Photoluminescence determination of well depth of $Ga_{0.47}In_{0.53}As/Al_{0.48}In_{0.52}As$ in an ultrathin single quantum well

K. Shum, P. P. Ho, and R. R. Alfano
Institute for Ultrafast Spectroscopy and Lasers, Photonic Engineering Laboratories, Physics Department and Electrical Engineering Department, The City College of New York, New York, New York 10031

D. F. Welch, G. W. Wicks, and L. F. Eastman
School of Electrical Engineering and National Research and Resource Facility for Submicron Structures, Cornell University, Ithaca, New York 14853
(Received 26 April 1985)

The photoluminescence spectra were measured from 4 to 90 K for single-quantum-well structures of (Ga, In)As/(Al, In)As with well widths $L_z = 14.5$ and 19.3 Å. The optical transitions were observed from $n = 1$ electrons in the conduction-band well to $n = 1$ heavy holes (hh) and light holes (lh) in the valence-band well. Using the observed energy separation between hh and lh subbands, the well depth $\Delta E_v = 120$ meV for holes in the valence band and the corresponding well depth $\Delta E_c = 740$ meV for electrons in the conduction band were determined. This gives the relation of $\Delta E_c = 0.85\Delta E_g$ which agrees with Dingle's rule for GaAs/(Al, Ga)As system.

INTRODUCTION

It is crucial for device design and applications to determine the well depths of a single-quantum well (SQW) in the conduction band (CB) and valence band (VB). Band discontinuities of semiconductors hetero-interface have been determined by photoemission spectroscopy, absorption spectroscopy, and capacitance-voltage measurements. In the latter two methods, there are many adjustable parameters in determining the conduction-band well energy ΔE_c and the valence-band well energy ΔE_c. In photoemission, the value of ΔE_v is directly obtained, however, the energy resolution is poor.[1] Optical methods offer convenient ways to measure these discontinuities. Dingle and his co-workers[2] have determined a value of $0.15\Delta E_g$ for well depth in the VB from absorption measurements on (Al,Ga)As/GaAs quantum wells where ΔE_g is the difference in the band gaps at the interface. This method in turn gave a value of $0.85\Delta E_g$ for the well depth in the CB. This value has been accepted for years and has become known as "Dingle rule." Recently, this relationship has become a subject of controversy. The reported values differ using various methods. Even for the most widely studied interface of (Al,Ga)As/GaAs consistent and accurate values have not been determined. Some researchers determined values of ΔE_c in range of $0.60\Delta E_c$ to $0.66\Delta E_g$ to explain their data.[3,4] Arnold *et al.*[5] deduced $\Delta E_c = 0.65\Delta E_g$ for the (Al,Ga)As/GaAs system using a current-voltage technique.

This paper reports on the first photoluminescence- (PL) spectroscopy determination of well depths $\Delta E_c = 740$ and $\Delta E_v = 120$ meV in the CB and VB for an (Al,In)As/(Ga,In)As ultrathin single-quantum well. The measured optical transitions for ultrathin wells which are separated by a large energy difference ΔE for the transitions from $n = 1$ electron subband in the CB to both $n = 1$ heavy hole (hh) and light hole (lh) subbands in the VB are the key behind this determination. The relationship for $\Delta E_c = 0.85\Delta E_g$ has been determined from these PL measurements. A theoretical calculation of ΔE versus L_z is presented to support the measurements of ΔE_v and ΔE_c.

EXPERIMENTAL METHOD

The samples were grown using a Varian 360 molecular-beam epitaxy (MBE) machine.[6] The structures were grown on a thermally cleaned InP substrate consisting of a 2500-Å-thick (Al,In)As layer followed by the (Ga,In)As single-quantum well of widths 14.5 and 19.3 Å, respectively, and a 100-Å cap layer of (Al,In)As. Each sample was attached to an aluminum plate by "super" glue and contained in a liquid Dewar. The sample was excited by a 488-nm argon-ion laser from 10 to 160 mW. The excitation area was about 200 μm in diameter. The photoluminescence was collected by a double $\frac{1}{2}$-m Spex spectrometer, detected by Hamamatsu R632 S-1 photomultiplier, and analyzed by a lock-in amplifier and a recorder. The temperature of sample was measured by a silicon diode connected to the cold finger on which the sample-aluminum plate combination was placed.

RESULTS

Various photoluminescene spectra were obtained as a function of lattice temperature T_L from 4 to 90 K for two single-quantum wells (SQW's) of well widths $L_z = 14.5$ and 19.3 Å. A set of typical spectra for $L_z = 14.5$ Å are shown in Fig. 1. The peaks are denoted by P_1, P_2, P_3, and P_4. The higher-energy set P_1 and P_2 are identified as arising from the radiative recombination of carriers in the barrier (Al,In)As. The lower-energy set P_3 and P_4 are identified as luminescence from the well (Ga,In)As, which are shifted above the bulk band gap $E_{gw} = 0.81$ eV, due to confinement of carriers in the quantum well.

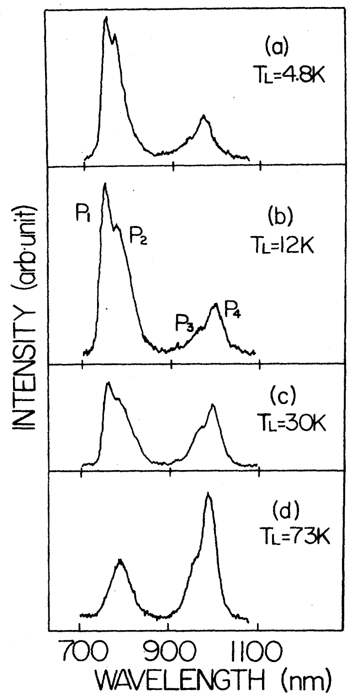

FIG. 1. Typical photoluminescence spectra of a (Al,In)As/(Ga,In)As SQW at well width $L_z = 14.5$ Å as a function of lattice temperature T_L. Excitation density power was about 10^2 W/cm^2. The peaks P_1, P_2, P_3, and P_4 denoted in this figure are explained in the text.

In order to determine precisely the band gap of (Al,In)As, the origin of the emission peaks P_1 and P_2 must be discussed. From spectra displayed in Fig. 1, it is quite clear that P_1 is stronger than P_2 at lower T_L and disappears when T_L is above 80 K. This temperature corresponds to thermal energy $k_B T_L = 7$ meV. The high-energy tail of P_1 displayed in Fig. 1(a) is fitted to $E^2 \exp(-E/k_B T_c)$ yielding a carrier temperature $T_c = 90$ K ($k_B T_c = 8$ meV). T_c is higher than T_L due to the heating from photoexcited energetic carriers. The three-dimensional exciton's binding energy in (Al,In)As is about 9 meV using the parameters $m_e = 0.118 m_0$, $m_{\text{hh}} = 0.677 m_0$, $K(\text{AlAs}) = 10.1$, and $K(\text{InAs}) = 14.6$. The disappearance of P_1 is caused by the lattice vibrational energy ionizing the exciton in the barrier. Thus, P_1 emission most likely arises from the annihilation of acceptor-bound exciton. The P_2 emission is broader than the P_1 and is weak at $T_L = 90$ K. This peak probably arises from the electron transitions from conduction-band edge to the shallow acceptor states. Furthermore, the intensity dependence of luminescence on pump intensity of the higher-energy set (P_1 and P_2) is plotted in Fig. 2. The luminescence intensity dependence varies as $I_e^{1.2}$. This confirms our speculation that the high-energy set is related to either impurity or exciton emission.[7] From the above identification of P_1 and P_2, the band gap of barrier (Al,In)As is determined to be $E_{\text{gb}} = E_{P_1} + E_B = 1.66 + 0.009 = 1.67$ eV at $T_L = 4$ K, where E_{P_1} is the peak energy of P_1 and E_B is binding energy of acceptor-bound exciton.

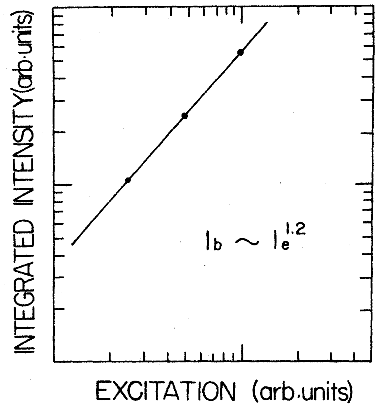

FIG. 2. Intensity dependence of emissions from barriers of (Al,In)As/(Ga,In)As SQW of well width $L_z = 14.5$ Å with respect to excitation intensity I_e.

The luminescence spectra of P_3 and P_4 emission for $L_z = 14.5$ and 19.3 Å are shown in Fig. 3. These arise from transitions in quantum-well region for both well widths. The peaks P_3 and P_4 are separated by energy differences $\Delta E = 47$ and 57 meV for $L_z = 14.5$ and 19.3 Å, respectively. The following argument is presented to support the assignment of the two peaks P_3 and P_4 arising from the radiative transitions from $n = 1$ electron states confined in the CB well to $n = 1$ hh and $n = 1$ lh states confined in the VB well. The excitation-power

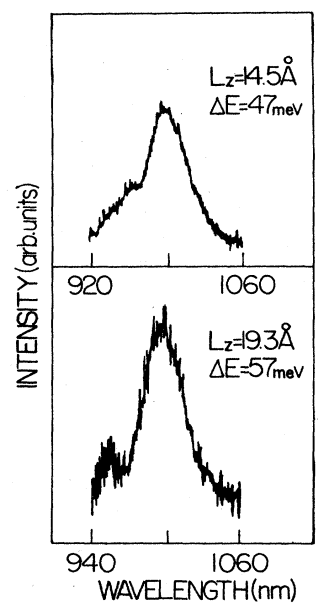

FIG. 3. SQW photoluminescence spectra from well GaInAs of two narrow wells. At lattice temperature $T_L = 7$ K. The energy separations $\Delta E = 47$ and 57 meV between hh and lh subbands for $L_z = 14.5$ and 19.3 Å, respectively, are indicated on each curve.

dependence of luminescence intensity of P_3 and P_4 emission from $L_z = 14.5$-Å quantum well is displayed in Fig. 4. The ratio of intensity of peaks P_3 and P_4 is defined by $R_p = I_3/I_4$, where I_3 and I_4 are the peak intensity for P_3 and P_4, respectively. The electron temperature T_c from each spectrum is determined by fitting the high-energy tail of P_3 to $E^2\exp(-E/k_B T_c)$. The most salient feature of spectra shown in Fig. 4 is that the ratio R_p increases as electron temperature T_c increases. The R_p versus kT_c is plotted in Fig. 5. The cross dots are the peak intensity ratios measured from Fig. 4. The solid curve is fitted to $R_p = C\exp(-\Delta E/k_B T_c)$, where ΔE is energy separation depicted in the inset of Fig. 5. A value of $C = 5.2$ takes care of the overlap of transitions from electron subband to hh and lh subband tails. The value of C depends on the well width L_z, lh, and hh intersubband scattering and other factors. The value of ΔE extracted from this fit is 47 meV. Thus, the energy ΔE determined by this method is the same as the energy separation between lh and hh subbands in the quantum well $L_z = 14.5$ Å measured from the photoluminescence spectra. This implies that holes in the VB are nondegenerate (Maxwell-Boltzmann). The populations of holes in the two subbands change with the electron temperature T_c. The inset of Fig. 5 shows this feature. This argument supports the model involving transitions from $n = 1$ electron subband to two $n = 1$ hole subbands.

In this section, the energy separation ΔE between hh and lh subbands as a function of well width L_z are calculated to support the above data for the two thin wells as long as well depth ΔE_v in the VB is set to be 120 meV. The following assumptions are used in the model: (1) the quantum well is simulated by an finite square well with width L_z; (2) the well depth ΔE_v is used as an adjustable parameter to be determined by fitting the observed energy separation ΔE between hh and lh subbands at different well width L_z, and (3) the effective kinetic energy operator is obtained from three-dimensional effective-mass approximation, i.e., to take hh and lh effective mass

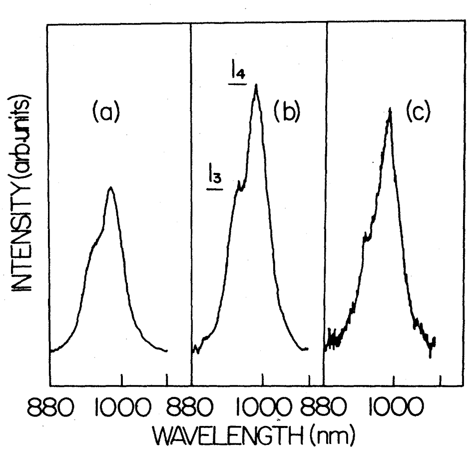

FIG. 4. SQW photoluminescence spectra from well region for $L_z = 14.5$ Å with different excitation power P_e. The peak intensity are denoted as I_3 and I_4, (a) $P_e = 160$ mW, (b) $P_e = 80$ mW, (c) $P_e = 40$ mW.

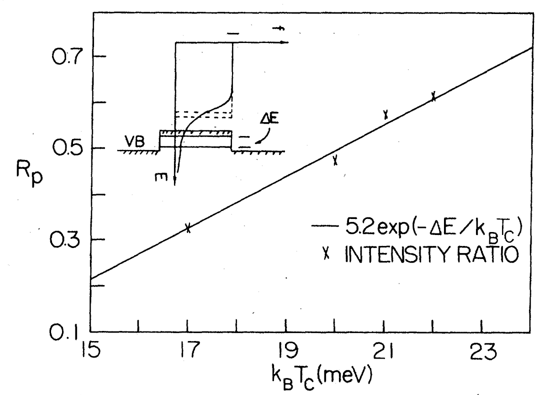

FIG. 5. Ratio of peak intensity of I_3 and I_4 with respect to the energy of carriers $k_B T_c$. T_c is the carrier temperature obtained by fitting each high-energy tail to $E^2\exp(-E/k_B T_c)$. Inset shows that nondegenerate holes populate in hh and lh subbands in the VB of the SQW, where f is Fermi-Dirac function.

$(m_{\rm hh}, m_{\rm lh})$ from the band edge of (Al,In)As and (Ga,In)As compounds. This is a reasonable approximation because the quantum well for localizing holes in the valence band is shallow. Therefore, the energy dependence on the effective mass of holes is negligible. However, for an electron in the conduction band one must consider the energy dependence on the effective mass.

Due to the continuity of wave functions and their spatial derivatives at the boundaries, the eigenenergy value E_n in the valence band well is determined for a finite well by 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 well and barrier, respectively, and n is the number of the localized states in the well. The value n is controlled by value of p. For $L_z = 14.5$ and 19.3 Å, only one state ($n = 1$) exists in both the CB and VB wells. The values of masses[9] used in this calculation are $m_{w\rm hh} = 0.6094 m_0$, $m_{w\rm lh} = 0.0491 m_0$, $m_{b\rm hh} = 0.6768 m_0$, and $m_{b\rm lh} = 0.0860 m_0$.

Various values of parameter ΔE_v have been used in Eq. (1) to calculate ΔE versus L_z. The calculated results ΔE versus L_z for parameters $\Delta E_v = 100$, 120, and 140 meV are plotted in Fig. 6. The inset shows the schematic energy-band diagram of a SQW. The dots in Fig. 6 locate the position of the measured ΔE for the two wells. The best fit to observed energy separations between hh and lh of 47 and 57 meV at well width $L_z = 14.5$ and 19.3 Å is for the parameter $\Delta E_v = 120$ meV. The fit of the theoretical calculation to experimental data for the well widths of $L_z = 14.5$ and 19.3 Å demonstrates that well depth in the VB is $\Delta E_v = 120$ meV. The corresponding well depth for the CB is $\Delta E_c = 740$ meV which is $0.86\Delta E_g$. The results of this photoluminescence method agree well with Dingle's relationship $\Delta E_c = 0.85\Delta E_g$ for

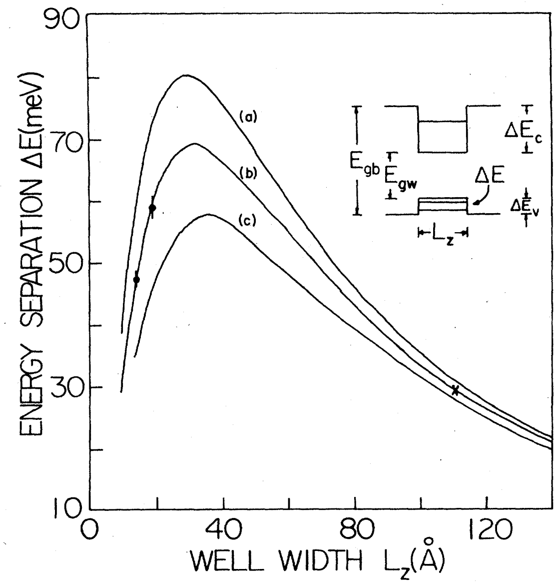

FIG. 6. Calculated energy separation ΔE between hh and lh subbands with respect to well width L_z with ΔE_v as a parameter. (a) $\Delta E_v = 140$ meV, (b) $\Delta E_v = 120$ meV, (c) $\Delta E_v = 100$ meV. Inset shows the approximate band diagram of a SQW. The dots are our data for PL and X is the absorption data given in Ref. 13.

(Al,Ga)As/Ga(As) system obtained by absorption. However, it deviates from the result of $0.73\Delta E_g$ at room temperature obtained by Morgan *et al.*[10] for (Al,In)As/(Ga,In)As who used the current-voltage method. The methods use to determine the well depths may account for this discrepancy. The current-voltage method may have systematic errors due to the background-carrier profile, concentration density of states, and the thermal energy of the free carriers.[11] The photoluminescence method requires the knowledge of hh and lh masses and interaction of carriers among the hh and the lh in subbands. However, the energy separation ΔE between hh and lh subbands is rather insensitive to the precise values of masses. For an ultrathin quantum well, the energy separation ΔE is large enough to be observed in photoluminescence spectra and the coupling between hh and lh could be neglected. Our results agree well with Harrison's linear-combination of atomic orbitals (LCAO) approach[12] and photoemission studies of Katnani and Margaritondo[1] within their limited accuracy (± 100 meV). By using interpolation method, the absolute position of the valence-band maximum can be obtained from the table given in Ref. 12. This yields a value of $\Delta E_v = 22$ meV. The large uncertainty in theoretical approach allows the agreement with our value of $\Delta E_v = 120$ meV.

From the result of theoretical calculation shown in Fig. 6, three salient features appear. First, the value of ΔE is extremely sensitive to the energy discontinuity ΔE_v for an ultrathin SQW of thickness $L_z = 14.5$ and 19.3 Å. This enables us to determine ΔE_v as well as ΔE_c very accurately (± 3 meV). Second, for thick wells of $L_z > 80$ Å, the value of ΔE is insensitive to the choice of ΔE_v. Therefore, it is difficult in practice to determine ΔE_v for thick wells. A recent paper[13] reported the value of $\Delta E_v = 290$ meV for (Ga,In)As/(Al, In)As system using the absorption spectra of a quantum well with L_z varying from 85 to 165 Å. The energies measured for the optical transitions for $L_z = 110$ Å well given in Ref. 13 can also be fitted well to the absorption transition using the value of $\Delta E_v = 120$ meV determined by us. The thickness of quantum wells studied by Weiner *et al.*[13] is in an insensitive range for determination of ΔE_v by fitting the measured optical transitions (see Fig. 6). This will result in an inaccurate determination of ΔE_v. Furthermore, they measured $\Delta E = 29$ meV for $n = 1$ hh and lh subbands of $L_z \equiv 110$-Å well which exactly agrees with our results shown in Fig. 6. This adds further support to our determination using a PL method. Third, there is a maximum energy separation ΔE_m which occurs at well width L_{zm} for a given ΔE_v. This feature may explain maximum quantum efficiency measured by Welch, etc.[6] Moreover, the value of ΔE_m increases and L_{zm} decreases with increasing ΔE_v.

In conclusion, the well depths ΔE_c and ΔE_v in the CB and VB for the SQW of (Al,In)As/(Ga,In)As have been determined to be 740 and 120 meV, respectively. This has been accomplished by fitting the transitions from $n = 1$ electron states to hh and lh states for both $L_z = 14.5$ and 19.3 Å SQW's. It should be pointed out that the (Al,In)As/(Ga,In)As structure may possess new characteristics which are not displayed in the (Al,Ga)As/GaAs system, which arise from the much deeper well depth in the CB for the (Ga,In)As/(Al,In)As system by a factor of over 2 than the AlGaAs well. Some of these characteristics are the following: increase of the electron effective mass in both well and barrier region; the hot-carrier temperature dependence on the well width L_z; the larger degeneracy and mobility of two-dimensional electron-hole system and the enhanced interaction strength of electrons and phonons due to the reduced dimensionality and more effective localization.

ACKNOWLEDGMENTS

We thank S. S. Yao for performing some of the measurements and Dr. K. Bajaj for helpful discussions. This research is supported by U.S. Air Force Office of Scientific Research (AFOSR), Department of the Air Force.

[1] A. D. Katnani and G. Margaritondo, Phys. Rev. B **28**, 1944 (1983).
[2] R. Dingle, A. C. Gossard, and W. Wiegmann, Phys. Rev. Lett. **34**, 1327 (1975).
[3] See, for example, R. C. Miller, D. A. Kleinman, and A. C. Gossard, Phys. Rev. B **29**, 7085 (1984).
[4] C. M. Wu and E. S. Yang, J. Appl. Phys. **51**, 2261 (1980).
[5] D. Arnold, A. Ketterson, J. Henderson, J. Klem, and H. Morkoç, Appl. Phys. Lett. **45**, 1237 (1984).
[6] D. F. Welch, G. W. Wicks, and L. F. Eastman, Appl. Phys.

Lett. **43**, 762 (1983).
[7]S. S. Yao and R. R. Alfano, Phys. Rev. Lett. **49**, 69 (1982).
[8]Frank Stern and Sankar Das Sarma, Phys. Rev. B **30**, 840 (1984); Tsin-Fu Jiang, Solid State Commun. **50**, 589 (1984).
[9]P. Lawaetz, Phys. Rev. B **10**, 3460 (1971).
[10]D. V. Morgan, K. Board, C. E. C. Wood, and L. F. Eastman, Phys. Status Solidi A **72**, 251 (1982).
[11]S. R. Forrest, P. H. Schmit, R. Binlson, and M. L. Kaplan, Appl. Phys. Lett. **45**, 1199 (1984).
[12]W. A. Harrison, J. Vac. Sci. Technol. **14**, 1016 (1977).
[13]J. S. Weiner, D. S. Chemla, D.A.B. Miller, T. H. Wood, D. Sivco, and A. Y. Cho, Appl. Phys. Lett. **47**, 619 (1985).