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Conduction and valence band offsets of ZnO/β-Ga_2O_3 interface measured by X-ray photoelectron spectroscopy

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Abstract

We have studied the band alignment of ZnO/β-Ga_2O_3 heterojunction fabricated by atomic layer deposition at 150ºC using X-ray photoelectron spectroscopy. The conduction and valence band offsets at ZnO/Ga_2O_3 interfaces are 1.27±0.1eV and 0.20±0.1eV, respectively. These results are useful to the understanding and design of ZnO/β-Ga_2O_3 based heterojunction devices.

1. Introduction

Beta-gallium oxide (β-Ga_2O_3) has attracted much attention due to its large bandgap of 4.6~4.9 eV, high bulk electron mobility and eminent chemical stability [1]. Therefore, numerous Ga_2O_3 based devices including solar-blind photodetectors[2] and metal-oxide-semiconductor field-effect transistors (MOSFETs)[3] have been demonstrated with excellent properties. However, limitations still exist in Ga_2O_3 based devices, such as the slow response (~seconds) of most of the Ga_2O_3 based photodetectors [4] and the poor ohmic contact between Ga_2O_3 and most of metals [5]. Forming a heterojunction of Ga_2O_3 and metal oxide semiconductor with a high electron concentration has been confirmed as an effective resolution for both above problems because the modulation of energy barrier at the interface.

ZnO has attracted much attention because it has a large exciton binding energy of 60 meV, high electron concentration of $>10^{19}$ cm^{-3}, the lattice mismatch between ZnO and Ga_2O_3 is within 5%[6]. Atomic-layer-deposited ZnO on wide-bandgap semiconductors can reduce interface disorder and yield more controllable sample to examine the energy band alignment, which plays an important role in the carrier transport process [7]. In this work, the band alignment of ZnO on single crystal β-Ga_2O_3 was characterized by X-ray photoelectron spectroscopy (XPS).

2. Experiment

Sn-doped β-Ga_2O_3 was alternately cleaned in acetone, isopropanol by ultrasonic cleaning for each 10 min, subsequently rinsed with deionized water to remove residual organic solvents. After that, the Ga_2O_3 substrate was transferred into an ALD reactor (Wuxi MNT Micro Nanotech co., LTD, China). Both 30 nm and 5 nm ZnO films were deposited on cleaned β-Ga_2O_3 using Zn $(C_2H_5)_2$ (DEZ) and H_2O at the temperature of 150 ºC. The growth rate of ZnO was ~1.6 Å per cycle. ZnO(30 nm)/β-Ga_2O_3 was used as bulk standard and the ZnO(5 nm)/β-Ga_2O_3 was used to determine the band alignment. A bare bulk β-Ga_2O_3 was used as control sample. XPS (AXIS Ultra DLD, Shimadzu) measurement with a step of 0.1 eV was performed on bare β-Ga_2O_3, 30 nm and 5 nm ZnO. To identify the bandgap, the optical transmittance spectra of Ga_2O_3 and ZnO were measured by ultraviolet-visible (UV-VIS) spectroscopy (Lambda 750, PerkinElmer, USA).

3. Results and Discussion

Fig. 1 shows the plot of $(\alpha h\nu)^2$ versus $h\nu$ for the β-Ga_2O_3 substrate. The $(\alpha h\nu)^2$ as a function of photon energy for the as-deposited ZnO film is shown in the inset of Fig.1. The optical band gap (E_g) of the ZnO film and β-Ga_2O_3 can be evaluated by the Tauc's relation [8]: $(\alpha h\nu)^{1/n} = A(h\nu - E_g)$, where α is the absorption coefficient, A is a constant, $h\nu$ is the incident photon energy, E_g is the optical energy bandgap, n is 1/2 for the direct bandgap and 2 for the indirect bandgap. Here, both ZnO and β-Ga_2O_3 have typical direct band gap that make the value of n is 1/2. Subsequently, E_g can be extracted by extrapolating the straight line portion to the energy bias at α = 0. Therefore, the extracted E_g for ZnO and β-Ga_2O_3 are 3.18 eV and 4.65 eV, respectively.

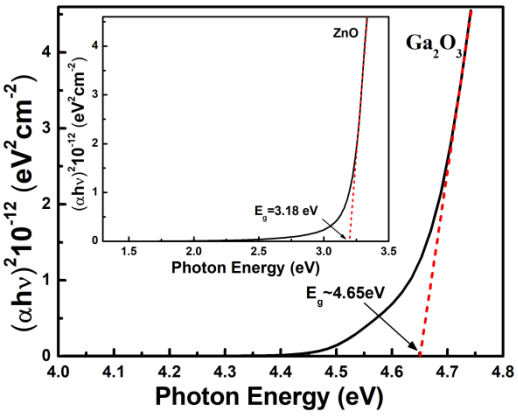

Fig.1 The plot of $(\alpha h\nu)^2$ versus $h\nu$ for β-Ga_2O_3 substrate. Inset shows $(\alpha h\nu)^2$ as a function of $h\nu$ for ZnO film grown on quartz glass.

Furthermore, the valence band offset (VBO) can be determined by Kraut's method using the following equation [9]:

$$\Delta E_V = (E_{Ga\ 2p}^{Ga_2O_3} - E_{VBM}^{Ga_2O_3}) - (E_{Zn\ 2p}^{ZnO} - E_{VBM}^{ZnO}) - (E_{Ga\ 2p}^{Ga_2O_3} - E_{Zn\ 2p}^{ZnO}) \quad (1)$$

where $E_{Ga\ 2p}^{Ga_2O_3} - E_{VBM}^{Ga_2O_3}$ $(E_{Zn\ 2p}^{ZnO} - E_{VBM}^{ZnO})$ corresponds to the energy difference between Ga 2p (Zn 2p) core level (CL)

and VBM of bulk β-Ga_2O_3 (ZnO), and $E_{Ga\ 2p}^{Ga_2O_3} - E_{Zn\ 2p}^{ZnO}$ denotes as the energy difference between Ga 2p core level and Zn 2p core level. Fig. 2 shows all CL spectra including Zn 2p of ZnO(30 nm)/β-Ga_2O_3 and ZnO(5 nm)/β-Ga_2O_3, Ga 2p of bulk Ga_2O_3 and ZnO(5 nm)/β-Ga_2O_3, as well as valence band spectra from bulk Ga_2O_3 and ZnO(30 nm)/β-Ga_2O_3. Fig. 2(a) shows the CL spectra of Zn 2p on the ZnO(30 nm)/β-Ga_2O_3, which is quiet symmetrical indicating the uniform bonding state, and the peak located at 1020.84±0.1 eV corresponds the Zn-O bond. The VBM can be extracted by linearly fitting the leading edge of the valence band and the flat energy distribution from the XPS measurements. By extrapolating the two fitted lines as shown in Fig. 2(a), the VBM of ZnO is obtained to be 2.11±0.1 eV. In Fig. 2(b), the peak located at 1117.78±0.1 eV is attributed to the Ga-O bond and the VBM is deduced to be 2.74±0.1 eV according to the method mentioned above. The CLs difference of Zn 2p and Ga 2p in the ZnO(5 nm)/β-Ga_2O_3 is 96.11±0.1 eV as shown in Fig. 2(c). According to equation (1), the valence band offset at the interface of ZnO/Ga_2O_3 is determined to be 0.20±0.1 eV.

Based on the calculated E_g and ΔE_V, the conduction band alignment (ΔE_C) at ZnO/Ga_2O_3 interface can be easily deduced from the following equation：

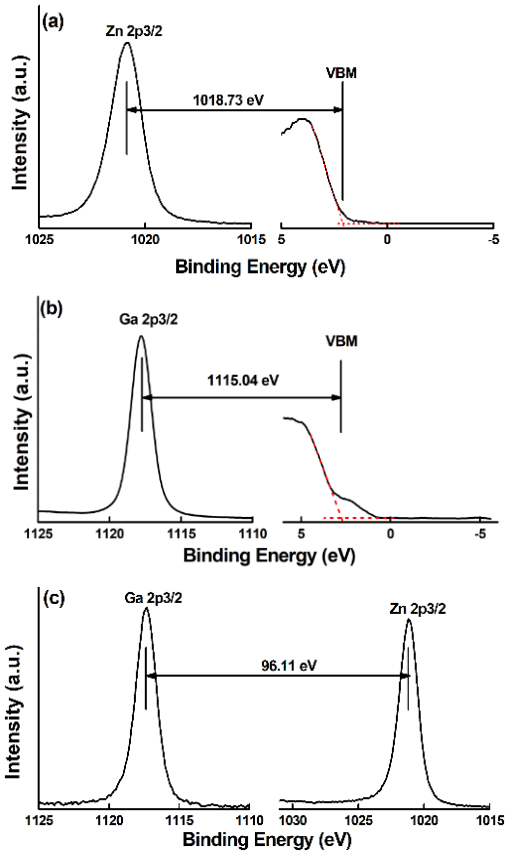

Fig.2 High resolution XPS spectra for core level and valence band maximum(VBM) of (a) Zn 2p core level spectrum and VBM from 30nm ZnO/β-Ga_2O_3 (b) Ga 2p core level spectrum and VBM from bare β-Ga_2O_3 (c) the core level spectra of Ga 2p and Zn 2p obtained from high resolution XPS spectra of 5nm ZnO/β-Ga_2O_3.

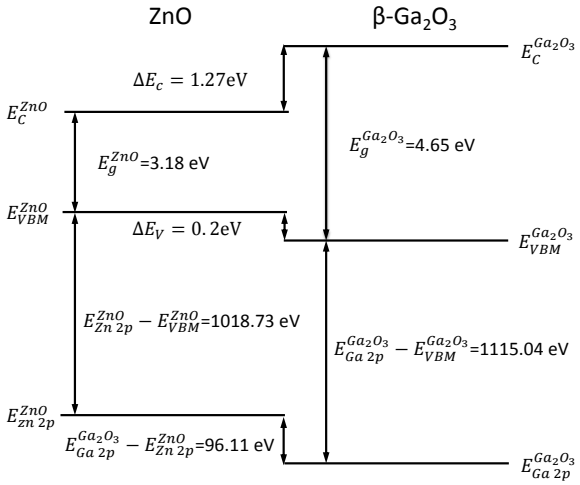

Fig.3 Schematic band alignment diagram of ZnO/β-Ga_2O_3 heterojunction.

$$\Delta E_C = (E_g^{Ga_2O_3} - E_g^{ZnO} - \Delta E_V). \quad (2)$$

where $E_g^{Ga_2O_3}$ and E_g^{ZnO} are the energy bandgap for Ga_2O_3 and ZnO, respectively. Thereby, the result of ΔE_C is 1.27±0.1 eV. The detailed energy band diagram for ZnO/Ga_2O_3 is presented in Fig. 3. The interface has a type-I band alignment, where the conduction band edge and valence band edge of ZnO are located within the bandgap of Ga_2O_3. The conduction band offset ΔE_C is much larger than ΔE_V, which is beneficial to the impact ionization of the electrons generating an avalanche multiplication effect.

4. Conclusions

The energy band alignment at atomic-layer-deposited ZnO/β-Ga_2O_3 was determined by XPS. A type-I band alignment forms at the ZnO/Ga_2O_3 interface with conduction band offset of 1.27±0.1 eV and valence band offset of 0.20±0.1 eV. The large conduction band offset is beneficial to the impact ionization of the electrons generating an avalanche multiplication effect in photodetector applications.

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