Binding of Shallow Donor Impurities in Quantum-Well Structures

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Far-infrared magnetospectroscopy has been carried out on shallow donor impurities doped in the central region of GaAs quantum wells in GaAs-$Al_xGa_{1-x}As$ multiple-quantum-well structures. Quantum-well widths between 80 and 450 Å were investigated. Results are in very good agreement with recent effective-mass calculations for isolated impurities at the center of GaAs quantum wells.

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The nature of isolated hydrogenic impurities in confined geometries has received theoretical attention for nearly twenty years.[1] One system especially suitable for controlled, systematic experimental investigations is that of shallow impurities in GaAs-$Al_xGa_{1-x}As$ quantum wells (QW's) grown by molecular beam epitaxy (MBE). For shallow donors such as Si in GaAs-AlGaAs structures it is thought that the one-band effective mass approximation is applicable, even though the matching conditions for the wave functions at the well boundaries are not yet well established. Variational calculations by several authors[2–4] are in general agreement in their prediction of substantial shifts in the impurity energies relative to the bulk values as the width of the QW's approaches the effective Bohr diameter (~ 200 Å) of the impurities. The direction and magnitude of the shifts depend on the position of the impurity center along the growth axis of the QW, as well as the width and depth of the well.

Experimental investigations of this system have thus far been confined to photoluminescence[5,6] and, more recently, Raman scattering[7] measurements. We report detailed far-infrared spectroscopy of intraimpurity transitions on a series of center-doped QW's over a wide range of magnetic fields.[8] These measurements are more sensitive, more extensive, and less ambiguous than previous studies, and allow us to identify positively the absorption features associated with donor impurities doped in the QW center, and to make detailed comparison with recent theoretical calculations. Results are in very good agreement with theory, and are thus consistent with the use of the effective-mass approximation and simple wave-function matching conditions in this case.

The samples investigated consisted of a set of GaAs-AlGaAs multiple QW's grown on semi-insulating GaAs substrates by MBE. Quantum-well widths varied from 80 to 450 Å.[9] The mole fraction of the aluminium in the barriers (0.31 ± 0.03 for the three narrowest wells and 0.25 ± 0.03 for the wide well) and the well widths were determined from photoluminescence[6] measurements. In each case the central third of the QW's was doped with Si at a nominal density of 1×10^{16} cm^{-3}, except for the 450-Å well which was doped at 5×10^{15} cm^{-3}. The width of the doped region was estimated from the product of the growth rate and the time the shutter on the Si effusion cell was open. The AlGaAs barriers were all at least 125 Å thick to minimize interaction between adjacent wells.

Spectroscopic measurements were made with a far-infrared Fourier-transform spectrometer in conjunction with He-cooled photoconductive detectors and a superconducting-magnet system. Samples were maintained at approximately 4.2 K in He exchange gas in the Faraday geometry with the QW growth axis parallel to the applied magnetic field (except for one set of runs in which the sample was tilted at 45°). In this configuration, considering the temperature of the sample and the dipole selection rules, the predominant transitions are $1s \rightarrow 2p^+$ and $1s \rightarrow 2p^-$ in the usual spectroscopic notation, where + and − refer to the azimuthal quantum numbers +1 and −1, respectively. Cooled filters limited the radiation reaching the sample to frequencies less than about 400 cm^{-1}. For comparison purposes measurements were also made on a "bulk" MBE-grown GaAs sample 6 μm thick doped with Si at 1.3×10^{15} cm^{-3}.

Figure 1 shows three transmission measurements made on a sample consisting of twenty 210-Å wells doped with Si at 1×10^{16} cm^{-3} over the central 75 Å of each well. The top spectrum was taken immediately after the sample was cooled to He temperature. No

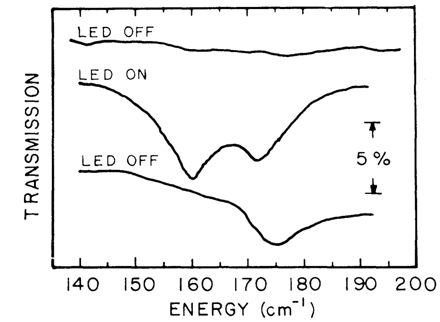

FIG. 1. Transmission spectra at 9 T obtained from the 210-Å-well sample with the center 75 Å doped. The three traces from top to bottom correspond to measurements made before, during, and after illumination of the sample by a red-light-emitting diode. The low-energy peak with the LED on occurs at the energy of the bulk $1s$-$2p^+$ transition.

significant features are present. The middle spectrum was taken with a red light-emitting diode (LED) illuminating the sample. The transmission minimum at 160 cm^{-1} is due to impurities in the bulk substrate neutralized by the pump light. This was verified by measurements made on untreated substrate material which also verified that the transmission minimum occurred at the same photon energy as the bulk impurity line in the MBE-grown bulk Si-doped sample. The minimum at 172 cm^{-1} is due to absorption by the impurities confined in the QW's. This identification is confirmed by measurements made with the growth axis of the sample inclined at 45° to the magnetic field axis. In this configuration the transmission minimum identified as arising from the sample substrate remains at the same frequency as that observed with the sample in the normal configuration. On the other hand, the minimum attributed to the confined impurities shifts to lower energy, occurring, within the experimental uncertainty, at an energy determined by the component of magnetic field along the growth direction. These measurements, repeated at several values of total magnetic field, demonstrate the two-dimensional nature of the impurity states. The bottom spectrum was obtained after turning the LED off; under this condition only the confined impurity line remains clearly discernible. This persistent effect is attributed to a mechanism similar to that responsible for the persistent photoeffects observed in modulation-doped heterostructures.[10] Upon cooling of the sample under "dark" conditions the donor impurities in the well center are ionized, likely as a result of charge transfer to acceptor states or deep electron traps in the AlGaAs; thus no impurity absorption is possible. Illuminating the sample with light of photon energy greater than the AlGaAs band gap releases electrons from traps in the AlGaAs as well as creating electron-hole pairs in both the GaAs and the AlGaAs. A large

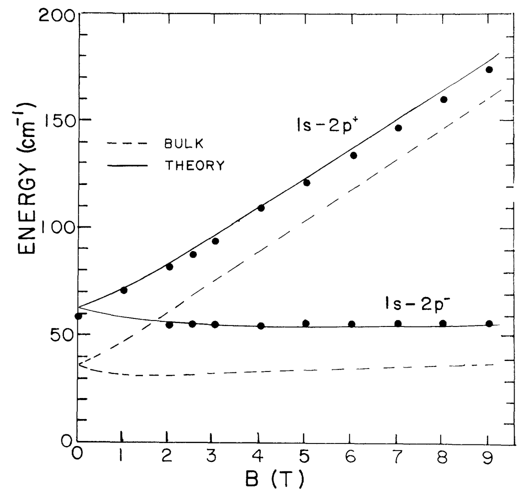

FIG. 2. Energy of $1s$-$2p^+$ and $1s$-$2p^-$ transitions for the 210-Å-well sample. Experimental data are indicated by solid circles. The solid line is the result of a calculation (Ref. 12) interpolated for the 210-Å well width. The broken line indicates the energy of the corresponding transition observed in the bulk doped sample.

fraction of these photoexcited electrons and holes are trapped in the QW's, neutralizing ionized impurities in the wells in steady state, and permitting the shallow donor transitions to be observed. Transitions are observed from both the Si impurities in the QW's and the residual donor impurities in the bulk GaAs substrate under steady-state conditions. After turn-off of the illumination, since the time required for the excess electrons to recombine with traps in the AlGaAs is extremely long at low temperatures, the impurity absorption from the neutral donors in the QW's persists.

The fact that with the LED on both bulk and confined impurity absorption lines (transmission minima) are present is a valuable tool for making accurate measurements in the wider wells. Since the transmission minima for impurities in wider wells are shifted a small amount from the corresponding bulk positions, the ability to produce a reference bulk absorption line simultaneously is a great advantage in resolving small shifts, as well as in demonstrating unambiguously the presence of the confined impurity. A series of measurements as a function of illumination intensity demonstrated that the energy of the confined impurity line was largely independent of illumination intensity. Small shifts, as apparent in Fig. 1, are at the limit of the resolution of the present measurements.[11]

The results of measurements made on a sample having QW widths of 210 Å along with measurements on a bulk GaAs sample are shown in Fig. 2. Also shown are the results of a very recent calculation[12] interpolated for the 210-Å well width. As predicted, both the $1s$-$2p^+$ and the $1s$-$2p^-$ transition energies are increased relative to the bulk values, and theory and experiment are in remarkably good agreement. It is also evident from this figure that the shift due to confinement decreases slightly as the magnetic field increases. This is readily understood by considering the effect of the magnetic field on the impurity state. As the magnetic field increases the wave functions become more localized about the impurity center, and the quantum-well confinement becomes less important.

Figure 3 compares the observed $1s$-$2p^+$ transition energies for four different well widths with the calculations of Ref. 12. There is good agreement between theory and experiment in all but the narrowest wells, for which the measured values are consistently less than those predicted. The solid lines are calculated for an Al mole fraction of 0.3 and a conduction-band–edge discontinuity that is 85% of the total band-gap difference; this results in a conduction-band–edge discontinuity (barrier height) of 0.323 eV. Recent results, however, indicate that the conduction-band–edge discontinuity may be closer to 57% of the total band-gap difference.[13] For the present samples this translates to a conduction-band–edge energy discontinuity of 0.217 eV. The dotted line in Fig. 3 is the theoretical result for a conduction-band–edge discontinuity of 0.154 eV. There is little effect on the results for QW widths greater than about 200 Å, but for narrower wells the smaller barrier height gives transition energies in better agreement with experiment, but still higher.

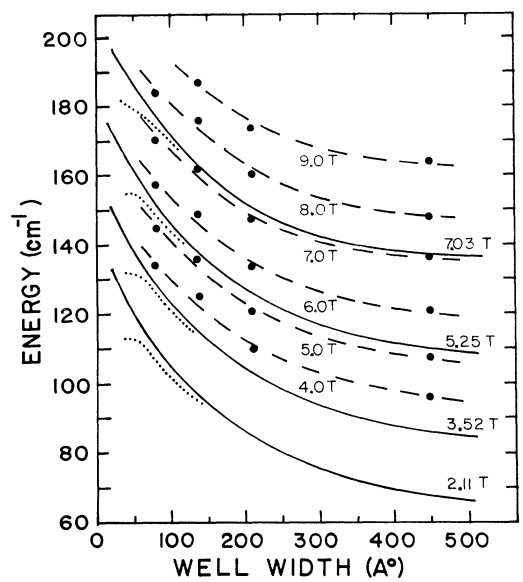

FIG. 3. Energy of the $1s$-$2p^+$ transition vs well width at various magnetic fields. Solid circles connected by the broken line are experimental values. The solid and dotted lines are the results of calculations (Ref. 12) for potential barriers of 0.323 and 0.154 eV, respectively.

In regard to possible sources of systematic differences between experiment and theory, it should be noted that the theoretical calculations are performed for an impurity located at the exact center of the well, while the samples have the dopant impurities distributed over at least the central one-third of the well, and perhaps more if there is substantial diffusion or redistribution during growth. Since off-center impurities have reduced binding energies relative to impurities at the center, a distribution of impurity positions about the center should, at the very least, produce an asymmetric line broadened to lower energies and perhaps a distinct low-energy line if there is a substantial impurity density at the edges of the QW's. For wells that are relatively wide compared to the impurity effective Bohr diameter the broadening effect should be small; however, for narrow wells it could lower the peak energy of the absorption profile relative to that of impurities at the exact center of the well. Experimentally, there is evidence of broadening or weak additional absorption towards lower energy, as in the bottom trace of Fig. 1, where the low-energy "tail" extends to about 150 cm^{-1}. Calculations predict that the $1s$-$2p^+$ transition for edgelike donors should occur at about 145 cm^{-1} for this sample at 9 T. Measurements made on an intentionally edge-doped sample show an absorption at the energy predicted for an edgelike state, broadened to higher energy, and no significant absorption at the energy corresponding to a centered impurity state. Taken together, these results set an upper bound on any significant redistribution of the dopant at 50–100 Å. Far-infrared laser measurements and higher-resolution Fourier-transform spectroscopy performed on the wider center-doped samples do show some structure in the low-energy tail of the absorption, but no features that can be clearly identified with an edgelike state. Finally, it should also be noted that the uncertainty in determination of the well widths may be an important source of systematic differences in quantitative comparisons with theory, since the energy shift due to confinement varies rapidly with width for narrow wells.

With the above caveats, the overall agreement of the present measurements with theory is very good for impurities located at the center of QW's; this supports the use of the one-band effective-mass approximation for impurities in these systems. These results, due to the relative insensitivity of impurities in the well center to the detailed nature of the boundaries, do not provide a stringent test of the validity of the wave-function matching conditions at the heterojunction boundaries. Experiments on impurities doped at the edges of the wells should be considerably more sensitive to the matching conditions.

The present measurements also indicate that for all samples the selective doping appears to be effective;

no appreciable absorption features that could be assigned to edgelike impurities are observed in the samples that are selectively doped at the center. However, there are additional weaker absorption features observed at energies lower than the transition energy of the centered impurities in different samples under varying conditions of magnetic field and pump light. These features are presently not well understood and are undergoing further investigation.[14]

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[1]Jules D. Levine, Phys. Rev. **140**, A586 (1965).

[2]G. Bastard, Phys. Rev. B **24**, 4714 (1981).

[3]C. Mailhiot, Yia-Chung Chang, and T. C. McGill, Phys. Rev. B **26**, 4449 (1982).

[4]R. L. Greene and K. K. Bajaj, Solid State Commun. **45**, 825 (1983).

[5]B. V. Shanabrook and J. Comas, Surf. Sci. **142**, 504 (1984).

[6]R. C. Miller, A. C. Gossard, W. T. Tsang, and O. Munteanu, Phys. Rev. B **25**, 3871 (1982).

[7]B. V. Shanabrook, J. Comas, T. A. Perry, and R. Merlin, Phys. Rev. B **29**, 7096 (1984).

[8]Preliminary measurements were recently presented. N. C. Jarosik, B. D. McCombe, B. V. Shanabrook, R. J. Wagner, J. Comas, and G. Wicks, in *Proceedings of the Seventeenth International Conference on the Physics of Semiconductors, San Francisco, 1984,* edited by D. J. Chadi (Springer, New York, 1985).

[9]The samples with 80-, 138-, and 210-Å-wide wells were all grown in a single run under identical conditions at Cornell University (growth temperature 680 °C). The sample with 450-Å-wide wells was grown in a separate run in a different MBE system at the Naval Research Laboratory (growth temperature 650 °C).

[10]H. L. Stormer, R. Dingle, A. C. Gossard, W. Wiegmann, and M. D. Sturge, Solid State Commun. **29**, 705 (1979).

[11]Both the sensitivity and resolution of these measurements are limited by residual interference effects within the wedged sample.

[12]R. L. Greene and K. K. Bajaj, Phys. Rev. B **31**, 913 (1985).

[13]R. C. Miller, D. A. Kleinman, and A. C. Gossard, Phys. Rev. B **29**, 7085 (1984).

[14]R. J. Wagner, B. V. Shanabrook, J. E. Furneaux, J. Comas, N. C. Jarosik, and B. D. McCombe, in Proceedings of the Tenth International Conference on Gallium Arsenide and Related Compounds, Biarritz, France, 1984 (to be published).