Electron Localization by a Metastable Donor Level in n-GaAs: A New Mechanism Limiting the Free-Carrier Density

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We observe in Si-doped GaAs, by capacitance transient spectroscopy, electronic occupation of a highly localized state of the donor-related *DX* center. The emission and capture kinetics are those of a metastable state which lies above the conduction-band edge. The state is so spatially localized that its emission kinetics are not measurably perturbed by neighboring Si atoms (donors or acceptors) at an average distance $\simeq 3.5$ nm. Occupation of this state is therefore a previously unsuspected mechanism which can limit the free-carrier density in very heavily doped n-GaAs.

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The maximum equilibrium free-carrier concentrations, n_0, obtained in heavily doped n-type GaAs are typically $(5-7)\times 10^{18}$ cm^{-3}, limited by donor self-compensation. Compensating acceptors are produced when dopant atoms are incorporated into certain complex defects, or, in the case of column-IV dopants, when the dopant atoms occupy As lattice sites (site switching). By use of low-temperature growth techniques, such as molecular beam epitaxy (MBE), self-compensation is suppressed and considerably higher values of n_0 are obtained. Under these conditions we demonstrate a new mechanism, distinct from, and acting in addition to, self-compensation, which limits n_0. This mechanism involves electron localization by a donor state associated with the *DX* center.[1] We show that in GaAs this electronic state is energetically resonant with the conduction band, that it is metastable, and that *even in highly degenerate material* it strongly localizes electrons.

The relative importance of lattice relaxation and symmetry principles in the determination of the properties of the *DX* center is currently a subject of debate.[1,2] However, the existence of a metastable donor level in GaAs has been argued by one of us[3] solely on the basis of experimental results. Briefly summarized, various n-type dopants introduced into the semiconductor alloy $Al_xGa_{1-x}As$ give rise to a "deep donor level" which displays a characteristic thermally activated electron-capture cross section. Hall data from various laboratories,[4] summarized in Fig. 1(a), indicate a donor level, E_{DX}, measured with respect to the Γ band edge, E_g^Γ, which tends to track the L-band edge in the direct-gap alloy composition range. Extrapolation to low Al mole fractions, $x \lesssim 0.22$, suggests a resonant level lying about 170 meV above E_g^Γ in GaAs. The existence of this level in n-GaAs is demonstrated by the observation of the thermally activated electron capture and emission when it is brought into the direct gap by application of hydrostatic pressure.[5,6] Even in GaAs, all or nearly all donors give rise to the level.[5,6] The metastability and vanishingly small radiative decay rate of the *resonant* level is demonstrated by its persistent population in n-$Al_xGa_{1-x}As$ $(x<0.22)$ under nonequilibrium conditions by a hot-electron capture process.[3,7] These properties can also be inferred from the alloy dependence of the thermal emission and capture rates. The activation energies for thermal capture, E_c, and thermal emission, E_e, are found to be larger than $E_g^\Gamma - E_{DX}$, so that capture and emission can be viewed as occurring over an effective repulsive barrier as shown in Fig. 1(b).[1] While $E_g^\Gamma - E_{DX}$ goes to zero at $x\simeq 0.22$, E_e is independent of

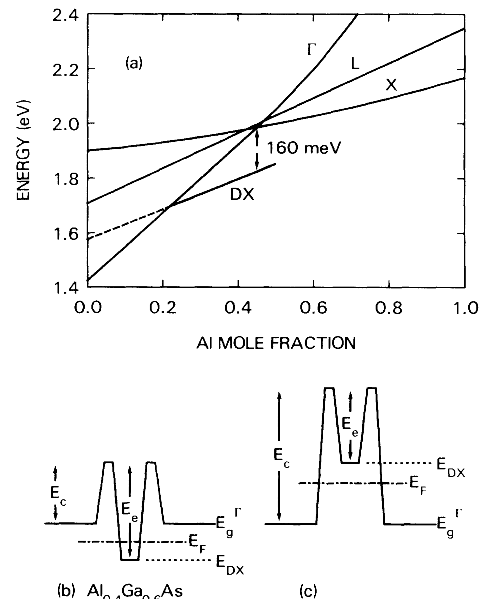

FIG. 1. (a) Lower conduction-band edges in $Al_xGa_{1-x}As$ as functions of x. Extrapolation (dashed line) of Hall measurements from various laboratories indicates that the deep level associated with the *DX* center becomes resonant with the Γ band for $x\lesssim 0.22$. (b) Effective potential barrier for electron capture to and emission from the deep level in $Al_xGa_{1-x}As$, $x\simeq 0.4$ (after Ref. 3). (c) Effective potential barrier for the metastable state in GaAs.

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x and E_c becomes *larger* as x is reduced.[8] Extrapolating this behavior to GaAs, one expects the effective barrier of a metastable state as shown in Fig. 1(c).

We have now observed the equilibrium occupation of this state in heavily doped GaAs as the Fermi level, E_F, approaches E_{DX}. We have employed capacitance transient spectroscopy, which yields an unmistakable spectroscopic signature of electron capture and emission from the highly localized level. Our samples were epitaxially grown by MBE on n-type Si-doped GaAs substrates. Each growth consisted of a 1-μm layer of GaAs doped $\simeq 1\times10^{18}$ cm^{-3}, a 50-nm layer of heavily Si-doped GaAs, followed by a 25-mm layer of nominally undoped GaAs. Low-resistance Ohmic contacts were alloyed to the back of the substrate, and Ti/Pt/Au rectifying (Schottky) contacts were vacuum evaporated on the front. Bias voltages sufficient to change the occupation of donor states in the upper 5 nm of the heavily doped layer could be applied between electrode and substrate. The 25-nm undoped "spacer" layer beneath the Schottky contact reduced tunneling currents to levels acceptable for the accurate measurement of the resulting capacitance transients. n_0 in each heavily doped layer was determined from the frequency shift, ω_p, of the Raman-scattered light from the bulk plasmon mode.[9] At the carrier concentrations of interest, we have

$$\omega_p^2 = n_0 e^2/\epsilon_\infty m_c, \quad (1)$$

where ϵ_∞ is the optical dielectric constant, and $m_c = \hbar^2 k/(dE/dk)$ is the optical (or conductivity) effective mass for a Γ band electron, evaluated at the Fermi level. The nonparabolicity of the band was treated as in the work of Heiblum *et al.*[10] Thus we write the "energy effective mass," $m(E) = \hbar^2 k^2/2E(k)$, as

$$m(E) = m_{c0}(1-\alpha E), \quad (2)$$

where $\alpha = -0.834$ eV^{-1} is the nonparabolicity coefficient, and $m_{c0} = 0.067 m_0$ is the band-edge effective mass, both at $T=0$ K. The optical effective mass in (1) is then given by

$$m_c = m_{c0}[1-4\alpha(\hbar^2 k_F^2/2m_{c0})]^{1/2}, \quad (3)$$

where k_F is the Fermi wave number.

TABLE I. Characteristics of four heavily doped GaAs layers: Si-doping concentration, N_{Si}; net donor concentration, $N_D - N_A$; carrier concentration, n_0; and relative magnitude of the DX center capacitance transient, $\Delta C/C$, each determined as described in the text.

Layer	N_{Si} (cm^{-3})	$N_D - N_A$ (cm^{-3})	n_0 (cm^{-3})	$\Delta C/C$
1	4.3×10^{19}	6.0×10^{18}	6.0×10^{18}	1.4×10^{-4}
2	2.3×10^{19}	1.0×10^{19}	8.4×10^{18}	2.4×10^{-4}
3	2.2×10^{19}	1.1×10^{19}	1.0×10^{19}	5.2×10^{-4}
4	1.9×10^{19}	1.1×10^{19}	1.1×10^{19}	5.8×10^{-4}

Table I gives the values of n_0 for four heavily doped layers grown at substrate temperatures between 530 and 570 °C, along with the net fixed charge density, $N_D - N_A$, in the upper 5 nm determined by capacitance-voltage (C-V) profiling, and the chemical concentration of Si atoms, N_{Si}, determined by secondary-ion mass spectroscopy (SIMS). The SIMS depth profiles of the dopant concentrations showed only modest diffusion of Si into the spacer layer. Within the experimental accuracy, $n_0 = N_D - N_A$, as expected, while in all cases, $N_{Si} > n_0$, indicating substantial self-compensation of the Si donors. To determine the total donor concentration, N_D, we assumed $N_{Si} = N_D + N_A$.

Capacitance transients produced by electron emission from the resonant level were studied by standard techniques of deep-level transient spectroscopy (DLTS).[11] A positive bias voltage (+0.5 V) was applied to the metal electrode for sufficient time to fill the localized states near the edge of the heavily doped layer. The sample was then reverse biased (−1.0 V), and the capacitance transient resulting from the emptying of states in this edge region was measured. Because this region is much thinner than the undoped spacer layer, the magnitude of the capacitance transient, ΔC, is much less than C, the quiescent capacitance at −1.0 V. Values of $\Delta C/C$ are listed in Table I, and the corresponding DLTS signals are shown in Fig. 2. As expected from our picture of a resonant donor state, the signal increases monotonically with n_0. No signal was observed in samples with

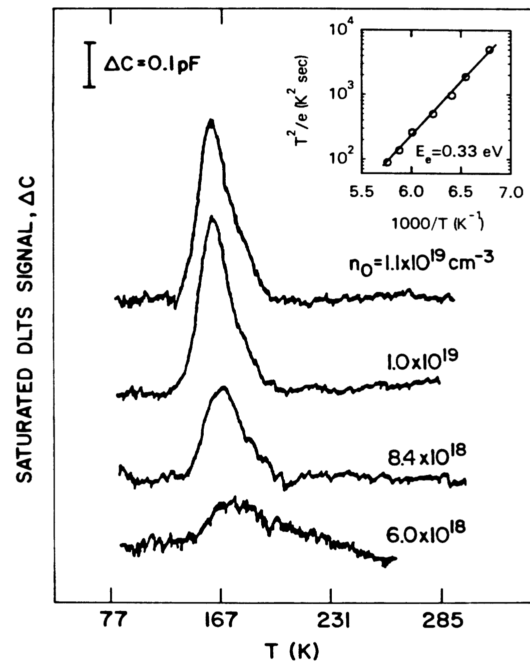

FIG. 2. DLTS peaks due to electron emission from the metastable state in heavily doped n-GaAs samples with varying free-carrier densities. Inset: Determination of the thermal activation energy for electron emission.

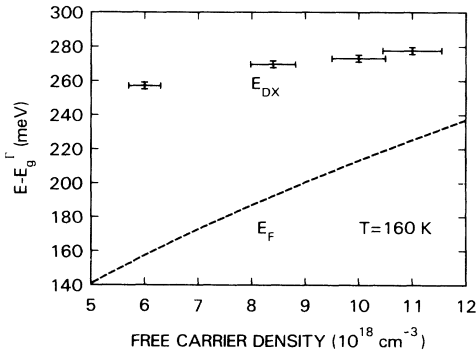

FIG. 3. Energy of the resonant donor level (error bars) and the Fermi level (dashed line) with respect to the direct band edge as functions of the carrier concentration. Error bars account for statistical variations in the measurements but exclude possible systematic errors in measurement or modeling.

$n_0 < 6\times10^{18}$ cm^{-3}.

There is no doubt that these peaks represent a spectroscopic signature of electron emission from the *DX* center. The change in emission rate with temperature (inset to Fig. 2) yields an activation energy for the thermal emission, $E_e = 0.33 \pm 0.02$ eV, in perfect agreement[12] with the value found for the *DX* center in GaAs under hydrostatic pressure.[5] As in Ref. 5, the peaks are slightly asymmetric, and the linewidth is narrower than in $Al_xGa_{1-x}As$, consistent with the absence of alloy broadening[13] in GaAs. In fact, our peak half width, $\Delta T/T = 0.11$, is about equal to the instrumental resolution of DLTS, demonstrating strong spatial localization of the state which is *not measurably perturbed* by neighboring Si atoms (donors or acceptors) at an average distance $\simeq 3.5$ nm. We also observe the most distinctive signature of the *DX* center, the extraordinarily small ($\simeq 10^{-26}$ cm^2 at $T = 142$ K) thermally activated capture cross section. While detailed analysis of the isothermal capture transients will be presented elsewhere, we note that the dependence on free-carrier density is similar to that found in $Al_xGa_{1-x}As$.[14] From the thermal activation of the capture rate, we find an effective capture barrier with respect to the Γ band edge, $E_c = 0.55 \pm 0.05$ eV. Thus $E_c > E_e$, as illustrated in Fig. 1(c).

Very similar emission and capture kinetics have been reported for a resonant donor level in InSb.[15] However, the donor concentrations was over 4 orders of magnitude lower than in the present case. Our measurements demonstrate a state which localizes electrons even in very heavily doped degenerate material. To estimate the resulting reduction in n_0 in our samples, we note that in thermal equilibrium the concentration of occupied *DX* levels in the charge-neutral interior of the heavily doped layer is

$$n_{DX} = N_{DX}\left[1 + \frac{1}{g}\exp\left(\frac{E_{DX} - E_F}{kT}\right)\right]^{-1}, \quad (4)$$

where N_{DX} is the chemical concentration of *DX* centers, and g is the level degeneracy. $E_F(n_0)$ is found by our performing the Fermi integral over the nonparabolic density of states found with use of Eq. (2), subject to the charge neutrality condition, $n_0 + n_{DX} = N_D - N_A$. Since care was taken to use filling times sufficiently long to saturate the DLTS signals, $\Delta C/C$ is a measure of n_{DX}. However, because the signal represents electron emission from the edge of a highly degenerate region, the approximations customarily used to relate n_{DX} to $\Delta C/C$ are invalid. Therefore, a self-consistent numerical solution of the Poisson equation with use of Fermi-Dirac statistics to determine the trap occupation, and the Thomas-Fermi approximation to determine $E_F - E_g^\Gamma$ outside the charge neutral region, is used in the calculation of the capacitance of the structure.

Figure 3 shows the results of modeling of the relative magnitude of the capacitance transients, with use of $E_{DX} - E_F$ as a free parameter. We assumed $N_{DX} = N_D$, consistent with hydrostatic pressure results,[5,6,16] a level degeneracy, $g = 2$, and a steplike modulation of the donor density. Alteration of these assumptions ($N_{DX} = 0.5N_D$, $g = 8$, diffused donor profile) did not alter the general nature of the results. $E_{DX} - E_g^\Gamma$ was found to be considerably larger than the 170 meV estimated from Fig. 1 and to increase with increasing n_0. This upward movement of the level is also inferred from hydrostatic-pressure data.[16] The calculations show a significant occupation of the metastable state at $T = 160$ K, reaching $n_{DX}/n_0 \simeq 0.06$ at $n_0 = 1.1\times10^{19}$ cm^{-3}. Further increases in n_0 are obtained only at the cost of ever increasing donor neutralization through occupation of the metastable state. A straightforward extrapolation of the trend in Fig. 3 suggests that E_F reaches E_{DX} at $n_0 \simeq (1.5-2)\times10^{19}$ cm^{-3}. If $N_{DX} > N_D - N_A$, this will be the maximum possible value of n_0 in *n*-GaAs. A similar limit is inferred from hydrostatic-pressure experiments.[16] If we exclude *C-V* measurements of $N_D - N_A$, which measure the fixed charge, including *DX* centers, in a depletion region, then indeed, for all donors except Ge,[17] we are unaware of any published reports which significantly exceed this value.

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[1]D. V. Lang, R. A. Logan, and M. Jaros, Phys. Rev. B **19**, 1015 (1979); D. V. Lang, in *Deep Centers in Semiconductors*, edited by S. T. Pantelides (Gordon and Breach, New York, 1986), pp. 489–539.

[2]H. P. Hjalmarson and T. J. Drummond, Appl. Phys. Lett. **48**, 656 (1986); A. Oshiyama and S. Ohnishi, Phys. Rev. B **33**, 4320 (1986); E. Yamaguchi, Jpn. J. Appl. Phys. Pt. 2 **25**, L643

(1986); T. N. Morgan, Phys. Rev. B **34**, 2664 (1986); J. C. M. Henning and J. P. M. Ansems, Semicond. Sci. Technol. **2**, 1 (1987).

[3]T. N. Theis, in *Defects in Semiconductors,* edited by H. J. von Bardeleben (Trans Tech, Aedermannsdorf, Switzerland, 1986), pp. 393–398.

[4]N. Chand, T. Henderson, J. Klem, W. T. Masselink, R. Fischer, Y. C. Chang, and H. Morkoç, Phys. Rev. B **30**, 4481 (1984), and references therein.

[5]M. Mizuta, M. Tachikawa, H. Kukimoto, and S. Minomura, Jpn. J. Appl. Phys. Pt. 2 **24**, L143 (1985).

[6]M. Tachikawa, T. Fujisawa, H. Kukimoto, A. Shibata, G. Oomi, and S. Minomura, Jpn. J. Appl. Phys. Pt. 2 **24**, L893 (1985).

[7]T. N. Theis, B. D. Parker, P. M. Solomon, and S. L. Wright, Appl. Phys. Lett. **49**, 1542 (1986).

[8]P. M. Mooney, E. Calleja, S. L. Wright, and M. Heiblum, in Ref. 3, pp. 417–422.

[9]A. Mooradian and A. L. McWhorter, in *Light Scattering Spectra in Solids,* edited by G. B. Wright (Springer-Verlag, New York, 1969), pp. 297–308.

[10]M. Heiblum, M. V. Fischetti, W. P. Dumke, D. J. Frank, I. M. Anderson, C. M. Knoedler, and L. Osterling, Phys. Rev. Lett. **58**, 816 (1987).

[11]G. L. Miller, D. V. Lang, and L. C. Kimerling, Annu. Rev. Mater. Sci. **7**, 377 (1977).

[12]Note, however, that E_e in GaAs is smaller than in $Al_xGa_{1-x}As$. Since E_e is constant for $x > 0.14$ (Refs. 7 and 8), the change is *not* simply related to band structure.

[13]E. Calleja, P. M. Mooney, S. L. Wright, and M. Heiblum, Appl. Phys. Lett. **49**, 657 (1986).

[14]N. S. Caswell, P. M. Mooney, S. L. Wright, and P. M. Solomon, Appl. Phys. Lett. **48**, 1093 (1986).

[15]L. Dmowksi, M. Baj, P. Ioannides, and R. Piotrzkowski, Phys. Rev. B **26**, 4495 (1982).

[16]D. K. Maude, J. C. Portal, L. Dmowski, T. Foster, L. Eaves, M. Nathan, M. Heiblum, J. J. Harris, and R. B. Beall, Phys. Rev. Lett. **59**, 815 (1987).

[17]A. Li, A. G. Milnes, Z. Y. Chen, Y. F. Shao, and S. B. Wang, J. Vac. Sci. Technol. B **3**, 629 (1985).