$2E_g$ Transitions in GaSb-AlSb Quantum-Well Structures

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Photoluminescence emission at twice the fundamental band-gap energy is observed in GaSb-AlSb multiple quantum-well structures for well thicknesses below 42 Å, whereas it is not observed for larger thicknesses. The intensity of the emission increases dramatically with decreasing well width below this value. The appearance of these novel features is traced to changes in the character of the band-edge wave functions due to quantum-well confinement.

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The properties of semiconductor quantum-well structures have attracted a great deal of experimental and theoretical interest recently.[1] The most common form of a quantum well consists of a layer of a semiconductor with a smaller band gap (here GaSb, see inset of Fig. 1) between layers of a second semiconductor material with a larger band gap (here AlSb), with "straddling" band lineup such that the lowest-lying electron and hole states in the conduction and valence bands are localized in the region of the material with the smaller gap. Then both electron and hole states are quantized into a series of subbands (denoted by $n = 1,2,\ldots$) whose energies depend on the well width. Such systems have been found to give rise to novel electronic, optical, and transport properties which are of great interest both scientifically and also for device applications.[1]

In the present optical studies of GaSb-AlSb quantum-well structures, we have observed novel photoluminescence spectra corresponding to the simultaneous recombination of two electrons and two holes in semiconductor quantum-well systems. These features are not observed in the corresponding bulk system.[2] They result from carrier confinement and are observed only in structures with well widths less than 42 Å. The corresponding recombination intensities are found to increase dramatically for decreasing well widths below this value. We relate the appearance of these size-dependent transitions to the mixing of wave functions away from the center of the bulk Brillouin zone to form the subband functions. Although such mixing has been studied theoretically,[3] there has been little experimental evidence to date relating to this effect.[4]

The GaSb-AlSb quantum-well system is especially attractive for the present studies. In bulk GaSb, the direct gap, which is at the Γ point, and the indirect gap at the L point lie about 0.80 and 0.89 eV above the valence-band edge, respectively.[5] The difference in the band gaps of AlSb and GaSb at the Γ point is large, 1.5 eV, and it occurs mainly in the conduction band.[6] The strong confinement allows the subbands in the conduction band to move especially high in energy, giving rise to substantial wave-function modifications which will be of interest here. In addition, because the electron mass at the Γ point is much smaller than that at the L point,[5] this

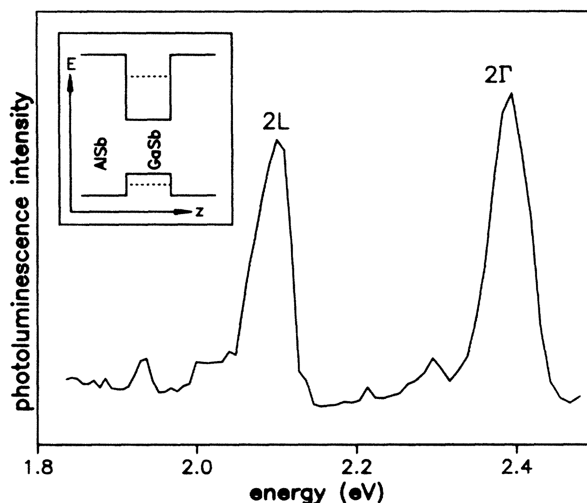

FIG. 1. Photoluminescence spectrum in the energy range close to twice the energy gap for a 20-Å GaSb-AlSb multiple quantum-well sample. Inset: Schematic energy-band diagram in real space for a quantum-well structure. It is important for the present study that in GaSb-AlSb potential wells are formed both at the Γ point and close to the L point of the conduction band (Ref. 7).

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quantum-well system changes over from direct gap to indirect gap[7] for well thicknesses less than approximately 39 Å; this feature offers a unique opportunity to study recombination corresponding to both of these gaps.

The experiments were performed on a series of molecular-beam-epitaxy–grown multiple quantum-well structures with well widths L_z between 115 and 20 Å. Details concerning the growth and structure of the samples are given by Griffiths *et al.*[8] All measurements were performed at 2 K. The samples were excited slightly above the direct-gap transition by a cw neodymium-doped yttrium aluminum garnet laser ($\lambda_L = 1.064$ nm) for $L_z \geq 25$ Å and by a dye laser ($\lambda_L = 880$ nm) for $L_z = 20$ Å. The photoluminescence at twice the band-gap energy (denoted as $2E_g$ transitions) was detected by a GaAs photomultiplier. Because the $2E_g$ transitions are rather weak, typically 1 count per second for fully opened monochromator slits, great care was taken to suppress any background light. For this purpose the optical path was completely shielded from external stray light, and a 1-m double monochromator was used. In order to avoid high-energy components of the excitation, the laser beam always was passed through a $\frac{1}{4}$-m monochromator set at the laser wavelength.

Figure 1 shows a typical photoluminescence spectrum, which is for a sample with $L_z = 20$ Å, in the energy range between 1.8 and 2.5 eV. It has been shown in previous investigations[7] of the $1E_g$ transition that this sample has an indirect band gap at the L point. The $1E_g^L$ transition from the lowest-lying ($n=1$) subband at the L point in the conduction band to the $n=1$ heavy-hole subband occurs at 1.050 eV. The $1E_g^\Gamma$ transition between the first subbands at the Γ point is observed at 1.205 eV. The spectrum in the energy range around twice the band gap (Fig. 1) displays pronounced emission lines at 2.10 eV ($2E_g^L$) and at 2.40 eV ($2E_g^\Gamma$) which are situated at precisely twice the corresponding $1E_g$ transition energies.

Very good agreement between the energies of the $2E_g^L$ and the $2E_g^\Gamma$ luminescence lines and twice the values of the corresponding $1E_g$ transitions is observed for all indirect-gap samples as well as for direct-gap samples with $L_z \leq 42$ Å. Figure 2 shows our experimental data for the $2E_g^\Gamma$ (full circles) and the $2E_g^L$ (full squares) transition energies compared to twice the values of the respective $1E_g$ transitions (open symbols) as a function of the well widths. For all samples the agreement is better than 10 meV. The solid lines represent twice the calculated values of the $n=1$ transition energies for the Γ and L emissions, respectively.[7] It should be noted in Fig. 2 that we observe $2E_g$ transitions only for well widths below a certain value (42 Å).

The $2E_g$ transition at the Γ point involves the four-particle dipole matrix element $\langle c_1c_2|\hat{d}|v_1v_2\rangle$ between two holes in the valence band and two electrons in the conduction band. In systems with inversion symmetry like bulk Si this transition is strictly forbidden because

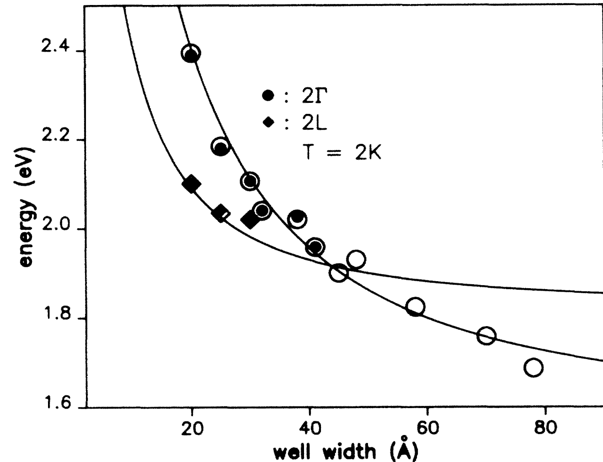

FIG. 2. Comparison of the positions in energy of the observed $2E_g^\Gamma$ and the $2E_g^L$ transitions (solid symbols) with twice the values of the respective $1E_g$ transitions (open symbols). The solid lines are twice the calculated values of the $1E_g$ transitions (Ref. 7).

each wave function has a definite parity, and each of the pairs c_1c_2 and v_1v_2 is even under inversion. For bulk GaSb and the other III-V zinc-blende systems inversion symmetry is absent, and the point group is T_d. For such systems we find from group theory that the four-particle matrix element at the Γ point is nonzero. Nevertheless, the wave function at the edge of the bulk conduction band has Γ_1 symmetry and transforms like an s state, and the valence-band edge has Γ_{15} symmetry and transforms like a p state. Therefore, on physical grounds the four-particle matrix element is expected to be small for bulk GaSb and for related III-V systems, and in the limit in which the potentials of the Ga and Sb atoms become identical this transition becomes strictly forbidden.

In order to account for the appearance of $2E_g^\Gamma$ transitions in the case of quantum wells it is necessary to consider the changes in the character of the band-edge wave functions upon confinement. The wave-vector component parallel to the well ($k_\parallel$) remains a good quantum number, but that perpendicular to it (k_z) is not. The wave function at the bottom of the lowest subband is composed from all of the bulk states which have zero $k_\parallel$ and have an energy equal to that of the subband. In the case of the conduction band in GaSb, as the subband energy moves up from the bulk Γ point (for finite well thicknesses) the wave function begins to include increasingly large contributions having p-like symmetry from the bulk bands having finite k_z near zone center. The appearance of these terms can be understood from $\mathbf{k}\cdot\mathbf{p}$ perturbation theory.[9,10] As the width of the well decreases the subband energies move farther away from the bulk band edges, and the magnitude of these admixtures increases. These admixtures give contributions to the matrix element which are large compared to that of

the bulk Γ point.

From the above arguments we expect that the intensity of the $2E_g^\Gamma$ transition will increase with decreasing well thickness. In Fig. 3 we show the intensity of the $2E_g^\Gamma$ transition as a function of the well width for $L_z \leq 42$ Å. As predicted by the above arguments we observe a dramatic increase of the intensity with decreasing well width. Between the thickest sample for which we observe the $2E_g^\Gamma$ transitions ($L_z = 41$ Å) and the thinnest sample ($L_z = 20$ Å) the intensity increases by more than three orders of magnitude. No indication of $2E_g^\Gamma$ transitions is seen in samples with well thicknesses greater than 42 Å. As indicated by our semilogarithmic plot, the intensity of the $2E_g^\Gamma$ transition increases approximately exponentially with decreasing well width. The dip in the $2E_g^\Gamma$ intensity which occurs around 35 Å might be associated with the change from direct to indirect band-gap structure which occurs in this well-width range.[7]

We observe a similar dependence on well width of the intensity of the $2E_g$ transition at the L point. The $2E_g^L$ transition occurs at twice the energy of the $1E_g^L$ transition and shows no evidence of a phonon shift. From the fact that the GaSb typically shows a substantial[5] (10^{16} cm^{-3}) hole concentration we suggest that both the $1E_g^L$ and the $2E_g^L$ transitions occur via shallow impurity (acceptor) levels. The conduction band at the L point has Γ_1 s-like symmetry, and therefore the argument given above concerning the admixture of wave functions having symmetries different from the bulk for decreasing quantum-well widths also holds for the L point.

Finally we point out that internal frequency doubling does not provide an appropriate explanation of the $2E_g$ lines observed here. This process is allowed at the Γ point. Because the intensity for internal frequency doubling at the energy gap varies in proportion to the density of states, only a very weak variation of the emission intensity with L_z is expected, which is in contradiction with our experimental results.[11,12] Furthermore, internal frequency doubling should not occur at the L point.

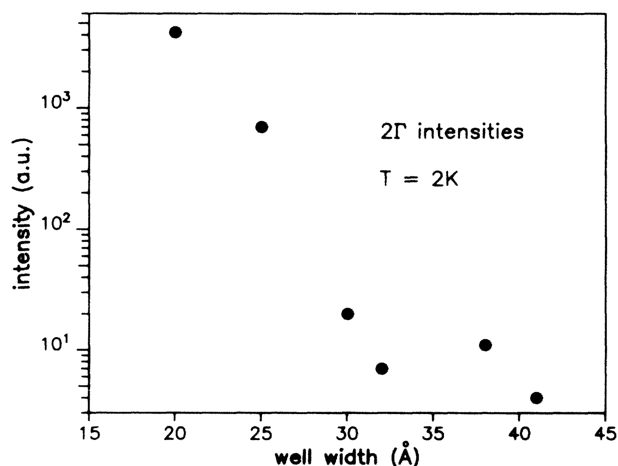

FIG. 3. Intensity dependence of the $2E_g^\Gamma$ transition in the GaSb-AlSb quantum wells as a function of the well width.

In summary, we have observed novel emissions at twice the gap energy at both the direct and indirect gaps in quantum-well structures. These four-particle transitions are not observed at the direct gaps of corresponding bulk materials. We have related the appearance of these transitions to the presence of contributions corresponding to states away from the bulk edges in the quantum-well subband wave functions. It should be noted that such wave-function admixtures give rise to the breakdown of bulk selection rules in confined geometries and that such effects should be a general feature of confined electronic systems.

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