Determination of valence-band discontinuity via optical transitions in ultrathin quantum wells

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The energy separation (ΔE) between the heavy-hole and the light-hole subbands as a function of the well width for ultrathin quantum-well structures is calculated using a single-band particle-in-a-box model. It is found that the most sensitive range for the well width (L_z) to determine accurately the valence-band discontinuity (ΔE_v) is between 15 and 80 Å, whereas it is insensitive for $L_z > 80$ Å using optical transitions in quantum wells. A controversial issue for the determination of ΔE_v can then be resolved by measuring the ΔE's in the sensitive well-width range. Results for the GaAs-Al$_x$Ga$_{1-x}$As system are presented and compared with the available experimental data in the sensitive range yielding good agreement with Dingle's initial work.

A fundamental and long-standing problem in the study of the semiconductor microstructures is the determination of the band-edge discontinuities (ΔE_c and ΔE_v) of the heterojunctions.[1-6] The intrinsic asymmetry associated with ΔE_c and ΔE_v for electrons in the conduction band and holes in the valence band, respectively, has produced spectacular effects for photonic devices such as quantum-well lasers, photodetectors, and high-speed logic elements. Four methods commonly employed to measure ΔE_v as well as ΔE_c are photoemission spectroscopy,[1] capacitance-voltage (C-V) techniques,[2] optical transition measurements,[3] and the charge-transfer method.[7] The first method is direct; however, its accuracy is limited and cannot be improved thus far beyond a value of about 0.15 eV. This is not sufficient for most practical applications and critical testing of theories. The second method is not a direct method since it is based on the average properties of the transport of carriers. It is difficult to obtain accurate values of ΔE_v or ΔE_c from the C-V technique because of the numerical uncertainties of the quantities used in the determination procedure such as the Fermi-energy levels and band bendings. The third method is the one that the initial determination of ΔE_v by Dingle and his co-workers[3] was based on. Although this optical method provides a convenient way to obtain the values of ΔE_v and ΔE_c, there have been excessive recent claims[4,5] that Dingle's 15-85 rule for the band offset contribution for ΔE_v and ΔE_c found for the GaAs/Al$_x$Ga$_{1-x}$As system is in error. In addition, the charge-transfer method[7] was utilized to investigate the orientational independence of band offset at GaAs/(Al,Ga)As heterointerfaces. In spite of many measurement techniques utilized, the magnitudes of ΔE_c and ΔE_v for the GaAs/Al$_x$Ga$_{1-x}$As system remain a controversial subject.[6]

Recently, Shum and his co-workers[8] have determined ΔE_c as well as ΔE_v for the Ga$_x$In$_{1-x}$As/Al$_x$In$_{1-x}$As system without any ambiguity by photoluminescence studies of two ultrathin quantum wells. They found that the energy separation (ΔE) between the maxima of $n = 1$ heavy-hole (hh) and light-hole (lh) subbands are most sensitive to the band offset for well widths (L_z) ranging from 15 to 80 Å. This was a key finding that enabled them to use a single-band particle-in-a-box model for their determination, yield-

ing a 15-85 split. However, their results are in quantitative disagreement with those reported by earlier studies[9,10] using the C-V profiling technique. The method used to determine the band discontinuities may account for this discrepancy. The C-V method may have systematic errors due to background-carrier profile, concentration density of states, and thermal energy of the free carriers.[6,11] Furthermore, those who employ this method usually take the values of the band gaps from the literature rather than determining them simultaneously as Shum et al.[8] did for their determination.

In this paper, the simple model used in Ref. 8 for calculating ΔE is further justified and the approach for determination of the valence-band offset of the Ga$_x$In$_{1-x}$As/Al$_x$In$_{1-x}$As system is extended to determine the counterpart at GaAs/Al$_x$Ga$_{1-x}$As heterointerfaces. It is shown that one can also determine ΔE_v and ΔE_c very accurately for the GaAs/Al$_x$Ga$_{1-x}$As system by measuring the values of ΔE's from optical transitions for a set of ultrathin quantum wells: 15 Å $< L_z < 80$ Å. The calculated results of ΔE vs L_z are presented and compared with available experimental data[12-16] in the literature. Our results indicate that the fraction (Q_v) to the total band discontinuity (ΔE_g) for the GaAs/Al$_x$Ga$_{1-x}$As system is not a close issue, and this issue can be settled by systematically measuring data of ΔE's in sensitive well-width range. With the limited data available, it was noticed that Dingle's rule may still be valid.

The values of eigenenergy (E_n) are determined for a finite quantum well in the valence band by the following equation:[8]

$$\tan(p\,\sigma_n) = \frac{2\sigma_n(m_w/m_b)^{1/2}(1-\sigma_n)^{1/2}}{(m_w/m_b + 1)\sigma_n^2 - 1} , \quad (1)$$

where $\sigma_n = E_n/\Delta E_v$ and $p = L_z(2\Delta E_v m_w)^{1/2}/\hbar$ are two dimensionless variables; m_w and m_b are the effective mass in the well and the barrier, respectively, and n is the number of subbands in the well. The value n is controlled by the value of p. From Eq. (1), one can easily evaluate the values of eigenenergies for hh and lh as well as the ΔE as a function of L_z by a given set of parameters of ΔE_v and hole masses.

The assumptions used to derive Eq. (1) and to calculate ΔE vs L_z are highlighted in this section. First, the quantum well for holes in the valence band is simulated by a finite square well with a well width L_z. This is a reasonably good approximation confirmed by photoemission measurements at the interface of heterojunctions.[1] Second, the potential-well depth ΔE_v is used as an adjustable parameter which is determined by fitting the observed energy separation ΔE between hh and lh subbands at a different well width L_z. Third, the effective kinetic energy operator is obtained from three-dimensional effective-mass approximation; that is, the effective masses of hh and lh (m_{hh}, m_{lh}) from the band-edge of GaAs and $Al_xGa_{1-x}As$ compounds are used. This is a reasonable approximation because the quantum well for localized holes in the valence band is shallow. In this situation, the energy dependence of the effective mass of the holes is negligible. However, for the electrons in the conduction band one must consider the energy dependence of the effective mass of the electrons. It should be argued whether or not an effective-mass approach based on the band model is still valid for an ultrathin quantum well structure. We may take note of the fact that the conductivities and other electrical properties of most semiconductors are virtually unchanged upon melting,[17] suggesting that a band structure is preserved even though there is no longer any long-range order. This is not surprising if we recall that in the band model the influence of everything beyond one or two atomic spacings is lumped into a self-consistent field. Furthermore, the wave function for valence electrons piles up electronic charge on the cores of the positive ions, thereby valence electrons are more localized on the nuclei than conduction electrons. Therefore, the influence on the effective mass of holes due to the reduced dimensionality can be expected to be small. The last assumption in our model is to use the boundary conditions that the effective mass wave function and its spatial derivative are continuous at the boundaries.

Various values of the parameter $\Delta E_v = Q_v \Delta E_g$, where $\Delta E_g = 1247x$ meV is assumed, and various sets of hole masses have been used in Eq. (1) to generate ΔE vs L_z curves 1–7 in Fig. 1 for the $GaAs/Al_xGa_{1-x}As$ quantum well structure to test the validity of our approach. The change in hole effective masses is essential[18] to describe the measured spectra by Miller and co-workers,[12,13] in particular, for $\Delta n \neq 0$ transitions. Relying on that, an apparent new valence-band offset was determined for the $GaAs/Al_xGa_{1-x}As$ system. Careful attention was paid to choosing the values of hole effective masses by which the band offset ΔE_v and Q_v are determined by us based on the available experimental data.[12-16] We have chosen here to use the most reliable measured cyclotron masses[19] in the [100] L_z direction ($0.087m_0$ for lh, $0.403m_0$ for hh, respectively) for our determination. In order to further eliminate the possible deviations due to the simple constant-mass picture, various sets of hole masses for GaAs were tested in such a way that the curves of ΔE vs L_z would deviate most from the curve using the above masses. For example, the solid curve 4 was calculated using the [100] masses[19] and a value of $\Delta E_v = 75$ meV. The masses for generating curves 1, 2, and 3 are the density-of-states effective masses,[18] the masses initially used by Dingle,[3] and the new set of masses proposed by Miller, Kleinman, and Gossard,[5] respectively. The same value of $\Delta E_v = 185$ meV was used for those three dot-dash curves. Variations on hole effective masses cannot compensate for
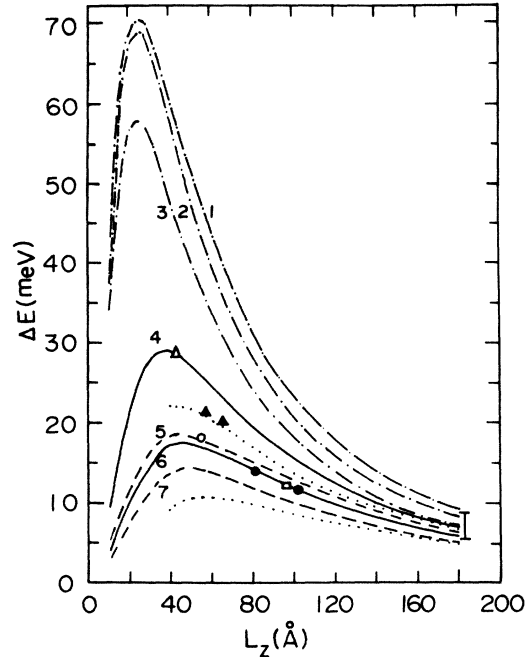

FIG. 1. The calculated energy separation ΔE between the hh and lh subbands as a function of well width L_z for various ΔE_v and hole masses described in Table I for $GaAs/Al_xGa_{1-x}As$ quantum well structures. Two dot curves were extrapolated from Ref. 27, where exciton binding energies were calculated. The composition numbers x for upper and lower dash curves were 0.30 and 0.15, respectively. The open triangle corrresponds to the data taken from the excitation spectrum at 6 K (Ref. 12). The solid triangles correspond to the data from the excitation spectrum (Ref. 15). The open circle corresponds to the data taken from the photoluminescence spectrum at 300 K (Ref. 14). The square corresponds to the data taken from the absorption spectrum at 300 K (Ref. 16). Two solid circles correspond to the data from the excitation spectrum at 5 K (Ref. 13). The error bar illustrates the insensitivity of ΔE vs L_z to the choice of ΔE_v.

the larger calculated ΔE than the measured ΔE due to large value of $\Delta E_v(Q_v = 0.40)$. The effective masses for the holes of alloy barriers were obtained from a linear extrapolation as a function of x from the hole masses of AlAs defined by Luttinger parameters $\gamma_1 = 3.45$ and $\gamma_2 = 0.68$ given in Ref. 20. All parameters used for the various curves plotted in Fig. 1 are described in Table I.

There are two most significant features appearing in those

TABLE I. The parameters used for generating curves plotted in Fig. 1. Unit of mass is in m_0.

Curve	x	Q_v	ΔE_v	m_{hh}	m_{lh}	Ref. for mass
1	0.37	0.40	185	0.620	0.074	18
2	0.37	0.40	185	0.450	0.080	3
3	0.37	0.40	185	0.340	0.094	5
4	0.37	0.16	75	0.403	0.087	19
5	0.30	0.12	46	0.450	0.080	3
6	0.30	0.12	46	0.403	0.087	19
7	0.30	0.12	46	0.340	0.094	5

curves plotted in Fig. 1 despite the very different masses used. First, there are two distinct regions for well widths L_z from calculated curves. One *region* is called the *sensitive range* (15 Å $< L_z <$ 80 Å) in which ΔE's are very sensitive to the value of ΔE_v in spite of various sets of masses for hh and lh (see Table I). In this region, it is possible to determine ΔE_v very accurately by fitting ΔE's to the experimental data. One can also cleary show whether or not the recent trend of determination of ΔE_v is correct and was determined without any ambiguity. The other region ($L_z >$ 80 Å) is called the *insensitive range* in which ΔE's are very insensitive to the choice of ΔE_v. In fact, the lowest-energy levels can often be adequately found by using the "infinite-well" approximation for thick wells. Therefore, it is very hard in practice to determine ΔE_v by fitting transition energies from the thick quantum wells. Since most previous optical measurements were performed on quantum wells with $L_z >$ 80 Å, this feature from the curves explains why different values of Q_v were obtained from study to study. Our calculations also show that varying Q_v from 0.10 to 0.50 does not alter the energies of low-lying optical transitions by much for $L_z >$ 100 Å. For example, for a single quantum well with the values of $L_z =$ 100 Å and $x =$ 0.30, the calculated variation of energy for $n = 1$ electron to $n = 1$ heavy-hole transition is only 3 meV for a wide variation of Q_v from 0.10 to 0.50. The energy separation between $n = 2$ hh and lh subbands is not sensitive at all to ΔE_v when $L_z >$ 180 Å (see similar work in Ref. 21 in this respect). Second, there is a maximum energy separation (ΔE_m) occurring at well width (L_{zm}) for a given ΔE_v. The value of ΔE_m increases and L_{zm} decreases with increasing ΔE_v. At L_{zm}, the population in the light-hole band will be depleted, giving rise to a higher light emission from the recombination of electrons in the conduction band and heavy holes in the valence band. This may result in a corresponding maximum quantum yield for quantum well lasers.

Three key advantages should be emphasized here for determining ΔE_v in the sensitive range of well widths by fitting the experimental data ΔE to the calculated ΔE. First, the mixing between the hh and lh bulk states can be neglected since the values of ΔE are relatively large. Furthermore, from the results of the multiband effective-mass approach, the valence-band mixing affects higher subbands ($n > 1$) resulting in a poor description of the dispersion of hold bands and ambiguous identification of transitions among all pairs of valence and conduction subbands[22] and possible impurity states involved. However, lowest subbands ($n = 1$) remain unaffected. Therefore, the envelope-function approximation for $n = 1$ subbands is realistic.[23] One can almost exactly determine ΔE at defined well widths. This accuracy is crucial to infer band offsets. Second, the influence of band bending can also be neglected since the wells are thin enough. Third, the effects of any possible symmetric, linear interface grading are to increase the eigenenergies of all confinement states.[24] Although it may be sensitive for $L_z <$ 50 Å, ΔE, which is the energy difference of hh and lh states, may remain relatively unchanged. It should be pointed out that the effects of errors in the determination of L_z can be overcome by systematically comparing the derived value of L_z using the contouring approach[25] with that determined by the reflection high-energy electron diffraction (RHEED) oscillation technique or real-time layer growth rate. In fact, one can estimate Al composition x as accurately as 0.4%.[26] Therefore, by know-

ing x and the nearly exact measured energies of transitions from $n = 1$ electron states to both hh and lh states, the well width L_z can be determined very accurately since those transitions depend strongly on this parameter (because L_z is small).

Since the energy difference of electron-hh exciton and electron-lh exciton is relatively small (< 2 meV), we did not include the dependence of exciton binding energy on L_z in our calculation. However, we took 1–2 meV reduction from the measured ΔE to account for the binding-energy difference. In order to further justify this point, the two dot curves are also plotted in Fig. 1 from the data in Table I of Ref. 27 in which the different exciton binding energy for hh and lh at different L_z was considered. The upper one corresponds to $x =$ 0.3 ($\Delta E_v =$ 45 meV for $Q_v =$ 0.12), while the lower one corresponds to $x =$ 0.15 ($\Delta E_v =$ 22 meV for $Q_v =$ 0.12). The masses used[16] were $m_{whh} =$ 0.45m_0, $m_{wlh} =$ 0.082m_0, $m_{bhh} = (0.45 + 0.2x)m_0$, and $m_{blh} = (0.082 + 0.068x)m_0$, which are different from the masses we used. However, all three features discussed above are preserved.

In this section, the available experimental data[12-16] of ΔE vs L_z in the *sensitive range* are used to determine ΔE_v and Q_v according to our calculation. The data denoted by the triangle at location ($L_z =$ 42 Å, $\Delta E =$ 28.5 meV in Fig. 1 were taken from the excitation spectrum at 6 K given in Ref. 12. The composition number x for the Al is 0.37. These data yield a value of $\Delta E_v =$ 75 meV which corresponds to a fraction $Q_v =$ 0.16. We note that even if the masses used for this fit were given for $x =$ 0.3 rather than for $x =$ 0.37, the value of $\Delta E_v =$ 76.5 meV would be obtained. This is evidence that energy separation ΔE is insensitive to the precise masses of hh and lh as long as the ratio of m_{hh}/m_{lh} remains relatively unchanged. Using the data denoted by solid triangles in Fig. 1 from the other group[15] yields $Q_v =$ 0.14. Data on ΔE from Refs. 13, 14, and 16 are also displayed in Fig. 1. Using our calculation, the data consistently yield a fraction $Q_v =$ 0.12. It is interesting to note that the samples cited here were mainly grown in the [100] direction at Bell and Philips laboratories (except the sample studied in Ref. 12). Those samples consistently showed a fraction Q_v that was approximately the same when the most accurate optical data ΔE and the most reliable effective masses in the growth direction were used in the sensitive range.

Recently, there have been reports suggesting $Q_v =$ 0.40.[5] It is necessary to show how $Q_v =$ 0.40 fails to fit the experimental data[12-16] in the *sensitive range*. For example, let us take the data of Ref. 12. When $Q_v =$ 0.40 ($\Delta E_v' =$ 185 meV for $x =$ 0.37) and the *new* set of masses (0.340m_0, 0.094m_0) for hh and lh of GaAs proposed by Miller *et al.*[5] for the GaAs/Al$_x$Ga$_{1-x}$As system were used by us for data fitting, a value of $\Delta E' =$ 46 meV was obtained which does not fit the observed value of $\Delta E =$ 28.5 meV.[12] Including nonparabolicity in our calculation only makes an insignificant reduction of about 1.5 meV from 46 meV. Also, our calculation does not yield the observed values of ΔE (Refs. 13–16) using $Q_v =$ 0.40 for both the conventional masses[19] and the *new* set of masses.[5] It should be pointed out here that a *new* set of mass parameters,[5] including the fraction $Q_v =$ 0.40 for the GaAs/Al$_x$Ga$_{1-x}$As system, deduced from the measurements of optical transitions in thick quantum wells (for $L_z >$ 80 Å) and in parabolic quantum wells, are not determined uniquely. These results[5] are subject to large errors for finding Q_v because of the insensitivity of ΔE vs

L_z for the choice of ΔE_v for $L_z > 80$ Å. Moreover, using a smaller value of effective mass for hh in quantum wells over the conventional bulk value is not consistent with the K·p theory, since effective mass for a particle away from the band edge is, in general, larger than at the edge.[28]

Data from various sources[12-16] are summarized in Table II. The values of ΔE_v and Q_v are obtained by our model. Our determinations in the *sensitive range* are clearly more favorable and support Dingle's initial work.

In conclusion, we have used a simple model for calculating the energy separation ΔE between maxima of hh and lh subbands and showed how the valence-band discontinuity at the interface of different semiconductors can be determined by fitting this right quantity to the experimental data measured in the right region of parameter space (the *sensitive* region of well thicknesses). Experimental data in the sensitive range are compared with the calculated results for the GaAs/Al$_x$Ga$_{1-x}$As system yielding an agreement with Dingle's initial work:[3] $\Delta E_v \approx 0.12\Delta E_g$. Most recently, resonance Raman scattering[29] and pressure dependent photoluminescence measurements[30] have shown a $Q_v \sim 0.29$ for thick wells. To precisely determine ΔE_v using optical transitions in quantum well structures, more measurements should be performed in the sensitive range of well width: 15 Å $< L_z < 80$ Å.

TABLE II. The available experimental data of ΔE in the literature. The values of ΔE_v and Q_v are obtained by our model. The prime denotes the corresponding values using Miller's *new* set of parameters $(0.34m_0$ for hh mass, $0.094m_0$ for lh mass, and $Q_v = 0.40)$ given in Ref. 5. Unit of energy is in meV.

ΔE	L_z	X	ΔE_v	Q_v	$\Delta E_v'$	$\Delta E'$
28.5[a]	42	0.37	75	0.16	185	46
21[b]	56.6	0.36	63	0.14	180	33
20[b]	65	0.36	63	0.14	180	29
18[c]	55	0.33	49	0.12	165	34
12[d]	96	0.30	46	0.12	150	17
14[e]	81	0.30	46	0.12	150	21
11.5[e]	102	0.30	46	0.12	150	15

[a]From Ref. 12. [d]From Ref. 16.
[b]From Ref. 15. [e]From Ref. 13.
[c]From Ref. 14.

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