Picosecond far-infrared studies of intra-acceptor dynamics in bulk GaAs and δ-doped AlAs/GaAs quantum wells

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We report direct pump-probe measurements of the excited-state lifetime of a carrier bound to a shallow impurity in a semiconductor. The dynamics of intra-acceptor level scattering were studied for the cases of uniformly doped GaAs:Be and also a δ-doped AlAs/GaAs multiple-quantum-well sample. The experimental technique used to measure the scattering rate was a balanced pump-probe system using a free-electron laser as a source of intense far-infrared picosecond pulses. The hole relaxation time from the $2p$ state to $1s$ ground state of the acceptor was measured as a function of temperature for the two main absorption lines. It was found that in the bulk these transitions have a lifetime of the order of 350 ps independent of temperature up to the thermalization temperature of the acceptor. Studies of the 15-nm δ-doped GaAs quantum well in AlAs barriers show that in this quantum-confined system, where the transition energies are governed by the well width, the lifetime of the excited state is much shorter, of the order of 80 ps. We suggest that the relaxation process is by acoustic phonon emission and that the effect of the superlattice periodicity is to relax the strict k conservation rules of the bulk increasing the acoustic phonon emission rate.

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Studies of shallow impurity states in semiconductors have been given fresh impetus by interest in potential devices such as far-infrared emitters/detectors and even possible applications in quantum computing.[1–3] In particular, the use of intra-impurity states as light emitters was recently demonstrated by Hubers *et al.*,[4] who detected radiative emission at 58 μm due to transitions between the internal states of phosphorus donors in silicon under optical pumping; they also were able to demonstrate population inversion between the $2p_0$ and $1s(E,T)$ internal transition of the donors opening the possibility of a solid-state terahertz laser system based on shallow impurities.

Any solid-state technology based on such transitions will need to demonstrate tunability of the transition energy; this can be achieved by quantum confinement of the impurity but the effect of the confinement on the interlevel dynamics is unknown. More generally, the internal transitions of a shallow impurity form a zero-dimensional system with many analogies to the quantum-dot systems whose carrier dynamics are the subject of much current research.[5,6]

Unlike the Stranski-Krastonov self-organized dot systems where large dot-size variations are observed, established growth technology can, in a controlled manner, tune these transitions by δ-doping within quantum-well structures. Indeed, several researchers have previously demonstrated the tunability of the impurity transitions in the $Al_xGa_{1-x}As/GaAs$ quantum-well system.[7–9] Most of the applications mentioned above rely on the internal impurity transitions having a much longer excited-state lifetime than carriers excited either further up the band in bulk systems or into an upper subband in two-dimensional (2D) systems. In these intensively studied systems the large density of available carrier states (bulk dispersion or in-plane k states in the 3D and 2D cases, respectively) gives rise to rapid relaxation processes for photoexcited carriers. Here we report a direct study of the carrier dynamics for intra-acceptor transitions in bulk GaAs and in the AlAs/GaAs quantum-well semiconductor systems.

The recent availability of free-electron lasers as sources of intense far-infrared radiation has enabled many studies of carrier relaxation in semiconductor systems of bulk, 2D, and 0D nature. In particular, it has extended the wavelength range that such measurements can be conducted well into the far-infrared region. The free-electron laser for infrared experiment (FELIX) at Rijnuizen in the Netherlands provides pulses that are typically 50–100 cycles in duration and high peak power (0.5–2 MW), allowing transient measurements on a 0.5–10-ps time scale and has been used in several such carrier relaxation studies. In particular Murdin *et al.*[10] have studied the intersubband scattering times for electrons in $Al_xGa_{1-x}As/GaAs$ multiple quantum wells (MQW's). More recently Cole *et al.*[11] published similar data for hole scattering. In terms of quantum cascade devices such measurements are of critical importance for interpreting device efficiency. The extremely rapid transfer of carriers in these systems ($\tau \approx 1-5$ ps) is the result of longitudinal optical (LO) phonon emission from the high-energy tail of the carrier population in the upper subband.

One possible solution to the problem of increasing the nonradiative lifetimes for carriers in these systems is to remove the dispersion in the system by use of a 3D confining potential. This has the added advantage of removing the se-

lection rule for 2D systems requiring the electric field of the interaction to lie normal to the plane of the wells. This is important as it not only makes the optical experiments on the system simpler but also opens the door to surface-emitting/detecting type devices. Shallow impurity states provide just such an environment for the bound carrier and studies of these states provide a very useful analogy in the absence of precise energy-level control in other artificial 0D systems.

It has been only relatively recently that the Lyman series of the beryllium acceptor in GaAs was studied in detail by infrared absorption.[12] In practice the suppression of impurity-band formation requires a doping concentration of less than a few 10^{16} Be atoms/cm^3, which in a typical epilayer sample with an areal doping concentration of 10^{12} Be atoms/cm^2 will produce only approximately 10% absorption from the strongest absorption line. As a result of this small absorption cross section, earlier work[13] utilized photoconductivity, a more sensitive technique but with a much more complex mechanism to interpret. Raman spectroscopy can also be used to observe scattering between even-parity states as has been demonstrated in residually doped *p*-type bulk GaAs (Ref. 14) as well as modulation-doped GaAs/$Al_xGa_{1-x}As$ quantum wells.[8] These previous studies did not extend to the excited-state dynamics as the experimental techniques to do this were only developed recently, although a recent study of Si:P used bleaching under intense far-infrared illumination and measured $2p$-$1s$ scattering time for this donor state of the order of 10 ns.[15]

Both samples were grown on 2-in. semi-insulating GaAs substates in a VG V90 H 4-in. reactor equipped with all solid sources. The growth of the layers was performed under exact stoichiometric conditions using the technique of stoichiometric low-temperature (SLT) growth,[16] which ensures high quality optical materials even at relatively low growth temperatures. Under these conditions, the quantum-well structures were grown at 540 °C, which ensured negligible diffusion of the Be δ layers. Previous studies have observed that the intra-acceptor transitions of Be in bulk GaAs are only observed at low doping density (below 3×10^{16} atoms/cm^3) due to impurity-band effects that smear out or obscure the sharp absorption lines at higher concentrations.

For this study two samples were used, The first was a single 1-μm-thick epilayer of GaAs doped at 10^{16} atoms/cm^3 (10^{12} atoms/cm^2)—used as a bulk GaAs:Be reference sample. The second sample was a 20-nm period AlAs/GaAs quantum-well structure with 15-nm-thick GaAs wells. The center of each of the GaAs wells was δ doped to an areal density of 5×10^{10} atoms/cm^3, and the structure contained 50 periods, giving a total areal density of 2.5×10^{12} atoms/cm^2. The areal doping density used 5×10^{10} atoms/cm^3 corresponds to a bulk density (assuming a 5-nm diffusion region) of approximately 10^{17}, which is close to the lower limit of the density required for impurity-band formation in a δ-doped system. We observe that in Ref. 9 sharp impurity lines were observed in doped quantum wells for a somewhat greater doping density than this and also (as noted below) the observed transition from our samples is well defined. In the ensuing discussion we therefore assume that we are below the doping level needed for impurity banding effects to become significant.

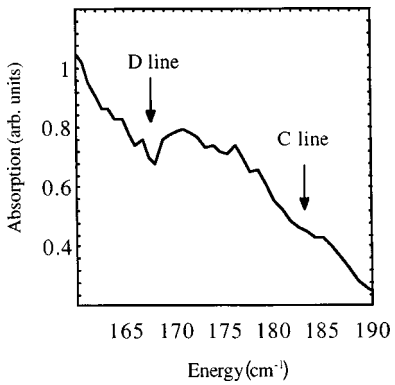

FIG. 1. Epilayer Sample transmission as measured by FELIX.

For the infrared-absorption/pump-probe experiments the samples were thinned and wedged to approximately a 5° angle to prevent Fabry-Perot fringing. Four such pieces of each sample were then stacked to increase further the total absorption due to the acceptors. All spectra (pump probe and linear absorption) were recorded with the sample in the dark (i.e., no above-band-gap illumination present).

The experiments were conducted with the samples cooled to 4 K in a He continuous-flow cryostat with polypropylene windows. Preliminary measurements of the thick epilayer sample transmission by scanning the free-electron laser (FEL) wavelength in the region 160–200 cm^{-1} (60–50 μm) clearly showed the absorption lines to be studied (Fig. 1). The weak line at 166 cm^{-1} is due to acoustic phonon absorption.[13] The spectrum in Fig. 1 was taken using a pump beam of approximately 2 mW integrated intensity, 0.5 MW peak power. The two observed lines are centered on 167 and 183 cm^{-1} and are the result of the $1s$ to $2p$ transition of holes bound to isolated acceptors. The observed energy positions correspond to the $1S_{3/2}\Gamma_8$-$2P_{5/2}\Gamma_8$ and $1S_{3/2}\Gamma_8$-$2P_{5/2}\Gamma_7$ transitions of the bulk acceptor as reported by previous workers, these transitions are usually referred to as the *D* and *C* lines and their measured energies correspond exactly to those reported by Lewis *et al.*[12] for a similar Be-doped GaAs epilayer. The lines were also found to thermalize completely by 70 K in agreement with those observed by previous workers.

By comparison with our own Fourier-transform infrared (FTIR) measurements of the same sample some bleaching of the *D* line was evident (approximately 30% after allowing for the bandwidth of the FEL). Due to strong lattice absorption the total transmission through the samples is of the order of a few percent. The pump-probe experiments were conducted at the FELIX facility using the balanced pump-probe technique first implemented in this wavelength regime by Langerak and co-workers.[11,17] This technique uses two probe pulses, one preceding and one following the pump pulse (with a 40-ns total pulse separation). A fast Ge:Ga detector is then biased to the 25-MHz sinusoidal reference signal from FELIX as the pump pulse is scanned through a delay line. The effect is to use the preceding pulse as a reference to

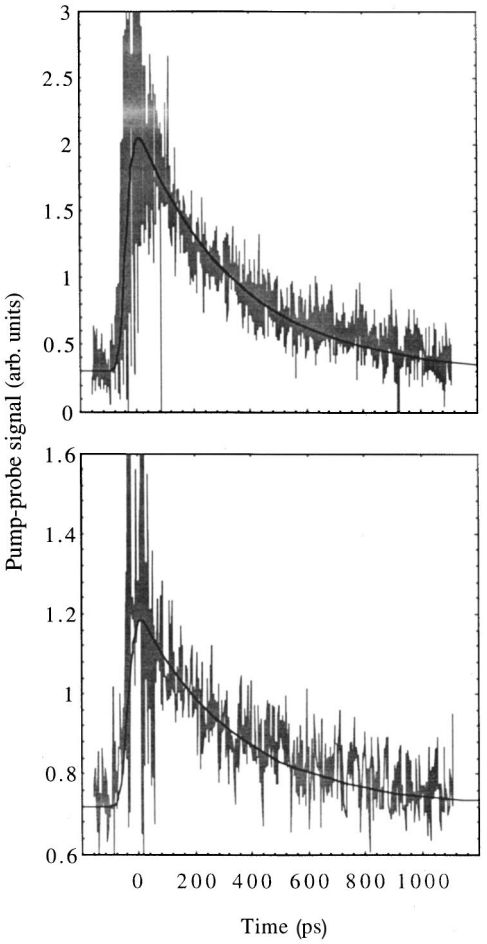

FIG. 2. The pump-probe signal for the (a) *C*-line and (b) *D*-line intra-acceptor transitions in the bulk GaAs:Be sample 1. The solid curve is calculated by a rate model according to the lifetimes for the *C* line of 340 ps and for the *D* line 350 ps as described in the text.

balance the effect of pulse power variation on the signal obtained from the second probe pulse. It has been demonstrated previously that the technique is very efficient at removing signal jitter and can resolve absorption changes due to the pump beam of less than 0.5% even for samples whose transmission is very low, as in this case. Thus the FELIX facility provides a unique capability for the experiments described.

Balanced pump-probe measurements were performed on the observed absorption lines using a probe pulse of approximately 10% of the pump beam. The pump-probe signals for the *D* and *C* lines as a function of delay are shown in Figs. 2(a) and 2(b).

The two-level rate equation for a homogeneously broadened system is[11]

$$\frac{dN_{2P}}{dt}=\frac{\sigma}{\hbar\omega}I(t)(N_{1S}-N_{2P})-\frac{N_{2P}}{\tau}, \tag{1}$$

where N_{1S} and N_{2P} are the number of acceptors with holes in the $1S$ and $2P$ states, respectively, σ is the absorption cross section, τ is the lifetime of the transition, and $I(t)$ is the intensity of the laser pulse with time, which is taken to be a Gaussian with width 15 ps (the pulse length of FELIX when operated at 60 μm as determined by pulse autocorrelation). The absorption change observed is calculated as[11]

$$A=\int_{-\infty}^{+\infty}\frac{\sigma}{\hbar\omega}I(t-t_d)(N_{1S}-N_{2P})dt. \tag{2}$$

The solid lines in Fig. 2 are generated as fits with $\tau=350\pm10$ ps for the *D* line and $\tau=340\pm20$ ps for the *C* line. The temperature dependence of the *D*-line transition rate was also studied, the lifetime was found to be constant within experimental error up to a temperature of 40 K at which point thermalization of the acceptors was evident.

The experiment was repeated for the δ-doped sample. The energy states of a shallow acceptor in GaAs can be thought of as a spin-$\frac{3}{2}$ particle in a Coulomb field with a further energy-level splitting due to the cubic crystal field. The effect of confining the acceptor in a quantum well is twofold; first the binding energy is increased and second there is a symmetry lowering effect from T_d symmetry to D_{2d} symmetry by confinement in a ([100]-oriented) quantum well. It has been previously calculated theoretically and demonstrated experimentally that the confinement on an acceptor state in a quantum well increases both the binding energy of the acceptor and the magnitude of the $1s$-$2p$ transition. As in the case of the excitonic binding energy the atomic impurity level can have its binding energy increased by up to a factor of 4 by complete 2D confinement.

It proved impossible to record an equivalent spectrum for the δ-doped MQW sample as the absorption change expected is of the order 0.5%—well below the pulse power variation of the FEL, but this change is within the range at which a balanced pump-probe signal can be obtained. Although there is no previous data on acceptors confined in GaAs quantum wells in pure AlAs barriers, Reeder, Mercy, and McCombe[9] studied Be acceptors in GaAs wells with $Al_{0.3}Ga_{0.7}As$ barriers. They observed shifted *D*- and *C*-line energies of 195 and 213 cm^{-1}, respectively for acceptors doped over the central $\frac{1}{3}$ of a 15-nm well, in good agreement with the theoretical predictions Masselink, Chang, and Morkoc.[7] At the relatively large well thickness used here the effect of the increased valence-band offset of AlAs relative to the $Al_{0.3}Ga_{0.7}As$ would be expected to be negligible. As noted in Ref. 8, the doping of a central region of the well will result in a distribution of binding energies dependent of the exact acceptor position. In the present study δ doping was attempted and although clearly some diffusion of Be is to be expected we would expect that the Be distribution will be more localized at the center of the well, resulting in an absorption linewidth in our samples significantly less than that observed in Ref. 9 but centered on a similar position in energy.

The experiment was repeated for the MQW sample. Tuning the laser in the 51–53 μm region, the pump probe signal due to the *D*-line transition was weakly observed at 52.4 μm (191 cm^{-1}) and is shown in Fig. 3. The signal is shown for a range of temperatures up to 60 K at which point the acceptor

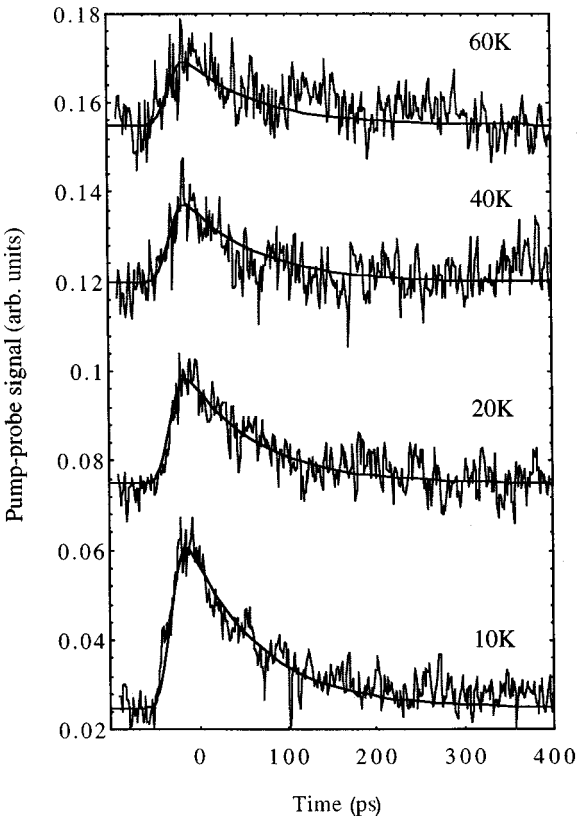

FIG. 3. Temperature dependence of pump-probe signal from the Be *D*-line transition in the multi-quantum-well sample as taken at the sample temperatures indicated. The fitted curves all correspond to a decay of 80 ps.

thermalizes as in the bulk case, confirming the signal's electronic origin. Also as in the bulk case, there is no measurable change in the lifetime with temperature. Evidently this transition has been shifted up in energy by the quantum confinement effect from its bulk value of 167 cm^{-1} by 24 cm^{-1} (3 meV). This compares to a shift of 28 cm^{-1} reported in Ref. 9 for a sample with a similar quantum-well width but doped throughout the center of the well rather than δ doped as in this case. The *C* line for our quantum-well sample is expected to occur in the region 200–210 cm^{-1} but was not observed due to the strong lattice absorption in this region. The fits in Fig. 3 were obtained in the same manner as in the case of sample 1 and correspond to an excited-state lifetime of $\tau = 80$ ps, a factor of 4–5 times less than that observed in the bulk case.

The radiative lifetime for the *D* transition is unknown but we can estimate a lifetime from the absorption cross section (or indeed by assuming a purely hydrogenic impurity), and this gives a value of the order of 0.1–1 ms. We can conclude that the observed lifetimes are clearly nonradiative, in agreement with what has been observed in Si:P.[5]

The nature of the nonradiative scattering channel cannot be assigned with complete certainty. However, the observed independence of the decay with temperature suggests that the observed recombination is not due to carrier-carrier scattering as in this case we would expect to observe a change in the transition rate as the impurities ionize. Since the energy of the transitions considered is below that of the optical phonon bands a phonon-relaxation process at this energy can only involve acoustic phonon emission. For the bulk case this must be multiphonon scattering in order to conserve momentum. However, in the case of the MQW sample a relatively small degree of confinement produces a dramatic reduction in the excited-state lifetime. Hence the most likely process to explain this behavior is relaxation of the *k* conservation by the phonon zone folding effect in the QW.[18] We note that a similar effect has been observed in persistent photoconductivity measurements on *n*-type GaAs, where the decay rate reduces from 10 ns in the bulk to less than 1 ns in a $Al_xGa_{1-x}As$ quantum well,[19] although this measurement will include a capture time component.

In conclusion, we have demonstrated far-infrared pump-probe measurements of the excited-state lifetime for main infrared-active $1s$-$2p$ transition of Be acceptors in GaAs. It is found that the scattering rate is orders of magnitude slower than intraband scattering at similar energies in the bulk case. The scattering rate is also found to be independent of temperature, in agreement with the expected behavior for a shallow impurity state for which the carrier is localized in all three directions (in analogy with the 0D quantum-dot carrier levels[5]). This is in contrast to the free-carrier intersubband scattering in the 2D quantum-well system, which shows a strong temperature dependence due to phonon emission via momentum transfer in the plane of the wells. Finally, we demonstrated that quantum confinement of the impurity state enables the intra-acceptor states to be tuned in energy but that relaxation of the *k*-selection rules for phonon transitions results in an enhanced interlevel scattering rate between levels in these systems.

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