Bandgap and band offsets determination of semiconductor heterostructures using three-terminal ballistic carrier spectroscopy

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Utilizing ambipolar tunnel emission of ballistic electrons and holes, we have developed a model-independent method to self-consistently measure bandgaps of semiconductors and band offsets at semiconductor heterojunctions. Lattice-matched GaAs/AlGaAs and GaAs/(Al,Ga1-x)0.51In0.49P (100) single-barrier heterostructures are studied at 4.2 K. For the GaAs/AlGaAs interface, the measured band offset ratio is 60.4:39.6 (±2%). For the heterojunction GaAs/AlGaNP (100) interface, this ratio varies with the Al composition and is distributed more in the valence band. The indirect-gap X band offsets observed at the GaAs/AlGaNP interface deviates from predictions by the transitivity rule. © 2009 American Institute of Physics. [doi:10.1063/1.3224914]

Among the most important properties of semiconductors are their bandgaps and how the total bandgap difference distributes between the conduction band offset ΔEC and the valence band offset ΔEV at the heterojunction (HJ) interface between two semiconductors. Understanding such properties is crucial for the design of HJ devices.

Traditionally, bandgaps are measured mostly with optical spectroscopies such as absorption and photoluminescence (PL).¹ Band offsets are measured electrically by thermionic emission and C-V profiling, optically by absorption and PL, and optoelectrically by photoelectron spectroscopies. However, each of these methods has certain limitations.² With a transistor setup, ballistic electron/hole emission spectroscopy (BEES/BHES) utilize ballistic injection of electrons/holes to probe the band offsets of HJs underneath a metal-semiconductor (m-s) interface.³ However, to obtain the genuine barrier heights, a delta doping is needed to reach a flat-band condition across the HJ, which introduces a source of error due to the doping level.⁴ Most of the aforementioned methods require separately designed n-type and p-type HJs to measure ΔEC and ΔEV independently, therefore, the results are not necessarily self-consistent.

In this letter, we report that the bandgap Eg of a semiconductor, as well as both ΔEC and ΔEV at a semiconductor HJ, can be measured on the same device. In contrast with previous BEES studies, our method utilizes selective injection of electrons and holes into the same m-s interface, realized by a collector bias Vc, which tunes the electric field (E-field) in the depletion region.² This enables measurement of the energy maxima in both the conduction band (CB) and the valence band (VB) of the HJ collector. Summing these two values gives the Eg of the corresponding constituent layer. An advantage of our method over optical spectroscopies is the absence of the generation and recombination of electron-hole pairs, therefore, it is free of exciton effects. In our previous report,⁵ however, only one material (Al0.4Ga0.6As) was studied, therefore, band offset information was not obtained. Here we demonstrate that this method allows a precise measurement of ΔEC and ΔEV of a buried HJ over a wide range of constituent compositions.

As a proof of concept, ternary AlGaAs and quaternary AlGaNP III-V alloys are studied. Lattice-matched GaAs/AlGaAs and GaAs/AlGaNP single-barrier (SB) HJs are epitaxially grown on Zn-doped p-GaAs (100) substrates. After growing a 500 nm p-doped (5×10¹⁸ cm⁻³) GaAs buffer layer (layer “4” in Fig. 1, and so forth), the unintentionally doped SB HJ is formed, with a 45 nm GaAs layer (‘3”), a 50 nm AlGaAs or AlGaNP barrier layer (‘2”), and a 5 nm GaAs cap layer (‘1”) for surface passivation. Samples with Al m fraction x=0.0, 0.1, 0.2, 0.3, 0.42, 0.6, 0.8, and 1.0 for Al,Ga1-xAs, and x=0.0, 0.2, 0.35, 0.5, 0.7, 0.85, and 1.0 for Al,Ga1-xIn0.51P are grown under exactly the same condition for each alloy system. Monolithic metal-base transis-

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![FIG. 1.](Color online) Band diagrams (insets) and collector-current (Ic) spectra of Al0.4Ga0.6As sample taken at 4.2 K illustrating the direct and secondary BEES/BHES processes. Letter “E,” “B,” and “C” stand for emitter, base, and collector, respectively. Emitter current Ic=0.8(0.4) mA at Vf=±1.7 V, and the flat-band Vf=±0.5 V for this particular device.
tors, using planar Al/AlOx/Al tunnel junctions as the tunnel emitters, are fabricated using a shadow-mask technique. The GaAs surfaces were treated in a 1:10 solution of NH4OH:H2O for 60 s prior to Al evaporation. All the devices were characterized at 4.2 K to suppress the thermally excited currents.

Ambipolar carrier injection is made possible using BEES/BHES and their secondary/reverse processes (s-BEES/s-BHES) (Fig. 1). For example, in a s-BHES process, hot electrons tunnel into the base from a negatively biased emitter (Vc<0) with the p-type collector unbiased or in reverse bias [Fig. 1(c)]. The repulsive E-field in the CB prevents them from being collected across the m-s interface. Rather, they excite electron-hole pairs in the metal base in an Auger-like process. As a result, hot holes are produced and some of them may be ballistically injected into the VB of the collector and probe the VB barrier height φv. Under a forward Vc, the E-field in the CB becomes attractive to collect hot electrons injected by the direct BEES process, and the CB barrier height φc is probed [Fig. 1(a)]. Similar mechanisms apply for positive Vc [Figs. 1(b) and 1(d)]. Ec of the barrier layer is hence determined by summing these two barriers. The energy resolution of s-BEES is arguably superior to that of BEES owing to the quartic spectral shape of the two-step Auger process, i.e., near the threshold, the collector transfer ratio α=kIc/Ib=(eVE−φv(Vc))4.6 versus α=(eVE−φv(Vc))2 for BEES. Shown in Figs. 2(a) and 2(b), we found that a linear fit of α4.6=α0(εVE−φv(Vc)), with only two free parameters, gives φv(Vc) with a typical resolution ~2 meV at 4.2 K (kBT=0.4 meV), compared with ~20 meV resolution in typical BEES fitted by a multi-valley valley–Kaiser model. The present fitting process does not require band parameters, e.g., effective masses, making it model independent. Note that the measured apparent barrier heights are subject to an image force lowering effect due to the E-field across the HJ. Therefore a series of BEES/s-BEES spectra are measured under constant Vc at small intervals (0.1 V or less). The measured barrier heights indeed depend on Vc [Fig. 2(c)]. φv and φc near the flat-band condition, where the transition from hole to electron injection occurs (telling from the polarity reversal of Ic), are used to calculate the Ec and band offsets.

The main results from the ternary AlGaAs alloy are shown in Fig. 3. The measured φv and φc as functions of Al composition x are shown in Figs. 3(b) and 3(c), respectively. φv increases linearly with x in the full range of Al composition (0<x<1), which is expected because all the VB maxima of AlGaAs are located at the Brillouin zone center. ∆Ey(x) of GaAs/AlGa1−xAs is obtained by ∆Ey(x)=φv(x)−φv(0), where φv(0) is the value for GaAs. Here it is assumed that the Fermi level pinning position at the m-s interface (with regard to the vacuum level) remains unchanged for devices with different Al compositions, as supported by the fact that the measured φv shows a nearly perfect linear dependence on x. A linear fit gives ∆Ey(x)=(0.57±0.01)x (eV). ∆Ec(x) of GaAs/AlGa1−xAs is derived from ∆Ec(x)=φc(x)−Ec(0)+φc(0), where Ec(0) is the value for GaAs (taken as 1.519 eV at 4.2 K). The derived ∆Ec(x) increases linearly with x in the direct regime, i.e., ∆Ec(x)=(0.87±0.01)x (eV) for x<0.42. A direct-indirect transition of the CB minima at x=0.42 is indicated by the abrupt slope change at this composition. In the indirect-gap regime, ∆Ec(x) slowly increases with x. The direct-gap Γ band offset ratio r=∆Ec/∆Ey is found to be 60.4:39.6 (±2%), which agrees with the 60:40 rule.8

It is found that for samples with x=0 and 0.1, although φv can be readily measured both by BEES and s-BEES, φc cannot be measured due to the overwhelming internal hole current under the forward VC needed for electron injection. For x=0.2, the measured Ec of AlGa1−xAs [Fig. 3(a)] agree well with the established values7 (within 2%). In the direct-gap regime, no obvious band bowing effect was observed.9 In the indirect-gap regime, Ec of L valley instead of the lower lying X valley in the CB is observed. This may be attributed to the short mean free path of X electrons in GaAs materials,10 consistent with BEES results on direct-gap GaAs/AlGa1−xAs(x≈0.42) SB HJs.11

The main results from the quaternary AlGaInP alloy are shown in Fig. 4. Figures 4(b) and 4(c) show the measured φv.
Fig. 4. Al composition $x$ dependence of (a) $E_g$ of (Al$_{1-x}$Ga$_x$)$_{0.51}$In$_{0.49}$P (solid lines are from Ref. 7), (b) $\phi_v$ and $\Delta E_G$ of GaAs/(Al$_{1-x}$Ga$_x$)$_{0.5}$In$_{0.5}$P, and (c) $\phi_C$ and $\Delta E_C$ of GaAs/(Al$_{1-x}$Ga$_x$)$_{0.5}$In$_{0.5}$P. Dotted lines and dashed line are deduced from Refs. 12 and 13, respectively. Vertical arrows show the transition at $x \approx 0.7$.

and $\phi_C$, as well as $\Delta E_V(x)$ and $\Delta E_C(x)$ derived the same way as above. $\Delta E_V(x)$ shows a linear dependence on $x$ for $0 < x < 0.7$ as $\Delta E_V(x) = 0.293 + 0.306x$ (eV) (±3%), which can be explained by an argument similar to the case for AlGaAs. For $x > 0.7$, $\Delta E_V(x)$ decreases with $x$ as $\Delta E_V(x) = 0.541 - 0.037x$ (±4%). $\Delta E_C(x)$ shows a more complicated behavior. In the direct-gap regime ($0 < x < 0.5$), $\Delta E_C(x)$ increases linearly with $x$ as $\Delta E_C = 1.72 + 0.358x$ (±7%). The measured $\Gamma$ band offsets agree well with the expected values deduced by the transitivity rule, i.e., adding $\Delta E_C = 0.31$ eV and $\Delta E_C = 0.18$ eV of the GaInP-GaAs HJ to the reported $\Delta E_V$ and $\Delta E_C$ on AlGaInP-GaInP HJ $^{12,13}$ respectively. At $x > 0.5$, $\Delta E_C$ starts to decrease signaling a direct-indirect transition of the CB minima. Surprisingly, $\Delta E_C$ increases with $x$ again at $x > 0.7$ as $\Delta E_C = 0.242 + 0.097x$ (±1%). The measured $E_g$ of (Al$_{1-x}$Ga$_x$)$_{0.51}$In$_{0.49}$P [Fig. 4(a)] match well with the established values' (within 0.4%). The indirect $E_g$ is found to be from the $X$ valley in the CB. $E_g$ does not show a transition at $x \approx 0.7$ because the opposite trends in the CB and the VB at $x > 0.7$ are effectively canceled out. The $\Gamma$ band offset ratio $r$ for heteroanion GaAs/AlGaInP HJs increases from 37:63 at $x = 0$ to 44:56 at $x = 0.5$ (±8%). The band offsets tend to distribute more in the VB, as predicted by the common anion rule.$^5$

It is intriguing that the observed indirect band offsets deviate from predictions by the transivity rule. Strain effects should be minimal since all the epilayers were grown at the same temperature and the AlGaInP layers are nearly lattice-matched (with ±0.1% compressive strain measured by x-ray diffraction) to the GaAs substrates. The ordering effect in AlGaInP alloys can be excluded because it would cause a lowering of the $E_g$.$^4$ which is not observed in our case. We tentatively attribute the breakdown of the transitivity rule as a result of the interfacial dipoles$^{15}$ formed at the polar GaAs/AlGaInP (100) interface, which awaits further investigation.

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