Material Properties of Beta-Gallium Oxide

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## Work Plan

### Year 1

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### Year 3

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<td>OSU Task 7</td>
<td>Evaluation of Traps in $\beta$-$(\text{Al},\text{Ga})_2\text{O}_3$ and Heterostructures</td>
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1. ‘New’ electronic material – $\beta$-Ga$_2$O$_3$

2. Growth studies
   Homoepitaxy
   Heterostructures

3. Process and transport

4. Defect spectroscopy

5. Conclusion and ongoing work
## Wide Bandgap Semiconducting Oxides

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<td>dominant donor, $p$-doping, surface accumulation</td>
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<td>In$_2$O$_3$</td>
<td>Bixbyite</td>
<td>2.70</td>
<td>conductivity</td>
<td>YSZ, CeO$_2$</td>
<td>dominant donor, mobility, surface accumulation</td>
<td>MBE</td>
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<td>SnO$_2$</td>
<td>Rutile</td>
<td>3.65</td>
<td>conductivity</td>
<td>TiO$_2$</td>
<td>dominant donor, $p$-doping, surface accumulation</td>
<td>MBE</td>
<td>TCO, sensors, light emitters</td>
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<tr>
<td>Ga$_2$O$_3$</td>
<td>Monoclinic Rhombohedr.</td>
<td>4.90</td>
<td>conductivity</td>
<td>Sapphire</td>
<td>bulk crystals; dominant donor; UV transparent</td>
<td>MBE</td>
<td>Power</td>
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<tr>
<td>TiO$_2$</td>
<td>Rutile, Anatase</td>
<td>3.10</td>
<td>high-$K$, conductivity</td>
<td>Sapphire, TiO$_2$</td>
<td>dielectric; $n$-type conductivity</td>
<td>Hybrid MBE</td>
<td>CMOS; tunable capacitors; photocatalysis</td>
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<tr>
<td>SrTiO$_3$</td>
<td>Perovskite</td>
<td>3.25</td>
<td>high-$K$, piezoelectric</td>
<td>SrTiO$_3$</td>
<td>dielectric; $n$-type conductivity, piezoelectric</td>
<td>Hybrid MBE</td>
<td>CMOS; tunable capacitors</td>
</tr>
</tbody>
</table>
**Crystal structure**

β-gallia structure

\[ a = 12.2 \text{ Å} \]
\[ b = 3.0 \text{ Å} \]
\[ c = 5.8 \text{ Å} \]
\[ \alpha = 90.0^\circ \]
\[ \beta = 103.7^\circ \]
\[ \gamma = 90.0^\circ \]

- Pulling speed: 10 mm/h
- Size: 70 mm x 50 mm x 3 mm

**Ga\textsubscript{2}O\textsubscript{3} bulk** (Edge-defined film-fed growth (EFG) method)


**Physical Properties**

Direct, dipole *disallowed* bandgap
4.9 eV gap
Naturally n-type

Cleavage on (100) and (001)
Poor growth on cleavage planes
Excellent growth on noncleavage planes

n-type doping
Sn, Si, Ge (Sb in development)

Deep acceptor doping
Mg

Alloys and heterostructures possible
Group III site
$\beta-(\text{Al,In,Ga})_2\text{O}_3$

ARPES studies on $\beta-\text{Ga}_2\text{O}_3$

~4.9 eV gap
Valence bands

Mohamed et al., APL 97, 211903 (2010)
Growth Studies
Dedicated Oxide MBE at UCSB

Plasma-assisted MBE Growth
- Activated oxygen from O$_2$ plasma (1-2% atomic O)
- Sn, Ga, In, Sb, Mg effusion cells
- Base pressure \(\sim 10^{-10}\) Torr
- Oxygen plasma cleaning prior to growth

Used extensively for SnO$_2$ and In$_2$O$_3$

Materials Characterization
Extensive suite of characterization tools
  - AFM, HRXRD, SIMS, XPS, TEM, atom probe
  - T-dependence Hall, I-V, CV, …
**Experimental Details**

**Substrate**
- β-Ga$_2$O$_3$ (010) (Tamura Corp.)
- 5 x 5 mm$^2$
- XRD (020) $\omega$-rocking scan: 83 arcsec
- 2.2 deg miscut
- Sn-doped (conductive) and Fe-doped (insulating)

**Growth** 620 (RF Plasma MBE)

Oxygen plasma:
- O BEP: $\sim$1 x 10$^{-5}$ Torr
- Plasma power: 200 W
- Active O BEP: $\sim$1 x 10$^{-7}$ Torr

Sample cleaning:
- Acetone and Isopropanol
- *In situ* O plasma cleaning (30 min, 850° C)
Growth Parameter Refinement: Ga Flux

Homoepitaxial Growth

~100 nm UID β-Ga$_2$O$_3$  $T_{\text{sub}}$: 700 °C

$\Phi_{\text{Ga}} - \Phi_{\text{O}^*} = -0.2$ nm/min  $\Phi_{\text{Ga}} - \Phi_{\text{O}^*} = +0.2$ nm/min

O-rich growth results in favorable surface morphology
Excess Ga: rms roughness ↑, step-bunching ↑, clusters at step edges
(Clusters not removed by HCl – not Ga droplets)
Growth Parameter Refinement: 
Substrate Temp and Growth Rate

Homoepitaxial Growth

\[ \sim 100 \text{ nm UID } \beta-\text{Ga}_2\text{O}_3 \quad \Phi_{\text{Ga}} - \Phi_{\text{O}*} = -0.2 \text{ nm/min} \]

Increasing Substrate Temperature 
Enhanced Step-bunching / Surface Roughness

<table>
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<tr>
<th>Temperature</th>
<th>RMS Roughness</th>
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<tr>
<td>600 °C</td>
<td>0.431 nm</td>
</tr>
<tr>
<td>650 °C</td>
<td>0.529 nm</td>
</tr>
<tr>
<td>700 °C</td>
<td>1.468 nm</td>
</tr>
</tbody>
</table>

Optimal Temp Range: 600 – 675 °C

Peak of 3.2 nm/min (~200 nm/hr) at 60 Torr O₂ foreline
45% improvement over previous PAMBE growth
\( \beta-(\text{Al}_x\text{Ga}_{1-x})_2\text{O}_3 \) Alloys: Solubility

Solubility of \( \text{Al}_2\text{O}_3 \) in \( \beta-\text{Ga}_2\text{O}_3 \) drastically reduced below 800 °C by formation of \( \text{AlGaO}_3 \) intermediate compound.

In the typical \( \beta-\text{Ga}_2\text{O}_3 \) homoepitaxy temperature range solubility 20-30\% \( \text{Al}_2\text{O}_3 \)

V. G. Hill et al, J Am Cer Soc 35, 135 (1952)
\[ \beta-(\text{Al}_{x}\text{Ga}_{1-x})_2\text{O}_3 \] (010) Grown by PAMBE at 600 °C

O-rich growth - ~60 nm layers - ~3 nm/min

Phase stability limit of ~15% Al\textsubscript{2}O\textsubscript{3} at 600 °C (Composition confirmed by EDS)
$\beta-(Al_xGa_{1-x})_2O_3$ (010)

O-rich growth - ~60 nm layers - ~3 nm/min

Distinct layer peak with $x = \sim 0.18$ at 650 °C
Increased phase stability limit at 650 °C since layer peak with $x = \sim 0.18$ at 600 °C was indistinguishable
Peak roughness at phase stability limit

Increasing phase stability limit with increasing temp
Phase stability limit of ~18% Al$_2$O$_3$ at 650 °C
Phase stability limit of ~20% Al$_2$O$_3$ at 700 °C
Process and Transport Studies
ICP- Superior etching technique

BCl$_3$ – 20 SCCM
~15 mT chamber pressure

200 nm etch depth (all BCl$_3$)

ICP yields much higher etch rates and smoother surfaces than RIE

Circular TLM measurements on etched Sn-doped $\beta$-Ga$_2$O$_3$ substrates in progress to correlate roughness to contact resistance
Preliminary Sn-doping Study

O-rich growth - ~200 nm layers - ~3 nm/min

Sn-doping inhibits step-bunching SnO_2 surface segregation for h >250 nm

Electron concentrations spanning 10^{16}-10^{20} cm^{-3}

Mobility of ~120 cm²/Vs (current record) ~1.5x GaN BFOM, similar HFOM
Contact and Defect Spectroscopy Studies
Initial Ni/β-Ga$_2$O$_3$ (010) Schottky Diode Screening

Very high quality devices

Diode size: 300 x 300 µm$^2$

UID β-Ga$_2$O$_3$ (010)

8 nm Ni / Ti/Au

200 nm

Current Density (A/cm$^2$)

Voltage (V)

Capacitance (pF)

Frequency (Hz)

300 K

Ideal C-V

No observable capacitance dispersion

Leakage below detection limit

n ~ 1.04
Although unintentionally doped, n-type conductivity via C-V and Hall
- Hall measured electron density of $1.1 \times 10^{17} \text{ cm}^{-3}$, with a mobility of $20 \text{ cm}^2/\text{V-s}$
- C-V revealed n-type doping density of $1.5 \times 10^{17} \text{ cm}^{-3}$ (assuming $\varepsilon_{\text{Ga}_2\text{O}_3}=10^*$)
Ni/β-Ga$_2$O$_3$ (010) Schottky barrier height

SBH determined by **internal photoemission (IPE)** and confirmed by C-V

→ Ni/Ga$_2$O$_3$ SBH is 1.55 eV at 300 K with small T dependence

- Theoretical prediction of ideal SBH:

  \[
  \Phi_B = \Phi_m - \chi
  \]

  - Work function for Ni ~ 5.1 eV
  - Electron affinity for Ga$_2$O$_3$ ~ 3.5 eV\[^1\]
  
  Calculated ideal SBH ~ 1.55 eV

Evidence that Ni/(010)Ga$_2$O$_3$ SBH may be unpinned!
- Plan to test different metals and orientations
- Note Ni/(100) Ga$_2$O$_3$ SBH = 1.1 eV\[^2\]

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DLTS results to explore traps within ~ 1 eV of $E_C$

### DLTS spectrum

- **RW 10 s^{-1}**
- $V_R = -0.5$ V
- $V_F = 0$ V
- $E_C - 0.62$ eV
- $E_C - 0.82$ eV
- $E_C - 1.00$ eV

### Arrhenius plot

- **Red = (010) Ga$_2$O$_3$ (this work)**
- **Black = (100) Ga$_2$O$_3$**

<table>
<thead>
<tr>
<th>$E_C$ (eV)</th>
<th>$N_T$ (cm$^{-3}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$E_C - 0.62$ eV</td>
<td>$3.4 \times 10^{14}$ (low $10^{14} \sim$ mid $10^{15}$)</td>
</tr>
<tr>
<td>$E_C - 0.82$ eV</td>
<td>$2.4 \times 10^{16}$ (mid $10^{16}$)</td>
</tr>
<tr>
<td>$E_C - 1.00$ eV</td>
<td>$2.8 \times 10^{15}$ (low $10^{14} \sim$ mid $10^{15}$)</td>
</tr>
</tbody>
</table>


- Same DLTS traps appear in both crystal orientations for different sources
- Trap concentration for $E_C - 0.82$ eV trap is similar; possible growth sensitivity for $E_C - 0.62$ eV and $E_C - 1.00$ eV
DLOS exploring traps in 4.8 eV bandgap: energy level determination

Optical Cross Section Spectrum from Photocapacitance transient analysis provides energy levels

\[
\sigma_n^0 \propto \frac{1}{\Phi(h\nu)} \frac{dC}{dt}_{t=0} \quad E_G = 4.8 \text{ eV}
\]

\[
E_C - 4.42 \text{ eV}
\]

\[
E_C - 2.4 \text{ eV}
\]

Fitting with Lucovsky model \cite{1}

\[
\sigma_n^0(h\nu) \propto \frac{E_i^{1/2}(h\nu - E_i)^{3/2}}{(h\nu)^3}
\]

Steady State Photocapacitance provides concentrations

\[
\begin{array}{c}
\text{RT} \\
V_R = -0.5 \text{ V} \\
V_F = 0 \text{ V}
\end{array}
\]

\[
E_G \sim 4.8 \text{ eV}
\]

\[
E_C - 4.42 \text{ eV}
\]

\[
E_C - 2.4 \text{ eV}
\]

<table>
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<tr>
<th>Energy level</th>
<th>(N_T \ (\text{cm}^{-3}))</th>
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<tbody>
<tr>
<td>(E_C - 2.4 \text{ eV}) *</td>
<td>(1.5 \times 10^{15})</td>
</tr>
<tr>
<td>(E_C - 4.42 \text{ eV})</td>
<td>(1.0 \times 10^{16})</td>
</tr>
</tbody>
</table>

* broadness indicates significant lattice relaxation, under study now \cite{2}

\cite{1} G. Lucovsky, Solid State Commun. 3, p299 (1965).

\cite{2} A. Armstrong et al, J. Appl. Phys. 98, 053704 (2005).
Summary

Research highlights:
• Optimized (010) β-Ga$_2$O$_3$ homoepitaxial growth
• Developed β-(Al$_x$Ga$_{1-x}$)$_2$O$_3$/Ga$_2$O$_3$ heterostructures
  • Establish Al solubility limit
• Developed RIE and ICP etch technology of (010) β-Ga$_2$O$_3$
• High electron mobility in β-Ga$_2$O$_3$
• High quality Ni/Ga$_2$O$_3$ Schottky diodes
• SBH appears to be unpinned at 1.5~1.6 eV over wide range of temperatures
• DLTS and DLOS trap studies

Next steps:
• characterize MBE grown epilayers as function of doping (Si, Sn, etc), growth conditions
• Explore AlGaO/GaO heterostructures
• Measure SBH with different metal/orientation
• Variable temperature Hall, C-T to determine activation energy for background donor

\[
\begin{align*}
E_C - 0.62 \text{ eV} \\
E_C - 1.00 \text{ eV} & \quad E_C - 0.82 \text{ eV} \\
E_C - 2.4 \text{ eV} \\
E_C - 4.42 \text{ eV} \\
E_V & \quad N_T \sim 1 \times 10^{16} \text{ cm}^{-3}
\end{align*}
\]
Background Slides
Deep level transient/optical spectroscopy (DLTS/DLOS)

- Probe entire $E_G$ to $\sim 5.5\ eV$
- $<0.02\ eV$ energy resolution
- Sensitive to $N_T > 10^{-5}N_D$

Energies:
- DLTS: $E_C$ to $E_C - 1\ eV$
- DLOS: $E_C - 1\ eV$ to $E_V$

Semi-transparent Schottky
- n-GaN, uid(n)-InGaN, or n-AlGaN
- n+GaN:Si epi
- GaN template

Advanced Defect Characterization
OSU

Nano-DLTS/DLOS/SPM
DLTS and DLOS

**• Trap modulation:**

**Quiescent Condition**

\[ V < 0 \]

**Electrical pulse to fill traps**

\[ V = 0 \]

**Trap emission (Thermal/Optical)**

\[ V < 0 \]

- Capacitance transient

**DLTS: thermal emission**

Arrhenius plot & DLTS spectra

Full coverage of \( E_G \)

**DLOS: optical emission**

Steady State Photocapacitance

\[ N_{T1} \]

\[ N_{T2} \]

\[ E_G \]

\[ E_T, N_T \]

\[ E_T, N_T \]

\[ \text{slope, peak height} \]

\[ \text{onset, step height} \]
Growth Rate of $\beta$-$\text{Ga}_2\text{O}_3$ by MBE

**Goal:** Growth diagram of $\beta$-$\text{Ga}_2\text{O}_3$ (010)

Growth T: 800°C
O$_2$: 1 sccm
Ga: 2x10$^{-7}$ Torr

(100) & (001): Cleavage plane
Small growth rate


$\text{Ga}_2\text{O}_3 + 4\text{Ga} \rightarrow 3\text{Ga}_2\text{O}↑$
Narrow growth window


$\beta$-$\text{Ga}_2\text{O}_3$ (100)
O plasma: 200 W
DLTS can’t “see” mid-gap states!

Wide bandgap reveals limitations for trap detection approaches based on thermal carrier emission (e.g. DLTS)

$$e_n = \sigma_n < v_n > N_C \exp\left(\frac{E_t - E_C}{k_B T}\right)$$

Exponentially worsens with increasing Eg – even worse for AlGaN!

300K time constant

- $E_C$  
  - $E_{T1} = E_C - 0.6$ eV  
  - $\rightarrow \sim 30$ ms

- $E_{T2} = E_C - 1.3$ eV  
  - $\rightarrow \sim 63$ yrs
Defining Energy States in III-Nitrides

0K band-gap variation of InGaN and AlGaN alloys

\[ E_g(\text{In}_x\text{Ga}_{1-x}\text{N}) = 3.42(1-x)+0.77x-1.43x(1-x) \]
\[ E_{\text{vac}}-E_v = 6.92-0.35x \]
\[ E_g(\text{Al}_x\text{Ga}_{1-x}\text{N}) = 3.42+2.86x-x(1-x) \]
\[ E_{\text{vac}}-E_v = 6.92+1.26-0.5x(1-x) \]

References:
Fang et al., APL 82, 1562 (2003).
Hierro et al., APL 80, 805 (2002).
Hierro et al., PSSB 228, 309 (2001).
Armstrong et al., APL 84, 374 (2004).
Hierro et al., APL 76, 3064 (2000).
Hierro et al., APL 77, 1499 (2000).
Armstrong et al., APL 84, 374 (2004).
K. B. Nam et al., APL 86, 222108 (2005).

InGaN bandgaps:
J.Wu et al. APL80, 4741 (2004).
S. X. Li et al., PRB 71, 161201 (2005).

AlGaN bandgaps:
Yun et al., JAP 92, 4837 (2002).
C. I. Wu, JAP4249 (1998)
Additional Slides
$\beta-(Al_{0.15}Ga_{0.85})_2O_3/Ga_2O_3$ (010) Superlattice at 650 °C

Cross-sectional TEM taken in [201] zone axis projection
Roughly normal to bunched steps

Homogeneous alloy distribution and abrupt interfaces
β-(Al$_{0.15}$Ga$_{0.85}$)$_2$O$_3$ (010) Temperature Optimization

O-rich growth - ~60 nm layers - ~3 nm/min

Increasing Temperature $\rightarrow$ Enhanced Step-bunching

Inclusion of Al$_2$O$_3$ Suppresses Step-bunching

Smoothest β-(Al$_{0.15}$Ga$_{0.85}$)$_2$O$_3$ (010) grown at 650 °C
RIE of $\beta$-$\text{Ga}_2\text{O}_3$ (010), (-201), (100)

Average of ≥ 3 timed etches

$\text{BCl}_3/\text{Cl}_2$ – 10/10 SCCM
10 mT chamber pressure

$\text{BCl}_3$ does not etch SPR 220 or NLOF 2020 PR (Cl$_2$ etches PR >100 nm/min)
Active components and products of etch unknown – presumably GaCl$_3$

Reduced etch rate on (100)
Suitable etch rates ≥ 200 W

Pure $\text{BCl}_3$ etch most effective
Reduced discrepancy in etch rates between planes with pure $\text{BCl}_3$

200 W RF
10 mT chamber pressure