Materials Letters 230 (2018) 135–138

Contents lists available at ScienceDirect

Materials Letters

journal homepage: www.elsevier.com/locate/mlblue

Determination of N-polar AlN/GaN heterojunction valance-band offsets by X-ray photoelectron spectroscopy

Jin-Juan Du [a], Sheng-Rui Xu [a,*], Jin-Cheng Zhang [a], Pei-Xian Li [b], Zhi-Yu Lin [a], Ying Zhao [a], Ruo-Shi Peng [a], Xiao-Meng Fan [a], Hong-Chang Tao [a], Yue Hao [a]

[a] Wide Bandgap Semiconductor Technology Disciplines State Key Laboratory, School of Microelectronics, Xi'dian University, Xi'an 710071, China
[b] Wide Bandgap Semiconductor Technology Disciplines State Key Laboratory, School of Advanced Materials and Nanotechnology, Xi'dian University, Xi'an 710071, China

ARTICLE INFO

Article history:
Received 1 May 2018
Received in revised form 27 June 2018
Accepted 21 July 2018
Available online 23 July 2018

Keywords:
N-polar AlN/GaN heterojunction
Planar
Vicinal
Valance band offset
X-ray photoelectron spectroscopy

ABSTRACT

The N-polar AlN/GaN heterojunctions were grown by metal organic chemical vapor deposition on planar and vicinal sapphire substrates. The valence-band offsets (VBOs) were directly determined to be 2.18 ± 0.15 eV and 2.05 ± 0.15 eV for N-polar AlN/GaN heterojunctions grown on planar and vicinal sapphire substrates by X-ray photoelectron spectroscopy measurement, respectively.

1. Introduction

AlN, GaN and their alloys materials are widely used in fabrication of electronic and optoelectronic devices, particularly, light-emitting diodes (LEDs) [1,2]. At present, it is a usual method to deposit AlGaN layer upon GaN as the electron block layer (EBL) in LEDs. Consequently, accurate determination of the valance band offset (VBO) ΔE_V and conduction band offset (CBO) ΔE_C at the AlN/GaN heterojunction interface is crucial to obtaining the electronic properties of AlGaN alloys and designing, modeling and fabricating the GaN-based LEDs. X-ray photoelectron spectroscopy (XPS) is a direct and powerful tool for measuring the valance-band discontinuities of heterojunction [3–5]. In fact, the VBO of Ga-polar AlN/GaN heterojunction by XPS measurement has been determined elsewhere [5–7]. However, comparing with the Ga-polar GaN, the N-polar GaN may provide many superior advantages for LEDs application, for example, a weaker polarization effect due to the opposite direction of the piezoelectric and spontaneous polarization in the N-polar GaN [8–10]. **Many theoretical studies have researched the new structures of N-polar GaN-based LED by simulating the optical and electrical characteristics** [11–13]. Nevertheless, it is impossible to set the accurate value of the simulation parameters, such as the VBO, which has a significant effect on the accuracy of simulation results. Therefore, it is very important to calculate the VBO of N-polar AlN/GaN heterojunction. **Whereas, the study about the VBO determination based on N-polar AlN/GaN heterojunction are barely reported.**

As we know, the N-polar GaN films have a poor crystal quality and surface morphology, so the vicinal sapphire substrate would be a suitable selection to improve the crystal quality [14,15] (**Fig. S1**). As a consequence, we prepared the N-polar AlN/GaN heterojunctions on planar and vicinal sapphire substrates to determine their VBO values by XPS measurement. Meanwhile, the Ga-polar AlN/GaN heterojunction acted as the reference to verify the accuracy of this experiment.

2. Experiment

The AlN/GaN heterojunctions were grown by metal organic chemical vapor deposition (MOCVD) on different substrates. To determine the VBOs of different AlN/GaN heterojunctions, we prepared three groups of substrates, namely planar sapphire substrates for Ga-polarity, planar sapphire substrates for N-polarity and vicinal sapphire substrates for N-polarity, and each group included three kinds of samples. The direction of vicinal sapphire substrate was inclined from *c*-axis toward the

* Corresponding author.
E-mail address: shengruixidian@126.com (S.-R. Xu).

https://doi.org/10.1016/j.matlet.2018.07.091
0167-577X/

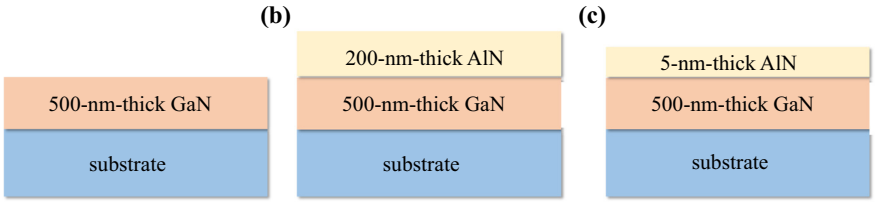

Fig. 1. The structure schematic diagram of (a) GaN sample, (b) AlN sample and (c) GaN/AlN sample on three different kinds of substrates.

m-plane by 4°. Moreover, the N-polar substrates were obtained by treating with H_2 at 1200 °C to clean the surface and then exposing them to high temperature with an NH_3 flow of 150 mmol/min at 1100 °C for 5 min in the reaction chamber before the growth process. The three kinds of samples of each group of substrates were GaN sample, AlN sample and AlN/GaN sample. The sample with a 500-nm-thick GaN layer grown on the substrate was used as the GaN sample. The AlN sample consisted of a 500-nm-thick GaN layer and a 200-nm-thick AlN layer. A 5-nm-thick AlN layer was deposited on a 500-nm-thick GaN layer as the AlN/GaN sample. The structure schematic diagram of three kinds of samples was shown in Fig. 1. XPS measurements were performed on an Auger Electron Spectrometer (Escalab 250Xi) and a monochromatic Al κα with energy 1486.7 eV is used as the X-ray radiation source. Argon ion sputtering was performed in the analytical chamber to each of the samples. Since both the Al 2p and Ga 2p3 core-level (CL) electrons need to escape from the valance band to be collected by the vacuum energy level during the XPS measurement, the position of the valance band could be determined. By bombarding the surface of those samples, the parameters of the AlN bulk material, AlN/GaN heterojunction and GaN bulk material were obtained to calculate the VBO of Ga-polar and two N-polar AlN/GaN heterojunctions.

3. Results and discussion

The VBO of two different semiconductor materials is determined by the valance band (VB) and core-level (CL) from bulklike materials and a heterojunction interface [3–5]. The valance-band offset (ΔE_V) of the AlN/GaN heterojunction could be calculated from the following formula:

$$\Delta E_V = \Delta E_{CL} + \left(E_{Al2p} - E_{VBM}\right)_{AlN} - \left(E_{Ga2p3} - E_{VBM}\right)_{GaN} \quad (1)$$

where the energy difference $\Delta E_{CL} = \left(E_{Al2p}^{AlN} - E_{Ga2p3}^{GaN}\right)$ between the measured Al 2p and Ga 2p3 CLs is determined from the AlN/GaN sample. The $\left(E_{Al2p} - E_{VBM}\right)_{AlN}$ and $\left(E_{Ga2p3} - E_{VBM}\right)_{GaN}$ respect difference in binding energies between the Al 2p, Ga 2p3 CLs and the valance-band maximum (VBM) of the AlN and GaN bulk material constants for AlN and GaN sample. Particularly, the CL peaks are fitted by using Shirley backgrounds and Voigt (mixed Lorentzian–Gaussian) functions. Moreover, the VBM positions are determined by linear extrapolation of the low binding energy edge of valance-band spectra to the base lines [16,17]. The XPS spectra for Ga-polar AlN/GaN heterojunction grown on planar sapphire substrate, N-polar AlN/GaN heterojunction grown on planar sapphire substrate and N-polar AlN/GaN heterojunction grown on vicinal sapphire substrate were shown in Fig. 2(a)–(f), Fig. 2(A)–(F) and Fig. 2(I)–(VI), respectively. The parameters derived from XPS measurement used here were given in Table 1. The Al spectra from AlN sample and AlN/GaN sample were fitted by two components: Al-O and Al-N bonds. It is clearly noticed that the binding energy of the Al-O bond was about 1.10 eV larger than that of the Al-N bond [18]. **For Ga 2p3 spectra, the difference in binding energy between Ga–N and Ga–O was about 1.2 eV, which is consistent with the literatures** [19,20]**.**

By fitting the spectra with different parameters from Table 1, the uncertainties of CL and VBM positions were respectively estimated to be lower than 0.03 and 0.1 eV. The room-temperature VBO value of Ga-polar AlN/GaN heterojunction was determined to be 0.84 ± 0.15 eV by substituting these parameters in Eq. (1), and the CBO value was 1.96 ± 0.15 eV owing to the different band-gap E_g between AlN (E_g = 6.2 eV) and GaN (E_g = 3.4 eV) [21]. The VBO value of Ga-polar AlN/GaN heterojunction was comparable to the experimental value of 0.82 ± 0.15 eV determined from XPS by H. Li et al. [6], which confirmed the accuracy of this experiment. Correspondingly, the VBO values of N-polar samples grown on planar and vicinal substrates were calculated as 2.18 ± 0.15 eV and 2.05 ± 0.15 eV, respectively, while the CBOs were 0.62 ± 0.15 eV and 0.75 ± 0.15 eV. At the interface of N-polar samples, the bands aligned in a type-I straddling configuration, which was shown in Fig. 3.

4. Conclusions

In summary, we have measured the valance band offset of N-polar AlN/GaN heterojunctions grown on planar and vicinal sapphire substrates to be 2.18 ± 0.15 eV and 2.05 ± 0.15 eV by X-ray photoelectron spectroscopy. Considering the potential application of N-polar GaN, the accurate determination of the valance band offsets of N-polar AlN/GaN heterojunctions is beneficial to the simulation and design of N-polar GaN-based devices.

Acknowledgements

This work was supported by The National Key R&D Program of China (2016YFB0400800, 2016YFB0400801), the National Natural Science Foundation of China (Grant No. 61574108, 61334002, 61474086, 51302306), the Fundamental Research Funds for the Central Universities (Grant No. JBZ171101).