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Valence band offset of $ZnO/Zn_{0.85}Mg_{0.15}O$ heterojunction measured by x-ray photoelectron spectroscopy

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X-ray photoelectron spectroscopy was used to measure the valence band offset at the $ZnO/Zn_{0.85}Mg_{0.15}O$ heterojunction grown by plasma-assisted molecular beam epitaxy. The valence band offset (ΔE_V) is determined to be 0.13 eV. According to the experimental band gap of 3.68 eV for the $Zn_{0.85}Mg_{0.15}O$, the conduction band offset (ΔE_C) in this system was calculated to be 0.18 eV. The $\Delta Ec:\Delta Ev$ in $ZnO/Zn_{0.85}Mg_{0.15}O$ heterojunction was estimated to be 3:2. © *2008 American Institute of Physics*. [DOI: 10.1063/1.2977478]

ZnO with a wide band gap of 3.37 eV and an exciton binding energy of 60 meV has been under intensive investigation for its potential use in blue and ultraviolet (UV) optoelectronic devices.[1,2] Recently, many groups have fabricated homojunction or heterojunction light-emitting diodes (LEDs) based on ZnO and realized electroluminescence (EL).[3–6] In order to construct optical and electrical confinement structures, a barrier material with larger band gap has to be proposed. ZnMgO alloy is one of the most promising barrier materials because its lattice constant is very close to that of ZnO in which carriers and photons are confined in well layers.[7,8] To improve the EL emission in UV region, ZnO/ZnMgO quantum well structures had been applied in fabricating LEDs.[9] In designing LED structures in ZnMgO/ZnO quantum well structures, it is wanted to have the valence and conduction band offsets between the well and barrier layer. Although ZnMgO/ZnO quantum wells and supperlattice structures have been frequently reported, there has been little information on the conduction and valence band offsets between ZnO and ZnMgO.[10,11] Moreover, experimental data on band alignment of ZnO/ZnMgO heterojunctions are still less. X-ray photoelectron spectroscopy (XPS) has been demonstrated to be a direct and powerful tool for measuring the band discontinuities of heterojunctions,[12–16] which was usually used to characterize the band configuration at the interface of heterostructures.

In this letter, we report an XPS study on the valence band offset (ΔE_V) at a $Zn_{0.85}Mg_{0.15}O/ZnO$ heterojunction. The ZnO and $Zn_{0.85}Mg_{0.15}O$ layers were grown by plasma-assisted molecular beam epitaxy (P-MBE) on sapphire substrate and no phase separation was detected at this Mg concentration.

The samples (ZnO, $Zn_{0.85}Mg_{0.15}O$, and $ZnO/Zn_{0.85}Mg_{0.15}O$ heterostructure) were grown on *c*-sapphire substrates by P-MBE. Elemental Zn (99.9999%) and Mg (99.999%) contained in separate Knudsen cells were used as the group-II precursors, while oxygen (O_2, 99.999%) treated in a radio frequency (rf) plasma cell as the group-VI precursor. The background vacuum in the growth chamber was about 1×10^{-9} mbar. The oxygen flow rate was controlled by a mass flow controller. During the growth, the rf power of oxygen plasma was fixed at 300 W. The oxygen flow rate was fixed at 0.8 SCCM (SCCM denotes standard cubic centimeter per minute at STP), and the Zn source and Mg source were maintained at 240 and 260 °C, respectively. The films were grown at 650 °C. A 500-nm-thick ZnO, 500 nm $Zn_{0.85}Mg_{0.15}O$, and 5 nm ZnO/500 nm $Zn_{0.85}Mg_{0.15}O$ were fabricated on *c*-sapphire substrates, respectively. Reflection high-energy electron diffraction was used to monitor the epitaxial growth of the single wurtzite phase ZnO and $Zn_{0.85}Mg_{0.15}O$. Its nominal carrier concentration and Hall mobility were 2.5×10^{18} cm^{-3} and 14 $cm^2/V\,s$, respectively. By x-ray diffraction (XRD) measurements, the single (0002) reflection peak with full width at half maximum (FWHM) of 0.08° is observed in ZnO film, which indicates that high quality film was obtained. The Mg composition was verified to be about 15% by the calibrated XPS measurements. The band gap of our ZnMgO determined from photoluminescence measurements was 3.68 eV. No phase sepa-

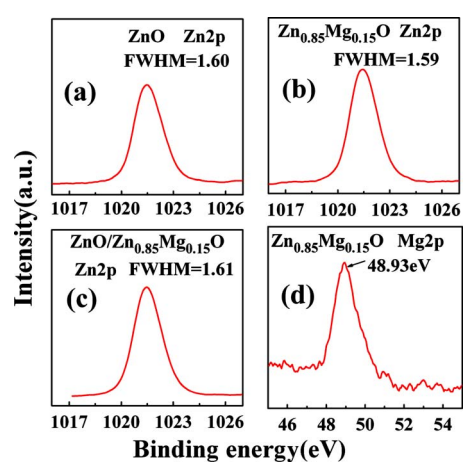

FIG. 1. (Color online) CL Zn $2p3/2$ spectra of ZnO (a) and $Zn_{0.85}Mg_{0.15}O$ (b) and ZnO/ZnMgO (c) samples, Mg $2p$ spectra of $ZnO/Zn_{0.85}Mg_{0.15}O$ (d) sample.

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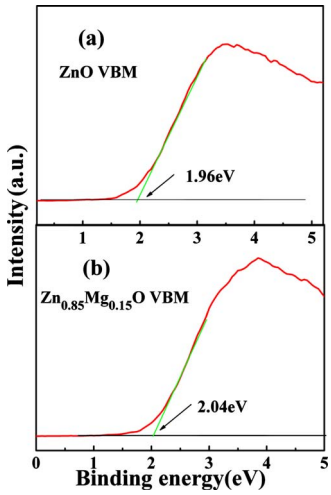

FIG. 2. (Color online) The VB spectra for ZnO (a) and $Zn_{0.85}Mg_{0.15}O$ (b) samples. The VBM values are determined by linear extrapolation of the leading edge to the base line.

ration was observed in the ZnMgO films, as confirmed by XRD and optical-absorption spectra. The XPS was performed by an ESCALAB 250 XPS instrument with Al $K\alpha$ ($h\nu$=1486.6 eV) as the radiation source, which is competent for precisely calibrating work function and Fermi energy level. All XPS spectra were calibrated by the $C\,1s$ peak (284.6 eV). The air absorption and contaminations on surfaces may influence the precise of measurements. To get rid of the contamination effect, all the samples were subjected to a surface cleaning procedure by Ar+ bombardment. After the bombardment, peaks related to impurities were greatly reduced.

XPS has been extensively employed in determining the ΔE_V at heterojunction interfaces, which lies on a core-level photoemission-based method. Appropriate shallow core-level peaks were referenced to the top of the valence band for the ZnO and ZnMgO thick films, using a linear extrapolation method to determine the valence band maximum (VBM). The resulting binding energy differences between the core peaks and valence band minimum for the single layer were then combined with core-level binding energy differences for the heterojunction sample to obtain the ΔE_V. This standard method can be depicted by the formula as follows. As shown on the ZnO and $Zn_{0.85}Mg_{0.15}O$ band diagram in Figs. 1 and 2. The ΔE_V is obtained by the following expression:

$$\Delta Ev = (E_{\mathrm{Zn}\,2p}^{\mathrm{ZnO}} - E_{\mathrm{VBM}}^{\mathrm{ZnO}}) - (E_{\mathrm{Zn}\,2p}^{\mathrm{ZnMgO}} - E_{\mathrm{VBM}}^{\mathrm{ZnMgO}}) + \Delta E_{\mathrm{CL}}, \quad (1)$$

where $(E_{\mathrm{Zn}\,2p}^{\mathrm{ZnO}} - E_{\mathrm{VBM}}^{\mathrm{ZnO}})$ is the energy difference between Zn $2p$ and VBM in the ZnO film, $(E_{\mathrm{Zn}\,2p}^{\mathrm{ZnMgO}} - E_{\mathrm{VBM}}^{\mathrm{ZnMgO}})$ is the energy difference between Zn $2p$ and VBM in the ZnMgO film, $\Delta E_{\mathrm{CL}} = (E_{\mathrm{Zn}\,2p}^{\mathrm{ZnO}} - E_{\mathrm{Zn}\,2p}^{\mathrm{ZnMgO}})$ is the energy difference between Zn $2p$ core levels (CLs) in the ZnO/ZnMgO heterojunction, respectively. The CL spectra of Zn $2p3/2$ recorded on the ZnO sample is shown in Fig. 1(a), which are quite symmetric, indicating the uniform bonding state. The only peak located at 1021.55 eV corresponds to the Zn–O bond. Similarly, the CL of Zn $2p3/2$ in ZnMgO is determined to be 1021.50 eV in Fig. 1(b). The Zn $2p3/2$ of the ZnO/ZnMgO heterojunction is shown in Fig. 1(c). The FWHM of Zn $2p3/2$ peak of ZnO/ZnMgO (1.61 eV) has no obvious difference with that of the Zn $2p3/2$ in the ZnO (1.60 eV) and ZnMgO (1.59 eV) samples. Therefore, it can be considered that the Zn $2p$ from the ZnO layer and ZnMgO layer in the ZnO/ZnMgO heterojunction coincides in the spectra, and the $\Delta E_{\mathrm{CL}} = (E_{\mathrm{Zn}\,2p}^{\mathrm{ZnO}} - E_{\mathrm{Zn}\,2p}^{\mathrm{ZnMgO}}) = 0$. Figure 1(d) is the Mg $2p$ of the ZnO/ZnMgO heterojunction, which also supports that the Zn $2p$ of ZnO/ZnMgO is composed of Zn $2p$ of ZnO and ZnMgO.

The valence band (VB) spectra recorded on ZnO and ZnMgO samples are shown in Fig. 2. This linear method has already been widely used to determine the VBM of semiconductors.[17,18] Figure 2(a) shows the VB XPS spectra of the ZnO sample. A VBM value of 1.96 eV is deduced from the VB spectra by linear fitting as depicted above. The VB XPS spectra recorded on ZnMgO in Fig. 2(b) shows a VBM of 2.04 eV by the same method.

Table I shows a summary of the band offset results. The ΔE_V of $ZnO/Zn_{0.85}Mg_{0.15}O$ heterojunction is calculated to be 0.13 eV by placing those experimental values into Eq. (1).

Figure 3 shows the schematic diagram of the energy band lineups in the ZnO/ZnMgO heterostructure with all of the energy scales included. The conduction-band offset (ΔE_C) can be calculated by $\Delta Ec = E_g^{\mathrm{ZnO}} - E_g^{\mathrm{ZnMgO}} - \Delta Ev$. The band gaps of ZnO and $Zn_{0.85}Mg_{0.15}O$ are 3.37 and 3.68 eV at room temperature, respectively. So the ΔE_C is estimated to be −0.18 eV, indicating that a type-I alignment for $ZnO/Zn_{0.85}Mg_{0.15}O$ heterojunction. The band gap difference of 0.31 eV between the $Zn_{0.85}Mg_{0.15}O$ and ZnO has an almost 3:2 ratio between ΔE_C and ΔE_V. Coli and Bajaj have demonstrated that $\Delta E_C/\Delta E_V$ is in the range 3/2–7/3 in ZnO/ZnMgO superlattice,[11] which supports the rationality of our results.

In the ΔE_V measurements, strain is an important impact factor. The critical thickness of the ZnO/MgO is reported to

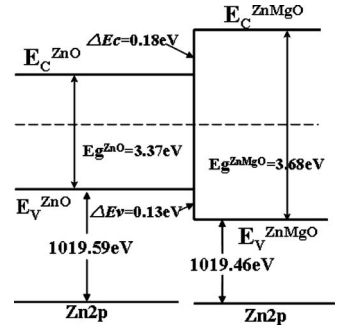

FIG. 3. Energy band diagram of thin $ZnO/Zn_{0.85}Mg_{0.15}O$ heterojunction interface. A type-I heterojunction is formed.

TABLE I. Values of band offsets determined in our experiment.

ZnO Zn $2p3$	ZnO VBM	Zn $2p3$-ZnO VBM	ZnMgO Zn $2p3$	ZnMgO VBM	Zn $2p3$-ZnMgO VBM	ZnO/ZnMgO Zn $2p3$-Zn $2p3$	Valence band offset ΔE_V
1021.55 (eV)	1.96 (eV)	1019.59 (eV)	1021.50 (eV)	2.04 (eV)	1019.46 (eV)	0 (eV)	0.13 (eV)

be 5.5 nm.[19] The lattice mismatch between ZnO/MgO is larger than that between $ZnO/Zn_{0.85}Mg_{0.15}O$. For the ZnO film grown on $Zn_{0.85}Mg_{0.15}O$, 5 nm is far below the critical thickness. Therefore, the ZnO on $Zn_{0.85}Mg_{0.15}O$ suffers tensile strain.[20] Fortunately, the strain is so small that it can be neglected in our work. For example, the *c*-axis lattice constant of the $Zn_{0.85}Mg_{0.15}O$ (namely ZnO *c*-axis lattice constant) is 0.5178 nm determined by XRD, which shows a 0.48% mismatch with ZnO. According to the biaxial relaxation coefficient $R^B=-\varepsilon_{zz}/\varepsilon_{xx}$, [$\varepsilon_{xx}$ and ε_{zz} are the strain perpendicular and parallel to *c*-axis direction, respectively, the R^B is 1.035 for ZnO (Ref. 21)], the *a*-axis strain is about 0.46%. In ZnO/MgO heterostructure, the 8.3% mismatch brings a shift of 220 meV on ΔE_V.[22] By linear extrapolation method, the strain in $ZnO/Zn_{0.85}Mg_{0.15}O$ is less than 12 meV, the error from which is acceptable in this work.

In summary, XPS determinations of the ΔE_V of $ZnO/Zn_{0.85}Mg_{0.15}O$ heterojunctions were performed, which shows a type-I band alignment with $\Delta E_V=0.13$ eV and $\Delta E_C=0.18$ eV. The determination of the band alignment indicates that $ZnO/Zn_{0.85}Mg_{0.15}O$ is competent for confining both electron and hole, which is important for the design and application of ZnO based devices.

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