Valence and conduction band offsets in AZO/Ga$_2$O$_3$ heterostructures

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**Abstract**

We report on the determination of band offsets in rf-sputtered Aluminum Zinc Oxide (AZO)/single crystal $\beta$-Ga$_2$O$_3$ (AZO/Ga$_2$O$_3$) heterostructures using X-Ray Photoelectron Spectroscopy. The bandgaps of the materials were determined by Reflection Electron Energy Loss Spectroscopy as 4.6 eV for Ga$_2$O$_3$ and 3.2 eV for AZO. The valence band offset was determined to be $-0.61 \pm 0.23$ eV, while the conduction band offset was determined to be $-0.79 \pm 0.34$ eV. The AZO/Ga$_2$O$_3$ system has a nested, or straddling, gap (type I) alignment and provides a convenient method for reducing contact resistance on Ga$_2$O$_3$-based device structures.

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1. Introduction

There is significant recent interest in the development of the $\beta$-polytype of Ga$_2$O$_3$ [1–12]. This has a wide bandgap of ~4.6 eV, can be grown in bulk form from melt sources and has a theoretical breakdown field of ~8 MV cm$^{-1}$, which is higher than either GaN or SiC [1–5]. Ga$_2$O$_3$ is promising for solar blind UV detectors [13], as well as extreme environment electronics (high temperature, high radiation, and high voltage (low power) switching) [1–12]. High quality bulk Ga$_2$O$_3$ crystals can be grown by edge-defined film-fed (EFG) growth using Ir crucibles, by Czochralski or by float zone with excellent quality and control of conductivity. Excellent results for Ga$_2$O$_3$-based power rectifiers, metal-semiconductor field effect transistors (MESFETs) and metal-oxide field effect transistors (MOSFETs) have been reported [1,3–7,9–12], along with various types of solar blind photodetectors [13]. One common limitation noted in these results is the need for improved Ohmic contacting processes [1,3,4]. High quality Ohmic contacts are a prerequisite for any device and should provide low contact resistance at moderate anneal temperatures. Additional contact resistance leads to slower device switching speeds as well as reliability issues due to local contact heating during current flow during device operation.

The usual approaches to lowering contact resistance involve surface etching or cleaning to reduce barrier height or increase of carrier concentration of the surface through preferential loss of oxygen [3,6,7,14–16]. To date, contact schemes involving deposition of Indium Tin Oxide (ITO) or dry etching in BCl$_3$/Ar to enhance the surface $n$-type conductivity, followed by Ti/Au annealed at 500 °C have been common [13,7,9]. Specific contact resistances of ~$4.6 \times 10^{-8}$ Ω cm$^{-2}$ were reported for Ti/Au contacts on n-Ga$_2$O$_3$ epitaxial layers in which Si was implanted and annealed at 925 °C, followed by dry etching, metal deposition and annealing at 470 °C [14,15]. Many published current-voltage (I-V) characteristics for contacts on Ga$_2$O$_3$ are only quasi-linear at low current and show the need for improved contact approaches. Cr has a low work function of 4.5 eV and is currently one of the best choices for Ohmic contacts on n-Ga$_2$O$_3$. For an n-type semiconductor, to achieve an Ohmic contact means that the work function of the metal must be close to or smaller than the electron affinity of the semiconductor (affinity of $\beta$-Ga$_2$O$_3$ is ~$-4.00 \pm 0.05$ eV) [16,17] and this limits the available options. Another approach is to deposit a transparent conducting oxide such as Aluminum Zinc Oxide (AZO).

AZO thin films have been widely studied for transparent and flexible device applications such as liquid crystal displays, plasma display panels, electronic paper displays, organic light emitting diode, solar cells, touch panels, gas sensors and other optoelectronics devices [18–24]. The most commonly used transparent
conducting oxide (TCO) material is ITO, because of its high conductivity and optical transparency over visible wavelengths. However, the relative scarcity and high cost of indium has focused attention on alternatives such as AZO [20]. To be used as a contact layer on Ga2O3, we need to establish the band alignment to ensure that there is no barrier to electron transport from the contact layer into the Ga2O3.

In this paper, we report on the determination of the band alignment in the AZO/Ga2O3 heterostructure. We employ X-Ray Photoelectron Spectroscopy (XPS) to determine the valence band offsets and by measuring the respective bandgaps of the AZO (3.2 eV) and Ga2O3 (4.6 eV), we were also able to determine the conduction band offset in AZO/Ga2O3 heterostructures.

2. Experimental

The AZO was deposited by RF magnetron sputtering on Ga2O3 and quartz substrates at room temperature using a 3-in. diameter target of pure AZO. The RF power was 125 W and the working pressure was 5 mTorr in a pure Ar ambient. The dc bias on the electrode under these conditions is in the range 30–40 V. The bulk β-phase Ga2O3 single crystals with (−201) surface orientation (Tamura Corporation, Japan) were grown by the edge-defined film-fed growth method. Hall effect measurements showed the sample was unintentionally n-type with an electron concentration of ~3 x 10^{17} cm^{-3}.

To obtain the valence band offsets, X-Ray Photoelectron Spectroscopy (XPS) survey scans were performed to determine the chemical state of the AZO and Ga2O3 and identify peaks for high resolution analysis [31]. Note that the Ga2O3 samples were cleaned using solvent rinses and loaded immediately were not exposed to air prior to the subsequent Reflection Electron Energy Loss Spectroscopy (REELS) measurements to avoid complications from surface contamination [26–28]. The latter may lead to less accurate band gap measurements when using REELS [29–33]. The samples for XPS were briefly exposed to ambient during transfer and loading into the XPS analysis chamber. A Physical Electronics PHI 5100 XPS with an aluminum x-ray source (energy 1486.6 eV) with source power 300 W was used, with an analysis area of 2 mm × 0.8 mm, a take-off angle of 50° and an acceptance angle of ±7°. The electron pass energy was 23.5 eV for the high resolution scans and 187.5 eV for the survey scans. The approximate escape depth (3 l sin θ) of the electrons was <80 Å [34]. All of the peaks are well-defined in this system and we didn’t need to curve fit the data.

Charge compensation was performed using an electron flood gun, due to the dielectric nature of the films. The charge compensation flood gun 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. An optimized peak fit to the carbon 1s spectrum on IGZO using only a simple peak model involving a single C-C peak at 284.8 eV can lead to errors of 0.5 eV or more. Therefore, additional peaks are generally added. In our work, we add one peak constrained to be 1.5 eV above the main peak and of equal FWHM. This higher binding energy peak is ascribed to alcohol (C-OH) and/or ester (C-O-C) functionality. A further high binding energy peak, attributed to O-C=O, is added with a position constraint of 3.7 eV above the main peak. All peaks are constrained to a peak area ratio of 2:1:1. During the measurements, all the samples and electron analyzers were electrically grounded so they were performing providing a common reference Fermi level. Differential charging is a serious concern for photoemission dielectric/semiconductor band offset measurements [32]. While the use of an electron flood gun does not guarantee that differential charging is not present and in some cases could make the problem worse, our experience with oxides on conducting substrates has been that the differential charging is minimized with the use of an electron gun. Calibrations with and without the gun.
and verified that was the case. This procedure has been described in
detail previously [29,30].

The valence band maximum (VBM) was determined by using a linear
extrapolation method, i.e. it is determined by linear fitting the
leading edge of the valence band and linearly fitting the flat energy
distribution and finding the intersection of these two lines. The
core-level peaks were referenced to the top of valence band for the
thick IGZO and the thick film of dielectrics. To determine the
valence band offset, the binding energy differences between the
valence band and the selected core peaks for the single thick layers
were combined with the core-level binding energy differences for
the heterojunction sample. Spectra from insulating samples can be
charge corrected by shifting all peaks to the adventitious C 1s
spectral component (C-C, C-H) binding energy set to 284.8 eV. The
C1s spectrum typically has C-C, C-O-C and O-C=O components
and optimization involves constraining these additional peaks. This
charge correction is used for chemical analysis, but not band offset
measurements. The method of Kraut et al.[31] using x-ray photo-
emission spectroscopy has been established as a reliable way to
determine band offsets at the hetero-junction interface. This
method has also been successfully used to provide insights into
interfacial properties between different materials [31]. It is based on
using an appropriate shallow core-level position as a reference.
Generally, this approach is based on the assumption that the energy
difference between the core-level positions and valence-band
maximum (VBM) are both fixed in the bulk.

Reflection electron energy loss spectroscopy (REELS) was
employed to measure the bandgaps of the AZO and Ga2O3. REELS is
a surface sensitive technique capable of analyzing electronic and
optical properties of ultrathin gate oxide materials because the
low-energy-loss region reflects the valence and conduction band
structures [33]. REELS spectra were obtained using a 1 kV electron
beam and the hemispherical electron analyzer.

3. Results and discussion

Fig. 1 shows the XPS survey scans of thick (200 nm) AZO, 1.5 nm
AZO on Ga2O3 and Ga2O3 bulk crystals. The spectra show the
films themselves free from contaminants (although there is adventiti-
ous carbon on the surface) and consistent with past published XPS
data on these materials [17].

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, and finding the inter-
section of these two lines, as shown Fig. 2 for the bulk Ga2O3 (a) and
thick AZO (b). The VBM was measured to be 3.2 ± 0.2 eV for Ga2O3,
which is consistent with previous reports [17] and 2.53 ± 0.2 eV for the AZO.

The bandgap of the Ga2O3 was determined to be 4.6 eV, as shown in the REELS spectra in Fig. 3 (a). The band gap was determined from the onset of the energy loss spectrum [33]. The measured band gap for the sputtered AZO was 3.2 ± 0.3 eV (Fig. 3(b)), which is consistent with literature values. The difference in bandgaps between AZO and Ga2O3 is therefore 1.4 eV and thus has the potential to provide a significant conduction band offset to enhance electron transport for improved Ohmic contacts. To determine the actual band alignment and the respective valence and conduction band offsets, we examined the core level spectra for the samples.

High resolution XPS spectra of the VBM-core delta region are shown in Fig. 4 for the Ga2O3 (a) and thick AZO (b) samples. These were used to determine the selected core level peak positions of the Ga2O3 and the AZO \((E_{\text{Core}}^{Ga_2O_3} - E_{\text{Core}}^{AZO})\). Fig. 5 shows the XPS spectra for the respective Ga2O3 to AZO-core delta regions \((E_{\text{Core}}^{Ga_2O_3} - E_{\text{Core}}^{AZO})\) of the heterostructure samples. These values are summarized in Table 1 for the three samples examined and these were then inserted into the following equation to calculate the valence band offset \(\Delta E_V\):

\[
\Delta E_V = (E_{\text{Core}}^{Ga_2O_3} - E_{\text{VBM}}^{Ga_2O_3}) - (E_{\text{Core}}^{AZO} - E_{\text{VBM}}^{AZO})
\]

Fig. 6 shows both a simplified and detailed band diagram of the AZO/Ga2O3 heterostructure. Our data shows this is a nested, type I alignment, with a valence band offset of 0.61 ± 0.23 eV and the conduction band offset \(\Delta E_C\) is then 0.79 ± 0.34 eV using the

![Fig. 5. High resolution XPS spectra for the Ga2O3 to AZO-core delta regions.](image)

![Fig. 6. Summary (a) and detailed (b) band diagrams for AZO/Ga2O3 heterostructure.](image)

<table>
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<th>Reference Ga2O3</th>
<th>Ga2O3 metal core VBM</th>
<th>Ga2O3 Metal Core level</th>
<th>Metal core - Ga2O3 VBM</th>
<th>Reference AZO</th>
<th>AZO VBM Zn 2p1/2 core level</th>
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</table>

Table 1
Values of band offsets determined in these experiments (eV).
following equation:
\[ \Delta E_C = E^{Ga_2O_3}_g - E^{AZO}_g - \Delta V \]

ie. \[ \Delta E_C = 4.6eV - 3.2eV - 0.61eV = 0.79eV. \] In these equations \( E^{Ga_2O_3}_g \) is the bandgap of the Ga2O3 and \( E^{AZO}_g \) is the bandgap of the AZO.

The fact that the AZO has a smaller bandgap and the correct alignment for electron transport from the contact into the Ga2O3 means that it is therefore a good choice as an enhancement layer for reducing Ohmic contact resistance on n-type Ga2O3. The lack of high quality Ohmic contacts is still a limiting issue on current Ga2O3 devices and thus any method that enhances electron transport across the contact/Ga2O3 heterointerface is valuable. This is a technique that is used in compound semiconductors, where smaller gap materials like InAs or InGaAs are used on GaAs to lower the Ohmic contact resistance. We should also point out the possibility of the band offsets when annealing such contacts, as it is usually found that post-deposition annealing further reduces contact resistance. Since AZO also has good thermodynamic stability of Ga2O3, in its undoped form it could also be a good choice as a surface passivation layer to prevent surface conductivity changes that are common in electronic oxides upon exposure to hydrogen-containing ambients [25,26].

4. Summary and conclusions

The AZO/Ga2O3 heterojunction has a nested gap alignment of band offsets with a valence band offset of \(-0.61\,eV \pm 0.06eV\) and a conduction band offset of \(-0.79\,eV \pm 0.80\,eV\) determined from XPS measurements. This is useful information for Ohmic contact schemes on n-type Ga2O3 devices.

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