Raman scattering from electrons bound to shallow donors in GaAs-$Al_xGa_{1-x}As$ quantum-well structures

B. V. Shanabrook and J. Comas
Naval Research Laboratory, Washington, D.C. 20375

T. A. Perry and R. Merlin
Department of Physics, University of Michigan, Ann Arbor, Michigan 48109
(Received 19 April 1984)

Transitions involving donor states were observed in resonant Raman scattering experiments on Si-doped GaAs-$Al_xGa_{1-x}As$ multiple quantum wells. The electronic scattering gradually transforms into photoluminescence as the exciting energy is tuned across the resonance. The largest contribution in the spectra is associated with $1S \rightarrow 2S$ transitions of donors near the center of the wells. The experimental results show good agreement with recent calculations.

Recently, the properties of shallow donors and acceptors in multiple quantum-well heterostructures (MQWH) have received much theoretical[1-5] and experimental[6-8] attention. Quantum confinement leads, generally speaking, to an increase in the binding energy (E_B) of these hydrogenic systems, and also to a dependence of E_B on the position of the impurity in the well.[1-5] These effects are expected to be of importance when the well thickness L becomes comparable to the Bohr radius of the impurity (a_0). Estimates of the binding energies of acceptors[7] and donors[8] in GaAs-Al_xGa_xAs MQWH obtained from photoluminescence (PL) data have revealed the predicted increase in E_B with decreasing L. These results, however, provide only approximate values of E_B which is not directly determined in PL measurements.

Electronic Raman scattering (ERS) has been shown to be a powerful tool for the study of the energy spectrum of MQWH.[9] To a lesser extent, it has also been applied to shallow donors in bulk GaAs.[10] In this Rapid Communication, we report the first results of ERS from impurity levels in MQWH. Our data confirm the expected behavior of E_B as a function of L and of its dependence on the impurity location.

The samples used in this work were grown by molecular-beam epitaxy on (001) GaAs substrates. They consist of ~ 30 periods of ≈ 125-Å-thick $Al_xGa_{1-x}As$ ($x = 0.19$ –0.22) and GaAs layers of different thickness L as indicated in Table I. Si donors ($a_0 \approx 100$ Å) were incorporated during growth at the center of the GaAs—slabs with dopant concentrations (n) shown in Table I. The width of the doping spike was nominally $\approx \frac{1}{3}L$ in all the samples.[8] The possibility of donor segregation during growth or diffusion, as previously suggested,[8] indicates that this width may be actually larger.

The samples just described differ from those referred to as modulation-doped MQWH[11] in that the donors are placed in the well material, i.e., GaAs. The electrons bound to the impurities are confined by the rectangular potential well arising from the conduction-band discontinuity at the interfaces. Because the $Al_xGa_{1-x}As$ layers are relatively thick the approximation that considers isolated quantum wells is valid here.

The resonant Raman experiments were performed in the range of the $E_0 + \Delta_0$ gap between the spin-orbit-split valence band and the lowest conduction band of GaAs. Spectra were recorded in the $z(x,x)\bar{z}$ and $z(x,y)\bar{z}$ backscattering configurations where z is normal to the layers and x,y are along two orthogonal equivalent [1,0,0] directions. Data was obtained at $T \sim 4$ K and power density $P \approx 40$ W/cm^2, using a DCM (4-dicyanomethylene-2-methyl-6-*p*-dimethylaminostyryl-4*H*-pyran) dye. Transverse optical phonons are not allowed in backscattering from a (100) face. The longitudinal optical (LO) mode of GaAs and the two LO modes of $Al_xGa_{1-x}As$ were observed in both scattering geometries due to the resonance. Other than the ERS related to donors discussed below, the samples with $L = 238$ and 460 Å show narrow structures that were assigned to $\epsilon_0 \rightarrow \epsilon_1$ and $\epsilon_0 \rightarrow \epsilon_2$ intersubband transitions. Table I shows a comparison

TABLE I. Sample parameters, measured and calculated (in parentheses) intersubband splittings, and energies of the D^0-h photoluminescence peaks and $1S \rightarrow 2S$ transitions (theoretical values for donors at the center of the well from Ref. 2 are in parentheses).

L (Å)	x	n (cm^{-3})	$\epsilon_0 \rightarrow \epsilon_1$ (cm^{-1})	$\epsilon_0 \rightarrow \epsilon_2$ (cm^{-1})	D^0-h(eV)	$1S \rightarrow 2S$ (cm^{-1})
88	0.19	5×10^{15}	(847)	· · ·	1.918	76(74)
153	0.21	1×10^{17}			1.887	
153	0.20	1×10^{16}	(382)	(982)	1.890	60(69)
153	0.21	1×10^{15}			1.891	
153	0.20	undoped			1.886	
238	0.20	5×10^{15}	174(184)	461(486)	1.872	50(61)
460	0.22	5×10^{15}	63(58)	165(157)	1.868	
∞					1.854	(33)

between the measured intersubband splittings and values obtained using the Kronig-Penney model. The observation of these transitions indicates that the lowest subband in the samples is partially occupied due to photoexcitation. The concentrations of free electrons (ρ) in the GaAs layers can be determined by comparing the positions of the intersubband peaks in the (x,x) and (x,y) configurations.[12] The latter gives the bare transition energy while (x,x) exhibits a shift roughly proportional to ρ due to depolarization effects.[12] No appreciable shifts were observed (< 1 cm^{-1}) setting an upper limit of $\rho \sim 5\times 10^9$ cm^{-2}. This value is in good agreement with an estimate of the steady-state electron concentration induced by optical pumping.

Figure 1 shows spectra of the sample with $L = 88$ Å for different excitation energies ω_L. The structure of interest is the broad band in the 50–250 cm^{-1} range, which shows a peculiar behavior as a function of ω_L. Above a certain energy, the band acts as PL (top spectrum in Fig. 1). As ω_L approaches the PL peak the structure becomes narrower, shifts to lower absolute energies, and finally transforms into inelastic scattering with maximum at 76 cm^{-1} (bottom spectrum). We found bands that exhibit an analogous behavior in all, but the sample with $L = 460$ Å where the structure appears to be always PL. The Raman shifts of the bands in different samples are plotted against ω_L in Fig. 2. No appreciable differences were observed between spectra in the (x,x) and (x,y) polarizations.

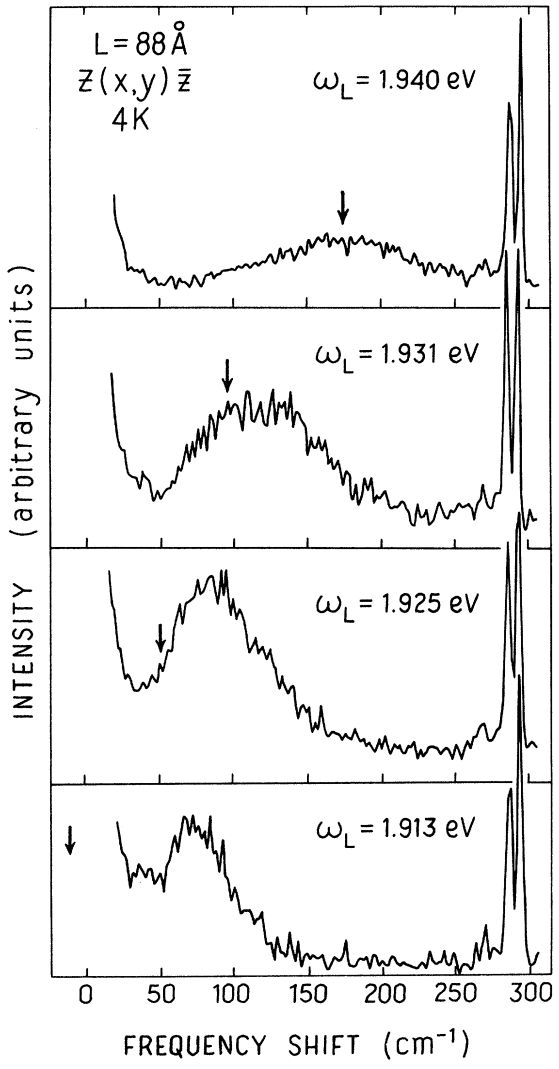

FIG. 1. Resonant Raman spectra of the sample with $L = 88$ Å for different incident photon energies ω_L. The narrow lines at 288 and 295 cm^{-1} are longitudinal optical phonons. The broad feature evolves from D^0-h photoluminescence (top spectrum) into ERS (bottom spectrum). The position of the D^0-h transition is indicated by arrows.

Luminescence associated with the $E_0+\Delta_0$ gap was originally observed in n-GaAs,[13] and ascribed to electron-hole recombination.[13,14] Data on the samples with $L = 153$ Å (see Table I) show a large increase in the intensity of the PL (relative to the LO mode of GaAs) as a function of n, indicating that it is impurity related. Based on this fact we assign it to D^0-h recombination with the hole in the split-off valence band. The shift of the PL peak to higher energies with decreasing L (see Fig. 2 and Table I) reflects the expected behavior of a gap in MQWH.

We now address the origin of the scattering. Transformation from Raman scattering to PL was first seen in CdSe where the Raman feature was identified as a two phonon mode.[15] Disorder-induced scattering by transverse acoustic phonons of GaAs is the only form of vibrational scattering that could have lead to structure in the range 50–80 cm^{-1}. Such a possibility, however, is inconsistent with the differences in peak position among the samples (see Fig. 2) and with the absence of features that could have been attributed to disorder-induced scattering by optical modes. These considerations and the fact that this form of scattering is not seen in undoped or other modulation-doped MQWH indicate that the bands are due to donor transitions. In Fig. 3, we show schematically the single-particle processes giving ERS and PL. To describe the ERS-PL transformation, however, we need to consider the complex $(e$-$h,D)$ involving e-h pairs and donor states.[16] For $\omega_L \lesssim E_0+\Delta_0$, the ERS-PL band is due to absorption and emission processes shown for the one-particle picture in Fig. 3 (left). Since the lifetime of the complex is too short for the intermediate state to be

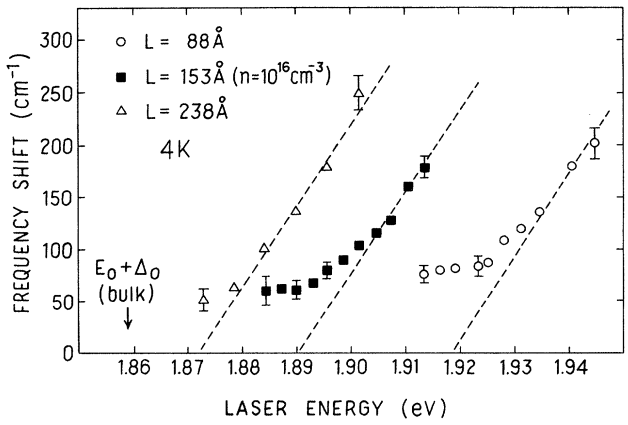

FIG. 2. Raman shift of the D^0-h/ERS peak as a function of ω_L. The dashed lines (slopes equal to unity) give the expected shifts of the D^0-h photoluminescence. Data are shown for three different samples.

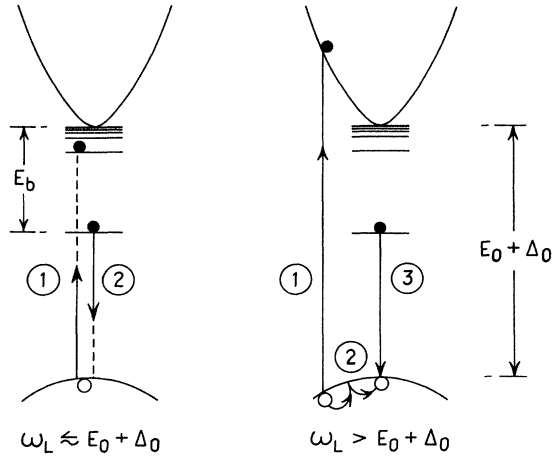

FIG. 3. Schematic single-particle diagrams of conduction, valence subbands, and donor levels showing the optical transitions that lead to ERS (left) and D^0-h recombination (right). Closed (open) circles indicate electron (hole) states.

able to relax, the whole process is resonant ERS. For large ω_L, i.e., such that the pair wave vector $k >> a_0^{-1}$, coupling between the $1S$ and the e-h states becomes negligible. The holes live probably long enough to allow relaxation to occur, as indicated in Fig. 3 (right). The ERS-PL band is now PL due to D^0-h recombination.

The $1S \rightarrow 2S$ transition gives normally the largest contribution to the scattering in the bulk.[17] Accordingly and consistent with our doping profiles, we ascribe the maxima of the Raman peaks to the $1S \rightarrow 2S$ transition energy corresponding to donors near the center of the wells. This assignment is supported by the comparison with calculated values[2] shown in Table I. The widths of the donor peaks reflect (i) the spread to impurity levels induced by the confinement,[3] (ii) contributions of transitions to higher donor states and (iii) donor-donor interactions. For the latter, an estimate is given by $e^2 n^{1/3}/\epsilon \approx 14\ \mathrm{cm}^{-1}$. The estimated broadening due to (ii) is $\sim 16\ \mathrm{cm}^{-1}$. Both values are too small to account for the measured widths of $\Gamma \sim 50$, 60, and 60 cm^{-1} for the samples with $L = 88$, 153, and 238 Å. The corresponding calculated values[2] of the difference in E_B for donors at the center and at the edge of the wells are $\Delta E_B = 32$, 38, and 43 cm^{-1}. This suggests that (i) is the dominant cause of broadening, and consequently, that Si diffusion is important.

This work was supported in part by a grant of the U.S. Army Research Office (Contract No. DAAG-29-82-K0057), and Research Corporation. Additional support was provided by the Office of Naval Research.

[1]G. Bastard, Phys. Rev. B 24, 4714 (1981).
[2]C. Mailhiot, Y. C. Chang, and T. C. McGill, Phys. Rev. B 26, 4449 (1982).
[3]G. Bastard, E. E. Mendez, L. L. Chang, and L. Esaki, Solid State Commun. 45, 367 (1983).
[4]R. L. Greene and K. K. Bajaj, Solid State Commun. 45, 825 (1983).
[5]W. T. Masselink, Y. C. Chang, and H. Morkoc, Phys. Rev. B 28, 7373 (1983).
[6]R. C. Miller, A. C. Gossard, W. T. Tsand, and O. Munteanu, Phys. Rev. B 25, 3871 (1982).
[7]R. C. Miller and A. C. Gossard, Phys. Rev. B 28, 3645 (1983).
[8]B. V. Shanabrook and J. Comas, in *Proceedings of the 5th International Conference on Electronic Properties of Two-Dimensional Systems* [Surf. Sci. (to be published)].
[9]For a review, see, A. Pinczuk, G. Abstreiter, and M. Cardona, in *Light Scattering in Solids IV,* Topics in Applied Physics, Vol. 54, edited by M. Cardona and G. Güntherodt (Springer, Berlin, 1984), Chap. 2.
[10]R. G. Ulbrich, N. V. Hieu, and C. Weisbuch, Phys. Rev. Lett. 46, 53 (1981).
[11]See, H. L. Störmer, J. Phys. Soc. Jpn. 49, Suppl. A, 1013 (1980), and references therein.
[12]See, e.g., A. Pinczuk, J. M. Worlock, H. L. Störmer, R. Dingle, W. Wiegmann, and A. C. Gossard, Solid State Commun. 36, 43 (1980), and references therein.
[13]A. Pinczuk, L. Brillson, E. Burstein, and E. Anastassakis, in *Light Scattering in Solids,* edited by M. Balkanski (Flammarion, Paris, 1971), p. 115.
[14]B. P. Zakharchenya, V. I. Zemskii, and D. N. Mirlin, Zh. Eksp. Teor. Fiz. 70, 1092 (1976) [Sov. Phys. JETP 43, 569 (1976)].
[15]P. Y. Yu and J. E. Smith Jr., Phys. Rev. Lett. 37, 622 (1976).
[16]P. Y. Yu and L. M. Falicov, Phys. Rev. B 24, 1144 (1981).
[17]See, e.g., P. Y. Yu, Phys. Rev. B 20, 5286 (1979).