RAPID COMMUNICATIONS

PHYSICAL REVIEW B VOLUME 39, NUMBER 8 15 MARCH 1989-I

# Pressure dependence of the valence-band discontinuity in GaAs/AlAs and GaAs/$Al_xGa_{1-x}As$ quantum-well structures

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(Received 21 November 1988)

We have performed high-pressure photoluminescence measurements on a type-II GaAs/AlAs superlattice at liquid-helium temperatures. The observed indirect transitions were found to have a pressure coefficient of $-2.4\pm0.1$ meV/kbar, significantly larger in magnitude than the coefficient of $-1.3$ meV/kbar reported for the indirect gap of GaAs. This is interpreted as evidence for a pressure dependence of the valence-band discontinuity ($\Delta E_V$) of approximately $+1$ meV/kbar. Our result is in excellent agreement with theoretical calculations of Van de Walle and Martin. Taken together with previously reported data, it suggests that the magnitude of $d\Delta E_V/dP$ is a linear function of the alloy composition of the barrier material. We show that the fractional conduction- and valence-band offsets of GaAs/$Al_{0.3}Ga_{0.7}As$ are pressure dependent.

## INTRODUCTION

For several years now there has been considerable interest in the optical properties of type-II superlattices.[1,2] A type-II superlattice is one in which the lowest-lying conduction- and valence-band minima are on opposite sides of the semiconductor heterojunction. A type-II configuration is produced in a $Al_xGa_{1-x}As$/GaAs system when the width and depth of the confining potential causes the first GaAs confined electron state to lie above the $X$- minima of the $Al_xGa_{1-x}As$ barriers. For example, a GaAs/AlAs superlattice is type II when the thickness of the GaAs is less than 35 Å and that of the AlAs is greater than 15 Å.[1]

A type-I $Al_xGa_{1-x}As$/GaAs superlattice, one in which the lowest-lying conduction- and valence-band minima are both in the GaAs, may be induced to change to type II with the application of hydrostatic pressure.[3] The pressure causes a decrease in the indirect gap of the $Al_xGa_{1-x}As$ of some 1.0 meV/kbar, and an increase in the confined Γ-related state in the GaAs of approximately 10 meV/kbar. With sufficient pressure the confined state in the GaAs is pushed above the $X$ minima in the $Al_xGa_{1-x}As$, which now become the lowest-lying conduction-band minima in the quantum-well system and hence produce a type-II configuration.

An important feature of such type-II systems is that the type-II recombination energy depends directly on the valence-band discontinuity $\Delta E_V$. A schematic band diagram of a GaAs/AlAs type-II superlattice is shown in Fig. 1 from which it is clear that $\Delta E_V$ is given by

$$\Delta E_V = E_{gB}^X - E_{PL} + \Delta_{1HH}^{\Gamma} + \Delta_{1e}^{X} - E_{EB}\,, \qquad (1)$$

where $\Delta_{1HH}^{\Gamma}$ and $\Delta_{1e}^{X}$ are the hole and electron confinement energies, respectively, $E_{gB}^X$ the indirect gap of the barrier material, $E_{EB}$ the exciton binding energy, and $E_{PL}$ the energy of the observed type-II recombination emission. The effective masses of the electrons[1] ($m^*=1.1m_0$) and holes[4] ($m^*=0.34m_0$) are relatively large and therefore the confinement energies are relatively small, compared with the valence-band discontinuity, and tend to be canceled by the small exciton term. A good estimate of $\Delta E_V$ (Ref. 1) may, therefore, be obtained from just the measured value of $E_{PL}$ and knowledge of $E_{gB}^X$. Similarly, measurements as a function of pressure give the pressure coefficient $d\Delta E_V/dP$ from $dE_{PL}/dP$ if $dE_{gB}/dP$ is known.

We have performed high-pressure, low-temperature photoluminescence (PL) measurements on a type-II GaAs/AlAs superlattice. In the analysis of our data, and

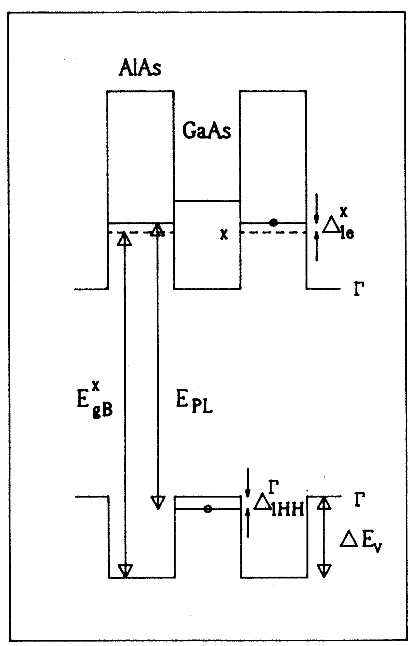


FIG. 1. A schematic representation of the band diagram of a type-II superlattice, defining the notation used in the text.

 

reported data, we assume that the pressure coefficient of the indirect gap in $Al_xGa_{1-x}As$ is independent of $x$ and equal to its value in bulk GaAs of $-1.3 \pm 0.1$ meV/kbar.[5] This is supported by the one measurement on bulk $Al_{0.3}Ga_{0.7}As$ which gave approximately $-1.0$ meV/kbar.[6] Consequently, we find that the valence-band discontinuity $\Delta E_V$ in the GaAs/AlAs superlattice increases at approximately 1 meV/kbar. We note that our result is supported by Van de Walle and Martin's[7] theoretical calculation of the pressure dependence of the valence-band discontinuity in GaAs/AlAs superlattices.

Inspection of reported high-pressure PL data for $GaAs/Al_xGa_{1-x}As$ quantum-well structures for various values of $x$ together with our data reported here shows that the type-II emissions have a pressure dependence $(dE_{PL}/dP)$ that is linearly dependent upon the value of $x$. Therefore, the above assumption implies that the pressure dependence of the valence-band discontinuity $(d\Delta E_V/dP)$ will also be linearly dependent upon alloy composition.

Until now it has generally been assumed that the fractional conduction- and valence-band offsets ($Q_C$ and $Q_V$) remain constant with pressure.[8-10] For the specific alloy composition $x=0.3$ we show that this is not the case, and in fact $Q_C$ and $Q_V$ decrease and increase, respectively, at a rate of $0.0013 \pm 0.0008$ kbar$^{-1}$.

## EXPERIMENTAL

The GaAs/AlAs superlattice used in these experiments was grown by molecular-beam epitaxy at Philips Research Laboratories, Redhill, and consisted of 60 periods of GaAs and AlAs. The GaAs thickness was measured by PL and transmission electron microscopy (TEM) to be $30 \pm 2$ Å and the AlAs to be $68 \pm 2$ Å.[1] The PL and excitation spectroscopy of the sample have already been discussed in some detail elsewhere.[1] The 8-K PL spectrum is shown in Fig. 2. The spectrum consists of five peaks, peak *A* being a relatively weak type-I recombination emission. Peak *B* has been assigned as a type-II emission involving the zero-phonon-assisted recombination of localized excitons formed from electrons in the $X_Z$ minimum in the AlAs and heavy holes in the GaAs. The remaining peaks, *C*, *D*, and *E*, are *X*-related-phonon-assisted emissions. The sample and a piece of bulk GaAs were mounted in a 0–8 kbar Be-Cu high-pressure cell[11] equipped with optical access. The pressure-transmitting fluid used was a 50:50 mixture of *n*-pentane and *iso*-pentane. The cell was inserted into a flow cryostat, but the changes in pressure were only made at room temperature to ensure hydrostatic conditions. The type-I recombination could not be observed at pressure because of a poorer signal-to-noise ratio with the pressure cell.

PL was excited by 10–100 mW of focused 514-nm argon ion laser radiation ($\sim 5\times10^2$ W cm$^{-2}$), analyzed by a 1*m* spectrometer, and detected by an ADC403 germanium diode detector. All the spectra were corrected for the spectral response of the detection system. The pressure-induced shifts in the spectra have been recorded as a function of the bulk GaAs band-edge emission (Fig. 3). This, as Venkateswaran *et al.*[12] pointed out, is a more accurate method of measuring pressure-related behavior. Any pressure coefficients may subsequently be deduced from the GaAs direct-gap pressure coefficient of 10.7 meV/kbar.[5]

## RESULTS

The PL peaks *B*, *C*, *D*, and *E* shift to lower energies by $-2.4 \pm 0.1$ meV/kbar with hydrostatic pressure, as shown in Figs. 3 and 4. To within experimental error the separations of the peaks remain constant.

Since the bulk moduli of GaAs and AlAs are very similar[7] we assume that the measured pressure effects are caused only by hydrostatic pressure, and that the effect of uniaxial stress is negligible. This assumption is further supported by a comparison of our hydrostatic pressure

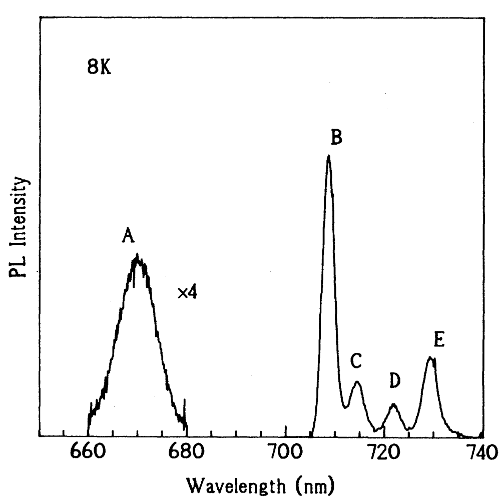


FIG. 2. The 8-K photoluminescence spectrum of the GaAs/AlAs superlattice at atmospheric pressure.

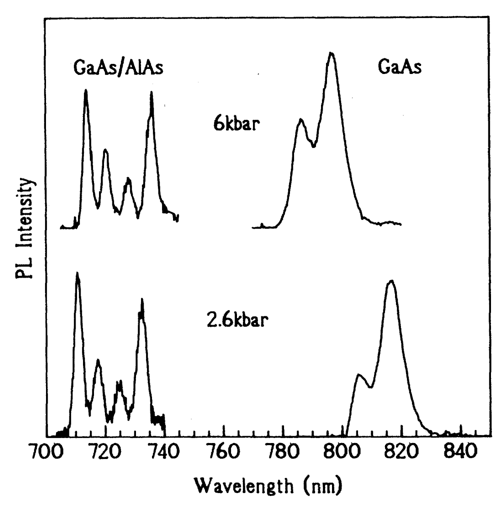


FIG. 3. Typical luminescence spectra of the GaAs/AlAs superlattice, together with bulk GaAs, at elevated pressures and 8 K.

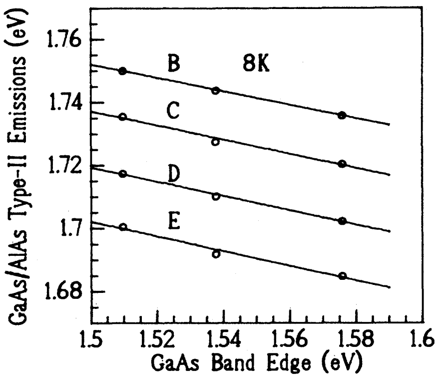


FIG. 4. The luminescence peak positions of the superlattice are plotted against the peak position of the bulk GaAs. The solid lines are least squares fits to the data.

data with data from recent uniaxial stress measurements[13] performed on a similar GaAs/AlAs superlattice, which showed that the relative spacings of the peaks and the intensity of peak $B$ are very sensitive to the application of uniaxial stress.

The measured pressure coefficients ($dE_{PL}/dP$) of type-II emissions from Wolford *et al.*[3] and Venkateswaran *et al.*[12] for various $Al_xGa_{1-x}As/GaAs$ superlattices with different alloy compositions and structures, together with our own measurement, are plotted against the aluminum concentration, shown in Fig. 5. The dependence is linear. The low scatter across the alloy range supports the assumption that uniaxial stresses are negligible since the data come from different samples in different experiments.

## DISCUSSION

While these pressure measurements confirm $X$-like nature of the PL spectra at liquid-helium temperatures, the pressure coefficient obtained is different from the reported value of $-1.3\pm0.1$ meV/kbar (Ref. 5) for the indirect gap in bulk GaAs. Since these measurements were made with respect to the bulk GaAs band edge, this small difference is significant and well outside experimental error.

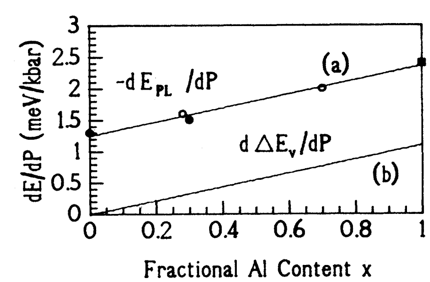


FIG. 5. (a) The pressure coefficient of type-II emissions from various samples is plotted against the alloy composition of the barrier. The open circles are from Ref. 3, the solid circles are from Ref. 11, and the square is our own data. The solid line is a least squares fit. Line (b) represents the change in the pressure coefficient of the valence-band discontinuity as a function of the alloy composition.

From Eq. (1) the pressure coefficient of the valence-band discontinuity is approximately,

$$d\Delta E_V/dP = dE^X_{gB}/dP - dE_{PL}/dP\ , \qquad (2)$$

where $dE^X_{gB}/dP$ is independent of alloy composition and equal to $-1.3$ meV/kbar. For the GaAs/AlAs superlattice therefore, $d\Delta E_V/dP$ is $+1.1\pm0.2$ meV/kbar. Furthermore, as shown in Fig. 5, $dE_{PL}/dP$ is linear with alloy composition ($x$) and so the constant $dE^X_{gB}/dP$ implies that the pressure coefficient $d\Delta E_V/dP$ is also linear in $x$, i.e.,

$$d\Delta E_V/dP = 1.1x \text{ (meV/kbar)}\ . \qquad (3)$$

This pressure dependence of the valence-band discontinuity is supported by theoretical calculations of Van de Walle and Martin,[7] who have predicted a value for $d\Delta E_V/dP$ in a GaAs/AlAs superlattice of $+0.8$ meV/kbar. Not surprisingly, the linear dependence on $x$ may be reproduced by the theory if the band gaps and valence-band deformation potentials of the ternary materials are deduced by linear interpolation.

Given the pressure dependence of the valence-band discontinuity, the conduction-band discontinuity pressure coefficient is given by

$$d\Delta E_C/dP = (dE^\Gamma_{gB}/dP - dE^\Gamma_{gW}/dP) - d\Delta E_V/dP\ , \qquad (4)$$

where $E^\Gamma_{gB}$ and $E^\Gamma_{gW}$ are the direct band gaps of the barrier and well materials, respectively. Since $dE^\Gamma_{gB}(x=1)/dP$ is not known, no conclusions for $\Delta E_C$ can be given for the GaAs/AlAs superlattice. However, for the alloy $Al_{0.3}Ga_{0.7}As$ the direct-gap pressure coefficient has been measured to be 9.9 meV/kbar.[14] From this and using Eq. (3), a superlattice with this ternary material in the barriers will have a value of $d\Delta E_C/dP$ of $-1.1\pm0.4$ meV/kbar. This can be expressed as a pressure dependence of the fractional valence and conduction offsets, i.e., $Q_V(x=0.3)$ increases at $0.0013\pm0.0008$ kbar$^{-1}$, and $Q_C(x=0.3)$ decreases at the same rate.

The change in $\Delta E_V$ with pressure is an order of magnitude smaller than the change in the direct gap of either the well or barrier material. Nonetheless, the change is significant in analyzing the behavior of quantum wells over the range of several tens of kbars. For example, it has important implications in modeling the behavior of type-I emissions in $GaAs/Al_x$- $Ga_{1-x}As$ quantum wells. Venkateswaran *et al.*[12] first pointed out that the pressure coefficients of the confined states in type-I $GaAs/Al_x$-$Ga_{1-x}As$ quantum wells are dependent upon their transition energy, i.e., the greater the confinement the smaller the pressure coefficient. Both Lefebvre, Gil, and Mathieu[8] and Gell *et al.*[10] have modeled this trend with the assumption of a pressure independent $Q_V$, and in the case of Gell *et al.* with the assumption that the pressure coefficients of the $\Gamma$ and $X$ band gaps of $Al_xGa_{1-x}As$ are the same as those of GaAs. Their fits, although indicating the right trend, are quantitatively unsatisfactory. We suggest that the fits may be improved by including the pressure dependence of $Q_V$.

A pressure-dependent offset ratio is not a property of the GaAs/$Al_xGa_{1-x}$As system alone. Recent high-pressure PL measurements by Lambkin *et al.*[15] show that the pressure behavior of type-I $Ga_xIn_{1-x}$As/InP quantum wells can only be successfully modeled when a pressure-dependent offset ratio is invoked. It is necessary, therefore, that band offset calculations are also capable of accurately modeling the behavior of the quantum-well systems under hydrostatic pressure, and this may prove a stringent test of the theory.

## CONCLUSION

We have performed high-pressure, low-temperature PL measurements on a GaAs/AlAs superlattice. The pressure coefficient of the type-II emissions was measured to be $-2.4 \pm 0.1$ meV/kbar. From this work and published data for $Ga_xAl_{1-x}$As quantum wells we find that the pressure coefficient of the type-II emissions from these wells is linearly dependent upon the alloy composition of the barrier material. We deduce that the GaAs/AlAs valence-band discontinuity increases at approximately 1.1 meV/kbar, in good agreement with theoretical calculations of Van de Walle and Martin.[7] Analysis of reported data conclusively shows that the fractional band offset for GaAs/$Al_{0.3}Ga_{0.7}$As barriers is pressure dependent, a fact which should be taken into consideration when interpreting pressure measurements of confinement energies and when developing theoretical models of the band offsets.

## ACKNOWLEDGMENT

J.D.L., A.R.A., and D.J.D. would like to thank the Science and Engineering Research Council for financial support.

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