Valence band offsets for CuI on (-201) bulk Ga$_2$O$_3$ and epitaxial (010) (Al$_{0.14}$Ga$_{0.86}$)$_2$O$_3$

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β-Ga2O3 is an attractive material for power electronic applications due to its wide bandgap, controlled n-type doping, and high quality, inexpensive substrate technology.1–7 A wide variety of lateral and vertical transistors and rectifiers have been reported,1,3–7 and (Al0.14Ga0.86)2O3/Ga2O3 heterostructures have also been demonstrated using modulation doping of the barrier layer.8–14 There is strong interest in these heterostructures involving β-(AlxGa1-x)2O3 monoclinic phase alloys, in which the bandgap can be varied from 4.8 to 6 eV.14,15 In terms of doping of these materials, controlled n-type doping with Sn, Si, and Ge has been demonstrated, but because of the relatively flat valence band, it is likely impossible to achieve conventional p-type doping of Ga2O3.16 While p-type conduction has been reported from Ga vacancies at high temperature,17 the predicted large ionization energies for acceptor dopants, the self-trapping of holes into polarons, and the presence of common n-type impurities and native n-type defects all work against achieving p-type conduction. This asymmetry in n-type versus p-type doping is common for many wide bandgap semiconductors.18–20 The absence of a p-type doping capability limits the type of device that can be fabricated, not only the ability to have p-n junctions but also in structures such as edge termination on power devices.

One option is to employ heterojunctions of Ga2O3 with p-type semiconductors such as SiC, NiO, Cu2O, CuI, or diamond.18–27 As an example, Watahiki et al.26 employed sputtered p-Cu2O and demonstrated 1.49 kV pn diodes with a specific on-resistance of 8.2 mΩ cm². Other groups have also reported heterojunctions of Ga2O3 with p-Cu2O.24,27 There is particular interest in p-type Cu,18–25 which is a wide-gap semiconductor with a zincblende-type structure at ambient conditions, used as a transparent electrode for improving hole collection in organic solar cells and also for forming a heterojunction with n-type oxides. Koehler et al.25 reported the p-CuI/n-Ga2O3 rectifying heterojunction with an on/off ratio of >10⁶ measured at room temperature, with ideality factor n = 1.18 as the junction turned on at higher bias. The current-voltage-temperature measurements degraded the junction, indicative of CuI oxidation and need for passivation.25 More work is needed to understand the characteristics of this system. In this letter, we report the band alignment for CuI on both Ga2O3 and (Al0.14Ga0.86)2O3 and find low barriers to hole transport.

The CuI films were grown in a two-step process.18–25 First, Cu was deposited by RF magnetron sputtering on Ga2O3 and (Al0.14Ga0.86)2O3 at room temperature using a 3-in. diameter target of pure (6N) copper. The RF power was 90 W, and the working pressure was 5 mTorr in pure Ar ambient (50 sccm flow rate). The dc bias on the electrode under these conditions is ~30–40 V. The samples were cleaned prior to deposition using rinses of acetone and isopropanol alcohol (IPA), N2 drying, and finally O2 exposure for 15 min. The commercial bulk β-phase Ga2O3 single crystals with the (-201) surface orientation (Tamura Corporation, Japan) were grown by the edge-defined-film-fed growth method. Hall data showed an n-type carrier concentration of ~3 × 10¹⁷ cm⁻³. The (Al0.14Ga0.86)2O3 was grown by Molecular Beam Epitaxy onto bulk (010) β-Ga2O3 substrates that were Sn-doped (6.3 × 10¹⁸ cm⁻³). These Aluminum Gallium Oxide (AGO) layers were doped with Si to produce an n-type carrier density of 10¹⁷ cm⁻³ determined by electrochemical capacitance-voltage measurements and were 55 nm thick. After the Cu deposition, the samples were placed in a Petri dish cover and mounted with a Teflon holder. 99.999% iodine particles were placed into the Petri dish and heated to 120 °C for 5 min using a hotplate. This forms a textured (111) film with a lattice parameter of 6.0546 Å.
Koehler et al.\textsuperscript{25} reported a carrier concentration of \(2 \times 10^{18} \text{cm}^{-3}\) and a mobility of \(\sim 7 \text{cm}^2/\text{V s}\) under these conditions. Two types of CuI films were formed—thin layers (1.5 nm) on the oxide samples and thick layers (150 nm) as references.

After iodination of Cu, the samples were directly placed into the XPS system to minimize oxidation of CuI. XPS survey scans were used to obtain the chemical state of CuI, Ga\(_2\)O\(_3\), and \((\text{Al}_{0.14}\text{Ga}_{0.86})\text{O}_3\) and identify peaks for high resolution analysis.\textsuperscript{28–33} An ULVAC PHI XPS with a monochromatic, Al X-ray source (energy 1486.6 eV) at a source power of 300 W was used. The analysis area was 10 \(\mu\text{m}\) in diameter, while a take-off angle of \(50^\circ\) and an acceptance angle of \(\pm 7^\circ\) were utilized. The electron pass energy was 23.5 eV for the high-resolution scans and 93.5 eV for the survey scans. The approximate escape depth (3 \(\lambda\) \(\sin\theta\)) of the electrons was 80 Å. In this system, all of the peaks are well-defined.

Charge compensation was performed using a dual beam charge neutralization system (low-energy electron beam and ion beam) to prevent charge buildup during data collection. The charge neutralization system is often not sufficient at eliminating all surface charge, and additional corrections must be performed. Using the known position of the adventitious carbon (C-C) line in the C 1s spectra at 284.8 eV, charge correction was performed. The samples and electron analyzers were electrically grounded to provide a common reference Fermi level. Differential charging was minimized with the use of an electron gun, verified using calibrations with and without the gun.\textsuperscript{31} Since CuI is conducting and the oxide samples are doped, we would not expect significant differential charging and no time-dependence of peak position was observed. We also checked by measuring the full-width at half maximum of the core level peaks that over-compensation during charge neutralization was not present.\textsuperscript{34}

Reflection electron energy loss spectroscopy (REELS)\textsuperscript{35} was employed to measure the bandgap of Ga\(_2\)O\(_3\). By taking a linear fit to the leading plasmon peak and finding its zero energy with the background, a direct measurement of valence to conduction band energy was made. REELS spectra were obtained using a 1 kV electron beam and the hemispherical electron analyzer. The bandgap of \((\text{Al}_{0.14}\text{Ga}_{0.86})\text{O}_3\) was determined from XPS O1s based electron energy loss measurements. The bandgap of CuI was assumed to be 3.1 ± 0.1 eV based on the many previously published reports.\textsuperscript{18–25} A slight deviation in the actual CuI bandgap could marginally affect conduction band offset values.

XPS confirmed the presence of CuI, with Cu in the +1 oxidation state (Cu 2p) and iodine in the −1 oxidation state (I 3d) based on the binding energies. The Cu 2p and iodine 4d showed that CuI was stoichiometric throughout the top 20 nm of the film, indicating that during synthesis, the iodine vapor reacts with more than just the Cu surface and creates a uniform CuI film.

Figure 1 shows the stacked XPS survey scans of thick (150 nm) CuI, 1.5 nm CuI on \((\text{Al}_{0.14}\text{Ga}_{0.86})\text{O}_3\), and \((\text{Al}_{0.14}\text{Ga}_{0.86})\text{O}_3\) reference samples. Only the expected elements are present, indicating no gross contamination or oxidation of CuI.

The valence band maximum (VBM) was determined by linearly fitting the leading edge of the valence band and the flat energy distribution from the XPS measurements\textsuperscript{31,33} and finding the intersection of these two lines, as shown in Fig. 2 for the thick CuI and the reference \((\text{Al}_{0.14}\text{Ga}_{0.86})\text{O}_3\) and Ga\(_2\)O\(_3\).
The VBMs were measured to be 0.95 ± 0.15 eV for CuI, 3.0 ± 0.2 eV for β-(Al0.14Ga0.86)2O3, and 3.20 eV ± 0.3 eV for Ga2O3.

The measured bandgap of β-Ga2O3 from the REELS data was 4.6 ± 0.2 eV.31 This was similar to the value obtained from XPS measurements of the type used for the alloy bandgap determination. For (Al0.14Ga0.86)2O3, the bandgap was determined to be 5.0 ± 0.3 eV, from XPS O1s based electron energy loss measurements. This is consistent with previous work on powdered samples of (AlxGa1-x)2O3 over the composition range x = 0–0.4.15 If we use the theoretical relationship derived by Peelaers et al.,14 we would expect a bandgap of 5.14 eV at our composition of x = 0.14, close to the measured result. The differences in bandgaps between CuI and β-(Al0.14Ga0.86)2O3 and β-Ga2O3 are therefore 1.9 and 1.5 eV, respectively.

To determine the band alignment and valence band offsets, we used the standard core level spectra approach32, which measures a core level and the valence band edge for each material and the shift of the core levels when the two materials have formed a heterojunction. The valence band offset is obtained from32

\[ \Delta E_V = (E_{\text{core}} - E_{\text{VBM}}^1) - (E_{\text{core}}^2 - E_{\text{VBM}}^2) - (E_{\text{core}}^1 - E_{\text{core}}^2). \]

It is important to use a well-defined core level since the offsets are small compared to the core level energy and more deviation is expected at higher core level energies.

High resolution XPS spectra of the VBM-core delta region are shown in Fig. 3 for the β-Ga2O3, β-(Al0.14Ga0.86)2O3 and thick CuI samples. These were used to determine the selected core level peak positions. Figure 4 shows the XPS spectra for the β-Ga2O3 and β-(Al0.14Ga0.86)2O3 to CuI core delta regions of the heterostructure samples. These values are summarized in Table I and were then used to calculate \( \Delta E_V \).

Figure 5 shows the measured band alignments of the CuI/β-Ga2O3 and CuI/β-(Al0.14Ga0.86)2O3 heterostructures. The latter is a nested, type I system, while the former is a staggered

**TABLE I. Summary of measured core levels in these experiments (eV).**

<table>
<thead>
<tr>
<th>Substrate</th>
<th>Core level VBM peak</th>
<th>Core level VBM</th>
<th>Core level VBM peak</th>
<th>Core level VBM</th>
<th>Core level VBM peak</th>
<th>Core level VBM</th>
<th>Core level VBM peak</th>
<th>Core level VBM</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ga2O3</td>
<td>Ga2p3/2 3.20</td>
<td>1111.10</td>
<td>1114.90</td>
<td>Cu 2p3 0.95</td>
<td>932.8</td>
<td>931.85</td>
<td>182.8</td>
<td>0.25</td>
</tr>
<tr>
<td>(AlGa)2O3</td>
<td>Ga2p3/2 3.00</td>
<td>1117.60</td>
<td>1114.60</td>
<td>Cu 2p3 0.95</td>
<td>932.8</td>
<td>931.85</td>
<td>182.8</td>
<td>−0.05</td>
</tr>
</tbody>
</table>
$\text{Ga}_2\text{O}_3$ $\text{CuI}$ $(\text{Al}_{0.14}\text{Ga}_{0.86})_2\text{O}_3$ $\text{CuI}$

![Band diagrams for CuI on Ga$_2$O$_3$ (left) and CuI on (Al$_{0.14}$Ga$_{0.86}$)$_2$O$_3$ (right).](image)

The band alignment for CuI on Ga$_2$O$_3$ and (Al$_{0.14}$Ga$_{0.86}$)$_2$O$_3$ is favorable for hole transport across the (Al$_{0.14}$Ga$_{0.86}$)$_2$O$_3$ heterostructure, the values are $0.05 \pm 0.02$ eV for the valence band offset and $1.85 \pm 0.35$ eV for the conduction band offset. These were obtained using the differences in bandgaps and the directly measured valence band offset, i.e., $\Delta E_C = E_{\text{CuI}} - E_{\text{Ga}_2\text{O}_3} = E_{\text{CuI}} - E_{\text{Ga}_2\text{O}_3}$. The shift from the pure binary to the $\beta$-(Al$_{0.14}$Ga$_{0.86}$)$_2$O$_3$ alloy with a relatively low Al content is enough to shift the alignment type, but note that the energy barriers to hole transport are small in both cases and auger well for the prospects of high quality p-n heterojunctions of CuI with both Ga$_2$O$_3$ and (Al$_{0.14}$Ga$_{0.86}$)$_2$O$_3$.

In conclusion, the band alignment for CuI on Ga$_2$O$_3$ and (Al$_{0.14}$Ga$_{0.86}$)$_2$O$_3$ is favorable for hole transport across the heterointerface and the low processing temperature is attractive for minimizing the formation of interface states. Electrical measurements are needed to demonstrate minority carrier injection at low biases in heterojunction samples.

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