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Electric-field effects on confined hydrogenic impurities in semiconductors

Byungsu Yoo and B. D. McCombe
State University of New York at Buffalo, Buffalo, New York 14260

W. Schaff
Cornell University, Ithaca, New York 14853
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We report the observation of electric-field effects on the electronic states of shallow impurities confined in semiconductor quantum wells. A *p*-"*i*"-*n* diode structure was used to produce the controllable electric field, and the states of donors doped in the well center were monitored by far-infrared magnetospectroscopy. A broadened, impurity-related peak is observed, which changes significantly both in shape and in position with electric field. Observed shifts and changes in the line profile are in good agreement with a variational calculation that incorporates the impurity distribution within the well.

Effects of external fields on the electronic states of hydrogenic systems have been of interest for many years. Effective-mass donor impurities in semiconductors can form nearly ideal hydrogenic systems in which the length and energy scales are dramatically changed relative to the hydrogen atom, e.g., for donors in GaAs the Bohr radius is 100 Å and the binding energy is 5.83 meV. This has permitted the high-magnetic-field limit to be explored in detail at normal laboratory magnetic fields, and the correspondences between the low-field and high-field quantum numbers to be established.[1] The effects of confinement of hydrogenic impurities has received considerable attention recently,[2–5] and the correspondences between the appropriate states in the limiting cases have also been established.[6] The corresponding large *electric-field* case cannot be studied in bulk semiconductors due to field ionization of the shallow impurities. The confining barriers of a quantum well (QW) in principle, permit large electric fields to be applied to shallow impurities without such ionization. However, the only reported experiments have been for *excitons* in QWs,[7] for which the hole states are complex; and calculations[8,9] of electric-field effects have been restricted to the ground state of shallow donors. We report the first experimental observation of the effects of large electric fields on the electronic states of shallow impurities confined in QWs, and a comparison of the far-infrared (FIR) measurements with variational calculations of the electronic states.[10]

The qualitative effects of an applied electric field on hydrogenic impurities in a quantum well can be understood by considering the changes in the confining potential. For zero electric field the envelope function for donors in the z direction has a maximum at the center of the well, leading to increased binding and transition energies for a well-center donor compared with those in the bulk. For impurities located away from the well center the binding and transition energies are decreased relative to those for the well center, and can be reduced below those for the bulk. A linear potential due to the applied electric field is superimposed on the square-well potential, and the peak of the envelope function in the z direction is displaced toward the lower potential-energy barrier. This leads to a separation of the peak in the probability density of the electron from any positive ion located near the well center or on the high-potential-energy side of the well, and a concomitant reduction in the (negative) potential energy. There is also an enhancement of the confinement leading to an increase in the kinetic energy for all low-lying states. Both effects conspire to decrease the binding and transition energies for such impurities. For the case of impurities located near the barrier on the *low*-potential-energy side of the well, both binding and transition energies *increase* as electric-field strength increases, and the position of the impurity ion that corresponds to the *maximum* binding energy is displaced increasingly toward the low-energy barrier with increasing electric field. Thus, depending on its location, the binding and transition energies of an impurity can be tuned in either direction through the application of an electric field.

A *p*-"*i*"-*n* diode structure grown by molecular-beam epitaxy was used in this study to provide an externally controllable electric field; the "*i*" region consisted of 20 wide (500 Å) GaAs quantum wells separated by 200-Å $Al_{0.3}Ga_{0.7}As$ barriers. Wide wells were used to emphasize the electric-field effects. Each of the wells was doped over the central $\frac{1}{3}$ with Si donors at a nominal sheet density of 1.7×10^{10} cm^{-2}. The top contact was 3000 Å of p^{++}-type (Be) $Al_{0.3}Ga_{0.7}As$, and the bottom contact was 3000 Å of n^{++}-type (Si) GaAs. Standard photolithography, etching, and evaporation techniques were used to create a large area mesa (2.5×2.5 mm^2) and to make sample contacts. A semitransparent (50 Å) Cr film was evaporated on the top surface as a Schottky contact. Ohmic contact to the n^{2+}-type GaAs region was made with Au:Ge. Low-temperature (4.2 K), far-IR magnetotransmission measurements were performed as a function of bias on the *p*-"*i*"-*n* diode in magnetic fields up to 9 T with a Fourier-transform interferometric spectrometer in conjunction with a Ge:Ga photoconductive detector and light-pipe and condensing-cone optics. In order to avoid electrical-leakage problems, observed under dc conditions, and to maintain neutrality of the donors in the wells (and thus a uni-

form electric field) during the measurements, an audio-frequency double-modulation scheme with phase-sensitive detection was employed (inset in Fig. 1). The bias is square wave modulated at 1 kHz between -2 V (zero electric field) and a value corresponding to a desired electric field. During the central 170 μsec of the $+2$ V half of the modulation cycle the sample is illuminated with low intensity red light from an *in situ* light-emitting diode (LED) to ensure neutrality of the donors. The majority of donors remain neutral during the 500 μsec of the second half (electric field nonzero) of the cycle. The lock-in-derived signal, referenced to the modulation voltage, is proportional to the difference between the sample transmission in the absence of an electric field and that in the presence of a desired electric field determined by the bias during the second half of the modulation cycle.

Figure 1 shows differential transmission spectra, obtained as described above, normalized to a background spectrum taken at 9 T. The sharp positive-going peak 2 at 162 cm^{-1} (2–3 cm^{-1} above the corresponding bulk transition due to confinement) is the $1s$-$2p(m=+1)$ (three-dimensional hydrogen-atom notation[6]) impurity transition[11] from well-center donors in the absence of an electric field. The negative-going peaks, cyclotron resonance (CR) and 1, arise from the nonzero electric-field portion of the modulation cycle. The moving broadened minimum (1) is the inhomogeneous line profile of ground-state- ($m=0$) to-first excited-state ($m=+1$) transitions for donors distributed around the central $\frac{1}{3}$ of the well in the presence of the electric field. The sensitivity of the absorption line profile to the impurity distribution increases as electric-field strength increases, and the impurity distribution is reflected strongly in the absorption line shape. At 9 T the average position of (1) shifts down by ~ 18 cm^{-1} in a nominal electric field of 1.14×10^4 V/cm [bias of 0.5 V in Fig. 2(a)]. At larger electric fields there is no well-defined minimum, and a confined cyclotron resonance peak labeled CR appears at 122 cm^{-1}. The electric-field dependence of the frequency positions of line 1 is summarized in Fig. 2(a) at several magnetic fields. The bars indicate the frequency region over which the (negative-going) absorption is 95% of the peak. The electric fields are estimated by assuming that the entire potential difference is dropped linearly across the "i" region ($\sim 17\,500$ Å) of the p-"i"-n structure; with this assumption the electric field corresponding to a bias of 4 V is 2.3×10^4 V/cm. This is an upper limit to the magnitude of the electric field, since there is a small potential drop at the top Schottky contact, as well as additional small potential drops in the cladding regions on either side of the multiple QW structure due to possible fixed charge from ionization of unintentional dopant in these regions.

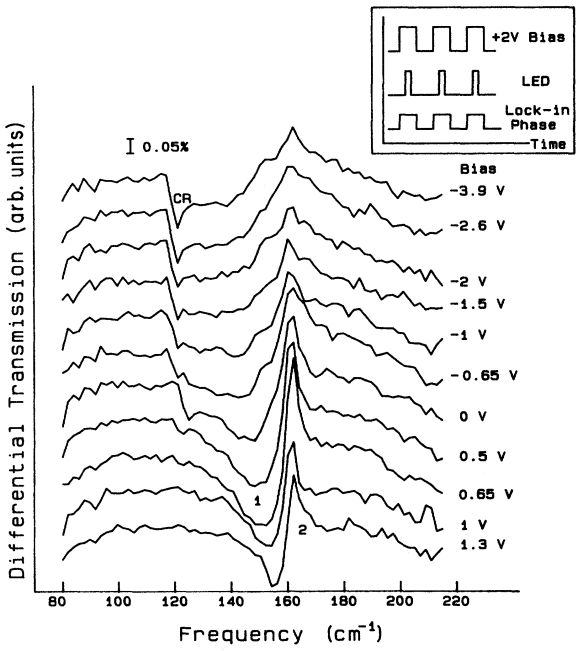

FIG. 1. Differential transmission spectra at 9 T, 4.2 K, and a number of bias voltages (during the LED-off part of the modulation cycle). The various spectral features, 1, 2, and CR, are discussed in the text. The modulation scheme is shown in the inset.

In order to provide a basis for interpretation of the experimental data, a variational calculation was carried out for the low-lying energy states of an effective-mass electron in the presence of a Coulomb potential in a single quantum well in the presence of an electric field at zero magnetic field. The Hamiltonian for this problem is

$$H=\frac{p^2}{2m^*}-\frac{e^2}{\epsilon[\rho^2+(z-z_i)^2]^{1/2}}+V_b\Theta(z^2-L^2/4)+|e|Fz\,, \tag{1}$$

where L is the quantum-well width, ϵ is the dielectric constant, z_i is the impurity position, F is the magnitude of the electric field, V_b is taken to be infinite to simplify the calculations, and $\Theta(x)$ is the step function. The trial functions were taken to be of the hydrogenic form,

$$\Psi(r)=N(\lambda,L)f(z,L)\rho^{|m|}e^{im\phi}\times\exp\{-(1/\lambda)[\rho^2+(z-z_i)^2]^{1/2}\}\,, \tag{2}$$

where λ is a variational parameter, m is the azimuthal quantum number, $N(\lambda,L)$ is a normalization constant, and $f(z)$ is the envelope function of the first subband. In this approximation coupling between the states associated with different subbands is ignored. The function $f(z)$ is taken to be a linear combination of two Airy functions with subband energy $E_z(L)$ and electric-field strength F. The ground ($m=0$) and first excited-state ($m=\pm1$) energies of the impurity at arbitrary positions in the quantum well were calculated from the minimization of the energy with respect to the variational parameter λ. Representative results for well-center donors are displayed in Fig. 2(b). In all cases the transition energies decrease as electric-field strength increases, with the most dramatic dependence for the wide wells. Although the magnetic field is not included directly in the calculation, it may be taken into account in an *ad hoc* fashion by adding the cyclotron energy to the calculated $1s$-$2p$ energy to provide a direct comparison with experiment. The energy separation between the two p-derived $m=+1$ and $m=-1$

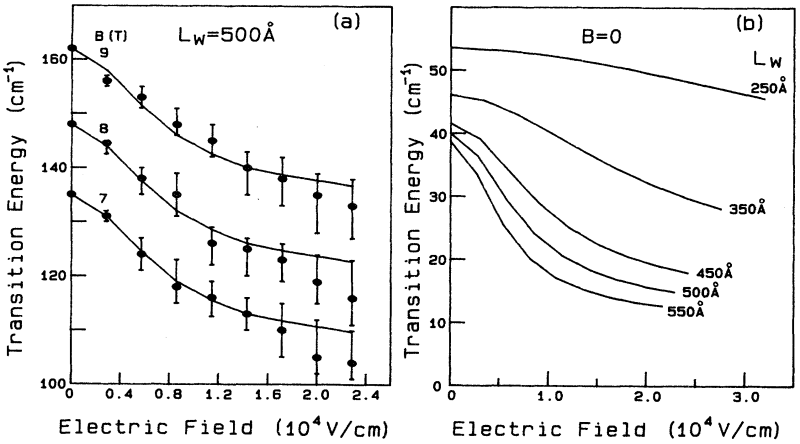

FIG. 2. (a) Electric-field dependence of the frequency positions of line 1 at three magnetic fields. Solid lines: calculated results from (b) for the 500-Å well with the measured cyclotron frequencies for each field added; solid circles: negative-going absorption minimum; bars: frequency range for which absorption is 95% of the minimum. (b) Variational calculation of the ground-state–to–first excited-state transition frequencies for a well-center donor vs electric field for several well widths.

states is equal to the cyclotron energy, and the $2p$-($m=-1$) like state is only weakly dependent on magnetic field; thus this procedure is expected to be reasonably accurate in this field region. The agreement in Fig. 2(a) between the experimental line positions (bars) and the calculated positions for a well-center impurity (solid lines) is reasonable. However, it should be emphasized that for electric fields $F > 1.14\times10^4$ V/cm, much of the shift of the line profile results from changes in the line shape due to "sampling" different parts of the impurity distribution, rather than a shift of the peak position for an impurity at some particular location in the well; this is discussed below. A clear manifestation of the decrease in binding energy with increasing electric field for a substantial fraction of the impurities can also be inferred in Fig. 1 from the appearance of a confined cyclotron resonance at about 0-V bias, and its increase of intensity for larger values of reverse bias. This is ascribed to increased thermal ionization at 4.2 K of donors in that part of the spatial distribution located in the higher-potential-energy region of the well; there is a large decrease in the binding energy for these impurity sites. Both cyclotron resonance and the impurity lines were verified to be confinement related by tilted-field experiments.

The impurity line (1) in the presence of a substantial electric field is clearly much broader than the corresponding line (2) at zero electric field. This is a result of the distribution of impurities over approximately $\frac{1}{3}$ of the wells ($\sim$170 Å), which leads to large inhomogeneous broadening in the presence of a finite electric field (see Fig. 3). Donors that are close to the low-potential-energy edge of the well have much larger binding (transition) energies than donors located close to the high-potential-energy edge; in addition, the square of the transition-matrix element increases substantially as the impurity is displaced from the well center toward the higher potential energies. Thus the detailed shape depends strongly on the form of the distribution in the presence of an electric field. In the square-well situation ($F=0$ in Fig. 3) the distribution away from the well center leads only to a low-frequency tail in the absorption line profile due to the large peak in the density of states for transition frequencies corresponding to impurities close to the well center.

In general, the impurity distribution, the positional dependence of the transition energies, and the dependence of the transition-matrix element, $\langle f|x|i\rangle$, on impurity position *all* contribute to the shape of the absorption line profile; the relative contributions depend on the magnitude of the electric field. The following line-shape function[3] for absorption of light polarized in the x direction was used to calculate the impurity absorption profile for comparison with experiment,

$$I(\omega)=\omega\int dz_i\,P(z_i)|\langle f|x|i\rangle|^2\left\{\frac{\Gamma/\pi}{(\omega-E_{fi}/\hbar)^2+\Gamma^2}\right\},$$

where $P(z_i)$ is the impurity distribution function, and Γ was taken to be 2 cm^{-1} to fit the $F=0$ line. A typical re-

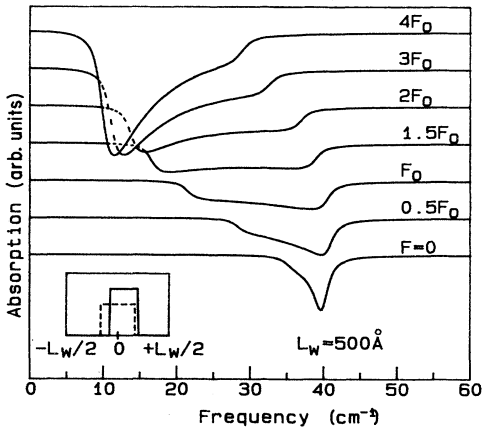

FIG. 3. Simulation of absorption line profile at $T=0$ and $B=0$ for several electric fields. $F_0=2.86\times10^3$ cm. The assumed and nominal impurity distributions are shown in the inset by solid and dashed lines, respectively.

sult for several values of electric field is displayed in Fig. 3. In this calculation all impurities were assumed to be neutral, i.e., finite temperature effects were not included. For this assumed off-center, rectangular profile the calculation gives rise to a shifting, broadened peak, with a shift and shape evolution in qualitative agreement with experiment. Several model impurity distributions have been simulated. The nominal centered (square) distribution does not yield absorption peaks that shift toward low frequency at small electric fields, as observed in the experimental data (see Fig. 1), but rather a very broad line with a peak that moves initially to *higher* frequencies due to the contribution of impurities located in the low-potential-energy region of the well. By displacing the impurity distribution slightly toward the higher-potential-energy region of the electric-field-modified well, the experimentally observed shifting, broadened line profile with a low-frequency transmission minimum absorption peak in high electric fields is qualitatively reproduced. This low-frequency peak results from the strong increase in oscillator strength for impurities displaced toward the high-potential-energy edge of the well coupled with the assumed sharp cutoff in the distribution. The line profile in the presence of an electric field is *much* more sensitive to the shape of the impurity distribution than that from a square well (see the $F=0$ and $F>0$ profiles in Fig. 3).

In conclusion, we have observed strong electric-field effects on confined shallow donors in QW structures. These results show that there is promise for tailoring a sharp absorption peak with a desired, tunable (by electric field) frequency response in such structures by spike doping in a precise region of the quantum well.

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[11]The intensity of peak 2 at +1.3 V appears smaller than that at 0.65 V. This is an artifact of the differential measurement. For small reverse bias the broadened, negative going absorption peak 1 partially overlaps peak 2 and reduces its apparent intensity. At large values of reverse bias peak 2 appears to decrease and broaden. This may be due to the existence of nonuniform electric fields during the first $\frac{1}{3}$ of the forward bias modulation.