Occupancy of Shallow Donor Impurities in Quasi-Two-Dimensional Systems: D^0 and D^- States

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Far-infrared magnetotransmission and photoconductivity measurements combined with visible-light, photon-dose experiments on wide-barrier GaAs/$Al_{0.3}Ga_{0.7}As$ multiple-quantum-well samples planar doped with Si donors in both well and barrier centers have provided unambiguous evidence for the existence of D^- ion states and the evolution of the occupancy of the donor-ion electronic states in the quantum wells with excess electrons in this quasi-2D system.

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The D^- ion in semiconductors is an analog of the H^- ion in atomic physics, in which two electrons are bound to one positively charged center. This is the simplest system upon which to test our understanding of many electron problems, since the two indistinguishable electrons mutually screen each other from the positive center, and the strong Coulomb repulsive interaction between the electrons must be taken into account. The H^- ion in a strong magnetic field has been of considerable interest in astrophysics, where fields are so strong ($>10^5$ T) that the so-called high magnetic field limit (half the cyclotron energy greater than the binding energy of the hydrogen atom) can be achieved. This region is inaccessible in the laboratory; however, for D^- ions in semiconductors the binding energy is a small fraction ($<5\times10^{-4}$) of that of H^-, the mass is much lighter, and one can study many-body effects in the high field limit at easily attainable laboratory magnetic fields.

In three-dimensional (3D) bulk semiconductors, ionizing transitions from the ground state of D^- ions to free electron Landau levels have been observed and identified [1]. Recently, the observation of D^- ions in quasi-two-dimensional (2D) systems, modulation-doped GaAs/AlGaAs multiple quantum wells (MQWs), has been reported by Huant, Najda, and Etienne [2], and very recently by Mueller *et al.* [3] in a wide-well sample. Similar spectroscopic features have been observed previously, but not identified [4,5]. In all previous work experimentally observed spectroscopic features were complicated by the existence of a number of possible transitions in the same spectral region, e.g., neutral barrier impurities (the strongest feature for the structures studied), neutral well impurities (at different locations in the well), cyclotron resonance (CR), and D^- ions. All of these transitions exhibit quasi-two-dimensional properties in tilted field experiments, have approximately the same slope with magnetic field at high fields, and appear in pairs with the same energy separation, $\hbar\omega_c$ (CR energy). Several theoretical calculations for the transition energies of quasi-2D D^- ions in magnetic fields have been carried out [6-8]. Results show the most prominent differences from other possible transitions in the *low* field region; D^- transitions have clearly larger slopes than CR, while all neutral donor transitions have smaller slopes than CR. Although previous observations [3-5] in the high field region are consistent with D^- transitions (from comparison with theoretical calculations), possible contributions from off-center impurities in the well and bulk donors complicate the interpretation. In addition, relative intensity variations among all spectroscopic features in a magnetic field at finite temperatures, which are determined by electron population of the different possible energy levels, have not yet been studied systematically. Interpretation of such studies is made difficult by the existence of neutral barrier donor states and off-center-well neutral donor states.

In the present work specially designed samples with very wide barriers (600 Å) δ doped with Si donors at the centers of both wells and barriers were used; with such large barrier widths the binding energy of barrier impurities is very small and can be neglected in the problem [9,10]. The concentration of dopant in wells and barriers is designed to be such that with all electrons in the wells the D^- ion transitions dominate the spectrum at low temperatures. A novel aspect of this work is the "photon dose" experiments, in which the number density of electrons in the wells is controlled by the accumulated illumination from an *in situ* red light-emitting diode (LED) [11]. Controlled progressive electron occupation of various states of donors in the wells, including D^+ ions, D^0 neutral donors, D^- ions, and finally free electrons in Landau levels, was realized and clearly observed on a single sample with increasing photon dose.

Several new results or insights have emerged from this work. The quasi-2D nature of the D^- transitions are most clearly seen at zero (or very low) magnetic field, where the binding energy in 2D is nearly a factor of 10 greater than that in 3D. Measurements of transition frequencies for a 100-Å well-width sample down to very low magnetic fields extrapolate to a zero field value that is, in fact, larger than the calculated binding energy for a strictly 2D limit [12]; it is significantly larger than the calculated ionization energy for this well width [6]. In addition, the observed D^- transitions in photoconductivity are all rather sharp; by contrast, in 3D such experiments exhibit a very broad photoresponse with an onset corresponding to the ionization frequency of the second electron, and a tail to higher frequency, which results from transitions to continuum states corresponding to free motion along the magnetic field. These continuum states are absent in quasi-2D. Finally, photon dose experiments on a single sample, combined with results for a sample having barrier doping larger than the well doping, have permitted a systematic study of controlled population of donor impurity states in the wells with electron density up to more than twice the number density of donors in the wells. These studies permit *unambiguous* identification of the D^- transitions. The large transition energy at zero field, the sharp lines observed in both transmission and photoconductivity measurements, and the metastable occupancy of the donor states at low temperatures are unique to quasi-two-dimensional quantum-well systems.

The three $GaAs/Al_{0.3}Ga_{0.7}As$ MQW samples were grown by molecular-beam epitaxy with 600-Å $Al_{0.3}$-$Ga_{0.7}As$ barriers separating the wells. Samples 1 and 2 have nominally the same doping (Si planar doped at 2×10^{10} cm^{-2} in both the well and barrier centers), but different well widths: sample 1, 200 ± 5 Å and sample 2, 96 ± 5 Å. Sample 3 is nominally identical to sample 1 except that the barrier doping is $\leq 4\times10^{10}$ cm^{-2}. Well widths were determined from photoluminescence (PL) and reflectivity measurements. A total of 20 well-barrier repetitions were sandwiched between two thick ($\sim$2000 Å) AlGaAs cladding barriers, and the entire structure was grown on a semi-insulating GaAs substrate and capped with a 100-Å GaAs layer. Far-infrared (FIR) transmission and photoconductivity spectra were obtained with Fourier-transform spectrometers in conjunction with a 9-T superconducting magnet and light-pipe, condensing-cone optics. All data were taken at liquid-^{4}He temperatures, and sample substrates were wedged to avoid multiple-reflection interference. For transmission measurements, Ge:Ga photoconductive detectors were used to cover the spectral region between 80 and 240 cm^{-1}. Photoconductivity measurements were carried out by an ac capacitive-coupling technique [13].

The inset to Fig. 1 shows typical transmission and photoconductivity spectra at 8 T for sample 1. Data were taken in the Faraday geometry (**B** parallel to FIR propagation direction and normal to the sample surface) after the samples have been exposed to a large (visible) photon flux. As checked by tilting the sample from the field direction, all high-frequency features are confinement related. The positions of the two low-frequency features are rather insensitive to the magnitude of the magnetic field; thus field tilting cannot be used as a test of confinement. Line A is the $1s\rightarrow 2p_+$ transition of D^0 at the well centers, whose behavior is well known [14]. The strong absorption line B at $\sim$146 cm^{-1} is in the region of a feature that has been attributed [2] to a transition from the ground singlet state of D^- ions to an excited state associated with the $N=1$ Landau level [15]. The sharp feature at the lowest energy ($\sim$107 cm^{-1}) is CR of localized electrons [16], which is shifted to slightly higher energy (3-4 cm^{-1}) than free electron CR at this well width. At higher temperatures the localized CR shifts down to the position of free electron CR. Photoconductivity measurements (the lower trace in the inset) do not show CR; the transitions $1s\rightarrow 2p_+$ of D^0 and $D^-(N=1)$ are clearly observed at the same positions as those in the tramsmittance spectra. In addition to these features, there are two weaker peaks at energies about $\hbar\omega_c$ below the $1s\rightarrow 2p_+$ and the $D^-(N=1)$ transitions, lines C and D, respectively. Line C is the $1s\rightarrow 2p_-$ transition of D^0; from its frequency position and relationship to line B, the lowest frequency feature, line D, could be reasonably assigned to the D^- ground state to an excited state associated with the $N=0$ Landau level [$D^-(N=0)$].

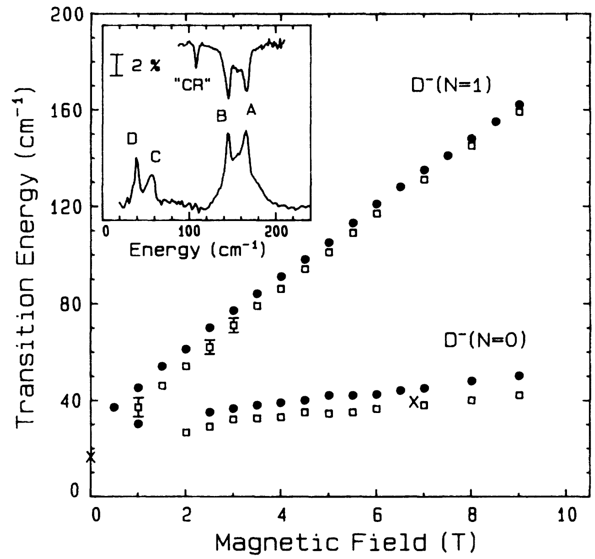

FIG. 1. Magnetic field dependence of D^- ion transition energies. □, sample 1; ●, sample 3; ×, calculation of Ref. [5]. Inset: Transmission (upper) and photoconductivity (lower) spectra for sample 1. Data were taken at 8 T and 4.2 K with the field normal to the sample surface.

A compilation of the transition energies for feature B for samples 1 and 2 as a function of magnetic field for both samples is shown in Fig. 1. The large error bars for data points around 3 T are due to crossing of the $D^-(N=1)$ and the D^0 $1s\rightarrow 2p_-$ transitions in this field region. It is clear that the slopes in the low field region ($B\lesssim 3$ T) are larger than those in the high field region, consistent with calculations for a D^- ion, and *opposite*

[14] to the behavior of D^0. Sample 2 has the larger transition energies by $\sim$3-4 cm^{-1} at high fields, consistent with calculations [7] for D^-. The B and D transitions for this sample [$D^-(N=1)$ and $D^-(N=0)$] extrapolate to $\sim 27\pm 2$ cm^{-1} at zero field. For sample 1 these transitions extrapolate to a zero field value of $\sim$20 cm^{-1}. Note that the separation between the two transitions for sample 1 at high fields is slightly larger than that for sample 2, since CR has a larger energy at a given magnetic field for sample 1 (the wider well sample) due to the nonparabolicity of the GaAs conduction band. Theoretical calculations [6] for the $D^-(N=0)$ ionizing transition (D^- ground state to $N=0$ Landau level continuum) in a 100 Å QW at $B=0$ and 6.76 T are also shown in Fig. 1.

The experimental results for the transition energies for D^- ions are in only fair agreement with the calculations; the measured energies are systematically higher than predicted by calculations in which transitions were assumed, i.e., D^- ground state to free electron Landau levels [6]. Larsen and McCann [8] have recently suggested that the observed features are due to intraimpurity transitions from the D^- ground state to D^- excited states lying *above* the corresponding Landau levels [$^1S \rightarrow {}^1P(M=\pm 1)$ in the usual atomic notation]; hence larger transition energies are predicted. The large systematic energy discrepancies between our experimental values and the ionizing transition calculation favor the latter interpretation.

Transmittance spectra for sample 1 at 8 T and 4.2 K for several accumulated photon doses (LED illumination time) are plotted in Fig. 2(a). The sample was tilted 20° from the field direction to avoid possible complications from bulk $1s\rightarrow 2p_+$ transitions, since $D^-(N=1)$ is very close to this transition when **B** is normal to the sample surface. After the sample was cooled to 4.2 K in the "dark," controlled doses of photons (successive short pulses of LED illumination) were applied to the sample to liberate electrons from trap states in the AlGaAs barriers, and introduce them into the GaAs wells. These electrons are metastable in the well and remain for days at low temperature [14]. Before LED illumination, all donors in the wells are ionized D^+ centers; hence there is no optical absorption from the wells. As the photon dose is increased, the first line to become detectable is that of neutral donors in the well centers. When the illumination time reaches $\sim$0.25 ms, the line that is attributed to D^- appears. Its absorption amplitude increases rapidly, and it becomes the dominant line at the highest dose. The CR line appears *after* the D^- line. The peak absorption in percent for all the three transitions is plotted in Fig. 3 as a function of the accumulated LED illumination time; these values of peak absorption are obtained by fitting the spectra with a sum of Lorentzian lines. The "turn-on" points move to higher photon dose for the three transitions in the sequence D^0, D^-, CR, clearly indicating that electrons populate the D^0 states first, then D^-, and finally the free electron states. The absorption amplitude of D^- ions increases much faster than that of the other two transitions, and crosses the D^0 curve at about 1 ms. At

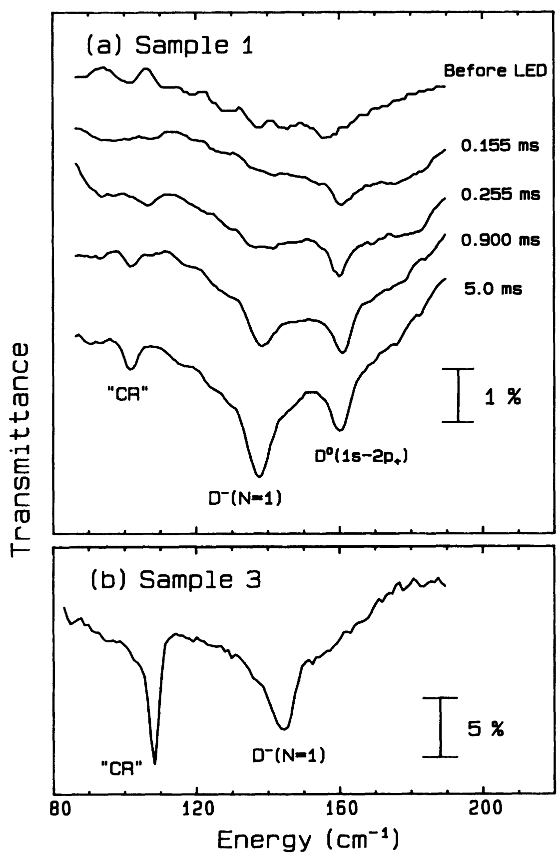

FIG. 2. (a) Transmission spectra of sample 1 at 8 T and 4.2 K for several accumulated LED illumination times. The sample surface is tilted 20° from the field direction. The spectrum before LED illumination is ratioed to a 0 T background, and is used as the background spectrum for all other spectra. (b) Transmission spectrum for sample 3 at 8 T and 4.2 K. The sample surface is normal to the magnetic field; thus the features occur at higher frequency than those of (a).

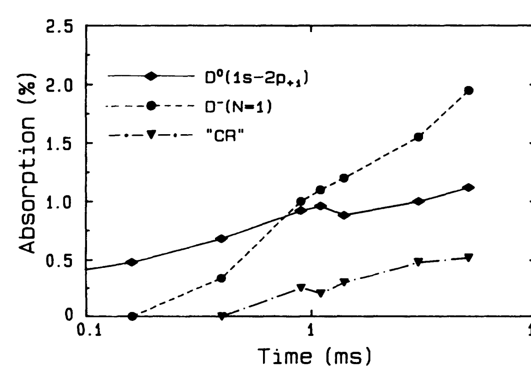

FIG. 3. Percentage peak absorption as a function of accumulated LED illumination time (logarithmic plot) for the $D^0(1s\rightarrow 2p_+)$, $D^-(N=1)$, and "CR" transitions of Fig. 2(a).

the highest dose, the absorptions of D^0 and CR are showing gradual saturation, but D^- is still increasing at this electron density. Studies of the temperature dependence of these lines at high magnetic fields are consistent with the assignments of the lines from these photon dose experiments; i.e., the binding energies of D^0 are significantly larger than those of D^- (for the second electron) over this field region. However, the fact that the D^0 transition does not *decrease* while the line attributed to D^- increases at large photon doses, makes this assignment possibly open to question. For example, edge impurity states have a smaller binding energy than center impurities, and thus an unusual peaked distribution of well impurities could give rise to a line in this region. Figure 2(b) shows a transmission spectrum at 8 T for sample 3, which is nominally identical to sample 1 except for a larger barrier doping density. *The D^0 line is not discernable*, while the feature attributed to D^- is much stronger. This result is consistent only with the existence of D^- states, and essentially all impurity ions in the well being doubly occupied with electrons at this temperature. The excess electrons appear in the much stronger cyclotron resonance.

The photon dose experiment and the temperature dependence studies on sample 1, combined with the results for sample 3 (barrier doping *larger* than well doping), have clearly demonstrated the sequence of electron population among the energy levels, and the effects of excess electrons in the wells. These results are qualitatively in agreement with expectations for D^- ions in the wells. At zero temperature, the intensity of the D^0 line should eventually *decrease* to zero as that of the D^- line increases, since, physically, both states involve the same impurity center. The data of Fig. 2(a) do not show a decrease of the D^0 line at the highest photon doses; this is primarily due to the fact that the barrier doping is actually somewhat less than the well doping (on average, there are less than two electrons available for each donor ion). However, sample 3, which has exactly the same structure as sample 1 but higher barrier doping ($\lesssim 4 \times 10^{10}$ cm^{-2}), shows no discernable D^0 line and a much stronger D^- line.

In summary, the qualitative population results, combined with the observed magnetic field dependence of the transitions at low fields and the well-width dependence, provide unambiguous identification of the D^- state and its quasi-2D nature in quantum wells. Discrepancies between the large observed transition energies near zero magnetic field and the calculated ionization energies for the same well width indicate the need for further theoretical examination of this problem.

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