# Band offsets of non-polar A-plane GaN/AlN and AlN/GaN heterostructures measured by X-ray photoemission spectroscopy

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**Abstract**

The band offsets of non-polar A-plane GaN/AlN and AlN/GaN heterojunctions are measured by X-ray photoemission spectroscopy. A large forward-backward asymmetry is observed in the non-polar GaN/AlN and AlN/GaN heterojunctions. The valence-band offsets in the non-polar A-plane GaN/AlN and AlN/GaN heterojunctions are determined to be 1.33 ± 0.16 and 0.73 ± 0.16 eV, respectively. The large valence-band offset difference of 0.6 eV between the non-polar GaN/AlN and AlN/GaN heterojunctions is considered to be due to piezoelectric strain effect in the non-polar heterojunction overlayers.

**Keywords:** GaN/AlN; Heterostructure; X-ray photoemission spectroscopy; Non-polar

## Background

During the last decade, group III-V nitrides are very promising semiconductor materials for application in high frequency heterojunction field-effect transistors (HFETs) [1-8]. Large band offsets at the heterojunctions are important to realize these device applications. To understand the band offsets between nitride materials at heterointerface is requested for fabricating devices. The heterojunction formed between GaN and AlN is particularly application-oriented because of their large band gap difference induced by the polarization properties of nitride materials [9-11]. Several groups have reported $\Delta E_V$ values for GaN/AlN heterojunctions fabricated by different growth techniques and determined the value of $\Delta E_V$ in a range from 0.5 to 1.4 eV [12]. However, these GaN/AlN heterojunctions reported were nearly deposited all on (0001) orientation substrates. Especially, Martin et al. reported valence-band offsets of GaN/AlN and AlN/GaN heterojunctions on C-plane sapphire substrates were 0.60 ± 0.24 and 0.57 ± 0.22 eV, respectively, both values were almost the same to each other [13]. In recent years, non-polar nitride heterostructure has

drawn great interest owing to its potential applications in normally-off HEMT, high-efficiency field-free deep-ultraviolet (UV) light emitting diodes (LEDs) with wavelengths of 200 to 300 nm or sensors and so on. Non-polar nitride can eliminate internal polarization fields because of the absence of spontaneous polarization in the non-polar materials. However, the valence-band offset of non-polar A-plane GaN/AlN heterostructures has been studied by few. In this paper, we studied valence-band offsets of non-polar A-plane GaN/AlN and AlN/GaN heterostructures deposited on R-plane sapphire substrates measured by X-ray photoemission spectroscopy (XPS).

## Methods

The samples investigated were grown on R-plane sapphire substrates by metal-organic chemical vapor deposition (MOCVD). Four samples were used in our XPS experiments, namely, a 1.5-μm-thick GaN layer, 250-nm AlN layer, 5-nm GaN/250-nm AlN heterojunction, and 5-nm AlN/1.5-μm GaN heterojunction. Triethylgallium (TEGa), trimethylaluminum (TMAl), and ammonia (NH₃) were used as the sources of Ga, Al, and N, respectively. The carrier gas was high-purity hydrogen. Before growing GaN and AlN layers, R-plane (10 $\bar{1}$ 2) sapphire substrates were thermally cleaned in H₂ ambient at 1,000°C for 10 min to remove the adsorbed water molecules and activate sapphire

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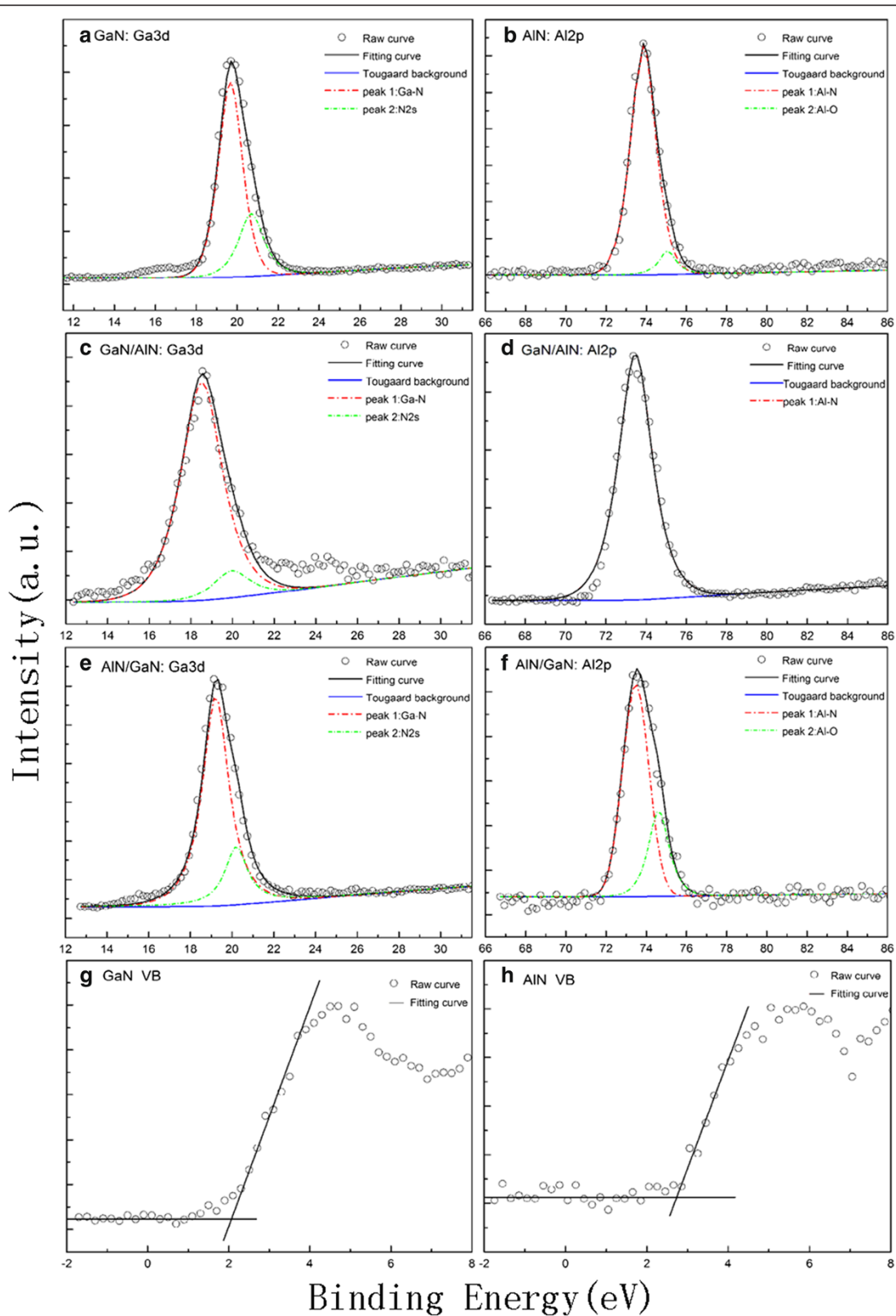Full list of author information is available at the end of the article

**Figure 1 XPS spectra of all samples.** Ga 3d XPS spectra for **(a)** GaN, **(c)** GaN/AlN, and **(e)** AlN/GaN samples and Al 2p XPS spectra for **(b)** AlN, **(d)** GaN/AlN, and **(f)** AlN/GaN. Experimental data points are fitted by Voigt (mixed Lorentzian-Gaussian) line shapes (solid lines) after the application of a Tougaard background. Also shown are VB spectra for **(g)** GaN and **(h)** AlN. The peak and VBM positions are summarized in Table 1.

surface. Then, sapphire substrates were nitridized for 5 min at 1,000°C under a mixed gas of $H_2$ and $NH_3$. The growth temperature of GaN and AlN layer was 1,000°C and 1,100°C, respectively. The XPS measurements were performed on a PHI Quantro SXM instrument (Physical Electronics, Inc., Chanhassen, MN, USA) with Al $K_\alpha$ radiation ($h\nu$ = 1,486.6 eV) at a pressure lower than $2 \times 10^{-9}$ Torr. Charged displacement was calibrated by C 1 s (approximately 285 eV) photoelectron peak from contamination to compensate the charge effect.

## Results and discussion

The valence-band offset ($\Delta E_V$) can be calculated from the following formula:

$$\Delta E_V = (\Delta E_{CL})_{A-B} + (E_{CL} - E_V)_B - (E_{CL} - E_V)_A \qquad (1)$$

where $A$ and $B$ represents the GaN or AlN, $\Delta E_{CL} = \pm$ ($E_{Ga3d}^{GaN} - E_{Al2p}^{AlN}$) is the energy difference between Ga 3d and Al 2p core levels (CLs), which are measured in the GaN/AlN (A-on-B) and AlN/GaN (B-on-A) heterojunction samples. ($E_{CL} - E_V$) is the GaN or AlN bulk constants, which is obtained by XPS measurement on the respective thick film. Ga 3d and Al 2p XPS spectra are shown in Figure 1a,b,c,d,e,f) fitted using Tougaard backgrounds and Voigt (mixed Lorentzian-Gaussian) functions. Since considerable accordance of the fitted lines to the original measured data, the uncertainty of the Ga 3d and Al 2p core level positions were less than 0.03 and 0.01 eV, respectively, as evaluated by numerous fittings with different parameters. Figure 1a,c,e shows the Ga 3d spectrum of GaN bulk film, GaN/AlN, and AlN/GaN heterojunctions, which were fitted by two peaks, attributed to the bonding configurations Ga-N and N 2 s, respectively. For Al 2p spectrum of AlN bulk film and AlN/GaN heterojunctions shown in Figure 1b,f, two fitting peaks are attributed to the bonding configurations Al-N and Al-O, respectively. The Al-O contribution is thought to be due to oxide contamination when samples are exposed to the air. For Al 2p spectrum of GaN/AlN heterojunctions shown in Figure 1d, only one fitting peak is attributed to the bonding configuration Al-N, which coincided with the sum fitting curve shown in black solid line (red dash and dot line represents the fitting peak of bonding configuration Al-N, not shown here). The VB XPS spectra for the thick GaN and AlN samples are shown in Figure 1g,h. The VBM positions were determined by linear extrapolation of the leading edges of VB spectra to the base lines in order to account for the finite instrument resolution. The VBM positions in the GaN and AlN VB XPS spectrum are determined to be 2.06 ± 0.03 and 2.74 ± 0.09 eV, respectively. The parameters deduced from Figure 1 are summarized in Table 1 for clarity. $\Delta E_V$ in the non-polar GaN/AlN and AlN/GaN

heterojunctions are calculated to be 1.33 ± 0.16 and 0.73 ± 0.16 eV, respectively, by substituting those experimental values into Equation (1).

Then, the conduction-band offsets ($\Delta E_C$) can be deduced from the following formula:

$$\Delta E_C = \left(E_g^A - E_g^B\right) - \Delta E_V \qquad (2)$$

Using room temperature band gaps for GaN and AlN (3.39 and 6.2 eV, respectively), $\Delta E_C$ in the non-polar GaN/AlN and AlN/GaN heterojunctions are calculated to be 1.48 ± 0.16 and 2.08 ± 0.16 eV, respectively, and the ratio of $\Delta E_C:\Delta E_V$ is close to 11:10 and 57:20, respectively.

From the calculated results, we can see that there exists a large band offset difference of 0.6 eV between the non-polar A-plane GaN/AlN and AlN/GaN heterojunctions, which may be due to the strain-induced piezoelectric fields in the non-polar films [14,15]. There is no spontaneous polarization but only piezoelectric polarization exists in the non-polar films. The heterojunction underlayers are thick enough to relax the strain caused by the lattice mismatch between GaN and AlN layers, but the heterojunction thin overlayers are only 5-nm thick and at least partially strained. The strain induces static electric fields via the piezoelectric effect. The strain-induced piezoelectric fields tend to decrease the apparent valence-band offsets for nitride materials [13].

The piezoelectric polarization $P_{PE}$ via the piezoelectric effect can be given by the following [16]:

$$P_{PE} = e_{33}\varepsilon_{zz} + e_{31}\left(\varepsilon_{xx} + \varepsilon_{yy}\right) \qquad (3)$$

Based on Hooke's law and the symmetry of wurtzite III-nitride material, the stress tensor can be represented

**Table 1 Binding energies (in eV) of the XPS peaks and VBM for GaN, AlN, GaN/AlN, and AlN/GaN samples**

| Sample | State | Binding energy(eV) | |
|---|---|---|---|
| GaN | Ga 3d | 19.70 ± 0.03 | Ga-N |
| | | 20.70 ± 0.03 | N2s |
| | VBM | 2.06 ± 0.03 | |
| AlN | Al 2p | 73.85 ± 0.01 | Al-N |
| | | 75.05 ± 0.01 | Al-O |
| | VBM | 2.74 ± 0.09 | |
| GaN/AlN | Al 2p | 73.36 ± 0.01 | Al-N |
| | Ga 3d | 18.56 ± 0.03 | Ga-N |
| | | 19.96 ± 0.03 | N2s |
| AlN/GaN | Al 2p | 73.43 ± 0.01 | Al-N |
| | | 74.63 ± 0.01 | Al-O |
| | Ga 3d | 19.23 ± 0.03 | Ga-N |
| | | 20.23 ± 0.03 | N2s |

by the following strain tensor and elastic stiffness coefficient:

$$\begin{pmatrix} \sigma_{xx} \\ \sigma_{yy} \\ \sigma_{zz} \\ \sigma_{yz} \\ \sigma_{xz} \\ \sigma_{xy} \end{pmatrix} = \begin{pmatrix} C_{11} & C_{12} & C_{13} & 0 & 0 & 0 \\ C_{12} & C_{11} & C_{13} & 0 & 0 & 0 \\ C_{13} & C_{13} & C_{33} & 0 & 0 & 0 \\ 0 & 0 & 0 & C_{44} & 0 & 0 \\ 0 & 0 & 0 & 0 & C_{44} & 0 \\ 0 & 0 & 0 & 0 & 0 & C_{66} \end{pmatrix} \begin{pmatrix} \varepsilon_{xx} \\ \varepsilon_{yy} \\ \varepsilon_{zz} \\ \varepsilon_{yz} \\ \varepsilon_{xz} \\ \varepsilon_{xy} \end{pmatrix} \quad (4)$$

where $C_{ij}$ is the elastic stiffness coefficient.

For A-plane III-nitride materials, the growth plane is in the y-z plane and the in-plane strain tensor is the bi-axial stress in which $\varepsilon_{yy} = \varepsilon_{zz}$, the out-plane strain tensor is $\varepsilon_{xx}$, and the other strain tensors are zero $\varepsilon_{xy} = \varepsilon_{yz} = \varepsilon_{zx} = 0$. Also, because there is not any restriction and effect along the growth direction of material, there is no stress along the growth direction, i.e., $\sigma_{xx} = 0$. Then, Equation (4) can be expressed as follows:

$$\varepsilon_{xx} = -\frac{C_{12}\varepsilon_{yy} + C_{13}\varepsilon_{zz}}{C_{11}} = -\frac{C_{12} + C_{13}}{C_{11}}\varepsilon_{zz} \quad (5)$$

Equation (5) is substituted into the Equation (3), and we can obtain the expression of the piezoelectric polarization $P_{PE}$ induced via the piezoelectric effect in the non-polar A-plane GaN/AlN and AlN/GaN hetero-junctions as follows:

$$P_{PE} = \frac{(a-a_0)}{a_0}\left[e_{31} - (e_{33} + e_{31})\frac{C_{11}}{C_{12} + C_{13}}\right] \quad (6)$$

Then, the field magnitude induced via the piezoelectric effect in the non-polar A-plane GaN/AlN and AlN/GaN heterojunctions is expressed as follows:

$$E = \frac{(a-a_0)}{\varepsilon a_0}\left[e_{31} - (e_{33} + e_{31})\frac{C_{11}}{C_{12} + C_{13}}\right] \quad (7)$$

where $a$ and $a_0$ are the lattice constants of the materials, $\varepsilon$ is the static dielectric constant, $e_{ij}$ is the piezoelectric coefficient, and $C_{ij}$ is the elastic stiffness coefficient. The values used in this work are given in Table 2 [13,16-19].

The calculated electric fields in the strained regions are GaN(on AlN) = $2.176 \times 10^8$ and AlN(on GaN) = $5.346 \times 10^8$ V/m. Assuming critical heterojunction over-layer thicknesses of about 2 nm, therefore we can esti-mate the band offsets caused by the strain-induced piezoelectric fields in the overlayers GaN and AlN of the non-polar A-plane GaN/AlN and AlN/GaN heterojunc-tions to be 0.4352 and 1.0692 eV, respectively. There ex-ists a band offset difference of 0.634 eV between them, which is almost equal to the valence-band discontinuity difference of 0.6 eV between non-polar GaN/AlN and AlN/GaN heterojunctions we measured. Figure 2 shows the energy band diagram of the non-polar A-plane GaN/
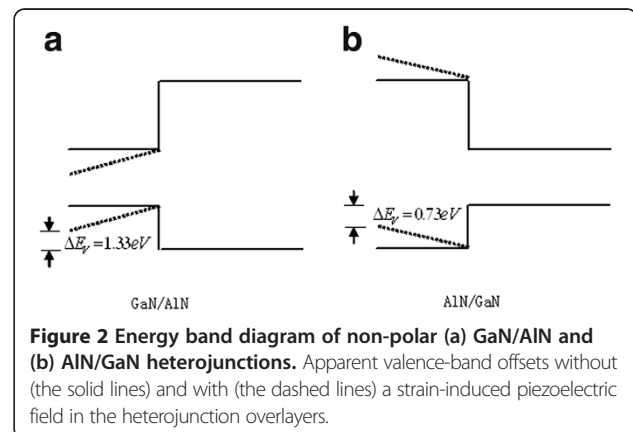
**Table 2 Values used for calculating strain-induced piezoelectric field [13,16-19]**

|  | AlN | GaN |
| --- | --- | --- |
| $a_0$(Å) | 3.112 | 3.189 |
| $\varepsilon$ | 8.5 | 10.0 |
| $e_{31}$(C.m$^{-2}$) | −0.600 | −0.490 |
| $e_{33}$(C.m$^{-2}$) | 1.460 | 0.730 |
| $C_{11}$(GPa) | 398 | 396 |
| $C_{12}$(GPa) | 140 | 144 |
| $C_{13}$(GPa) | 127 | 100 |

AlN and AlN/GaN heterojunction. The dashed and solid lines represent the apparent energy band with and with-out strain-induced piezoelectric field in the heterojunc-tion overlayers, respectively. Therefore, we can conclude that the large valence-band offsets between the non-polar A-plane GaN/AlN and AlN/GaN heterojunctions is most likely caused by the strain-induced piezoelectric fields in the heterojunction overlayers. Although we as-sume that the strain in the heterojunction overlayer can be released within 2 nm and obtain the above results, further analysis of the strain in the heterojunction over-layer and other physical properties will be discussed in our next paper in detail.

## Conclusions

This paper reports the study of valence-band offsets in the non-polar A-plane GaN/AlN and AlN/GaN hetero-junctions evaluated by XPS technique. The valence-band offsets in the non-polar GaN/AlN and AlN/GaN hetero-junctions are predicted to be 1.33 ± 0.16 and 0.73 ± 0.16 eV, respectively. There exists a large valence-band offset difference of 0.6 eV between the non-polar A-plane GaN/AlN and AlN/GaN heterojunctions, which is most likely caused by the strain-induced piezoelectric fields in the heterojunction overlayers.



**Figure 2 Energy band diagram of non-polar (a) GaN/AlN and (b) AlN/GaN heterojunctions.** Apparent valence-band offsets without (the solid lines) and with (the dashed lines) a strain-induced piezoelectric field in the heterojunction overlayers.

## Competing interests

The authors declare that they have no competing interests.

## Authors' contributions

## Acknowledgements

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