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Raman spectra of shallow acceptors in quantum-well structures

D. Gammon and R. Merlin
Department of Physics, University of Michigan, Ann Arbor, Michigan 48109-1120

W. T. Masselink* and H. Morkoc†
Coordinated Science Laboratory, University of Illinois at Urbana-Champaign, Urbana, Illinois 61801

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We report resonant Raman spectra of the shallow acceptor Be in GaAs-$Al_xGa_{1-x}As$ quantum-well structures. Samples preferentially doped at the center and at the edge of the wells with well widths in the range 70–165 Å were investigated. The data show transitions between acceptor levels derived from the bulk states $1S_{3/2}[\Gamma_8]$ and $2S_{3/2}[\Gamma_8]$. Confinement-induced splittings of these levels have been observed. The results are in good agreement with recent calculations.

Shallow impurities in semiconductor quantum-well structures (QWS's) form quasi-two-dimensional hydrogenic systems whose parameters can be both easily varied and controlled with great accuracy. Recent theoretical[1–4] and experimental[5–10] investigations of such systems have elucidated many of their interesting properties. Calculations[1–4] predict considerable confinement-induced shifts and splittings of impurity levels for $L \approx a_0$ (L is the well width and a_0 is the effective Bohr radius of the impurity). The magnitude and nature of these effects depend on the parameters of the structure and the position of the impurity in the well. Following the pioneering experimental work of Miller, Gossard, Tsang, and Munteanu,[5] there have been many reports of photoluminescence (acceptors[6,7] and donors[6,8]), and also far-infrared[9] (donors) and Raman scattering[10] (donors) measurements on GaAs-$Al_xGa_{1-x}As$ QWS's which have confirmed the expected occurrence of pronounced shifts in the impurity spectrum. A number of features of the problem, however, have so far escaped a clear experimental demonstration. In particular, splittings of impurity levels resulting from quantum confinement have not as yet been observed. Further, the available information on the position dependence of the spectrum is rather limited. Most experimental studies[5–10] have focused on the behavior of impurities placed in the central region of the wells. Edge-doped samples have received comparatively much less attention,[4] even though the determination of their spectra is relevant to the questions of (i) wave-function boundary conditions at the interface, and (ii) impurity segregation during growth. In this Rapid Communication we report resonant Raman scattering measurements of acceptor transitions in GaAs-$Al_xGa_{1-x}As$ QWS's doped with Be. Both center- and edge-doped samples were investigated. The data show energy shifts and clearly resolved splittings of the ground state $1S_{3/2}[\Gamma_8]$ and the excited state $2S_{3/2}[\Gamma_8]$ due to confinement. Results allow a precise determination of transition energies that can be compared with theoretical predictions.

The samples used in this work were grown by molecular-beam epitaxy on (001) Si-doped GaAs substrates with a 0.2–0.5-μm buffer layer on top. They consist of 20–50 periods of $\approx$100-Å-thick $Al_{0.3}Ga_{0.7}As$ barriers and GaAs layers of different thicknesses L, as indicated in Table I. For these structures, the overlap of wave functions associated with different wells can be neglected. Be acceptors ($a_0 \approx 20$ Å) were incorporated during growth at the center or edges of the GaAs slabs with dopant concentrations (p) shown in Table I. The width of the doping spike was nominally $L/2$ in the sample with $L = 92$ Å, and $L/3$ in the other center-doped QWS's. The edge-doped structure has no impurities in the central half of the wells. Values of L were determined from photoluminescence and absorption measurements.[11] The Al mole fraction in the barriers was determined from growth conditions and confirmed from the positions of longitudinal optical phonons in the Raman spectra.[12]

Resonant Raman experiments were performed using laser energies ω_L in the vicinity of the HH2 (LH2) exciton[13] [associated with the first excited conduction and heavy-hole (light-hole) states of the quantum wells] for the samples with $L = 70$, 92, and 108 Å ($L = 142$ and 165 Å). The resonances are very sharp, with widths less than ≈ 5 meV. The positions of the resonant maxima were found to be in good agreement with calculated transition energies using recently reported band-gap discontinuities.[14] Spectra were recorded in the $z(x',x')\bar{z}$, $z(x',y')\bar{z}$, and $z(x'+iy', x'\pm iy')\bar{z}$ backscattering configurations where z is normal to the layers and x',y' are along the [110] and [1$\bar{1}$0] directions. The point group of an impurity at the center of the wells is D_{2d}. The four scattering geometries allowed us to determine four [$\Gamma_1(A_1)$, $\Gamma_2(A_2)$, $\Gamma_3(B_1)$, and $\Gamma_4(B_2)$] out of the five irreducible components of the Raman tensor [the fifth representation, $\Gamma_5(E)$, was not accessible to our experiments as its determination requires photons polarized along

TABLE I. Sample parameters, measured and calculated (Ref. 4) (in parentheses) energies of acceptor transitions A ($1S_{3/2}[\Gamma_6] \rightarrow 2S_{3/2}[\Gamma_6]$), B ($1S_{3/2}[\Gamma_6] \rightarrow 2S_{3/2}[\Gamma_7]$), and C ($1S_{3/2}[\Gamma_6] \rightarrow 1S_{3/2}[\Gamma_7]$). Samples preferentially doped at the center (edge) of the wells are indicated by CD (ED).

L (Å)	p (cm^{-3})	A (meV)	B (meV)	C (meV)
70	7×10^{15} (CD)	28–31(32)	· · ·	5.7(5.5)
92	3×10^{16} (CD)	30.0(27)	· · ·	(2.3)
108	3×10^{16} (ED)	· · ·	· · ·	3.2(2.0)
142	2×10^{16} (CD)	27.5(25)	31.2(30)	· · ·
165	7×10^{15} (CD)	23.2(23)	27.0(27)	· · ·

z]. Data were obtained for temperatures T and power densities P in the ranges 2–60 K and 10–10^3 W cm^{-2}, respectively.

Our results are summarized in Figs. 1 and 2. The features of interest are labeled A, B, and C. As shown below, these lines are due to acceptor transitions between levels associated with the $1S_{3/2}[\Gamma_8]$ and $2S_{3/2}[\Gamma_8]$ states of the bulk. The samples with $L = 165$ Å and $L = 142$ Å show A- and B-type scattering, whereas the $L = 92$ Å structure exhibits only the A line. There is also some evidence of a relatively broad A-type feature in the sample with $L = 70$ Å. The C peak was observed in the latter structure and the edge-doped sample. Table I gives the measured positions of the lines. In all cases the A, B, and C scattering was found to be of roughly the same strength in the four irreducible representations. Other than the acceptor-related features, the spectra show the longitudinal optical phonon of GaAs at 36.9 meV, the interface modes (IF),[15] and the peaks indicated by X and h_{01} in Fig. 1. All these structures strongly resonant for $\omega_L \approx \omega(\mathrm{HH2}), \omega(\mathrm{LH2})$. X occurs at 39.4, 42.6, and 41.7 meV in the QWS's with $L = 165$, 142, and 70 Å. We have not been able to make a positive identification of this line. The weak L dependence of its position might suggest that the origin of X is vibrational as opposed to electronic. However, we do not know of any ~40-meV phonon that could couple to excitons localized in the wells to explain the resonant enhancement. The h_{01} peak was observed at 26.0 meV in the sample with $L = 92$ Å. As shown in Fig. 1, its intensity increases dramatically at large values of P. Unlike the A, B, and C lines, h_{01} shows a strong polarization dependence when probed with circularly polarized light; it appears mainly in $\Gamma_1 + \Gamma_2$. A calculation predicting 27.1 meV for the separation between the two lowest heavy-hole states in the wells, and the behavior as a function of P indicate that h_{01} is due to intersubband transitions of *photoexcited* holes.[16,17] The selection rules of the scattering are also consistent with this interpretation, since heavy-hole states transform like Γ_6 and $\Gamma_6 \times (\Gamma_1 + \Gamma_2)$ gives again Γ_6.

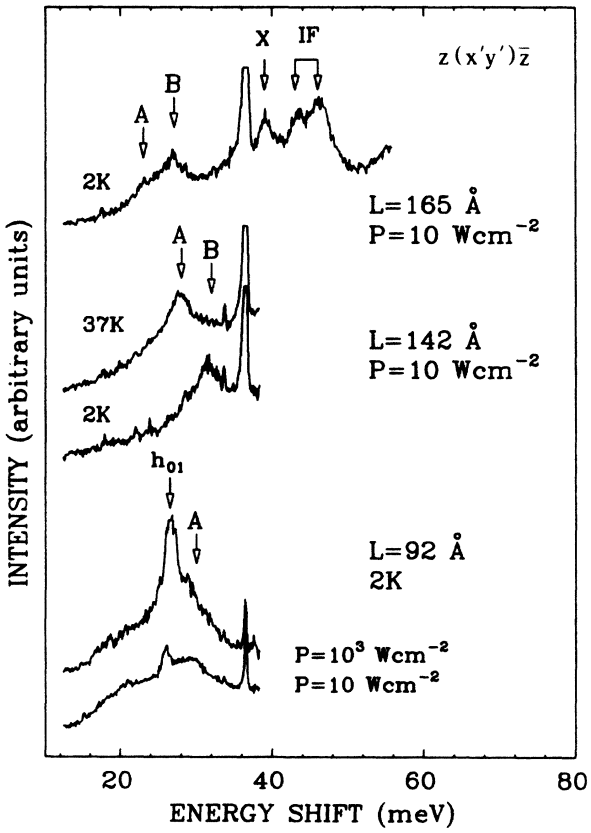

FIG. 1. Raman spectra showing acceptor transitions (peaks A and B) and also scattering by interface phonons (IF) and intersubband hole excitations (h_{01}). X is an unidentified feature (see text). The narrow lines at 34.0 and 36.9 meV are the transverse and longitudinal optical modes of GaAs. Data were taken at $\omega_L = 1.646$, 1.670, and 1.677 eV for $L = 165$, 142, and 92 Å, respectively.

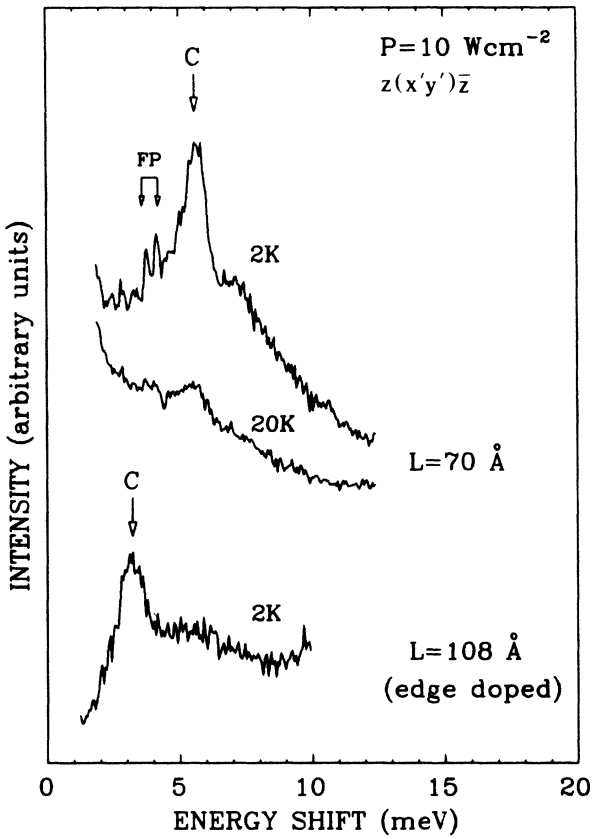

FIG. 2. The low-energy portion of the acceptor spectrum. The C line, on top of a luminescence background, corresponds to the transition $1S_{3/2}[\Gamma_6] \rightarrow 1S_{3/2}[\Gamma_7]$. The weak and narrow features labeled FP at 3.8 and 4.2 meV are folded acoustic phonons. Spectra were obtained at $\omega_L = 1.744$ eV ($L = 70$ Å) and $\omega_L = 1.635$ eV ($L = 108$ Å).

The temperature dependence of the scattering reveals some interesting features, particularly in the behavior of the A and B lines. At low values of P, the intensity of A increases substantially with temperature at the expense of a decrease in the intensity of B. This is shown in Fig. 1 for the structure with $L = 142$ Å (the sample with $L = 165$ Å behaves almost identically). During the intensity exchange, neither line shifts appreciably. An analogous, although weaker effect was also observed at $T = 2$ K using high power densities. We should point out that this effect does not orginate in a shift of the resonance with T or P. We have carefully checked against this possibility by varying ω_L in each situation. The A line in the QWS's with $L = 92$ Å becomes masked by the emergence of h_{01} at high T's or

P's. Because of this, we could not determine whether or not its behavior is the same as for the wider samples. Finally, the C peak shows a strong decrease in intensity with increasing temperature. For both the $L = 70$ Å (see Fig. 2) and the edge-doped sample, C could no longer be resolved for $T \gtrsim 25$ K.

Our assignment of A, B, and C to acceptor transitions is based, first, on the selection rules of the scattering and the fact that the lines can only be observed in samples doped with acceptors. As mentioned above A, B, and C show an almost equal contribution of all irreducible components, including the *antisymmetric* Γ_2. This indicates that their origin is electronic scattering. Impurity-induced phonon scattering can be discarded since associated Raman tensors are purely symmetric.[18] A comparison with Raman data on acceptors in bulk GaAs[19] provides a more definitive assignment for the lines. In the bulk, the dominant Raman feature is the transition $1S_{3/2}[\Gamma_8] \rightarrow 2S_{3/2}[\Gamma_8]$.[19] The fourfold degeneracy of Γ_8 states (T_d) is partially lifted in the D_{2d} group of QWS's giving rise to two Kramers doublets of symmetries Γ_6 and Γ_7.[4] A, B, and C can then be identified with the expected three transitions at low temperatures that result from confinement-induced splittings of the levels $1S_{3/2}[\Gamma_8]$ and $2S_{3/2}[\Gamma_8]$. This identification is supported by recent theoretical work on the acceptor spectra in QWS's.[4] The calculated L dependence of the four levels in question for an impurity at the center of the wells is reproduced in Fig. 3. By correlating the experimental results to the theoretical data,[4] we finally ascribe A, B, and C to the transitions $1S_{3/2}[\Gamma_6] \rightarrow 2S_{3/2}[\Gamma_6]$, $2S_{3/2}[\Gamma_7]$, and $1S_{3/2}[\Gamma_7]$. The measured and calculated transition energies for our structures are indicated in Table I. Except for the C line in the edge-doped sample, there is a very good agreement between the two sets of results. The small differences can in principle be accounted for by considering the experimental errors in the determination of well parameters; L, particularly, is only known to within 5–10%. This, however, does not explain the discrepancy for the edge-doped structure. Here, the position of C should be largely independent of L, for $L \gtrsim 95$ Å.[4] Calculations of edge-impurity spectra are very sensitive to boundary conditions at the interface. Accordingly, it is possible that the discrepancy originates in the inadequacy of the matching conditions used in the theoretical work.[4]

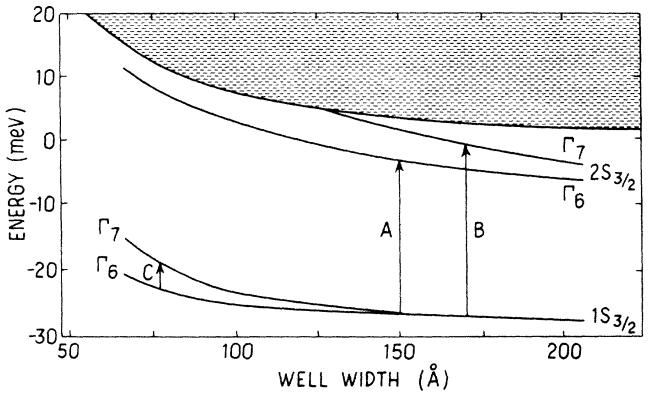

FIG. 3. The calculated well-width dependence of the spectrum of an acceptor at the center of a GaAs-$Al_{0.3}Ga_{0.7}As$ quantum-well structure (Ref. 4). Only the levels associated with the bulk states $1S_{3/2}[\Gamma_8]$ and $2S_{3/2}[\Gamma_8]$ are shown. Energies are given with respect to the position of the valence-band edge in the bulk. The dashed region denotes the continuum. Labels A, B, and C refer to corresponding Raman features in Figs. 1 and 2.

Some experimental features can be qualitatively understood by referring to the theoretical results of Ref. 4. For instance, the absence of the B line in the spectra of the narrower structures is likely due to the expected substantial increase in its linewidth, resulting from overlap with the continuum. As shown in Fig. 3, the crossing is predicted to occur at $L \approx 120$ Å. In addition, the calculated position of the C line in the wider samples is outside the range of our technique, explaining why C lines were not observed for these structures. Nevertheless, our failure to detect this transition in the sample with $L = 92$ Å appears to disagree with the prediction of a 2.3-meV shift. Another point of interest is the width of the acceptor lines. We find that the measured values are very close to estimates based on the calculated position dependence of the binding energy[4] and the nominal doping profile of the samples. This suggests that impurity segregation during growth is not important and, moreover, that (as expected for our low concentrations) acceptor-acceptor interactions do not contribute appreciably to the linewidths.

The temperature dependence of the C line is clearly consistent with our assignment; the decrease in its intensity results from depopulation of the ground state at high temperatures. Less well understood is the intensity exchange between lines A and B in the wider samples. In this regard, it is important to recognize that the character of A (B) becomes more $\Gamma_7 \rightarrow \Gamma_6$ ($\Gamma_7 \rightarrow \Gamma_7$) and less $\Gamma_6 \rightarrow \Gamma_6$ ($\Gamma_6 \rightarrow \Gamma_7$) as T increases (each line should actually give rise to two components at high T, but their expected separation[4] is much smaller than the peak widths). This suggests that the intensity exchange may be simply an indication of a much larger cross section for transitions involving states of different symmetries. However, we do not have an explanation as to why such excitations should dominate.

We finally discuss the selection rules of the scattering within a phenomenological approach. This can be done by considering an effective scattering Hamiltonian[20] given in terms of operators $\hat{O}[\Gamma_i]$ associated with fluctuations in the occupation number of acceptor states, transforming according to the Γ_i representation of the Raman tensor (the pseudo-angular-momentum of the hole is an example of such an operator; it transforms as $\Gamma_2 + \Gamma_5$). For the terms linear in $\hat{O}[\Gamma_i]$, an inspection of the D_{2d} character table shows that transitions between states of the same symmetry (different symmetry) should occur in $\Gamma_1 + \Gamma_2 + \Gamma_5$ ($\Gamma_3 + \Gamma_4 + \Gamma_5$). Second-order terms result in the same selection rules, except for $\hat{O}[\Gamma_5]\hat{O}[\Gamma_5]$. The latter leads to "forbidden" scattering by allowing *all* possible transitions (i.e., $\Gamma_6 \rightarrow \Gamma_6, \Gamma_7$ and $\Gamma_7 \rightarrow \Gamma_6, \Gamma_7$) in the representations $\Gamma_1 + \Gamma_2 + \Gamma_3 + \Gamma_4$. From this analysis, it is clear that an explanation of our data, showing almost no polarization dependence of the acceptor features, requires at least the consideration of quadratic terms. These and also higher-order terms can be expected to contribute significantly to the scattering because of its resonance nature.[20]

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*Also at Department of Physics, University of Illinois at Urbana-Champaign, Urbana, IL 61801.

†Also at Department of Electrical Engineering, University of Illinois at Urbana-Champaign, Urbana, IL 61801.

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