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X-ray photoelectron spectroscopy measurement of *n*-ZnO/*p*-NiO heterostructure valence-band offset

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Valence-band offset (VBO) of *n*-ZnO/*p*-NiO heterojunction has been investigated by x-ray photoelectron spectroscopy. Core levels of Zn 2*p* and Ni 2*p* were used to align the VBO of *n*-ZnO/*p*-NiO heterojunction. It was found that *n*-ZnO/*p*-NiO heterojunction has a type-II band alignment and its VBO is determined to be 2.60 ± 0.20 eV, and conduction-band offset is deduced to be 2.93 ± 0.20 eV. The experimental VBO value is in good agreement with the calculated value based on the electron affinity of ZnO and NiO. © *2009 American Institute of Physics*. [DOI: 10.1063/1.3072367]

ZnO is a promising semiconductor material in the field of blue and ultraviolet (UV) light-emitting diodes (LEDs) and laser diodes because of its direct wide band gap and high exciton binding energy.[1–3] Although ZnO-based *p*-*n* homojunction has been fabricated and realized electroluminescence, there are still many problems for *p*-type ZnO, for example, low acceptors solubility, instability, and low reproducibility.[4–12] Hence, these difficulties of *p*-type ZnO affects seriously the progress of ZnO-based *p*-*n* homojunction, which is a key structure for ZnO-based LEDs. Meanwhile, some researchers have tried to fabricate ZnO-based heterojunction LED for realizing electroluminescence in UV region.[13,14] NiO is a suitable material for fabricating ZnO-based heterojunction due to its *p*-type conductivity.[15] Recently, ZnO/NiO and MgZnO/NiO heterojunctions have been fabricated by various thin film preparation technology.[16,17] It is well known that properties in the interface of heterojunction are very essential for realizing the function of heterojunction. However, up to now, the knowledge of some properties in the interface of ZnO/NiO heterojunction is insufficient yet, for example, the band alignment of *n*-ZnO/*p*-NiO has not been determined precisely by x-ray photoelectron spectroscopy (XPS). In this paper, the valence-band offset (VBO) of *n*-ZnO/*p*-NiO heterojunction is measured by XPS and then the conduction-band offset (CBO) is also determined.

To measure VBO of ZnO/NiO heterojunction, three samples were used in our XPS experiments. A 500-nm-thick NiO thin film was grown on *c*-plane sapphire substrate by electron beam evaporation. The carrier concentration and Hall mobility of the *p*-type NiO thin film were determined by Hall measurements in van der Pauw configuration at room temperature to be 1.1×10^{16} cm^{-3} and 0.2 cm^2/V s, respectively. Then 600- and 8-nm-thick ZnO thin films were fabricated on the predeposited NiO thin film by plasma-assisted molecular beam epitaxy. The growth condition details of the ZnO layer can be found in our previous report.[18] The 600-nm-thick ZnO thin film has a carrier concentration and electron mobility of 1.3×10^{17} cm^{-3} and 8.6 cm^2/V s. XPS was performed by an ESCALAB 250 XPS instrument with Al $K\alpha$ ($h\nu = 1486.6$ eV) as the x-ray radiation source, which can precisely calibrate work function and Fermi energy level (E_F). All XPS spectra were calibrated by the C 1*s* peak (284.6 eV) from contamination to compensate the charge effect. The structure characterization was performed by using x-ray diffraction (XRD) with Cu $K\alpha$ radiation of 0.154 05 nm.

The calculation or measurement method of heterojunction band offset had been discussed in detail by Wei and Zunger.[19] In the present work, the VBO of *n*-ZnO/*p*-NiO heterojunction can be calculated by the following formula:

$$\Delta E_V = \Delta E_{\mathrm{CL}} + (E_{\mathrm{Ni}\,2p}^{\mathrm{NiO}} - E_{\mathrm{VBM}}^{\mathrm{NiO}}) - (E_{\mathrm{Zn}\,2p}^{\mathrm{ZnO}} - E_{\mathrm{VBM}}^{\mathrm{ZnO}}), \qquad (1)$$

where $\Delta E_{\mathrm{CL}} = E_{\mathrm{Zn}\,2p}^{\mathrm{ZnO}} - E_{\mathrm{Ni}\,2p}^{\mathrm{NiO}}$ is the energy difference between Zn 2*p* and Ni 2*p* core levels (CLs) in the ZnO/NiO heterojunction, $(E_{\mathrm{Ni}\,2p}^{\mathrm{NiO}} - E_{\mathrm{VBM}}^{\mathrm{NiO}})$ is the energy difference between Ni 2*p* and valence-band maximum (VBM) in the NiO thin film, and $(E_{\mathrm{Zn}\,2p}^{\mathrm{ZnO}} - E_{\mathrm{VBM}}^{\mathrm{ZnO}})$ is the energy difference between Zn 2*p* and VBM in the ZnO thin film.

The CL and VB edge XPS spectra for ZnO and NiO samples are shown in Fig. 1. Voigt (mixed Lorentzian–Gaussian) line shapes are used to fit all peaks. The VBM positions of the samples are obtained by linear extrapolation of the leading edge to the extended base line of the VB spectra. The parameters obtained from Fig. 1 are listed in Table I for clarity. The peak located at 1021.09 ± 0.05 eV in the CL spectrum of Zn 2*p*3/2 state recorded on the ZnO sample has a quite symmetric shape, as shown in Fig. 1(a), implying a uniform bonding state corresponding to the Zn–O bond. The CL spectra of Ni 2*p*3/2 are shown in Fig. 1(b), which consist of three components by careful Voigt fitting. All components of Ni 2*p*3/2 located at 853.95 ± 0.05, 855.83 ± 0.05, and 861.26 ± 0.05 eV are attributed to the Ni–O bonds.[20,21] The VB edge of ZnO shown in Fig. 1(c) is used to measure the VBM position. A VBM value of 1.75 ± 0.1 eV is deduced from the VB spectra by linear fitting depicted above. The VB spectra of NiO sample recorded in Fig. 1(c) gives a VBM of 0.36 ± 0.1 eV by the same method as ZnO. Additionally, the CLs of Zn 2*p*3/2 and Ni

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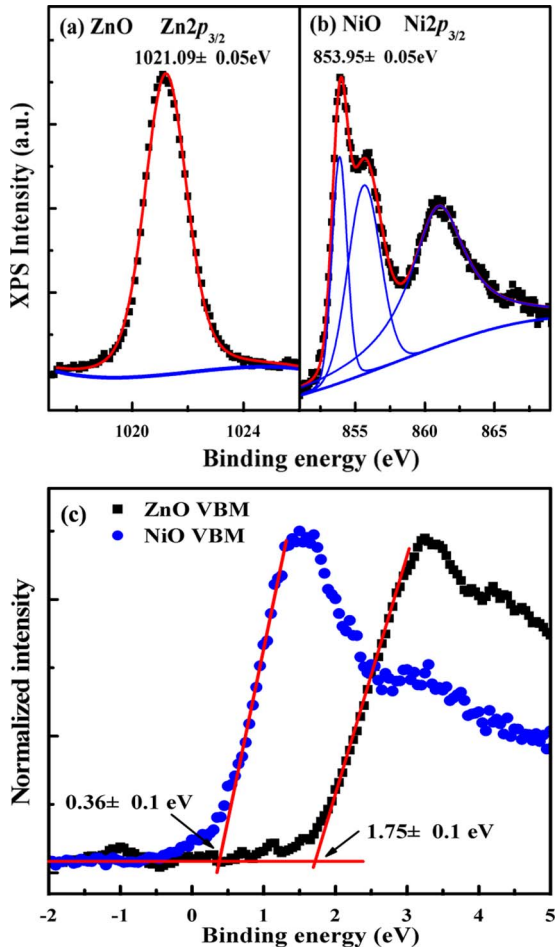

FIG. 1. (Color online) (a) CL of Zn $2p3/2$ recorded on ZnO sample, and (b) CL of Ni $2p3/2$ recorded on NiO sample. (c) The valence-band edge (VBE) spectra for ZnO and NiO samples. All peaks have been fitted to Voigt line shapes and the VBM values are determined by liner extrapolation of the leading edge to the base line.

$2p3/2$ in the ZnO/NiO heterojunction are shown in Figs. 2(a) and 2(b), respectively. Compared with the spectra recorded on the ZnO and NiO samples, the Zn $2p3/2$ peak of Zn–O bond in ZnO/NiO is shifted to ~0.93 eV to a binding energy of 1022.02 ± 0.05 eV, and the Ni $2p3/2$ CL of Ni–O bond is shifted to 853.67 ± 0.05 eV. According to Eq. (1), the VBO value is calculated to be 2.60 ± 0.20 eV.

It is well known that strain existing in the ZnO overlayer of the heterojunction will induce a piezoelectric field, which can affect the measured value, as explained by Martin *et al.*[22] The magnitude of strain is dependent on lattice mismatch

TABLE I. Peak positions of CL and VBM positions used to calculate the VBO of *n*-ZnO/*p*-NiO heterojunction.

Sample	Region	Binding energy (eV)
n-ZnO	Zn $2p3/2$	1021.09 ± 0.05
	VBM	1.75 ± 0.1
p-NiO	Ni $2p3/2$	853.95 ± 0.05
	VBM	0.36 ± 0.1
n-ZnO/*p*-NiO	Zn $2p3/2$	1022.02 ± 0.05
	Ni $2p3/2$	853.67 ± 0.05

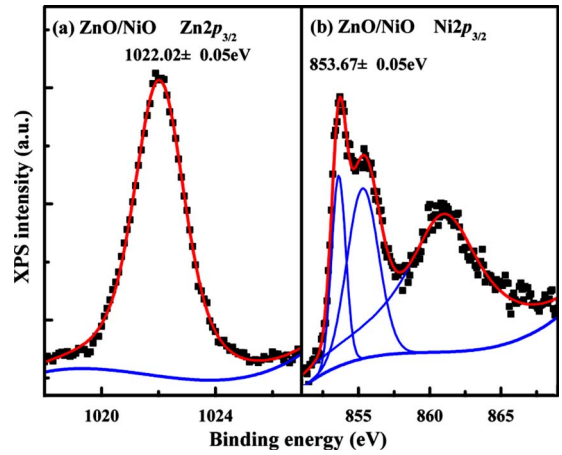

FIG. 2. (Color online) CLs of Zn $2p3/2$ and Ni $2p3/2$ in the *n*-ZnO/*p*-NiO heterojunction.

and film thickness. In order to determine the lattice mismatch between ZnO and NiO, an XRD plot, shown in Fig. 3, was recorded by standard θ-2θ scanning. The vertical coordinate is a logarithmic form for further detail. There are only two peaks recorded in the range of 25°–70°. The peak with large angle is from Al_2O_3 (006) and is used to calibrate the peak position of NiO thin film. The peak at 37.24° originates from cubic NiO (111), indicating the NiO thin film has a single orientation. According to Bragg's equation, the lattice constant of the NiO thin film is calculated to be 0.418 nm. It is deduced that the (111) plane of NiO with cubic structure has a hexagon lattice of 0.296 nm. The lattice constant of ZnO in the *a*-axis direction is 0.325 nm, is much larger than one of NiO (111). Therefore, the critical thickness is very thin. In the present experiment, the 8-nm-thick ZnO film grown on NiO layer is thick enough to be completely relaxed. Referring to the case of InN/ZnO heterojunction (the lattice mismatch is larger than that of ZnO/NiO), 1 ML (0.26 nm) thickness is approximately treated as completely relaxed for strain.[23] The lattice mismatch between ZnO/NiO is larger than that between InN/ZnO.[23] So, the critical thickness of ZnO grown on NiO is not more than 1 ML. The 8-nm-thick ZnO thin film grown on NiO layer should be relaxed and the strain-induced piezoelectric field is not considered in this work.

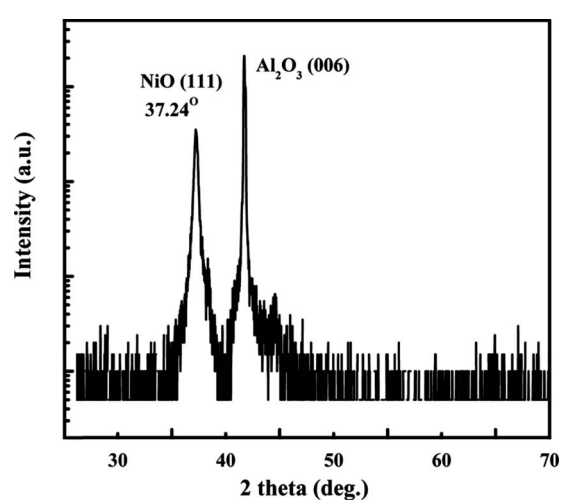

FIG. 3. XRD pattern of the NiO thin film on the sapphire substrate.

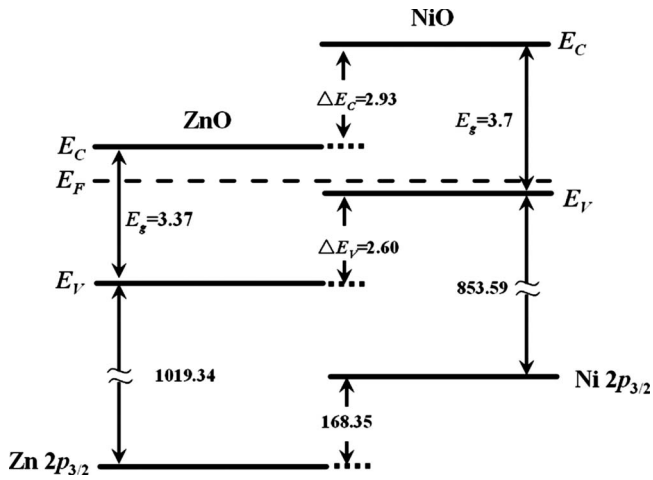

FIG. 4. Schematic diagram of type-II band alignment of a ZnO/NiO heterojunction.

According to Anderson's model, the CBO of ZnO/NiO heterojunction is 2.74 eV due to their electron affinities of 4.2 and 1.46 eV, respectively.[24,25] Consequently, the VBO is deduced to be 2.41 eV and well agreed with our experimental result. In addition, Ishida *et al.*[26] measured the VBO of ZnO/NiO:Li heterojunction to be 2.9 eV by photoelectron emission spectroscopy (PES). PES is slightly larger than our present result because of the acceptor impurities of Li doped into NiO.

The CBO can be estimated by $\Delta E_C = E_g^{\mathrm{ZnO}} - E_g^{\mathrm{NiO}} - \Delta E_V$. The band gaps of ZnO and NiO are 3.37 and 3.7 eV at room temperature, respectively. So the CBO is estimated to be 2.93 ± 0.20 eV, and the CB level of NiO is higher than that of ZnO. As a result, a type-II alignment forms at the interface of ZnO/NiO heterojunction. The schematic diagram of the band alignment is shown in Fig. 4. The ratio of CBO and VBO $\Delta E_C / \Delta E_V$ is estimated to be about 1.13.

In summary, we have presented an experimental determination of the band alignment of the ZnO/NiO heterojunction using XPS. A type-II band alignment with a VBO of $\Delta E_V = 2.60 \pm 0.20$ eV and CBO of $\Delta E_C = 2.93 \pm 0.20$ eV is obtained.

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