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Annealing temperature dependence of band alignment of NiO/ β -Ga₂O₃



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Abstract

The band alignment of sputtered NiO on β -Ga₂O₃ was measured by x-ray photoelectron spectroscopy for post-deposition annealing temperatures up to 600 °C. The band alignment is type II, staggered gap in all cases, with the magnitude of the conduction and valence band offsets increasing monotonically with annealing temperature. For the as-deposited heterojunction, $\Delta E_V = -0.9$ eV and $\Delta E_C = 0.2$ eV, while after 600 °C annealing the corresponding values are $\Delta E_V = -3.0$ eV and $\Delta E_C = 2.12$ eV. The bandgap of the NiO was reduced from 3.90 eV as-deposited to 3.72 eV after 600 °C annealing, which accounts for most of the absolute change in $\Delta E_V - \Delta E_C$. Differences in thermal budget may be at least partially responsible for the large spread in band offsets reported in the literature for this heterojunction. Other reasons could include interfacial disorder and contamination. Differential charging, which could shift peaks by different amounts and could potentially be a large source of error, was not observed in our samples.

Keywords: Ga₂O₃, band offsets, heterojunctions, wide bandgap semiconductor

(Some figures may appear in colour only in the online journal)

1. Introduction

There is considerable interest in developing Ga₂O₃ power electronics because of the lower resistive losses and higher energy conversion efficiency relative to Si power device switching [1–10]. Critical breakdown fields in lateral β -Ga₂O₃ transistors larger than the theoretical limits of SiC and GaN have been achieved [5]. There is particular interest in vertical Ga₂O₃ devices because of their larger conducting areas [10–28] and recently breakdown voltages of ~6 kV have been reported for β -Ga₂O₃ vertical rectifiers with edge termination consisting of a deep trench of SiO₂ [29]. For these unipolar devices, a number of variants have emerged. Fin field effect transistors (FinFETs) require that the surface potential in the channel region be tunable to enable accumulation and depletion, whereas planar rectifiers require that the surface region be depleted to avoid surface-related breakdown [2, 4, 7, 9, 17, 21]. Additionally, the latter benefit from narrow trenches and wide mesas/fins in order to achieve high device current density, whereas FinFETs need narrow fins to obtain enhancement mode (normally-off) behavior. These create entirely different requirements on the dielectric-semiconductor interface and the geometry of the fins [2, 3].

To overcome the absence of conventional p-type dopants for β -Ga₂O₃ and access the advantages of p-n junction devices, including higher breakdown voltage and flexibility in designing junction termination extension and p-type guard rings, a variety of p-type oxides have been integrated with n-type Ga₂O₃. These include SnO₂, Cu₂O, CuI and NiO for vertical p-n heterojunction power diodes [10, 13–35]. These typically show smaller leakage current than conventional

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planar rectifiers and also have larger turn-on voltages [20– 25]. The minority carrier nature of these devices should allow lower on-resistances and better on-state performance. In particular the focus has been on use of sputtered NiO [10, 16, 19–26]. The highest reported breakdown voltages for these heterojunctions are a static V_B of 2.41 kV [30], with specific on-resistance of 1.12 m Ω cm², producing a Baliga's figure of merit (FOM) of 5.18 GW cm² [25]. Large area devices (1 × 1 mm²) exhibited a forward current of 5 A and breakdown voltage 700 V (FOM 64 MW cm⁻²) [10] and a 9 mm² heterojunction rectifier, a surge current of 45 A was recorded in a 10 ms surge transient [21].

A point of contention in the literature has been the large spread in values reported for band offsets of NiO on Ga₂O₃. Gong et al [23] reported a staggered type II alignment with a valence band offset of -3.74 eV and a conduction band offset of 2.54 eV, determined from a combination of Ni2p_{3/2}, Ga2p^{3/2} and O 1 s and valence band maxima (VBM). Ghosh et al [35] reported a staggered type II alignment, with $\Delta E_{\rm V} = -1.6 \text{ eV}$ and $\Delta E_{\rm C} = 0.3$ eV. By contrast, Lu *et al* [16] reported a type II alignment with $\Delta E_{\rm V} = -2.3$ eV and $\Delta E_{\rm C} = 1.2$ eV, while Zhang *et al* [27] reported $\Delta E_{\rm V} = -2.1$ eV and $\Delta E_{\rm C} = 0.9$ eV. While it not unusual to see significant differences in valence band offsets for nominally similar deposition conditions in the same heterostructure, the spread in values for NiO/Ga₂O₃ needs further evaluation. It has been established previously in other dielectric/semiconductor systems that the biggest contributor to variability in reported conduction band offsets is the uncertainty in band gap of the dielectrics due to differences in measurement protocols and stoichiometry resulting from different deposition methods, chemistry and contamination [36, 37]. In terms of variations in valence band offset values, factors such as strain, defects/vacancies, stoichiometry, chemical bonding and interfacial contamination may play a role [37]. One other possible factor is the role of thermal budget. The thermal stability of NiO/Ga2O3 heterointerfaces is also of interest from the viewpoint that the metallurgical and electrical junctions are separated, whereas they coincide in a Schottky rectifier and should make the p-n junction less sensitive to thermal degradation.

In this paper we report measurements of the band alignment as a function of post-deposition annealing temperature up to 600 °C and see a monotonic increase in the values of the staggered band offsets with annealing temperature.

2. Experimental

We used vertical rectifier structures for the measurement of band alignments. These consisted of a 10 μ m thick, lightly Si doped epitaxial layer of Ga₂O₃ grown by halide vapor phase epitaxy with carrier concentration 2 × 10¹⁶ cm⁻³, on a (001) surface orientation Sn-doped β -Ga₂O₃ single crystal (Novel Crystal Technology, Japan).

The band gaps of NiO for as-deposited films and those after annealing at different temperatures were obtained using UV–Vis (Perkin-Elmer Lambda 800 UV/Vis spectrometer). These films were 60 nm thick and were sputtered on quartz. The absorbance spectrum were collected and Tauc plots were used to calculate the bandgap of the NiO. Since the depositions were done at room temperature and hence surface mobility is small, it is not expected that there will be much difference in the structure of the NiO deposited on quartz or Ga_2O_3 . This was done to avoid complications from possible defect-related absorption in the Ga_2O_3 .

The band alignments were obtained using the x-ray photoelectron spectroscopy (XPS) based technique initially developed by Kraut *et al* [38]. This requires preparation of three samples. In the first, the core levels and VBM positions are measured from a thick NiO layer and in the epitaxial Ga₂O₃. These same core level locations were re-measured in a NiO/Ga₂O₃ heterojunction consisting of 5 nm NiO sputtered on Ga₂O₃. The shift of the core level binding energy locations (Δ ECL) within the heterostructure determines the valence band offset (ΔE_V) from [36, 37]

$$\Delta E_{\rm V} = \Delta \text{ ECL} + (E_{\rm Core} - E_{\rm VBM})_{\rm Ref. NiO} - (E_{\rm Core} - E_{\rm VBM})_{\rm Ref. Ga2O_3}.$$

The XPS system was a Physical Instruments ULVAC PHI, with an Al x-ray source (energy 1486.6 eV, source power 300 W), analysis size of 100 μ m diameter, a take-off angle of 50° and acceptance angle of \pm 7°. The electron pass energy was 23.5 eV for high-resolution scans and 93.5 eV for survey scans. The total energy resolution of this XPS system is about 0.5 eV, and the accuracy of the observed binding energy is within 0.03 eV. We chose to measure the band offsets b XPS, because it reduces another source of variability if other methods such as capacitance or current–voltage is used, (i.e. past experimental studies, using XPS) and capacitance-voltage measurements, have yielded conflicting results on the band offset in many materials systems.

NiO was deposited by magnetron sputtering at 3 mTorr and 100 W of 13.56 MHz power using two targets to achieve a deposition rate around 0.2 Å s⁻¹. The Ar/O₂ ratio was used to control the doping in the NiO in the range 2×10^{18} -3 $\times 10^{19}$ cm⁻³ for separate device experiments, but was kept constant at 5 \times 10¹⁸ cm⁻³ for these band alignment experiments. The mobility was $<1 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$. The temperature of the sample during deposition was monitored by temperature-sensitive alloys placed next to the Ga2O3 and was <100 °C throughout. A representative cross-sectional transmission electron microscopy (TEM) image is shown in figure 1, in this case of a structure subsequently used for device measurements and consisting of a bilayer of NiO on the Ga_2O_3 . There is a small amount of near-surface damage in the top 10 nm of the Ga₂O₃ layer, which is likely due to sputteringinduced disorder during deposition of the NiO. However, the interface is atomically abrupt with no extended defects.

3. Results and discussion

To obtain the conduction band offsets, we also need to measure the bandgaps of the constituent layers within the heterojunction. This was done for separate layers of NiO annealed



Figure 1. High-resolution TEM image of the NiO/β -Ga₂O₃ heterojunction.

for 5 min at temperatures from 300 °C–600 °C under an O_2 ambient using rapid thermal annealing. We kept the annealing ambient constant and chose O_2 to avoid possibly creating oxygen vacancies which are known to strongly influence the electrical properties of many oxides. Figure 2(a) shows Ultraviolet–Visible Spectroscopy (UV–Vis) absorption data, while the corresponding Tauc plots are shown in figure 2(b). The extracted bandgap decreased with annealing temperature, from 3.90 eV for as-deposited films to 3.72 eV for those annealed at 600 °C, as tabulated in table 1.

The high resolution XPS spectra for the vacuum-core delta regions of Ga₂O₃ are shown in figure 3 for samples annealed at different temperatures up to 600 °C. The $\Delta E_{\rm V}$ values are then extracted from the shift of the core levels for the heterojunction samples with the thin NiO overlayers [36, 37]. The XPS spectra from which we extracted the core energy differences to VBM for thick NiO layers after different annealing temperatures are shown in figure 4. The corresponding VBMs are shown in table 1. The error bars in the different binding energies were combined in a root sum square relationship to determine the overall error bars in the valence band offsets [31]. Note that sample charging is not an issue when determining band offsets since we only need peak core shift deltas, which will shift all binding energies by the same amount. We also did not observe any differential charging, which could shift peaks by different amounts and could potentially be a large source of error.

Figure 5 shows the band alignment of NiO on Ga₂O₃ after the different annealing temperatures. The valence band offsets were 0.90 \pm 0.20 eV for the as-deposited heterojunction, 2.10 \pm 0.30 eV after annealing at 300 °C, 2.60 \pm 0.30 eV after annealing at 400 °C and 2.90 \pm 0.35 eV for annealing



Figure 2. (a) Absorbance spectrum and (b) Tauc plots for the extrapolation of bandgaps of NiO film as-deposited and annealed at different temperatures.

at 500 °C and 3.0 \pm 0.35 eV for annealing at 600 °C. The respective conduction band offsets are then 0.20 eV (as-deposited), 1.34 eV (300 °C), 1.76 eV (400 °C), 2.04 eV (500 °C) and 2.12 eV (600 °C). The band alignment is staggered, type II in all cases. The dominant effect in figure 5 is the elevation of the NiO bandgap in relation to GaO of about 2 eV. It has been shown that for dielectrics with type II band alignment with a negative $\Delta E_{\rm V}$, high temperatures and/or illumination can cause holes from Ga₂O₃ to move into the metal, greatly increasing the leakage current [39, 40]. Note that the band offsets increase monotonically with annealing temperature and will not provide any barrier to electrons moving into the Ga₂O, suggesting that NiO may not be an optimum choice as a guard-ring material on rectifiers, although Gong et al [23] noted that in addition to the band offset, there was an additional built-in potential of 0.78 V at the interface due to

Anneal T (°C)	$E_{\rm G}~({\rm eV})$			$\Delta E_{\rm V}$ (eV)		
As-deposited		3.90			0.9	
300		3.84			2.1	
400	3.76			2.6		
500	3.74			2.9		
600	3.72			3.0		
	Thick NiO			Thin NiO on Ga ₂ O ₃		
Anneal T (°C)	VBM	Core level peak (Ni 2p)	Core-VBM	Core level peak (Ga 2p3)	Core level peak (Ni 2p)	∆Core level
As-deposited	-0.6	853.4	854.0	1116.3	854.5	261.8
300	-1.8	853.2	855.0	1116.0	854.0	262.0
400	-1.9	853.1	855.0	1116.1	853.6	262.5
500	-1.9	853.4	855.3	1115.6	853.1	262.5
600	-1.7	853.7	855.4	1115.4	853.9	262.5

Table 1. (top) NiO bandgap measured by UV–Vis and (bottom) core level data measured by XPS data as a function of post-deposition annealing temperature.



Figure 3. Δ Core level calculations for interfaces of thin NiO/Ga₂O₃ as-deposited and annealed at different temperatures.



Figure 4. Core -VBM calculations for thick NiO film as-deposited and annealed at different temperatures.

the charge transfer across the p–n-junction. Based on separate device measurements on vertical rectifier structures, the entire NiO/Ga₂O₃ heterojunction also does not display thermal stability beyond 300 $^{\circ}$ C.

Our band offsets are only in general agreement with these of Gong *et al* [23] for the samples annealed at 600 °C, although they did not indicate any annealing of their samples. Similarly, the valence band offsets reported by Ghosh *et al* [35], Zhang *et al* [27] and Lu *et al* [16] would fall between a temperature cycle in the range ~275 °C-325 °C, judging from our data, if thermally-induced changes were the only cause. It is worth noting that the literature reports have the same general trend, just the magnitudes are significantly different. The fact that the sputter rate of NiO is slow does not allow for significant opportunity for sample heating during the deposition. Hays *et al* [37] also summarized other possible reasons for variations in band offsets between nominally similar systems, including different strain, interfacial disorder and contamination, stoichiometry and chemical bonding variations. At this stage, the exact cause cannot be isolated and awaits more experiments where deposition conditions are carefully controlled.

While annealing a sputtered material may change its crystallinity, preliminary TEM measurements on the NiO did not show significant structural changes with annealing and it is



Figure 5. Schematic of band alignments for NiO/Ga₂O₃ as a function of post-deposition annealing temperature.

difficult to quantify interfacial changes due to both materials being oxides, so that diffusion of oxygen cannot be quantified. However, this does suggest that changes in point defect population play a strong role in the changes in band alignment. This is reflected in the changes in bandgap of the NiO with annealing.

4. Conclusions

There is still additional work that must be done to better understand carrier transport across the NiO/Ga₂O₃ interface and how this varies with doping level in the NiO and annealing temperature. The large reported variations in band offsets in this system requires examination of less energetic deposition methods than sputtering. The NiO/Ga₂O₃ heterojunction is showing much promise for enhancing the capability of Ga₂O₃ power devices but must be optimized to obtain reproducible benefits.

Data availability statement

All data that support the findings of this study are included within the article (and any supplementary files).

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Conflict of interest

There are no competing financial interests in this paper.

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