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APPLIED PHYSICS LETTERS **93**, 242107 (2008)

# Valence band offset of InN/4*H*-SiC heterojunction measured by x-ray photoelectron spectroscopy

B. L. Zhang,[1,a)] G. S. Sun,[2] Y. Guo,[1] P. F. Zhang,[1] R. Q. Zhang,[1] H. B. Fan,[1] X. L. Liu,[1,b)] S. Y. Yang,[1] Q. S. Zhu,[1,c)] and Z. G. Wang[1]
[1]*Key Laboratory of Semiconductor Materials Science, Institute of Semiconductors, Chinese Academy of Sciences, P.O. Box 912, Beijing 100083, People's Republic of China*
[2]*Novel Semiconductor Material Laboratory, Institute of Semiconductors, Chinese Academy of Sciences, P.O. Box 912, Beijing 100083, People's Republic of China*

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The valence band offset (VBO) of InN/4*H*-SiC heterojunction has been directly measured by x-ray photoelectron spectroscopy. The VBO is determined to be $0.55 \pm 0.23$ eV and the conduction band offset is deduced to be $-2.01 \pm 0.23$ eV, indicating that the heterojunction has a type-I band alignment. The accurate determination of the valence and conduction band offsets is important for applications of InN/SiC optoelectronic devices. © *2008 American Institute of Physics*. [DOI: 10.1063/1.3046116]

Developments of III-nitride (InN, GaN, and AlN) based semiconductors have been attractive due to their outstanding properties. Recent research has been remarkably focused on InN due to its small electron effective mass, high electron drift velocity, and narrow band gap of 0.7 eV,[1] which makes InN suitable for high performance practical devices such as high electron mobility transistor,[2] heterojunction field-effect transistor,[3] etc. Lots of InN heterojunctions have been employed for device fabrication, among which InN/SiC heterojunction as a good candidate for InN devices because of the small lattice mismatch and the high thermal conductivity has been receiving attention very recently. Hashimoto and co-workers[4–6] reported InN grown on 3*c*-SiC using metal-organic vapor phase epitaxy technique. Losurdo *et al.*[7] and Ive *et al.*[8] grew InN films by molecular beam epitaxy on 4*H*-SiC and 6*H*-SiC templates. It is important to determine the energy band offset of the heterojunction for the design, modeling, and performance analyses of devices. However, to date, there is lack of experimental data available on the interface band alignment parameters for InN/SiC heterojunction. X-ray photoelectron spectroscopy (XPS) has been demonstrated to be a direct and powerful tool for measuring the valence band (VB) discontinuities of heterojunctions.[9–11] In this letter, we report on the experimental study of the electronic structure of the epitaxial model of InN/4*H*-SiC heterojunction. VB offset (VBO) value is determined experimentally by XPS, and conduction band offset (CBO) value is then calculated from the band gaps of InN and 4*H*-SiC.

To see the VBO value, three samples were used in our XPS experiments, namely, a bulk commercial Si-terminated *n*-type 4*H*-SiC substrate misoriented by 8° toward ⟨11−20⟩, a 400-nm-thick InN layer grown on *c*-plane sapphire, and a 5-nm-thick InN layer grown on the *n*-type commercial 4*H*-SiC substrate, respectively. The carrier concentration and the Hall mobility of the *n*-type 4*H*-SiC substrate were determined by Hall measurements in van der Pauw configuration at room temperature to be $6 \times 10^{16}$ cm$^{-3}$ and 350 cm$^2$/V s, respectively. The thick InN film and the heterostructure of InN/4*H*-SiC were grown by metal-organic chemical vapor deposition at 520 °C. In the growth, trimethylindium [$(CH_3)_3In$] and ammonia ($NH_3$) were used as precursors for In and N sources, respectively. Other growth condition details of InN layer can be found in our previous report.[12] The InN film has a wurtzite crystal structure. In x-ray diffraction measurement, the full width at half maximum of InN (0002) peak is only 200 arc sec, and its carrier concentration and Hall mobility were determined by Hall effect to be $5.7 \times 10^{19}$ cm$^{-3}$ and 365.6 cm$^2$/V s from testing a InN/*c*-plane sapphire sample grown under the same conditions. To get a high quality interface, the 4*H*-SiC substrate was *ex situ* cleaned by a standard Radio Corporation of America procedure followed by wet etching in HF solution in order to remove the surface oxide,[13] and before depositing the InN overlayer the 4*H*-SiC substrate was nitrided at 520 °C under an $NH_3$ flow to acquire a high quality interface.

XPS were performed on two instruments, VG MKII XPS and PHI Quantera SXM, with Al $K\alpha$ ($h\nu = 1486.6$ eV) as the monochromatic x-ray radiation source, which had been carefully calibrated on work function and Fermi energy level ($E_F$). The size and power of the x-ray spot are about 100 $\mu$m and 25 W, respectively. During the testing, because a large amount of electrons are excited and emitted from the sample, the sample is always positively charged and the electric field caused by the charge can affect the measured kinetic energy of photoelectron. Since only the relative energy position in each sample is needed to determine the VBO, the absolute energy calibration for a sample has no effect on the universal energy reference. The surface of all the samples was exposed to air so the impurities (e.g., oxygen and carbon) existing on the surfaces may prevent the precise determination of the positions of the VB maximum (VBM). To reduce the contamination effect, all the samples were subjected to a surface clean procedure by Ar$^+$ bombardment with a voltage of 1 kV at a low sputtering rate of 0.5 nm/min, which alleviated damage to the samples. The reduced thickness is calculated to be ~1 nm by the sputtering rate. After the bombardment, peaks related to impurities were greatly reduced, and no new peaks appeared. Based on the formula

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[a)] Electronic mail: zhangbaoli@semi.ac.cn.
[b)] Electronic mail: xlliu@semi.ac.cn.
[c)] Electronic mail: qszhu@semi.ac.cn.

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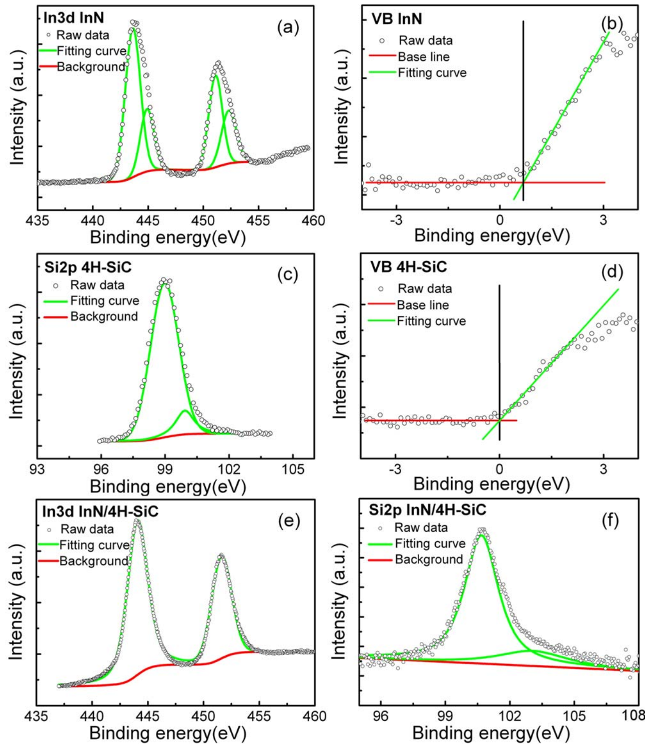

FIG. 1. (Color online) CL In $3d$ spectra recorded on (a) InN and (e) InN/4*H*-SiC samples, Si $2p$ spectra on (c) 4*H*-SiC and (f) InN/4*H*-SiC samples, and VB spectra for (b) InN and (d) 4*H*-SiC samples. All CL peaks have been fitted to the Voigt line shapes using a Shirley background, and the VBM values are determined by linear extrapolation of the leading edge to the base line.

$$\Delta E_v = \Delta E_{\mathrm{CL}} + (E^{\mathrm{SiC}}_{\mathrm{Si}\ 2p} - E^{\mathrm{SiC}}_{\mathrm{VBM}}) - (E^{\mathrm{InN}}_{\mathrm{In}\ 3d} - E^{\mathrm{InN}}_{\mathrm{VBM}}), \qquad (1)$$

from which the VBO ($\Delta E_v$) can be calculated, three parts of the relative energy differences, ($E^{\mathrm{SiC}}_{\mathrm{Si}\ 2p} - E^{\mathrm{SiC}}_{\mathrm{VBM}}$), ($E^{\mathrm{InN}}_{\mathrm{In}\ 3d} - E^{\mathrm{InN}}_{\mathrm{VBM}}$), and $\Delta E_{\mathrm{CL}}$, are required. $\Delta E_{\mathrm{CL}} = (E^{\mathrm{InN}}_{\mathrm{In}\ 3d} - E^{\mathrm{SiC}}_{\mathrm{Si}\ 2p})$ is the energy difference between In $3d$ and Si $2p$ core levels (CLs), which can be measured in the heterojunction sample. ($E^{\mathrm{SiC}}_{\mathrm{Si}\ 2p} - E^{\mathrm{SiC}}_{\mathrm{VBM}}$) and ($E^{\mathrm{InN}}_{\mathrm{In}\ 3d} - E^{\mathrm{InN}}_{\mathrm{VBM}}$) are the 4*H*-SiC and InN bulk constants, which can be obtained from the bulk 4*H*-SiC and thick InN film grown on sapphire by XPS measurement.

TABLE I. XPS CL spectra fitting results and VBM positions obtained by linear extrapolation of the leading edge to the extended base line of the VB spectra.

| Sample | State | Binding energy (eV) |
|---|---|---|
| InN | In $3d_{5/2}$ | $443.62 \pm 0.03$ (In–N) |
| | | $444.92 \pm 0.03$ (In–O) |
| | VBM | $0.68 \pm 0.1$ |
| 4*H*-SiC | Si $2p$ | $98.98 \pm 0.03$ (Si–C) |
| | | $99.88 \pm 0.03$ (Si–O) |
| | VBM | 0 |
| InN/4*H*-SiC | In $3d_{5/2}$ | $444.09 \pm 0.03$ (In–N) |
| | Si $2p$ | $100.68 \pm 0.03$ (Si–C) |
| | | $102.99 \pm 0.03$ (Si–O) |

Figure 1 shows all CL spectra including In $3d$ recorded on InN and InN/4*H*-SiC samples, Si $2p$ on 4*H*-SiC and InN/4*H*-SiC samples, as well as VB spectra recorded on InN and 4*H*-SiC samples. The CL spectra were fitted to Voigt (mixed Lorentzian–Gaussian) line shape with a Shirley background. The VBM positions in the VB spectra were determined by linear extrapolation of the leading edges of the VB spectra to the base lines in order to account for the instrument resolution induced tail.[10,14,15] Since considerable accordance of the fitted line to the original measured data has been obtained, the uncertainty of the CL position should be lower than 0.03 eV, as evaluated by numerous fittings with different parameters. The main uncertainty comes from the difficulty in determining the value of VBM exactly. The parameters deduced from Fig. 1 are summarized in Table I for clarity. The spin-orbit doublet with a splitting energy of 7.49 eV of In $3d$ spectrum in the InN sample is shown Fig. 1(a), which consists of two components by careful Voigt fitting. The first In $3d_{5/2}$ component located at 443.62 eV is attributed to the In–N bonds, and the second at 444.92 shifted by ∼1.3 eV is attributed to In–O bonds. The VBM position of InN is determined by linear extrapolation of the leading edge of the VB spectrum, as shown in Fig. 1(b) with an energy reference of $E^{\mathrm{InN}}_{\mathrm{VBM}} = 0.68$ eV. This linear method has already been widely used to determine the VBM of semiconductors with an accuracy of about ±0.1 eV. As a result, the energy difference of In $3d_{5/2}$ to InN VBM ($E^{\mathrm{InN}}_{\mathrm{In}\ 3d} - E^{\mathrm{InN}}_{\mathrm{VBM}}$) can be determined to be $442.94 \pm 0.13$ eV. The Si $2p$ CL peak consists of two components by careful Voigt fitting, as shown in Fig. 1(c). The prominent one located at ∼98.98 eV stems from the Si emitters within the 4*H*-SiC substrate that have four bonds to carbon atoms, and the other one which is shifted by ∼0.9 eV to a higher binding energy is attributed to the $\mathrm{Si}^{+}$ emitter atoms,[16] which are located at the surface of 4*H*-SiC substrate with one bond to oxygen and three bonds to carbon atoms. Moreover, the high ratio of the prominent peak intensity to the oxygen related peak indicates that only a small quantity of oxygen contamination exists in our samples. Using the same linear extrapolation methods mentioned above, the VB spectra recorded on 4*H*-SiC sample in Fig. 1(d) give a VBM of 0. The energy difference of Si $2p$ to 4*H*-SiC VBM ($E^{\mathrm{SiC}}_{\mathrm{Si}\ 2p} - E^{\mathrm{SiC}}_{\mathrm{VBM}}$) can be determined to be $98.98 \pm 0.13$ eV. The data shown in Figs. 1(c) and 1(d) are both from our previous report.[17] The In $3d$ and Si $2p$ in InN/4*H*-SiC heterojunction are shown in Figs. 1(e) and 1(f), respectively. The CL spectra of In $3d$ in InN/4*H*-SiC heterojunction are quite symmetric, which indicate that the quality of the thin InN film is higher than what we reported previously in Ref. 12. After subtraction of the background, the spectra of In $3d$ and Si $2p$ CLs were well Voigt fitted, and the energy difference between In $3d$ and Si $2p$ CLs can be determined to be $343.41 \pm 0.03$ eV. At the high energy side of Si $2p$, a peak centered at 102.99 eV attributed to the Si–O bonds as that mentioned above can be well fitted. The VBO value is calculated to be $0.55 \pm 0.23$ eV by substituting those values obtained in experiments into Eq. (1).

There are some factors that could impact the experimental result. As XPS measurements are spatially averaged due to the finite mean free path of elastic electrons (1.5–2 nm), band bending could induce a systematic error in our measurements. We checked that this error is much smaller than the average standard deviation of ±0.23 eV given above. Another factor that may affect the precision of the VBO value is the strain-induced piezoelectric field in the overlayer of the heterojunction, as described in Ref. 11. The heterojunction underlayer 4*H*-SiC is thick enough to be completely

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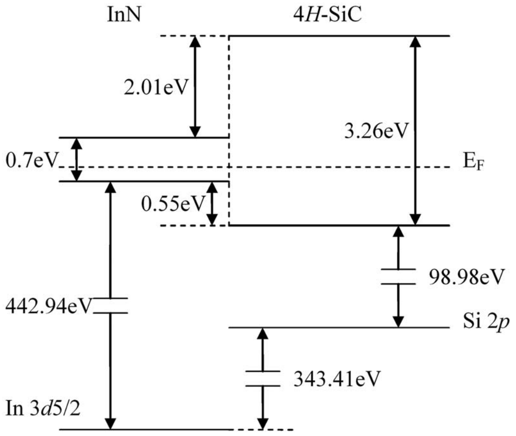

FIG. 2. Energy band diagram of InN/4*H*-SiC heterojunction. A type-I heterojunction is formed in the straddling arrangement.

relaxed. The overlayer (InN thin film) for our as-grown sample is as thick as 5 nm and can be approximately treated as completely relaxed. This approximation should not introduce much error since the critical thickness of the InN on GaN is as thin as 1 ML (~0.26 nm) (Ref. 18) and there is not much difference between the crystal constants of GaN and 4*H*-SiC. Because of this, the strain-induced piezoelectric field is not considered in this work. Since the energy separation between the VBM and $E_F$ can be changed by the band bending, the band bending could also impact the measured VBO values of the heterojunctions.[19] The energy band bends downward at the surface of the InN film and there is an electron accumulation layer, as shown by high resolution electron-energy-loss spectroscopy.[20] Since the electron accumulation layer extends to a deep depth into the film, the thin overlayer (~4 nm after $Ar^+$ sputtering) of the InN/4*H*-SiC sample can be treated as consisting of surface and interface. So, the band bending effect can be neglected in this experiment, as in the measurement of the band offset of the InN/4*H*-SiC heterojunction by others.[10,21] It has been previously noted that $\Delta E_v$ has transitive property.[22] It means for heterojunctions formed between three semiconductors (A, B, and C), if $\Delta E_v$ (A-B) and $\Delta E_v$ (C-B) are known, $\Delta E_v$ (C-A) is also specified. From the reported experiment data, $\Delta E_v$ (SiC−GaN)$=0.5\pm0.1$ eV,[23] $\Delta E_v$ (InN−GaN)$=1.05\pm0.25$ eV,[11] we can deduce $\Delta E_v$ (InN−SiC)$=0.55\pm0.35$ eV, which is comparable to our result, and thus, further confirms that the experimental obtained VBO value is somewhat reliable.

Finally, the CBO ($\Delta E_c$) can be estimated by the formula $\Delta E_c=(\Delta E_g^{\mathrm{InN}}-\Delta E_g^{\mathrm{SiC}})+\Delta E_v$. Using the band gap value ($\Delta E_g^{\mathrm{InN}}=0.7$ eV,[1] $\Delta E_g^{\mathrm{SiC}}=3.26$ eV,[24] the $\Delta E_c$ is deduced to be $-2.01\pm0.23$ eV and the ratio of $\Delta E_c/\Delta E_v$ is close to 40/11. As a result, a type-I band alignment forms at the interface of InN/4*H*-SiC heterojunction, as shown in Fig. 2.

In summary, the VBO of the InN/4*H*-SiC heterojunction has been measured by XPS. A type-I band alignment with a VBO of $\Delta E_v=0.55\pm0.23$ eV and CBO of $\Delta E_c=-2.01\pm0.23$ eV is obtained. The accurate determination of the band alignment of InN/4*H*-SiC is important for the applications of InN and SiC based devices.

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