

tive of the XPS spectrum and the low-energy region of the APS threshold over which effects due to the core-level width are expected to dominate. This close agreement strongly suggests that identical initial (core) energy states are involved for both XPS and APS in this case. However, as a result of the increasing predominance of final-state effects on the high-energy side of the APS threshold, there is no obvious correspondence between features in APS and the peak in the XPS core-level density of states from which the "binding energy" is usually determined.

¹R. L. Park and J. E. Houston, *Phys. Rev. B* **6**, 1073 (1972).

²J. A. Bearden and A. F. Burr, *Rev. Mod. Phys.* **39**, 125 (1967).

³See Ref. 1 and also J. E. Houston, R. L. Park, and G. E. Laramore, *Phys. Rev. Lett.* **30**, 846 (1973).

⁴R. L. Park, J. E. Houston, and D. G. Schreiner, *Rev. Sci. Instrum.* **41**, 1810 (1970).

⁵J. E. Houston and R. L. Park, *J. Chem. Phys.* **55**, 4601 (1971).

⁶E. J. McGuire, *Phys. Rev. A* **3**, 587 (1971).

Quantum States of Confined Carriers in Very Thin $\text{Al}_x\text{Ga}_{1-x}\text{As-GaAs-Al}_x\text{Ga}_{1-x}\text{As}$ Heterostructures

R. Dingle, W. Wiegmann, and C. H. Henry

Bell Laboratories, Murray Hill, New Jersey 07974

(Received 24 June 1974)

Quantum levels associated with the confinement of carriers in very thin, molecular-beam-grown $\text{Al}_x\text{Ga}_{1-x}\text{As-GaAs-Al}_x\text{Ga}_{1-x}\text{As}$ heterostructures result in pronounced structure in the GaAs optical absorption spectrum. Up to eight resolved exciton transitions, associated with different bound-electron and bound-hole states, have been observed. The heterostructure behaves as a simple rectangular potential well with a depth of $\approx 0.88\Delta E_g$ for confining electrons and $\approx 0.12\Delta E_g$ for confining holes, where ΔE_g is the difference in the semiconductor energy gaps.

One of the most elementary problems in quantum mechanics is that of a particle confined to a one-dimensional rectangular potential well.¹ In this Letter, we report the direct observation of numerous bound-electron and bound-hole states of rectangular potential wells, formed by a thin layer of GaAs sandwiched between $\text{Al}_x\text{Ga}_{1-x}\text{As}$ slabs. The levels are observed by measuring the optical absorption of the central GaAs layer of the structure. The presence of the bound states introduces a series of resolved exciton transitions in the above-band-gap absorption spectrum of GaAs layers less than 500 Å thick. A range of heterostructures, with central GaAs layers as thin as 70 Å, has been studied. The heterostructures produce two attractive potential wells of different depths, one for electrons and one for holes. Analysis of the spectra shows that the wells are extremely rectangular and that the electron and hole well depths are approximately 88 and 12% of ΔE_g , respectively.

The investigation was made possible by two recent developments. The first is the emergence of molecular-beam epitaxy^{2,3} (MBE) as a technique for the growth of layers of III-V semicon-

ductors. Our observations demonstrate the great precision of MBE in fabricating thin and uniform layers. The second is the development of selective chemical etches⁴ for the removal of the GaAs substrate without damaging the thin epitaxial layers of the heterostructure.

During the last decade there has been intense activity in the study of electrons confined to thin layers. These studies were primarily experiments on metals, superconductors, and metal-oxide-semiconductor devices.⁵ Recently, Chang, Esaki, and Tsu⁶ reported observing two levels in tunneling experiments involving $\text{GaAs-Al}_x\text{Ga}_{1-x}\text{As}$ heterostructures, grown by MBE, with GaAs thicknesses of 40–50 Å. This confining layer is thinner than any we have studied and in their experiment the applied electric field distorts the rectangular well into a trapezoidal shape. Nevertheless, the energies they quote are consistent with our more detailed observations.

With the use of MBE, the precision growth of multilayer $\text{GaAs-Al}_x\text{Ga}_{1-x}\text{As}$ heterostructures has been possible. The usual growth conditions are as follows: vacuum before growth, $\leq 1 \times 10^{-9}$ mm; vacuum during growth, $\sim 1 \times 10^{-7}$ mm (ar-

senic); As₄ source; {100} GaAs substrate; temperature, 600°C; and semiautomatic shuttering on the Al oven. At our growth rate, 1 μm per hour, the shutter time is equivalent to ~0.5 Å of growth. To increase the GaAs optical absorption, as many as fifty GaAs layers have been grown in a single structure. These GaAs layers are separated by Al_xGa_{1-x}As layers which are normally > 250 Å thick. The observed bound states penetrate only about 25 Å into the Al_xGa_{1-x}As layers. Consequently, the carriers are tightly bound to individual layers. Hence, we are studying energy levels of a single well, not energy bands of a superlattice. Although it is not possible to measure the electrical properties of the layers themselves, thicker layers, grown under identical conditions, are $p \sim 10^{14} - 10^{15} \text{ cm}^{-3}$ (GaAs) and $p \sim 10^{16} - 10^{17} \text{ cm}^{-3}$ (Al_xGa_{1-x}As). As a consequence of the $\approx 0.12\Delta E_g$ discontinuity in the valence band, the Al_xGa_{1-x}As layers will be depleted. Band bending of 1–10 meV in the Al_xGa_{1-x}As layers, caused by this depletion, should have a negligible effect on the energy levels. This was confirmed by the fact that the spectral features did not change when the thickness of the Al_xGa_{1-x}As layer was varied from 125 to 500 Å. Most data to be discussed here were obtained from structures with $x = 0.2 \pm 0.01$.

If a particle is completely confined to a layer of thickness L_z (by an infinite potential well) then the energies of the bound states are

$$E = E_n + (\hbar^2/2m)(k_x^2 + k_y^2), \quad (1)$$

where

$$E_n = (\hbar^2\pi^2/2m)(n/L_z)^2, \quad n = 1, 2, 3. \quad (2)$$

In reality the potential well is finite and the above solutions are inadequate for a quantitative analysis of the data. We have used a computer to obtain the eigenvalues for a well depth V_0 . The behavior of energy levels relative to those obtained for $V_0 = \infty$ is shown in Fig. 1. Both the level spacing and the number of bound states decrease as V_0 is decreased, but the $n=1$ state exists for all positive values of V_0 . Thus, for all attractive potential wells, at least one bound state will exist for each type of carrier.

There will be two series of bound-hole states associated with the $\pm \frac{3}{2}$ and $\pm \frac{1}{2}$ valence bands, quantized in the z direction. We will refer to these as the states of the heavy and light hole. The appropriate masses for calculating these states are $(\gamma_1 - 2\gamma_2)^{-1}m_0 \approx 0.45m_0$ and $(\gamma_1 + 2\gamma_2)^{-1}m_0 \approx 0.08m_0$, respectively.⁷ These masses deter-

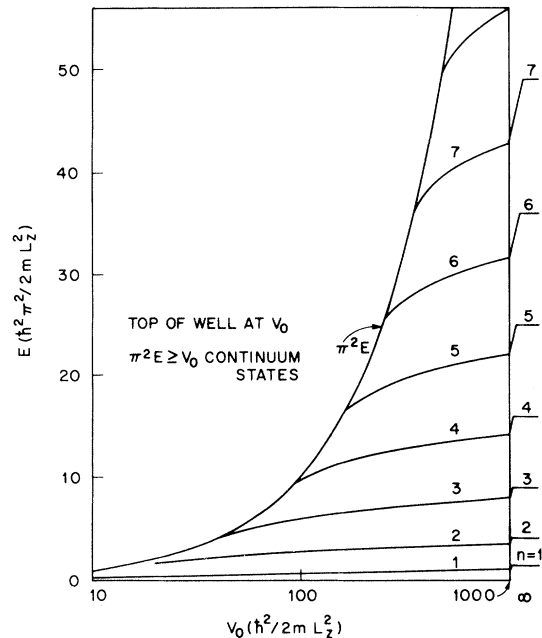


FIG. 1. Calculated energy levels of a particle in a symmetrical rectangular potential well of depth V_0 .

mine the k_z (001) dispersion of these bands. Coulomb attraction correlates the motion of the carriers in x and y directions, forming exciton states with peaks in the optical absorption spectrum. States with the same quantum number n have a substantially greater electron-hole overlap. Consequently, excitons with these states will dominate the optical absorption spectrum. Therefore we expect two series of exciton peaks, one series associated with equal- n states of the electron and the heavy hole and one series associated with equal- n states of the electron and the light hole.

Figure 2 displays typical absorption spectra of our structures in the band-edge region of GaAs at 2 K. Roughening the external surfaces with an etch removed all structure due to interference effects. There is negligible absorption in the Al_{0.2}Ga_{0.8}As layers below 1.75 eV. The trace labeled $L_z = 4000 \text{ Å}$ is typical of high-purity bulk GaAs and it shows none of the quantum effects central to this paper. It does, however, show the dominant excitonic⁸ contribution to the bulk GaAs band-edge absorption. The traces $L_z = 210 \text{ Å}$ and $L_z = 140 \text{ Å}$ show well-developed structure above the usual GaAs band gap. Moreover, the exciton peak of bulk GaAs moves smoothly to higher energy as L_z is reduced below 500 Å,

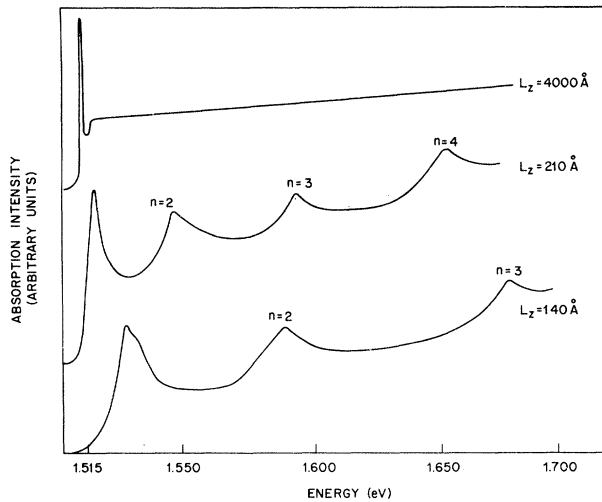


FIG. 2. Typical absorption spectra at 2 K. The traces labeled $L_z = 210 \text{ \AA}$ and $L_z = 140 \text{ \AA}$ show excitons associated with the electron and hole, each in the n th bound state. For $L_z = 4000 \text{ \AA}$, the absorption coefficient α (cm^{-1}) is about 2.5×10^4 at the exciton peak and $\approx 1 \times 10^4$ in the band-to-band region. Similar values are obtained for the thinner multilayers.

thereby becoming the lowest absorption feature in the quantum limit. The faint doubling of the lowest peak in the $L_z = 140\text{-\AA}$ spectrum is real. This splitting increases as L_z^{-2} and results in two resolved peaks in thinner layers. No doubling is observed for the $n = 2$ peak.

The single exciton series and the doubling of the lowest peak can be explained by assuming that the potential well for holes is weak. Then for layers with small L_z , for which two exciton series could be resolved, there is only one bound state for the light holes and consequently only the lowest exciton peak will double. The well depth for holes was determined by fitting the splitting of the lowest peak in a series of samples (see Fig. 3). It was found to be about 28 meV or $\approx 12\%$ of ΔE_g . In making this fit, the known heavy- and light-hole masses and the measured L_z were used. The well depth for electrons must therefore be about $0.88\Delta E_g = 220 \text{ meV}$.

Figure 3 is a plot of L_z versus the measured exciton energies. L_z was determined, within $\pm 10\%$, from the measured rate of growth of the epitaxial layer. The solid theoretical curves were constructed from the known electron mass $m_e = 0.0665m_0$,⁹ the known heavy-hole mass, and the known well depths. Absolute energies were determined by extrapolating the measured ener-

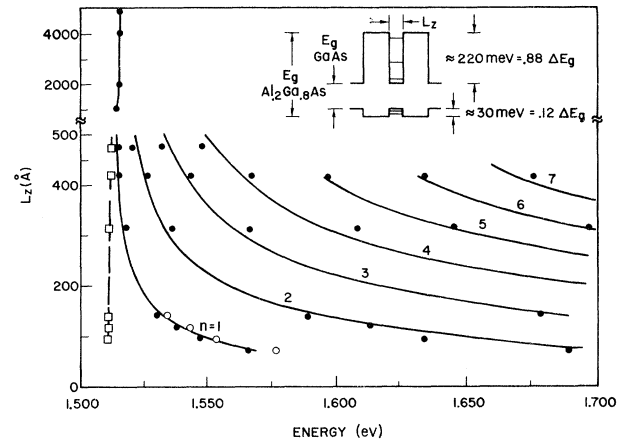


FIG. 3. The data points are a plot of the measured L_z versus the measured exciton energies. The open circles are resolved excitons associated with the light-hole $n = 1$ state. The open squares are the extrapolated energies for $n = 0$. The solid curves are the calculated energies for the excitons associated with the electron and heavy hole, each in the n th bound state.

gies to $n = 0$. These extrapolated energies are shown by the open squares. The calculated energies of the bound states for $n = 1, 2, \dots$ were then added to these energies. The excellent agreement between theory and experiment is a confirmation that the well depths and masses are correct and that the potential wells are quite rectangular. By varying the depth of the potential well for electrons, we found that a depth of $220 \pm 30 \text{ meV}$ was required to fit the data in Fig. 3, confirming the value deduced above. Attempts to fit the energies with eigenvalues of nonrectangular wells indicated that the potential step forming the side of the well occurs in less than 5 \AA .

The energy of the open squares in Fig. 3 is equal to the band-gap energy of GaAs minus the exciton binding energy. The energy of the squares decreases slowly with L_z and eventually saturates at $L_z < 200 \text{ \AA}$ at $1.512 \pm 0.001 \text{ eV}$, about 3 meV below the bulk exciton energy of 1.515 eV (2 K), indicating that the exciton binding energy increases from 4 meV⁸ to $\sim 7 \text{ meV}$ as a consequence of carrier confinement. This increase in binding energy agrees quite well with that expected¹⁰ for a three-dimensional exciton as it approaches the two-dimensional limit.

We have benefited from conversations with E. O. Kane, G. A. Baraff, A. C. Gossard, J. C. Hensel, and M. B. Panish. L. Kopf rendered valuable technical assistance.

¹W. Kauzmann, *Quantum Chemistry* (Academic, New York, 1957), p. 183.

²J. R. Arthur, *J. Appl. Phys.* **39**, 4032 (1968).

³A. Y. Cho, *J. Vac. Sci. Technol.* **8**, 531 (1971).

⁴R. A. Logan and F. K. Reinhart, *J. Appl. Phys.* **44**, 4172 (1973).

⁵Some recent publications are J. M. Rowell, *Phys. Rev. Lett.* **30**, 167 (1973), and *J. Vac. Sci. Technol.* **10**, 702 (1973); R. C. Jaklevic, J. Lambe, M. Mikkar, and W. C. Vassell, *Phys. Rev. Lett.* **26**, 88 (1971), and *Solid State Commun.* **10**, 199 (1972); R. A. Wheeler and R. W. Ralston, *Phys. Rev. Lett.* **27**, 925 (1971); D. C. Tsui, in *Proceedings of the Eleventh International Conference on the Physics of Semiconductors, Warsaw, Poland, 1972*, edited by The Polish Academy of Sciences (PWN—Polish Scientific Publishers, Warsaw,

1972), p. 109; A. Kamgar, P. Kneschawek, G. Dorga, and J. F. Koch, *Phys. Rev. Lett.* **32**, 125 (1974).

⁶L. L. Chang, L. Esaki, and R. Tsu, *Appl. Phys. Lett.* **24**, 593 (1974).

⁷The dispersion of the bands is discussed by J. C. Hensel and G. Feher, *Phys. Rev.* **129**, 1 (1963). The band parameters were taken from R. L. Aggarwal, in *Semiconductors and Semimetals*, edited by R. K. Willardson and A. C. Beer (Academic, New York, 1972), Vol. 9, p. 239.

⁸D. D. Sell, R. Dingle, S. E. Stokowski, and J. V. DiLorenzo, *Phys. Rev. Lett.* **27**, 1644 (1971).

⁹G. E. Stillman, C. M. Wolfe, and J. O. Dimmock, *Solid State Commun.* **7**, 921 (1969).

¹⁰E. O. Kane, *Phys. Rev.* **180**, 852 (1969), and private communication.

Matrix Element Dependence of Optical Excitation and Auger Decay of 5d Core Holes in Bi₂Te₃ †

Z. Hurych,* J. C. Shaffer, D. L. Davis, and T. A. Knecht

Department of Physics, Northern Illinois University, DeKalb, Illinois 60115

and

G. J. Lapeyre, P. L. Gobby, and J. A. Knapp

Department of Physics, Montana State University, Bozeman, Montana 59715

and

C. G. Olson

Ames Laboratory, Iowa State University, Ames, Iowa 50010

(Received 16 November 1973)

The spectral dependence of the Auger component of the uv photoemission and the far-uv reflectance show that the optical excitation of 5d core states cannot be described in terms of simple density of states indicating that matrix element effects must be included.

We report ultraviolet-photoelectron-spectroscopy data ($24 \text{ eV} < h\nu < 30 \text{ eV}$) for Bi₂Te₃ which contain information on optical transitions from 5d core states to conduction band states below the direct emission threshold. The emission in this photon energy region has a strong component resulting from energetically allowed Auger decay of core holes. Similar to previously reported works on other solids, the spectral dependence of Auger emission is found to exhibit the same features as the optical-reflectance spectra.¹ The central issue of this Letter is the evidence that the structure in both Auger and reflectance spectra cannot be explained in terms of a simple density-of-states model despite the fact that the initial state can be considered a core state. That is, the structure in the two spectra does not reflect directly the spin-orbit splitting of the 5d_{5/2}

and 5d_{3/2} core states, a fact which indicates the effect of matrix elements on core excitation.

This finding should also be of importance to soft-x-ray absorption spectroscopy.

A detailed description of the photoemission spectrometer, which utilizes the UWPSL 240-MeV storage ring, has been given elsewhere.² The overall energy resolution and the signal-to-noise ratio were better than 0.2 eV and 100:3, respectively. Rhombohedral (space group D_{3d}^5) single crystals³ of Bi₂Te₃ were grown from the 99.9999% purity elements using a previously described technique.⁴ Bi₂Te₃ is a strongly anisotropic semiconductor (band gap $E_g \sim 0.15 \text{ eV}$) of layered structure which results in excellent quality of *in situ* ($\sim 5 \times 10^{-10}$ Torr) cleaved surfaces.

The photoemission energy distribution curves (EDC's) are first used (Fig. 1) to determine the