Valence-band offset of epitaxial ZnO/MgO (111) heterojunction determined by x-ray photoelectron spectroscopy

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Valence-band offset of epitaxial ZnO/MgO (111) heterojunction determined by x-ray photoelectron spectroscopy

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The valence-band offset of ZnO/MgO (111) heterojunction has been directly measured by x-ray photoelectron spectroscopy. Excluding the strain effect, the valence-band offset is determined to be 0.87 ± 0.20 eV, and the conduction-band offset ΔE_C is deduced to be -3.59 ± 0.20 eV, indicating that ZnO/MgO heterojunction has a type-I band alignment. The conduction-band and valence-band offset of MgO/ZnO is used to interpret the origination of *p*-type conduction in undoped $Mg_xZn_{1-x}O$ alloy and deeper acceptor level in undoped and N-doped *p*-type $Mg_xZn_{1-x}O$ alloy than in ZnO. © *2008 American Institute of Physics*. [DOI: 10.1063/1.2924279]

Since ZnO has a large direct band gap and high exciton binding energy, it has been considered as a promising material in the field of blue and ultraviolet (UV) light-emitting devices (LEDs) and laser diodes (LDs).[1,2] Recently, many research groups have fabricated homo- or heterojunction LEDs based on ZnO and realized electroluminescence (EL).[3–8] To improve EL emission in UV region, some of them have applied the quantum well or superlattice structure to fabricate LEDs, in which carriers and photons are confined in well layers, for example, Ryu *et al.* have realized LDs based on BeZnO/ZnO multiple quantum well.[9] $Mg_xZn_{1-x}O$ alloy, another potential barrier material, has been proposed and widely investigated because MgO has a wider band gap of 7.83 eV than ZnO and has a good solid solution with ZnO.[10] Thus, $Mg_xZn_{1-x}O$ alloy has an adjustable band gap in the range from 3.37 to 7.83 eV, which is essential for acting as a barrier layer for $Mg_xZn_{1-x}O$/ZnO quantum well structure. The valence-band offset (VBO) of $Mg_xZn_{1-x}O$ with respect to ZnO is not only an important parameter for $Mg_xZn_{1-x}O$/ZnO quantum well structure, but also related to other properties of $Mg_xZn_{1-x}O$. For instance, acceptor levels in *p*-type MgZnO alloy are strongly dependent on the valence-band maximum (VBM) positions. The lower VBM position will result in deeper acceptor level,[11,12] which influences electrical properties of MgZnO alloy. Therefore, it is necessary to measure the VBO of MgZnO/ZnO heterostructure, especially of MgO/ZnO heterostructure. In the present work, the VBO of ZnO/MgO (111) heterojunction is determined by x-ray photoelectron spectroscopy (XPS).

To measure VBO of ZnO/MgO heterojunction, three samples were prepared on *c*-sapphire substrates by plasma-assisted molecular beam epitaxy. One is 650-nm-thick MgO thin film directly deposited on *c*-sapphire substrate. The others are 5 and 500-nm-thick ZnO films deposited on *c*-sapphire substrates with 650-nm-thick MgO buffer layers. The MgO buffer layers are used to suppress appearance of 30° rotation domain in ZnO layer.[13] The substrate temperature was fixed at 650 °C and the O_2 gas flux was 1.0 SCCM (SCCM denotes cubic centimeter per minute at STP) in the whole growth process for all samples. Zinc and magnesium source temperature was 235 and 325 °C, respectively. The 500-nm-thick ZnO thin film has a carrier concentration and electron mobility of 9.6×10^{16} cm^{-3} and 5.9 cm^2/V s. XPS was performed by an ESCALAB 250 XPS instrument with Al $K\alpha$ ($h\nu = 1486.6$ eV) x-ray radiation source, which can precisely calibrate work function and Fermi energy level. All XPS spectra were calibrated by the C 1*s* peak (284.6 eV).

The VBO of ZnO/MgO heterojunction can be calculated by the following formula:

$$\Delta E_V = \Delta E_{\mathrm{CL}} + (E^{\mathrm{MgO}}_{\mathrm{Mg}\ 1s} - E^{\mathrm{MgO}}_{\mathrm{VBM}}) - (E^{\mathrm{ZnO}}_{\mathrm{Zn}\ 2p} - E^{\mathrm{ZnO}}_{\mathrm{VBM}}), \quad (1)$$

where $\Delta E_{\mathrm{CL}} = E^{\mathrm{ZnO}}_{\mathrm{Zn}\ 2p} - E^{\mathrm{MgO}}_{\mathrm{Mg}\ 1s}$ is the energy difference between Zn 2*p* and Mg 1*s* core levels (CL) in the ZnO/MgO heterojunction, $(E^{\mathrm{MgO}}_{\mathrm{Mg}\ 1s} - E^{\mathrm{MgO}}_{\mathrm{VBM}})$ is the energy difference between Mg 1*s* and VBM in the MgO film, and $(E^{\mathrm{ZnO}}_{\mathrm{Zn}\ 2p} - E^{\mathrm{ZnO}}_{\mathrm{VBM}})$ is the energy difference between Zn 2*p* and VBM in the ZnO film. The CL and VB region XPS spectra for ZnO, MgO and ZnO/MgO 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 fitting peaks and VBM positions are listed in Table I. The peak located at 1020.82 ± 0.05 eV in the CL spectrum of Zn $2p_{3/2}$ state of ZnO has a symmetric shape, as shown in Fig. 1(a), implying a uniform Zn–O bonding state. The VB edge of ZnO shown in Fig. 1(b) is used to measure the VBM position. The VBM position is determined to be 1.92 ± 0.05 eV, which indicates the Fermi level is located at 1.45 eV below CBM and close to center of band gap. Similarly, the CL of Mg 1*s* and VBM position in MgO are determined to be 1301.65 ± 0.05 and 1.67 ± 0.05 eV, respectively, as shown in Figs. 1(c) and 1(d). Additionally, the CLs of Zn $2p_{3/2}$ and Mg 1*s* in the ZnO/MgO heterojunction are determined to be 1019.75 ± 0.05 and 1301.92 ± 0.05 eV, respectively, as shown in Figs. 1(e) and 1(f). According to Eq. (1), the VBO of ZnO/MgO heterojunction is determined to be 1.09 ± 0.20 eV. However, this result does not exclude the

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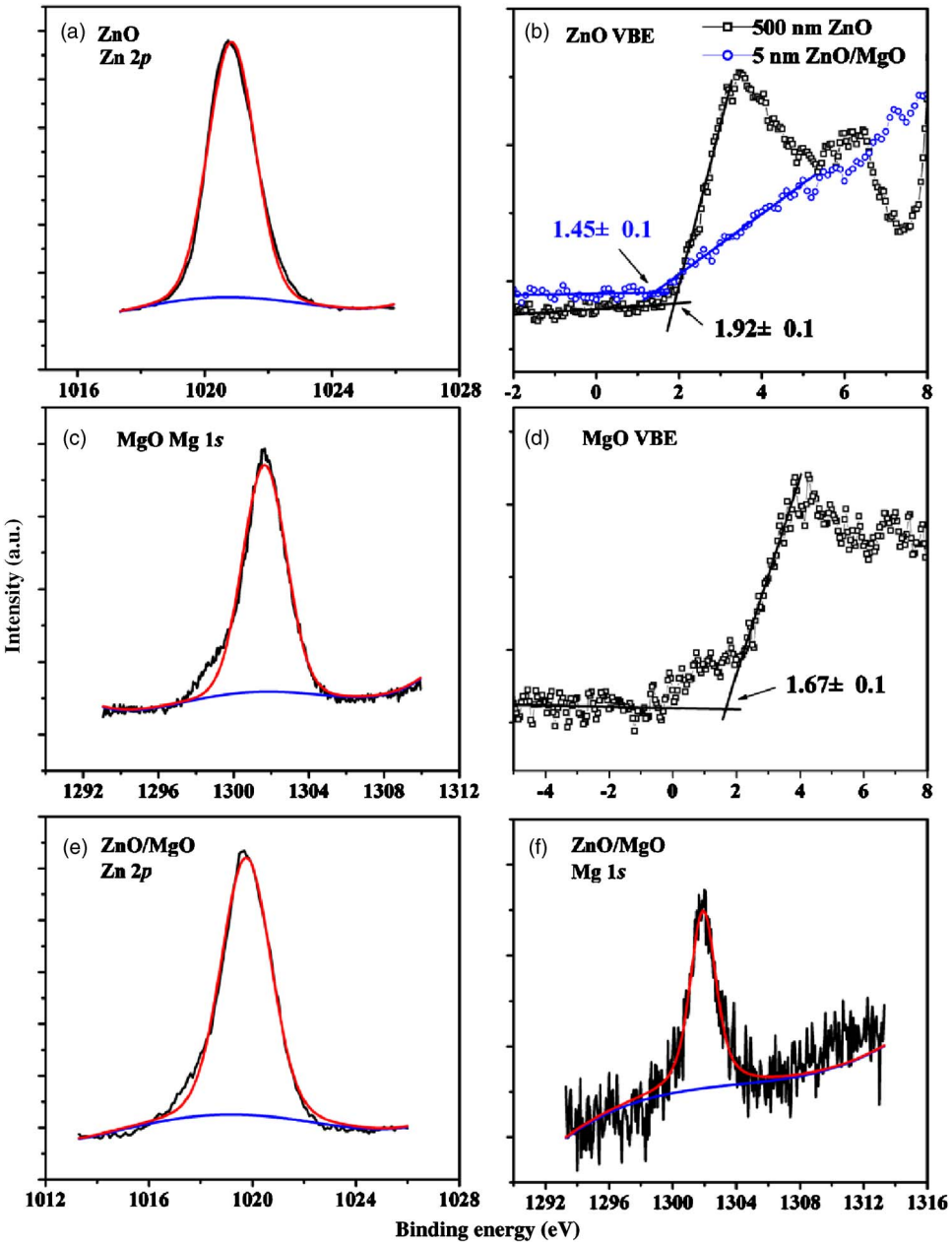

FIG. 1. (Color online) XPS spectra of all samples. Zn $2p_{3/2}$ core level (a) in ZnO and (e) in ZnO/MgO, Mg 1*s* core level (c) in MgO and (f) in ZnO/MgO. (b) The VBE of 500-nm-thick ZnO and 5-nm-thick ZnO grown on MgO buffer as well as (d) the VBE of MgO.

effect of biaxial strain on VBO. The 5-nm-thick ZnO thin film grown on MgO buffer is thinner than the critical thickness determined by Park *et al.*[14] So the 5-nm-thick ZnO thin film is subjected to large biaxial compressive strain. In order to get rid of the effect of biaxial strain on ZnO VBM, the VB edge of 5-nm-thick ZnO film is recorded, as shown in Fig. 1(b). The VBM position of 5-nm-thick ZnO film is determined to be 1.45 ± 0.10 eV, smaller in binding energy than that of 500-nm-thick ZnO film. On the other hand, the VBM position of 5-nm-thick ZnO film can be affected by the MgO layer below because the ZnO film is thin enough. The VBM position of MgO is 0.25 eV higher than that of 500-nm-thick ZnO film, implying that the MgO contributed to the VBM of ZnO is at most 0.25 eV in ZnO/MgO heterojunction. Getting rid of the contribution of MgO below to ZnO VBM, biaxial compressive strain induced VBO is evaluated to be 0.22 eV. As a result, the VBO of ZnO/MgO heterojunction is determined to be 0.87 ± 0.20 eV, in which the effect of biaxial strain is excluded. Zhang *et al.* measured the VBO of InN/ZnO and InN/MgO heterojunctions and obtained the values of 0.82 and 1.59 eV, respectively.[15,16] From these results, the VBO of ZnO/MgO heterojunction is deduced to be 0.77 eV, which is in good agreement with our result. The conduction-band (CB) offset can be calculated by $\Delta E_C = E_g^{\mathrm{ZnO}} - E_g^{\mathrm{MgO}} - \Delta E_V$. The band gaps of ZnO and MgO are 3.37 and 7.83 eV at room temperature, respectively. So the CB offset is estimated to be -3.59 ± 0.20 eV, indicating that

TABLE I. Peak positions of core level and VBM positions used to calculate the VBO of ZnO/MgO heterojunction.

Sample	Region	Binding energy (eV)
ZnO	Zn $2p3/2$	1020.82 ± 0.05
	VBM	1.92 ± 0.1
MgO	Mg 1*s*	1301.65 ± 0.05
	VBM	1.67 ± 0.1
ZnO/MgO	Zn $2p3/2$	1019.75 ± 0.05
	Mg 1*s*	1301.92 ± 0.05
	VBM	1.45 ± 0.1

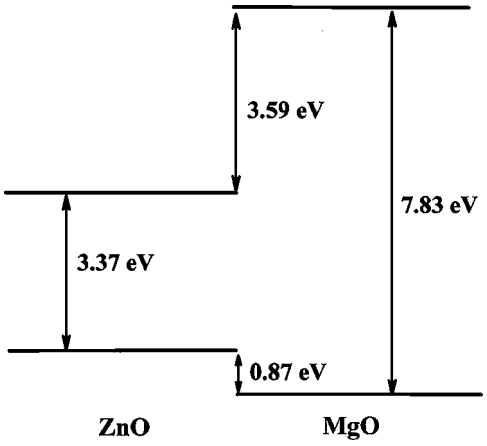

FIG. 2. Schematic diagram of type-*I* band alignment of a ZnO/MgO heterojunction.

a type-*I* alignment for ZnO/MgO heterojunction. The schematic diagram of the band alignment is shown in Fig. 2. The ratio of conduction-band offset (CBO) and VBO $\Delta E_C/\Delta E_V$ is estimated to be about 4. Ohtomo *et al.* obtained $\Delta E_C/\Delta E_V=9$ in $ZnO/Mg_{0.2}Zn_{0.8}O$ superlattice, which is larger than our result.[17] This difference can be due to the following: (i) $\Delta E_C/\Delta E_V$ is related to Mg content and (ii) MgO has a cubic structure but $Mg_{0.2}Zn_{0.8}O$ has a hexagonal structure.

The higher CBM and lower VBM of MgO with respect to ZnO imply that the $Mg_xZn_{1-x}O$ alloy has a higher CBM and lower VBM than ZnO. It can be used to explain origination of *p*-type conduction in undoped $Mg_xZn_{1-x}O$ alloy and the deeper acceptor level of *p*-type $Mg_xZn_{1-x}O$ alloy than that of *p*-type ZnO. In our previous experiments, it was found that, with the increase of Mg content, the undoped *n*-type $Mg_xZn_{1-x}O$ alloy gradually transform into *p*-type $Mg_xZn_{1-x}O$ with low hole concentration of $10^{15}-10^{16}$ cm^{-3}.[18] The transformation of conduction type is due to the shift to higher energy of CBM induced by Mg doping. The donor level in MgZnO alloy becomes much deeper than that in ZnO because the shift of CBM is much larger than that of VBM. As a result, the electron concentration goes down. When the electron concentration is lower than the background hole concentration, the transformation of conduction type occurs. On the other hand, it was also found that the undoped and N-doped *p*-type $Mg_xZn_{1-x}O$ alloy has a deeper acceptor level than in ZnO.[11,18,19] This is due to the lower VBM of MgO with respect to ZnO.

In conclusion, the VB alignment of a ZnO/MgO heterojunction has been determined to be 0.87 ± 0.20 eV, indicating ZnO/MgO heterojunction has a type-*I* band alignment with a CBO of -3.59 ± 0.20 eV. The higher CBM and lower VBM of MgO with respect to ZnO can be used to explain origination of *p*-type conduction in undoped $Mg_xZn_{1-x}O$ alloy and the deeper acceptor level of *p*-type $Mg_xZn_{1-x}O$ alloy than that of *p*-type ZnO.

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