PHYSICAL REVIEW B VOLUME 49, NUMBER 24 15 JUNE 1994-II

Absorption in InP/GaAs/InP type-II quantum wells

D. Hessman, M.-E. Pistol, J. Olajos, and L. Samuelson
Department of Solid State Physics, Box 118 Lund University, 221 00 Lund, Sweden
(Received 23 July 1993; revised manuscript received 24 March 1994)

Single strained layers of GaAs grown in between barriers of InP have been studied by absorption and photoluminescence-excitation spectroscopy. This structure is believed to be weakly type II, with the GaAs layer forming a quantum well for holes but a barrier for electrons. The absorption increases slowly close to the threshold and is similar to the photoluminescence-excitation spectrum. The absorption has been calculated using a single-band effective-mass model as well as using an eight-band effective-mass model, which include strain- and confinement-induced warping of the valence band. We find agreement between experiment and the results of both calculations with respct to the shape and magnitude of the absorption. No sharp excitonic peaks have been found.

I. INTRODUCTION

In a quantum well (QW), the difference in band gap between two semiconductors is offset by discontinuities in the conduction and valence bands. Depending on how the bands line up, the charge carriers (electrons and holes) will experience either a well or a barrier. If wells are formed for both electrons and holes the QW is called type I, whereas if one well and one barrier are formed the QW is called type II.[1] In this paper we will assume that a quantum well with a thin layer of GaAs strained to the surrounding InP is type II, with the GaAs layer acting as a barrier for the electrons and as a well for the holes. The absorption, due to transitions from the valence band to the conduction band, in a type-I QW has been studied both experimentally and theoretically.[1,2] The strength of the absorption has been found to be about 10^{-3} in a single GaAs/AlGaAs QW.[3] The absorption in a type-II QW is generally assumed to be several orders of magnitude smaller. The argument for this is that the spatial separation of electrons and holes should give a small overlap between the electron and hole wave functions and thus a low transition probability. However, an electron state with an energy close to the top of the barrier has a considerable penetration into the barrier, giving a large overlap with a localized hole state in the valence-band well; see Fig. 1. For a thick well this change from small to large overlap comes abruptly with increasing photon energy, as a real-space analogy to the abrupt change from indirect to direct transitions in an indirect-band-gap semiconductor. It is then tempting to distinguish the transitions as being either type II or type I, depending on whether the electrons and the holes are separated or not. However, if the well is thin, this picture might be misleading since the charge distribution is less distinct. Instead the magnitude of the overlap will increase continuously and slowly over an energy range determined by the thickness of the conduction-band barrier.

The wave-function penetration depends strongly on both the thickness and the height of the barrier. Specifically, a thin and low barrier will allow a large electron-hole overlap even for the lowest electron states, i.e., for states close to the conduction-band edge of the surrounding material. Since the luminescence is determined by the overlap of the lowest electron state and the highest hole state, such a type-II QW could be expected to have a strong luminescence intensity.

Strained layers of GaAs grown on InP have previously been spectroscopically studied by photoconductivity,[4,5] photoluminescence,[6,7] modulated reflectance,[7] Raman scattering,[7] and cathodoluminescence.[8] Studies under hydrostatic pressure have also been made.[9] These studies favor a type-II structure with a well for holes and a (low) barrier for electrons, although some controversy exists in the literature.[6,10] Theoretical calculations generally suggest that this system has a deep well for holes and a shallow well or a low barrier for electrons.[10,11] However, the accuracy of the parameters used in the calculations is not high enough to settle the type-I–type-II question from theory alone. GaAs grown on InP is not only interesting from a crystal growth[12] and physics point of view but has also been studied due to the device applications that are possible with integration of GaAs electronics and optoelectronic components made from InP.[13]

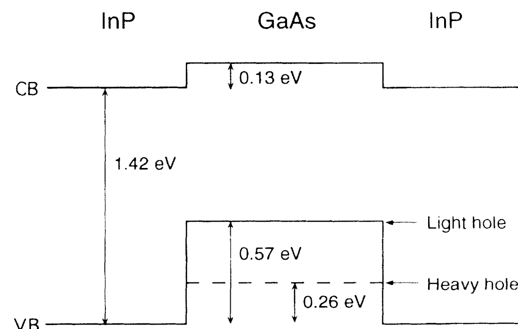

FIG. 1. Schematical description of the band-edge lineup of the GaAs/InP type-II quantum well. The values of the band offsets are calculated according to Ref. 7. In the valence band, due to the built-in strain, the QW formed by the light-hole bands (solid line) is deeper than the QW formed by the heavy-hole bands (dashed line).

 ©1994 The American Physical Society

This paper presents absorption measurements and photoluminescence excitation spectroscopy on single type-II QW's made of thin strained layers of GaAs in between barriers of InP, showing absorption spectra with onset close to the corresponding photoluminescence peaks and absorption strength similar to that of a type-I QW. The experimental results are compared to a simple single-band effective-mass model, which is then extended to include band mixing within an eight-band effective-mass model. Both models give good agreement with the experiments, including a magnitude of the absorption on the order of 0.1% at sufficiently high photon energy (100 meV above the photoluminescence transition energy). We present some experimental details in Sec. II, the calculations in Sec. III, and finally discuss the results in Sec. IV.

II. EXPERIMENTAL DETAILS

The samples used were grown by low-pressure metal-organic vapor-pulse epitaxy as described elsewhere[7] and consist of a (001)-oriented, Sn-doped InP substrate, a 2.5-μm InP buffer layer, a thin layer of GaAs, and finally a 250-Å capping layer. Two samples were grown, with GaAs thicknesses estimated from growth studies to be 18 and 28 Å.[7] This is believed to be below the critical thickness, as supported by cathodoluminescence experiments, showing no misfit dislocations.[8] The composition of the GaAs layer was determined by Raman spectroscopy, described in Ref. 7. As a reference sample the substrate with only the buffer layer grown was used.

A tunable sapphire:Ti laser was used for the photoluminescence excitation (PLE) measurements. The emission was dispersed by a double monochromator and detected by a liquid-nitrogen-cooled Ge detector. Some of the laser light was split off onto a thermopile, giving an intensity reference by which the PLE signal was normalized. The absorption measurements were done by measuring the light intensity transmitted by the samples $I_{\mathrm{sample}}(\omega)$ and the reference $I_{\mathrm{ref}}(\omega)$ using a Fourier transform infrared (FTIR) spectrometer. A tungsten lamp was used as a light source and the transmitted light was detected by either an InSb diode or a Si diode. The absorption spectra $A(\omega)$ were then obtained according to

$$A(\omega)=-\ln[I_{\mathrm{sample}}(\omega)/I_{\mathrm{ref}}(\omega)] , \quad (1)$$

which holds as long as $A(\omega)$ is small [i.e., $A(\omega)<0.05$] and if the spectra are measured under normal incidence. An estimation of the error in the measurement can be done if one considers the main source to the deviations from a perfectly flat base line in a FTIR spectrometer. Such deviations can occur due to slight fluctuations in the speed of the moving mirror of short duration or other abrupt processes. These events are rare, but when they happen they give rise to a deviation from the base line of maximum 1% in the total energy range measured (according to the manufacturer). Although care was taken during the measurements to ascertain the absence of invalid spectra, one still has to discuss the error limits within which the measured absolute absorbances are valid, especially when weak absolute signals are considered. Our estimate is that a possible background slope, which is not due to absorption processes in the QW, in the absorption spectra in Fig. 1 is less than 0.5%. All absorption measurements were performed at 10 K.

III. CALCULATIONS

When studying the type-II quantum well, it is instructive to first recall the type-I QW, in which the absorption in the simplest approach is proportional to the staircase-like two-dimensional density of states.[1] The absorption per unit thickness, i.e., the absorption coefficient, specifying the absorption properties of a bulk crystal is frequently used in literature to describe also the absorption of a QW. However, dividing the absorption by the QW width does not make sense since the well width dependence of the QW absorption has a steplike character. It is therefore more appropriate to discuss in terms of absorption per QW than to introduce an absorption coefficient. The type-II QW formed by a layer of GaAs in InP is believed to give a barrier for electrons in the conduction band and a well for holes in the valence band. In that case only the holes will be quantized and split into subbands as in the type-I case. The electron wave functions are, however, spread out over the whole crystal, slightly perturbed in the vicinity of the barrier. Increasing the photon energy above each subband threshold the absorption given will slowly start to increase. A further increase of the photon energy causes the absorption to approach a constant value, provided that the subband spacing of the holes is large enough. The rate by which the absorption approaches its maximum is a complicated function of the width and height of the conduction-band barrier, but the maximum value of the absorption is easily obtained by studying the limit of infinite photon energies.

As an input for the single-band calculation, a strain-shifted band lineup was established using linear deformation-potential theory.[7] According to this calculation, the barrier for the electrons is about 130 meV. Due to the strain, the degeneracy of the valence band is lifted, leading to an energy split between heavy- and light-hole bands. Of these bands, the light-hole band gives the deepest well, about 570 meV measured from the degenerate valence band of the unstrained InP. The heavy-hole well is about 260 meV deep. From these values the hole subband energies and the wave functions were obtained by an ordinary effective-mass calculation.[1] For the electrons, the 130-meV barrier is placed in the middle of an infinitely deep well of (macroscopic) width L_z in order to obtain the normalization.

The description with single parabolic bands is of course a naive simplification of the complicated valence-band structure. The mixing of light- and heavy-hole states in a QW is known to give a strongly nonparabolic energy dispersion, in some cases even a negative effective mass.[14] Such phenomena are expected to have a large influence on the absorption spectra. In this work the band mixing is included by using an eight-band $\mathbf{k}\cdot\mathbf{p}$ Hamiltonian[15–18] describing the light, heavy, and spin-orbit holes, in addition to the conduction band. The input parameters of the calculations are "conventional"[18] except that the un-

strained valence-band offset between InP and GaAs was chosen to be 0.38 eV instead of 0.34 eV.[7,8] The calculations have been performed on an infinite stack of thin GaAs layers separated by InP thick enough to give a negligible coupling between the GaAs layers. For the localized hole states, even rather closely spaced wells are essentially decoupled. The delocalized electron states, however, become confined between the GaAs barriers, and thus a much larger periodicity is needed in order to keep the artificially induced subband splitting reasonably small. This in turn increases the numerical work, since a larger number of plane waves have to be used in the expansion to maintain the accuracy. We used 43 plane waves for the expansion of the wave functions, and a superlattice period of about 700 Å was used to ensure negligible superlattice effects.

IV. RESULTS AND DISCUSSION

Figure 2 shows absorption and photoluminescence (PL) spectra of two different samples with GaAs layer thicknesses of 18 and 28 Å. For the 18-Å sample, a photoluminescence excitation spectrum is also shown. A PLE measurement on the thicker sample was not possible due to the limited wavelength region covered by the sapphire:Ti laser. The PL spectra show two peaks, of which the low-energy peak is believed to be a defect at the GaAs/InP interface. For the 18-Å sample, the splitting between the peaks is 26 meV and for the 28-Å sample the splitting is 35 meV. Lattice-matched QW's of GaInAs/InP are known to show monolayer splitting, i.e., within the area probed by the incident laser, more than one QW thickness is present, giving multiple peaks in luminescence.[19] One could therefore argue that a monolayer splitting is seen also here. An argument in favor of the defect interpretation is that no clear fluctuations in the relative intensity of the two peaks is observed when going across the sample. The high-energy peak is very close in energy to the onset of the corresponding absorption spectrum. The Stokes shift, estimated by the energy difference between the onset of the absorption and the extrapolated onset of the high energy PL peak, is approximately 10 meV. The PLE spectrum is in very good agreement with the absorption measurement except for energies above 1.25 eV, where the laser intensity was very low giving difficulties in the normalization. No sharp excitonic peaks are found, either in the PLE or in the absorption spectra.

Calculated absorption spectra using the two models described in Sec. III are shown in Fig. 3. Both models give two bound hole states, one with a light-hole character at $\mathbf{k}=0$ and one with a heavy-hole character. Due to the built-in strain, the light-hole state is highest in energy, i.e., closest to the conduction-band edge. The single-band model has an onset at 1.17 eV (1.06 eV) for the 18-Å- (28-Å-) thick QW, corresponding to an excitation from the top of the light-hole subband to the bottom of the conduction-band continuum. The absorption then increases slowly, with a tendency to flatten out, until the photon energy is high enough to start exciting the heavy-hole subband. This second onset occurs at 1.24 eV (1.21 eV) for the 18-Å (28-Å) sample. The eight-band model gives roughly the same shape of the absorption, with a tendency to lower energies, in particular for the heavy hole. A second difference is that the magnitude of the absorption calculated with the eight-band model is

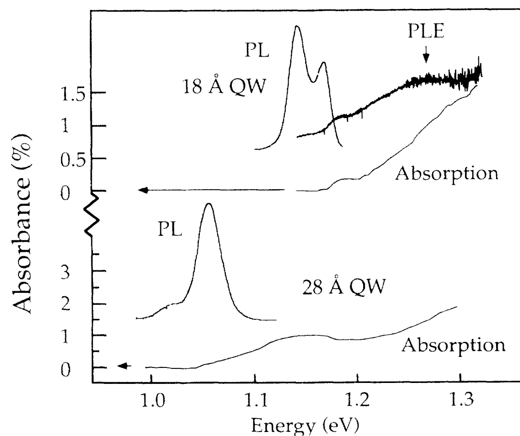

FIG. 2. Absorption and photoluminescence (PL) spectra of two GaAs/InP QW samples with estimated GaAs-layer thicknesses of 18 and 28 Å, respectively. For the 18-Å sample a photoluminescence excitation (PLE) spectrum (in arbitrary units) is also shown. In the PL spectra, the high-energy peaks are attributed to band to band transitions, while the low-energy peaks are believed to be related to an interface defect.

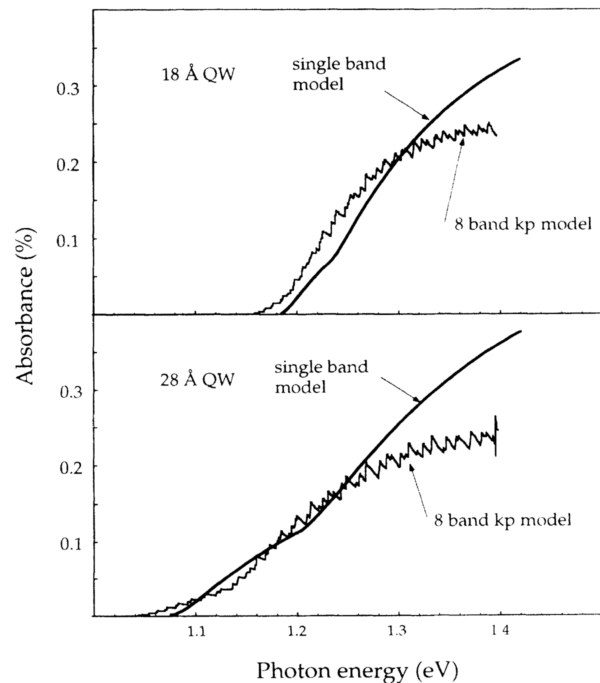

FIG. 3. Calculated absorption spectra for two GaAs/InP type-II QW samples with GaAs-layer thicknesses of 18 and 28 Å, respectively. Two models were used: a single-band model (dashed line) giving parabolic in-plane energy dispersion, and an eight-band $\mathbf{k}\cdot\mathbf{p}$ model (solid line) including the strong valence-band mixing due to strain and confinement. No excitonic effects were included in the two models.

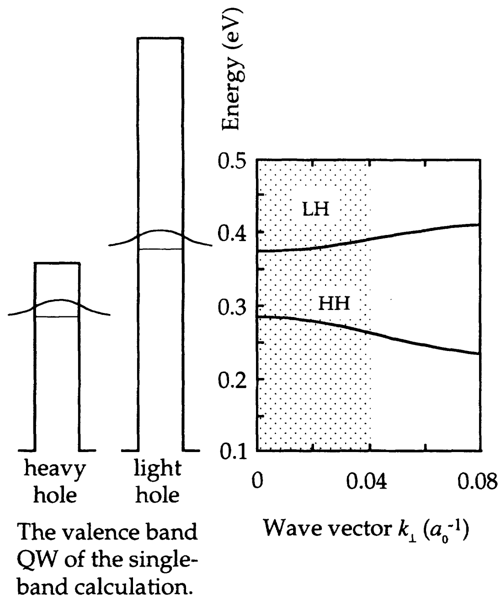

FIG. 4. The in-plane valence-band dispersion $E_j(k)$, with k along (001) of a strained layer of GaAs in between InP as calculated with the eight-band $\mathbf{k}\cdot\mathbf{p}$ model, the shaded area indicating the volume of k space sampled by the absorption. Two bound hole states are found, the ground state (LH) being constructed from light-hole and spin-orbit states at $\mathbf{k}=0$ and an excited state (HH) being constructed from heavy-hole states at $\mathbf{k}=0$. Note the electronlike mass of the LH state close to $k=0$. The energy is taken relative to the valence-band edge of InP, increasing values corresponding to deeper bound states. To the left, the heavy- and light-hole wells used in the single-band calculation are shown as a reference.

somewhat lower than that calculated with the single-band model at higher photon energies, i.e., above 1.3 eV.

The single-band model does not include any mixing of light-hole states with split-off band holes. Even more severe is that also the mixing between light- and heavy-hole states which occur at finite $\mathbf{k}$ is neglected. The in-plane energy dispersion of the valence band as given by the eight-band $\mathbf{k}\cdot\mathbf{p}$ model is shown in Fig. 4, for the 28-Å sample. The nonparabolicity of this curve, e.g., the negative (electronlike) effective mass, could be expected to have important implications on the absorption spectrum. However, as seen from Fig. 3, this is not the case. Quantitatively, the band-mixing model gives the same result as the single-band calculation. The reason for this is that even if the hole density of states might have van Hove singularities, the joint density of states involved in the absorption will be nonsingular due to the much lighter electron mass. The difference in absorption magnitude between the two models is mainly a consequence of the almost flat valence-band dispersion given by the light- and heavy-hole mixing, as compared to the parabolic bands of the single-band model. It can be seen from a comparison between Figs. 2 and 3 that the calculated absorption strength is somewhat lower than the measured absorption. We do not know the reason for this discrepancy.

In these discussions we have assumed that the structure is type II, based on the conclusion of Refs. 4 and 9, although a weakly type-I structure would give very similar absorption spectra. The reason is that there is very little difference between the electronic wave functions in a weakly type-II structure and in a weakly type-I structure. This makes it very difficult to determine if a structure is type II or type I, as noted in the Si/SiGe system.[20–22]

In summary, we have measured and modeled the absorption spectra of single InP/GaAs/InP type-II quantum wells and found good agreement between experiment and calculations based on both eight- and single-band effective-mass theory. The magnitude of the absorption is on the order of 0.1%, which is similar to the value found for type-I QW's. This is in agreement with what could be expected from simple theoretical considerations. The discrepancy between theory and experiment may be attributed to excitonic transitions, which were not included in our models.

ACKNOWLEDGMENTS

We gratefully acknowledge the helpful support in the growth of the samples by Dr. W. Seifert, Dr. J.-O. Fornell, and Dr. L.-Å. Ledebo at Epiquip AB. We also thank Professor D. Gershoni, who generously taught one of us (M.E.P.) to use his computer code which was used to carry out the multiband calculations. This work, which was performed within the nanometer consortium in Lund, was supported by the Swedish Natural Science Research Council and the Swedish National Board for Technical Development, as well as the Bank of Sweden Tercentenary Foundation.

[1]G. Bastard, *Wave Mechanics Applied to Semiconductor Heterostructures* (Les Editions de Physique, Paris, 1988).

[2]P. Voisin, C. Delalande, M. Voos, L. L. Chang, A. Segmuller, C. A. Chang, and L. Esaki, Phys. Rev. B **30**, 2276 (1984).

[3]C. Weisbuch and B. Vinter, *Quantum Semiconductor Structures: Fundamentals and Applications* (Academic, San Diego, 1991).

[4]D. Gershoni, H. Temkin, J. M. Vandenberg, S. N. G. Chu, R. A. Hamm, and M. B. Panish, Phys. Rev. Lett. **60**, 448 (1988).

[5]J. Barrau, B. Brousseau, M. Brousseau, R. J. Simes, and L. Goldstein, Electron. Lett. **28**, 786 (1992).

[6]R. Meyer, Hilde Hardtdegen, R. Carius, D. Grützmacher, M. Stollenwerk, P. Balk, A. Kux, and B. Meyer, J. Electron. Mat. **21**, 293 (1992).

[7]M.-E. Pistol, M. Gerling, D. Hessman, and L. Samuelson, Phys. Rev. B **45**, 3628 (1992).

[8]M.-E. Pistol, A. Gustafsson, M. Gerling, L. Samuelson, and H. Titze, J. Cryst. Growth **107**, 458 (1991).

[9]M. Gerling, M.-E. Pistol, L. Samuelson, W. Seifert, J.-O. Fornell, and L. Å. Ledebo, Appl. Phys. Lett. **59**, 806 (1991).

[10]T. Y. Wang and G. B. Stringfellow, J. Appl. Phys. **67**, 345 (1990).

[11]D. D. Nolte, J. Vac. Sci. Technol. B **7**, 820 (1989).
[12]I. Tanaka and S. Ohkouchi, Jpn. J. Appl. Phys. Lett. **30**, L1662 (1991).
[13]Y. H. Lo, R. Bhat, and T. P. Lee, Electron. Lett. **24**, 865 (1988).
[14]G. D. Sanders and Y.-C. Chang, Phys. Rev. B **35**, 1300 (1987).
[15]J. M. Luttinger and W. Kohn, Phys. Rev. **97**, 869 (1955).
[16]T. B. Bahder, Phys. Rev. B **41**, 11 992 (1990).
[17]G. A. Baraff and D. Gershoni, Phys. Rev. B **43**, 4011 (1991).
[18]D. Gershoni, C. H. Henry, and G. A. Baraff, IEEE J. Quantum Electron. **29**, 2433 (1993).
[19]W. Seifert, J.-O. Fornell, L.-Å. Ledebo, M.-E. Pistol, and L. Samuelson, Appl. Phys. Lett. **56**, 1128 (1990).
[20]R. People, J. C. Bean, D. V. Lang, A. M. Sergent, H. L. Störmer, K. W. Wecht, R. T. Lynch, and K. Baldwin, Appl. Phys. Lett. **45**, 1231 (1984).
[21]G. Abstreiter, H. Brugger, T. Wolf, H. Jarke, and H.-J. Herzog, Phys. Rev. Lett. **54**, 2441 (1985).
[22]M. Wachter, K. Thoube, R. Bauer, F. Schäffler, H.-J. Herzog, and E. Kasper, Thin Solid Films **227**, 10 (1992).