Energy band discontinuities in heterojunctions measured by internal photoemission

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(Received 6 May 1985; accepted for publication 12 June 1985)

A novel method involving internal photoemission has been developed to determine the conduction band discontinuity ΔE_c of heterojunctions. The method is straightforward, accurate, and assumes minimum unknowns; and has been applied to $\mathrm{GaAs/Al}_x\mathrm{Ga}_{1-x}\mathrm{As}$ heterojunctions. We have found for $x<0.4$ that $\Delta E_c \cong 0.62\, \Delta E_g$, where ΔE_g is the band-gap difference. For $x>0.4$, the apparent ΔE_c is considerably smaller.

One of the most important parameters of heterojunctions is the conduction (or valence) band discontinuity across the interface. The $\mathrm{GaAs/Al}_x\mathrm{Ga}_{1-x}\mathrm{As}$ heterojunctions are at present the most widely investigated and used in a variety of structures. Until recently it has been accepted widely that the difference between the energy gaps (ΔE_g) is distributed with a conduction (valence) band discontinuity $\Delta E_c = 0.85\,\Delta E_g$ ($\Delta E_v = 0.15\,\Delta E_g$).[1–3] Recent experimental results, which rely on photoluminescence from parabolic wells,[4] capacitance-voltage (C-V) profiling through[5] and thermionic emission above barriers,[6–8] and the carrier concentrations in selectively doped heterojunctions,[9] suggest that $\Delta E_c \cong 0.6\,\Delta E_g$, for $x \leqslant 0.4$. All those methods require rather elaborate analysis of the data.

In this letter we report on the measurement of ΔE_c utilizing a novel internal photoemission (IPE) method which can be universally used for many types of heterojunctions. Moreover, the method is very direct; the needed parameters are measured on the actual samples, resulting in an accurate determination of ΔE_c. The method is applied to GaAs/AlGaAs heterojunctions.

In an IPE measurement performed on a Schottky barrier, electrons are excited by photons above the barrier, and the photocurrent is measured. The dependence of the photocurrent per absorbed photon, Y, is found to be[10]

$$Y^{1/2} \propto h\nu - \Phi, \tag{1}$$

where $h\nu$ is the photon energy and Φ is the barrier height. The IPE method is most commonly used to determine barrier heights of metal-semiconductor junctions. The method is successful because of the high density of electrons in the metal which leads to relatively large currents and the ease of fabricating thin continuous metal films on top of semiconductors.

When an IPE experiment is performed on n^+: GaAs/AlGaAs heterojunctions, a few difficulties arise: (a) the density of electrons in the n^+: GaAs is $\sim 10^{18}\ \mathrm{cm}^{-3}$, which is 4–5 orders of magnitude less than in a metal, (b) the barrier height is <0.3 eV, a range where available photon sources have low output power, compared to ~ 0.9 eV or higher, the range of Schottky barrier heights to GaAs, (c) the heavy doping in the GaAs reduces the effective barrier height further (by some 50–100 meV due to degeneracy), thus complicating the interpretation of the results.

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We have chosen to combine a GaAs/AlGaAs heterojunction with a metal-GaAs Schottky barrier, where the intermediate common GaAs is very thin (as shown schematically in Fig. 1). Thus we have a large source of electrons, and we can measure barrier heights in the range of 1 eV. The total barrier height for the photo excited electrons is

$$\Phi_T = \Phi_1 - \eta + \Delta E_c - q\,\Delta V, \tag{2}$$

where Φ_1 is the metal-GaAs barrier height, ΔV is the voltage drop across the thin GaAs layer, and η is the image force and tunneling corrections.[11] When Φ_T and Φ_1 are measured experimentally via IPE, and ΔV and η are calculated from the known doping levels, ΔE_c can be obtained easily. Since ΔE_c is determined by the subtraction of two quantities measured by IPE, systematic inaccuracies are canceled, resulting in a more accurate ΔE_c.

All layers of the structure were grown *in situ* without breaking vacuum in a molecular beam epitaxy (MBE) system. The nominal background pressure with all sources hot was 2×10^{-11} Torr. Starting with a n^+: GaAs substrate, which was thoroughly cleaned and outgassed, a 1 μm GaAs buffer layer doped with Si to $\sim 10^{18}\ \mathrm{cm}^{-3}$ was grown (at 600 °C), followed by a transition region into $\mathrm{Al}_x\mathrm{Ga}_{1-x}\mathrm{As}$. In this region the Al flux was gradually increased to the desired Al mole fraction and the substrate temperature was increased to 700 °C, while the Si doping was decreased to $\sim 5\times10^{16}\ \mathrm{cm}^{-3}$ ($d_4 \cong 1000$ Å), thus avoiding an abrupt barrier with its own potential peak (as marked by the dotted line in Fig. 1). The doping in the AlGaAs prevents the increase in the apparent barrier height due to negative space charge which has been found to exist in AlGaAs,[6,12] and helps in electron collection due to the resultant band bending. The

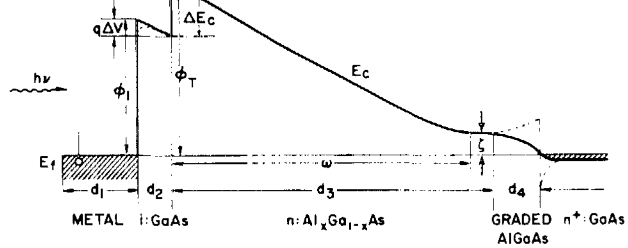

FIG. 1. Band diagram of the conduction band edge of the heterojunction. The dotted line at d_4 shows band alignment without grading, while those at the GaAs/AlGaAs and the Mo-GaAs interfaces show the band lowering due to image force and tunneling. ω is the depletion layer length in AlGaAs.

doped AlGaAs ($d_3 \cong 4000$ Å) was followed by a thin undoped GaAs, grown at 600 °C ($d_2 = 50$–150 Å, to minimize ΔV), and then by a thin molybdenum layer deposited *in situ* at ~ 180 °C ($d_1 \cong 150$ Å). To minimize the As background, about 3 h elapsed before the Mo deposition. It was found before that Mo grows epitaxially and does not react with GaAs at this temperature. Moreover, the Mo-GaAs barrier height is insensitive to the GaAs surface reconstruction, thus ensuring reproducible values of Φ_1 (Ref. 13). Each structure grown was analyzed for its Al mole fraction (by microprobe, with relative accuracy of $\pm 5\%$), and its AlGaAs net doping concentration $N = N_D - N_A$ (by C-V measurement).

Samples were prepared by etching 0.5×0.5-mm^2 square mesas to a depth of $\sim 1\,\mu$m, resulting in some undercutting under the Mo layers, thus minimizing edge effects. Gold dots (~ 1500 Å thick) 0.1×0.1 mm^2 in area, were evaporated at the corner of each square to facilitate top contact, while ~ 1500 Å of NiAuGe was evaporated on the back side and alloyed thereafter to form the back contact. Measurements were made with the samples immersed in liquid nitrogen. A tungsten bulb was used as a light source, followed by a grating monochromator. Long-pass optical filters were used to eliminate unwanted orders from the grating. All current measurements were made at dc, except when biasing was applied; then the light source was chopped and measurement done with a lock-in amplifier.

For a given N, the electric field at the GaAs/AlGaAs interface is[14]

$$F(0) = \left(\frac{2qN}{\epsilon_0 \epsilon}(\Phi_T - \zeta - kT)\right)^{1/2}, \tag{3}$$

where ϵ_0 and ϵ are the free space and relative dielectric constants of AlGaAs, respectively, and ζ is the energy difference between the bottom of the conduction band and the quasi-Fermi energy at 77 K when the sample is illuminated. Since the thin GaAs is undoped, the electric field in it is constant and related to $F(0)$ by the ratio of the dielectric constants of the AlGaAs and the GaAs. Hence, the potential drop across the GaAs layer is

$$\Delta V = \frac{\epsilon(\mathrm{AlGaAs})}{\epsilon(\mathrm{GaAs})} F(0)\, d_2, \tag{4}$$

where ϵ(AlGaAs) is obtained by a linear interpolation between $\epsilon(\mathrm{GaAs}) = 12.55$ and $\epsilon(\mathrm{AlAs}) = 9.25$ at 77 K[15] (assuming the same temperature dependence for GaAs and AlAs).[16] Finding the apparent barrier height from Eq. (1), and using the measured N and d_2 in Eqs. (3) and (4), the only calculated corrections are η and ζ.[17,18]

The detected current was corrected for spectral dependence of the source and monochromator combination, and $Y^{1/2}$ was plotted as a function of $h\nu$ for heterojunctions with different Al mole fractions (Fig. 2). The data were also plotted as $Y^{1/3}$ vs $h\nu$; a somewhat better fit to a straight line was observed in some cases (as was also observed by Powell[19] and DiMaria[20]), resulting only in a 10 meV reduction in Φ_T. Note the deviation from linearity which increases with Al mole fraction. Similar effects were observed in Mo-AlGaAs Schottky barriers, leading us to believe that they are not related to accumulation of electrons in the "notch" at the interface between the thin GaAs and the AlGaAs, and a subsequent tunneling thereafter. The nonlinear behavior of $Y^{1/2}$ for larger x is not clear, but all samples measured (more than one for each x), demonstrated a clear threshold which unambiguously led us to determine Φ_T with a spread of ± 10 meV.

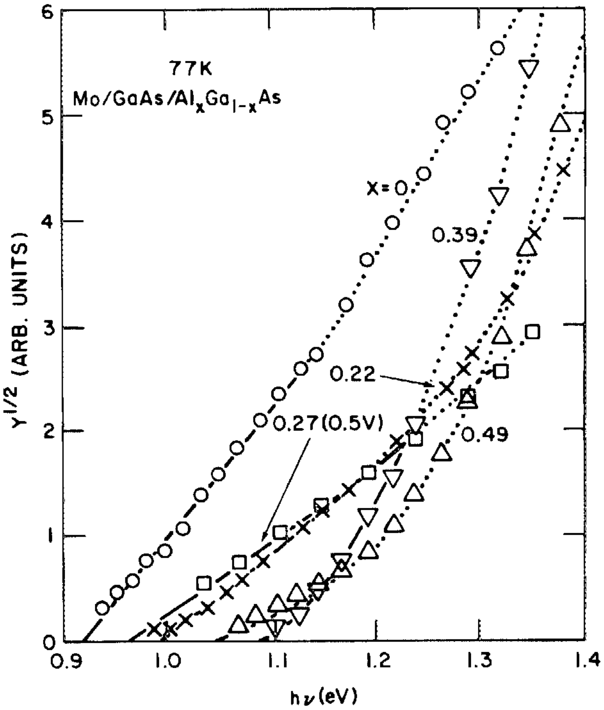

FIG. 2. Experimental results of the IPE measurements at 77 K. Note that $Y^{1/2}$ has the longest linear portion for $x = 0$, while for $x > 0$ the deviations from linearity are considerable. Fitting the straight lines was done to the lowest portion of each curve. Maximum current levels measured were in the 10^{-9} A range. The curve for $x = 0.45$ is not shown to avoid confusion.

While tunneling correction is estimated, the contributions of the image force and interface states to barrier lowering can be neglected at the GaAs/AlGaAs interface, due to the very similar dielectric constants and the very small number of interface states. However, all those effects are fully accounted for in calculating the corrections for Φ_1 (Ref. 17). AlGaAs is thought to have deep and shallow donor levels, both with activation energies which depend on x and N_D. However, at 77 K most electrons freeze into the deep levels, with a remaining number of free electrons which suggests that the Fermi level is shallow. At 77 K, for $x \leqslant 0.25$, shallow levels are dominant and $\zeta < 6$ meV. For $0.25 < x < 0.4$, ζ rises to about 25 meV, thereafter it drops again.[18] Since the sample is illuminated, the number of electrons in the conduction band is larger and the effective ζ is even smaller. Even though this is only an estimate, the maximum contribution to ΔV is only about 1%, and can be neglected.

N was determined by measuring C-V at 77 K under illumination, resembling the IPE conditions. Since the area and the dielectric constant are accurately known, the mistake in determining N is small and we estimate it to be less than $\pm 10\%$, which will affect ΔV by less than $\pm 5\%$. Since ΔV is linearly dependent on d_2, we have measured it (using step measurement apparatus) and got a very good agreement with the nominal thickness intended. Deviations from the nominal thickness are estimated by no more than $\pm 5\%$, leading to a total inaccuracy of $\pm 10\%$ in ΔV. Table I gives

TABLE I. Summary of measured and calculated parameters of the structures shown in Fig. 1. ΔE_c is determined with an accuracy of $\pm 0.1 \Delta V \pm 10$ mV.

x[%]	0	22	27	39	45	49
d_2[Å]	···	65	280	150	50	75
N[cm^{-3}]	1.5×10^{17}	1×10^{17}	4×10^{16}	5×10^{16}	4×10^{16}	4×10^{16}
Φ_T[eV]	0.92	1.00	0.965[a]	1.09	1.068	1.046
ΔV[meV]	···	110	203	180	52	78
η[meV]	50	20	8	10	10	10
ΔE_C[meV]	···	160	211	310	160	164
$\Delta E_C/\Delta E_g$[b]	···	0.60	0.63	0.64	0.30	0.30
ΔE_V[meV]	···	113	122	175	370	376

[a] Measured with forward bias 0.5 V.

[b] ΔE_g[meV] $= 12.55x$; $x \leqslant 37\%$. ΔE_g[meV] $= 380 + 3.12x + 0.0033x^2$; $x > 37\%$ (Refs. 21, 22, 23).

all relevant measured parameters including the calculated ΔV, η, and ΔE_c for different x, neglecting space charge effects in the thin GaAs.[21–23]

It is generally believed that $Al_x Ga_{1-x}As$ with $x \geqslant 0.43$ is an indirect material due to bands crossover ($x \equiv \langle 100 \rangle$ crosses $\Gamma \equiv \langle 000 \rangle$),[21] however, other reports suggest that the crossover point is at $x \cong 0.37$ (for example, Ref. 23). This seems to be supported by our previous results[24] of a discrepancy of about 0.06 in the Al concentration as determined by photoluminescence (using the data of Ref. 21) compared to absolute microprobe data. As given in Table I, we observe an average $\Delta E_c \cong 0.62 \Delta E_g$ for $x < 0.39$, which drops to $\Delta E_c \cong 0.3 \Delta E_g$ for $x > 0.39$. It has already been reported that ΔE_v is monotonically increasing with x ($0 < x < 1$), while ΔE_c rises up to the crossover point, and thereafter gradually drops,[8,9] but much more modestly than in our case. The lower than expected band discontinuity for $x > 0.39$ could be related to AlAs clusters (known to occur for large x); this would give rise to high- and low-barrier Schottky contacts in parallel. The coincidence with the crossover point is not yet understood.

In conclusion, using a modified internal photoemission method, we have shown that for $GaAs/Al_x Ga_{1-x}As$ heterojunctions for $x < 0.4$, the conduction band discontinuity can be given in the form ΔE_c [meV] $\cong 7.8\, x$[%], in close agreement with recent reports. The main advantages of this novel method of measurement are the ease of applying it to a variety of heterojunction materials which can be grown by MBE, and its accuracy.

We thank R. Savoy and F. Cardona for the Al mole fraction determinations, D. Thomas for processing the samples, and D. DeCain for technical assistance with the measurements. We also thank D. DiMaria, A. B. Fowler, and Frank Stern for helpful discussions.

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[17] See Ref. 11, p. 85. This correction reduces ΔE_c by 20–40 meV, but is not important in the GaAs layer, since d_2 is long enough relatively to the image force correction length.

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