Explanation of the formation of D^- ions in quantum wells

David M. Larsen
Department of Physics, University of Massachusetts–Lowell, Lowell, Massachusetts 01854
(Received 12 February 1993)

A simple model is proposed to explain why D^- ions can be present in significant concentrations at zero temperature in quantum wells even when they are less strongly bound than barrier donors. The model appears to account for certain recently reported experimental results in double planar doped quantum wells.

Although D^- ions are very difficult to detect in bulk GaAs, these hydrogenic donors with a second electron attached are commonly observed in GaAs/$Ga_{1-x}Al_xAs$ quantum-well structures which have been doped with shallow donor impurities. One reason is that D^- ions are more strongly bound in quantum wells than in bulk.[1] Another is that GaAs wells tend to be relatively rich in electrons, some of which are furnished by donors in the $Ga_{1-x}Al_xAs$ barriers.

If sufficiently dilute, donor impurities in the barrier can bind the electrons which they release into the quantum well. The resulting centers are called barrier donors; these donors are much less strongly bound than donors formed from positive ions near the center of the quantum well (called well donors) because the barrier-donor electron is prevented by the barrier from getting close to the positive ion to which it is bound. Nevertheless, calculations indicate that the electron in a barrier donor is more tightly bound than an electron attached to a neutral donor in the well, at least for the experimental conditions in recently reported far-infrared-absorption experiments.[2,3] Thus it has seemed paradoxical that observations indicate that D^- centers are often plentiful at low temperatures in such quantum-well structures. One might have expected that the extra electrons in the well contributed by the barrier ions would remain bound to those ions and not be captured by the neutral donors.

The purpose of this paper is to explain how significant populations of D^- centers can appear in thermal equilibrium at zero temperature in samples where the barrier donor is more tightly bound than the D^- ion. Investigated here is whether a model which ignores random potential fluctuations, but considers only isolated barrier-donor–well-donor pairs, can account, at least qualitatively, for the experimental data.

Under the assumption that barrier donors are more tightly bound than D^- ions, consider a neutral barrier donor and a "nearby" neutral well donor in a lightly doped quantum-well structure. To a first approximation, the electrostatic interaction energy between these donor centers is zero, because they are each neutral. Now consider the energy required to remove the electron from the barrier donor and place it on the neutral donor to form a D^- center. One pays an energy equal to the magnitude of the difference of the isolated-center binding energies of the barrier donor and the D^- ion, but one gains an energy equal to the electrostatic interaction energy of the (positive) barrier-donor ion and the (negative) D^- ion. This additional energy may suffice to favor the formation of the D^- center.

If potential fluctuations from charges external to the barrier-donor–well-donor pair of interest can be neglected, one can easily find the probability that a neutral donor in the well will convert to a D^- ion according to the reaction

$$B + D \rightarrow B^+ + D^- , \tag{1}$$

where B and D are neutral barrier and well donors, respectively, and B^+ is a "converted" barrier donor, a barrier-donor ion. If, as assumed here, this is the only reaction pertinent to the formation of B^+ or D^- ions, then the concentrations of D^- ions and of converted barrier donors must be equal.

Imagine a double planar doped (DPD) quantum-well structure, in which donor impurities are located in two parallel planes perpendicular to the growth direction (the z axis) of the structure. One of these planes lies in the barrier, the other in the center of the well. They are separated by a distance d. Donor impurities are randomly distributed within each plane but reside nowhere else. (Also, a magnetic field along z may be present.) Suppose that the binding energy of an isolated barrier donor exceeds the one-electron binding energy of an isolated D^- ion by an energy δ. Let n_B and n_W be the number of barrier impurities and well impurities, respectively, per unit area.

The distance of the ith barrier ion from the donor is $r_i=(\rho_i^2+d^2)^{1/2}$, where ρ_i is the distance from the center of the well donor to the projection of barrier ion i on the plane containing the well donors. Since d is a constant, the quantities ρ_i alone determine interimpurity distances of interest, and the problem is two dimensional. If the separation r of a barrier impurity from a chosen well donor is less than r_c given by

$$2/r_c=\delta , \tag{2}$$

where donor atomic units are employed in (2) and henceforth (lengths in units of a, the bulk donor Bohr radius, and energies in units of R^*, the bulk donor Rydberg energy[4]), then the attractive Coulomb energy between the D^- ion and the barrier ion exceeds the extra binding en-

ergy of the barrier donor and the conversion reaction of (1) is favored. In deriving Eq. (2), it is implicitly assumed that the electrostatic interaction can be well approximated by representing the D^- ion as a negative-point charge located at the position of the well-donor impurity atom. Taking $r_c=(\rho_c^2+d^2)^{1/2}$, one finds that D^- ion formation is favored if $\rho<\rho_c$, where

$$\rho_c=(4/\delta^2-d^2)^{1/2} . \tag{3}$$

Length ρ_c defines the radius of the "critical circle" centered on each well donor.

The basic premise of the present model can now be formulated concisely. It is assumed that in the ground-state configuration of the system, no unconverted barrier donor may lie inside the critical circle of any unconverted well donor. From this assumption one can construct a plausible algorithm for predicting the concentration x_M of D^- centers (or B^+ ions) in a given sample.

Suppose that one begins with a random array of barrier donors of concentration n_B and, starting from zero concentration, gradually adds well donors until the final concentration n_W is reached. At some intermediate point n well donors per unit area will have been added, of which η will have converted. The concentrations of unconverted barrier donors and well donors will be $n_B-\eta$ and $n-\eta$, respectively. If a very small additional concentration of well donors is added, the fraction of these which do not convert is $\exp[-(n_B-\eta)\xi]$, where $\xi=\pi a^2\rho_c^2$. This leads to the differential equation

$$\frac{d(n-\eta)}{dn}=\exp[-(n_B-\eta)\xi] ,$$

or equivalently,

$$\frac{d\eta}{dn}=1-\exp[-(n_B-\eta)\xi] . \tag{4}$$

Inverting both sides of (4) and integrating over η leads to

$$\int_0^{x_M}\{1-\exp[(x-R)\zeta]\}^{-1}dx=1 , \tag{5}$$

where $R=n_B/n_W$ and $\zeta=\xi n_W=\pi(n_W a^2)\rho_c^2$. The integral in Eq. (5) can be evaluated in terms of elementary functions, and x_M can be readily determined. Of interest in analyzing experimental spectra is the ratio of D^- ions to unconverted (neutral) barrier donors, which is given by $x_M/(R-x_M)$. Note that in the development above it is assumed that for all practical purposes a unique solution exists,[5] and that, despite the conversion of barrier donors, the unconverted barrier donors continue to obey Poisson statistics with respect to the added well donors.[6]

This model neglects potential fluctuations because it assumes that a well donor will convert if there is a B center close enough to it that their joint energy, calculated as if they were an isolated pair, is lowered by conversion. Although neglected, potential fluctuations of the kind envisioned by some other authors[2,3] must in reality play some role in the conversion process. It is expected that in many cases their effect on D^- populations will be small, since one expects the distribution of potential fluctuations acting on a D^--B^+ pair to be symmetrical about a mean of zero in the planar geometry envisioned here.

One case, however, in which the fluctuations may be especially important occurs when R is near 1 and (because δ is very small) ζ is much larger than 1. In this situation almost complete conversion is predicted by Eq. (5), but fluctuations could easily change this result. In the first place, the mean separation of D^--B^+ pairs allowed by the present model tends to be large, so that the potential fluctuations are relatively stronger compared to the Coulomb interaction between the pairs than when the pairs are closer together.[7] But even "weak" fluctuations might prevent conversion of a measurable fraction of well donors. The fluctuations favoring conversion would affect only the (small) population of unconverted centers, whereas those opposing conversion would act on the (large) population of converted centers. Thus it is to be expected that the present model would overestimate the amount of conversion in this case. (In the opposite case, when $\zeta\ll 1$, the few converted centers will consist of closely spaced D^--B^+ pairs which should be relatively insensitive to external potential fluctuations. In that case, however, the model should underestimate the conversion.)

It is of interest to compare the predictions of Eq. (5) to the available experimental data. The author is aware of only one systematic investigation of the relative absorption strengths of donor and D^- centers in quantum wells, and that is the work of Refs. 2 and 3. Absorption spectra are presented in those references for various values of n_W and n_B at two magnetic-field strengths (the magnetic-field strength affects δ, since the D^- binding increases more rapidly than the barrier-donor binding with increasing field) as well as at two different values of d. Although the strength of the absorption lines are proportional to the absorber concentrations, the relative strength of the absorption lines belonging to neutral donors and D^- ions is not a direct measure of their relative populations because of differences in oscillator strengths. (It can be expected that barrier donors, which, in the high magnetic fields of Refs. 2 and 3, have Landau-level-like wave functions, also have the strongest oscillator strengths of the three absorbing species present.) Nevertheless, trends can be discerned in the data which must be obeyed by an acceptable theory of D^- formation. For example, in Ref. 2 it is shown that, under the described conditions of the experiment, increasing R from 1 to 2 or 3 causes strong conversion of the well donors to D^- ions.

Table I has been constructed using Eq. (5), the data of Refs. 2 and 3, and calculations of δ described below; it shows the fraction of well donors which convert to D^- ions and the relative concentrations of D^- ions and barrier donors for various samples described in those references. Comparison of the tabulated results and the observed spectra[2,3] suggests that the present theory, for the most part, gives a qualitatively correct picture of the data. The two exceptions are for samples $F700$ and $G312$, in which δ is very small and the theory clearly overestimates the conversion, perhaps for the reasons discussed above.

Determination of δ presents the most difficult part of calculations which evaluate x_M from Eq. (5). For these calculations the effective mass m^* of the 10-nm wells was

TABLE I. Predictions of the present model for the fraction x_M of well impurities which have converted to D^- centers in various samples described in Refs. 2 and 3. Also shown are predicted ratios, $[D^-]/[B]$, of D^- ion concentrations to unconverted barrier-donor concentrations. One spectrum for each sample listed here is presented in Refs. 2 and 3 along with pertinent sample data from which δ, ζ, and R are calculated.

Sample	δ	ζ	R	x_M	$[D^-]/[B]$
*F*606	0.247	1.42	1.0	0.603	1.52
*G*612	0.310	1.91	1.0	0.677	2.10
*G*604	0.272	2.54	2.0	0.972	0.95
*G*610	0.272	2.45	3.0	0.997	0.50
*G*312	0.053	20.0	1.0	0.965	27.6
*F*700	0.012	737	1.0	1.000	> 1000.0
*F*704	0.225	2.03	2.0	0.947	0.90

taken to be $0.073m$, as determined from the positions of the barrier-donor transitions in Ref. 2, whereas m^* is assumed to be equal to the bulk value $0.0665m$ for the 37.6-nm well. (Here m is the electron mass in vacuum.) The D^- binding energies were evaluated from variational calculations of the total energies of well-center donor and D^- ions. The three-parameter donor trial functions employed are

$$\varphi(\rho,z)=\exp[-H\rho^2-\kappa(\rho^2+\alpha z^2)^{1/2}]g_1(z)\ , \tag{6}$$

where $g_1(z)$ is the ground-state wave function for a free electron in the quantum well. The quantum-well barriers are taken to be of finite height but of infinite width. Eight-parameter trial functions for the D^- center are of the form

$$\Psi(\mathbf{r})=[\Phi_I(\mathbf{r}_1)\Phi_0(\mathbf{r}_2)+\Phi_I(\mathbf{r}_2)\Phi_0(\mathbf{r}_1)][1+Cu]\ ,$$
$$u=[(x_1-x_2)^2+(y_1-y_2)^2+\alpha_c(z_1-z_2)^2]^{1/2}\ , \tag{7}$$

where each of the Φ orbitals take the same form as Eq. (6) but their parameters H, κ, and α are varied independently. For a well width L_W of 1, and for a dimensionless magnetic field γ also equal to 1, this ansatz gives a D^- binding energy of 0.753 compared to the results 0.77 ± 0.02 found in Ref. 1 and 0.747 in Ref. 8.

The barrier-donor binding was also calculated from trial functions of form (6), but with z in the exponential there replaced by $z-z_I$, where z_I is the z coordinate of the center of the barrier impurity. (The binding energies obtained here are significantly greater than those reported in Ref. 2 for $\gamma=1$ and 3.)

Two avenues of future research which would help in understanding the limits of accuracy of the present model suggest themselves. First, it would be interesting to do a computer simulation of the planar doping geometry assumed here. The simulation would explicitly take into account potential fluctuations from both nearby and more distant ions. Such calculations are contemplated for the near future. Second, for completeness it would be desirable to extend the experiments on DPD quantum wells into parameter regions where "weak" conversion of D^- occurs (note from Table I that x_M is never less than 0.5, which means that in all samples studied more than half of the original neutral donors are converted). It is expected that the present model should be relatively accurate in such regions.

[1]T. Pang and S. G. Louie, Phys. Rev. Lett. **65**, 1635 (1990).

[2]A. Mandray, S. Huant, and B. Etienne, Europhys. Lett. **20**, 181 (1992).

[3]S. Huant, A. Mandray, G. Martinez, M. Grynberg, and B. Etienne, Surf. Sci. **263**, 565 (1992).

[4]The "bulk" values referred to here are calculated for bulk GaAs using the bulk dielectric constant 12.58, but the electron effective mass characteristic of the *quantum well.* Concentrations in units of impurities per donor Bohr radius squared are denoted na^2.

[5]By "unique solution," we mean that the statistical distribution of possible D^- populations consistent with the requirements of the model has negligible width in the limit of an infinite system.

[6]It seems possible that the conversion of barrier donors could lead to a distribution of remaining barrier donors which has clumps in some regions and is "abnormally" devoid of donors in other regions in a way which would not be equivalent to a uniform reduction of the concentration of barrier donors. Such effects are ignored in this paper.

[7]It is expected that, not only do potential fluctuations of a given size more strongly determine whether a B-D pair will convert when the constituent B and D centers are well separated, but also that the presence of a high concentration of converted pairs increases the size of potential fluctuations in the sample.

[8]E. R. Mueller, D. M. Larsen, J. Waldman, and W. D. Goodhue, Phys. Rev. Lett. **68**, 2204 (1992).