~1991 as a tool to study the fundamentals of growth of silicon, germanium, and alloys of silicon germanium. The instrument is a custom tool that has a Thermionics three-pocket electron-beam evaporator as the source flange, which has three positions on the flange for installation of effusion cells. To form the flux beams from the electron beam sources, a copper plate with orifice holes cut into it is affixed atop the cooling shroud on the source flange. The instrument is an unusual geometry with a nearly one-meter source to substrate distance.

In 2010, the instrument was moved and converted to an oxide system. This process involved removal of many of the internal heating sources for bake out, conversion of the substrate heating element from a tungsten wire to a thicker tantalum wire, upgrading of the RHEED system to a new Staib Instruments system, and installation of new pumps and gauges.

The system has been used to grow lanthanum oxide and gadolinium oxide where the metallic fluxes are formed from e-beam evaporation and also magnesium oxide and calcium oxide, where the metallic fluxes are formed from custom effusion cells. To form a gallium flux, a new effusion cell needed to be procured. We worked with E-Science (Hudson, WI) to design an appropriate source for the custom Sandia instrument. The cell is an 85 cubic centimeter dual filament cell with a Titan crucible and an 11.4" in-vacuum length. The cell has an integrated cooling water jacket to aid in maintaining a well-controlled cell temperature. To control the cell temperature, two Sorensen DLM-600 DC power supplies, one for each the tip and body heating zones of the cell, were acquired. Two Eurotherm 2408 temperature/process controllers were acquired to provide PID controls of the DC power output to the cells. To install the cell, the source flange needed to be dropped from the system and the third effusion cell port made available. This required modifying the copper plate affixed to the cooling shroud to make an opening for the gallium flux. Also at the time of the opening, a shutter to block the gallium flux had to be installed. A pneumatic linear actuator was acquired from MDC vacuum and a custom shutter was designed and affixed to the end of the actuator. Efforts were made to ensure that the rotation of the source flange was correct such that the fixed radial position of the shutter was aligned over the gallium cell. Further, extensive efforts to ensure that the the linear translation of the shutter was efficient to both block and enable gallium flux to form a beam toward the substrate were undertaken. To provide a source of active oxygen, an existing InUSA ozone system had to be installed. In addition to installing the ozone generator, a directed gas nozzle was designed, with a large ~0.75" tube directed at the growth surface. An Agilent manual controlled leak valve was installed with the directed gas nozzle. The InUSA ozone generate required oxygen to be plumbed, but also nitrogen. The particular ozone generator requires a fixed concentration of nitrogen to form ozone. To provide sufficient control, two mass flow controllers were acquired from Omega Engineering. The oxygen mass flow controller was specified according the Sandia's pressure safety policy to be specially cleaned for oxygen service. The mass flow controllers were installed with the ozone generator and the ozone generator plumbed to the controlled leak valve. An ozone destruct unit was installed downstream of the ozone generator to destroy all unused ozone before venting to the building exhaust. Finally, installation of the gallium effusion cell required modifying the chilled water loop on the molecular-beam epitaxy tool to incorporate the cooling jacket on the cell. These modifications were made.

DISCUSSION: To install the gallium flux capability, the graphite effusion cell crucible had to be loaded with 99.999% pure gallium. The original crucible used in this work was an 85cc Titan crucible from E-Science. The crucible had a screw-on orifice with an 8° divergence angle. We chose to purchase gallium metal from Alfa Aesar and to melt the gallium to transfer it into the graphite crucible. A 5cc syringe was used to draw the molten gallium from the manufacturer-supplied container and inject it into the crucible. This process was done slowly and time was taken to ensure that the gallium solidified prior to injecting more gallium into the crucible. This care was taken as it is known that gallium undergoes a significant volume contraction upon freezing, which could crack the graphite crucible. Once a sufficient amount of gallium was added to the crucible, the crucible was loaded into the effusion cell, which was subsequently loaded into the molecular-beam epitaxy system. In the future, it is recommended to purchase gallium bars that do not require melting for filling the crucibles.



A concern developed among the research team that the standard 8° divergence angle on the Titan crucible orifice would result in a very broad gallium flux beam. This would result in coating of the internal walls of the molecular-beam epitaxy instrument with gallium metal – and also a coating of the substrate manipulator with gallium metal, in regions where there are electrical contacts and mechanical connections for manipulation. Beyond the concern of simply coating the internal components of the chamber with gallium was the concern that gallium has a relatively low melting temperature. This could result in gallium melting and flowing down the chamber components causing short circuits of electrical connections, interfering with mechanical operations, and, in general, damaging the system rendering it unusable for other on-going research. The decision was made by the principal investigator to not heat the effusion cell, which would melt the gallium, and perform a growth. Rather, the vendor of the effusion cell was contacted and a custom orifice was requested. The vendor was able to design and provide an orifice for the 85cc Titan crucible that reduced the divergence angle to 2°. This would limit the gallium flux beam to just the substrate platen. There was a lead-time associated with receiving the component, but it was decided that that time was worth the wait to avoid damaging the molecular-beam epitaxy instrument. In the interim, the gallium-loaded effusion cell remained in the system, as it would be cooled and remain in the solid state. This turned out to be an unfortunate decision.

In the summer of FY16 a power outage at the Labs caused the process chilled water for the molecular-beam epitaxy instrument to shut down. The heat exchanger had a built-in relay that prevented it from automatically turning back on. At the time of the power outage, the magnesium and calcium effusion cells were idling at 50°C, which resulted in a heating of the stagnant chilled water in the molecular-beam epitaxy instrument. Ultimately, this heating of the chilled water heated the chilled water jacket on the gallium effusion cell and caused the gallium metal in the graphite crucible to melt. Upon restoration of the chilled water power and cooling the water, it is believed that the gallium metal froze and underwent a volume contraction causing the graphite crucible to fracture and leak molten gallium into the effusion cell. This damage was identified upon removing the gallium effusion cell from the chamber to replace the 8° divergence angle orifice with the 2° divergence angle orifice. The damaged effusion cell and broken graphite crucible are shown in Figure 1 below. Ultimately, this damage to the gallium effusion cell prevented an opportunity to demonstrate oxide molecular-beam epitaxial growth of beta gallium oxide. Owing the late time in the fiscal year that the damage occurred, coupled with the limited budget resulted in an inability to repair the damage prior to the end of the fiscal year.



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Figure 1: (left) Graphite Titan effusion cell crucible after the freezing of gallium within it causing a rupture and (right) effusion cell with gallium metal and portions of the effusion cell in the bottom of the furnace.

The team did succeed, however, in generating a capability to grow gallium oxide films. We were able to demonstrate that the surface of the acquired gallium oxide single crystals was appropriate for epitaxial growth, as evidenced by the RHEED pattern shown in Figure 2. Clear diffraction streaks and points are observed, consistent with a smooth and well-ordered surface lattice. Should the effusion cell be repaired, demonstration of growth would be relatively straight-forward now that all necessary components exist: high activity oxygen, gallium source, and low divergence angle crucible orifice.

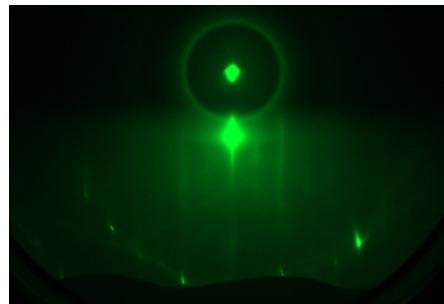


Figure 2: Reflection high-energy electron diffraction pattern of the surface of a beta gallium oxide single crystal. The streaks and spots along a ring are indicative of a smooth and well-ordered surface that is appropriate for epitaxial growth.

ANTICIPATED IMPACT: This project was originally proposed as a three-year project to study the growth of beta gallium oxide and gain a true fundamental understanding of the means in which dopants are incorporated and activated – and how the processing and resulting structure affect electronic and thermal transport within the material. Given budget limitations and perceived risk in growing beta gallium oxide, the project was reduced to \$100k for one year as a scoping study to minimize risk. It should be noted that in the original proposal, a one-year timeline to install a gallium oxide growth capability was anticipated and preliminary doping studies were to be performed on ceramic materials. Given the progress made toward installing the gallium oxide capability within this project, the project was re-proposed as a three study and



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expanded to include computational materials science to aid in understanding optical spectra necessary to characterize dopant energy levels. At the time of the proposing, however, Sandia had made significant investments in a competing materials system, aluminum gallium nitride. It was communicated to the team that the investment area had made significant investments in the nitride systems and that these precluded their ability to invest in other material systems, such as beta gallium oxide, and the project was not funded. Further internal investments and mission impacts will therefore have to come from more applied sources of funding. There is potential for this work to impact the new Power Bus Grand Challenge Laboratory Directed Research and Development project, where radiation hard power semiconductors and devices are sought. Much remains unknown about beta gallium oxide's radiation hardness, so there is opportunity there to learn new fundamental information, while making impacts in device research. This material system is currently not being considered for those purposes, but conversations will be had to explore the opportunity. Given this, further investment in this subject area and material system will likely require external proposal writing and funding.

This notwithstanding, the capability to growth beta gallium oxide now exists within Sandia and is one of three known active capabilities to do so within the United States, and the only epitaxial capability with in the DOE national laboratory complex. Sandia now has the capability to explore this promising power semiconductor material for future mission applications. The material does have potential advantages over other materials that are used or considered for use and performing growths and study of beta gallium oxide is something that could be established within a few months, if so desired.

There are a few paths that are being considered to build on the investments made in this project. The DOE Office of Electricity has standing interest in reliable power electronics for energy control and beta gallium oxide could be of great interest here. Power electronics are needed for energy conversion both into and out of energy storage systems. Increasing reliability and efficiency of the power switches is a significant challenge and an important parameter for broad scale deployment of grid-based energy storage. Additionally, beta gallium oxide could be of use in converting energy directly from renewable sources, such as photovoltaics and wind power. There are certainly opportunities in the Energy and Climate mission area for gallium oxide to have far reaching and deep impact. Further, both AFRL and ONR have put together broad agency announcements to develop programs in single crystal beta gallium oxide growth. It is anticipated that future proposal calls to study thin film systems will be forthcoming. This would build upon the Navy's significant investments in wide band gap semiconductors for their electric ship applications. Gallium oxide has advantages over the materials that are currently being studied, SiC and GaN, and this could present an opportunity for external investment in Sandia's capability.

The development of the beta gallium oxide growth capability required the installation of a high oxygen activity source into the Sandia oxide reactive molecular-beam epitaxy system. This new source of active oxygen enables the ability to growth other oxide materials that are otherwise difficult to grow in such a controlled environment as afforded by molecular-beam epitaxy. For example, the capability now exists to grow bismuth, lead, copper, and nickel oxide-containing oxides. Further, this can now be done with the atomic precision of molecular-beam epitaxy and would allow high structural- and chemically abrupt-interface material systems to be explored.



CONCLUSION: In conclusion, this project supported the development of a capability to prepare high-quality epitaxial beta gallium oxide thin films by oxide molecular-beam epitaxy. To achieve this goal, Sandia's existing oxide molecular-beam epitaxy instrument was upgraded to include a gallium effusion cell and ozone to effectively oxidize a gallium flux. An equipment failure occurred, which prevented a demonstration of film growth, but this equipment could be easily repaired and the capability remains within Sandia should further investment in this technology be of interest.

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