Investigation of the *DX* Center in Heavily Doped *n*-Type GaAs

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Shubnikov–de Haas and persistent-photoconductivity measurements are used to study the mobility, the free-electron density (n), and the occupancy of the *DX* center in heavily doped n-type GaAs [Si,Sn] as a function of doping level and hydrostatic pressure. The results show that the *DX* center produces a resonant donor level between the Γ and L conduction-band minima at a concentration comparable with the doping level. For the Si-doped samples, comparison with local vibration-mode measurements indicates that the *DX* level can be identified with $\mathrm{Si}_{\mathrm{Ga}}$.

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The *DX* center in n-type (Al,Ga)As has been a topic of considerable interest for over a decade.[1,2] The center, with the character of a deep donor level, is present in all n-type material and at concentrations comparable with the donor doping, irrespective of whether the donor is from Group IV or VI of the periodic table. The optical, capture, and emission cross sections of *DX* have been extensively reported (see Lang and Logan,[1] Nelson,[2] and Mooney *et al.*,[3] and references therein). These features give rise to the well-known persistent-photoconductivity effects (PPC) observed in n-type (Al,Ga)As at low temperatures. Several alternative models have been proposed for the nature of the defect giving rise to the PPC.[1,4–6] In particular, it has been suggested recently that the PPC is associated with states arising from substitutional donor impurities[5] rather than with defect-impurity complexes. The *DX* center has not been previously observed at atmospheric pressure in GaAs. However, Mizuta, Tachikawa, Kukimoto, and Minomura[7] have recently shown in deep-level transient spectroscopy measurements that *DX* centers become activated electrically in n-type GaAs and in n-type $\mathrm{Al}_x\mathrm{Ga}_{1-x}\mathrm{As}$, with low Al mole fraction at pressures above a critical value which decreases with increasing x.

In this Letter we investigate as a function of hydrostatic pressure up to 15 kbar, the free-carrier concentration, mobility, and the persistent photoconductivity, of a series of six n-type GaAs layers heavily doped $[(0.2\text{–}1.8)\times 10^{19}\ \mathrm{cm}^{-3}]$ with either Si or Sn. The layers (labeled a to f) were prepared by molecular-beam epitaxy. Samples a, d, e, and f were grown at Philips Research Laboratories, and samples b and c at IBM Thomas J. Watson Research Center. Enhanced doping was achieved by lowering the substrate during growth.[8] For samples a and d, the substrate temperature was 450 °C. The Si- or Sn-doped n^+ layers varied in thickness between 0.15 and 10 μm. The carrier concentration was measured at low temperature and with magnetic fields up to 18 T by use of the de Haas–Shubnikov effect (dHS). This measures the radius of the Fermi sphere in **k** space and yields directly the number (n) of conduction electrons in the Γ minimum. Pressure was applied by means of a liquid clamp cell manufactured by Unipress (Warsaw). An important feature of these cells is that the pressure can be applied at room temperature only. When measurements are subsequently made at low temperatures the applied pressure is "frozen in." Cooling to low temperatures is accompanied by a small decrease of pressure (typically $<10\%$). The pressure on the sample is continuously monitored *in situ* with a calibrated n-type InSb resistance manometer. The cooling procedure to the helium temperatures required for the dHS measurements involved a precool to 77 K of $\simeq 20$ min duration. The subsequent cooling to 4 K took place over $\simeq 5$ min. The occupation of the *DX* center is fixed at *some intermediate* temperature (probably about 120 K) at which the capture and emission rates become so slow that the electron population of the trap is no longer in equilibrium with the free-electron density. In order to study PPC, samples could be illuminated under pressure at low temperatures by means of a visible light-emitting diode mounted inside the cell.

Typical dHS measurements on a Si-doped sample with initial ($P=0$) carrier concentration of $1.1\times 10^{19}\ \mathrm{cm}^{-3}$ are shown in Fig. 1 for a range of applied pressure. The pressures quoted are those measured at 4.2 K. As P is increased, the period of the dHS oscillations increases, corresponding to a decrease in carrier concentration. Note also that the amplitude of the oscillations increases with pressure and that the oscillatory structure becomes observable down to lower magnetic fields. This is a clear indication that the mean collision time τ and mobility μ

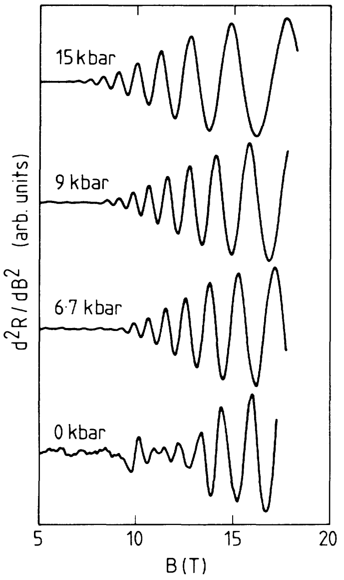

FIG. 1. Typical dHS oscillations in the second derivative of the transverse magnetoresistance of an Si-doped sample with initial ($P=0$) carrier concentration of 1.1×10^{19} cm^{-3}, $T=4$ K, $\mathbf{J}\perp\mathbf{B}$.

increases with increasing pressure since the amplitude of dHS structure is controlled by the factor $\omega_c\tau$, where $\omega_c=eB/m^*$ is the cyclotron frequency. Since the period $\Delta(1/B)$ of the dHS structure and the zero-field resistance give, respectively, the electron carrier concentration n, and the conductivity σ, the variation of μ with P can be determined. Typical results for some of the samples investigated are shown in Fig. 2. For the most heavily doped sample, n falls immediately on increasing the pressure above atmospheric [i.e., Fig. 2(d)]. This indicates that for this doping the *DX* level is very close to the Fermi energy and partially occupied even at atmospheric pressure. In the more lightly doped samples, e.g., Figs. 2(b), 2(e), and 2(f), the carrier concentration remains roughly constant up to a critical value P_c and then falls sharply. The sample doped at 2×10^{18} cm^{-3} [Fig. 2(c)] shows no significant change of n up to 15 kbar. It can be seen that in all samples a decrease in n with P is accompanied by an increase in μ. In lighter-doped samples, over the range of pressure for which n remains constant, μ is found to decrease slowly with pressure. This effect is associated with the increase of the electron effective mass of the Γ conduction band.

These results indicate that the loss of free carriers with increasing pressure is associated with capture at donor-like levels located between the Γ and L conduction-band minima. This capture process is described by the relation $D^++e^-\rightarrow D^0$. The neutralization of the ionized donors by electron capture and the corresponding decrease in ionized-impurity scattering explains the increases in mobility and in amplitude of the dHS structure.

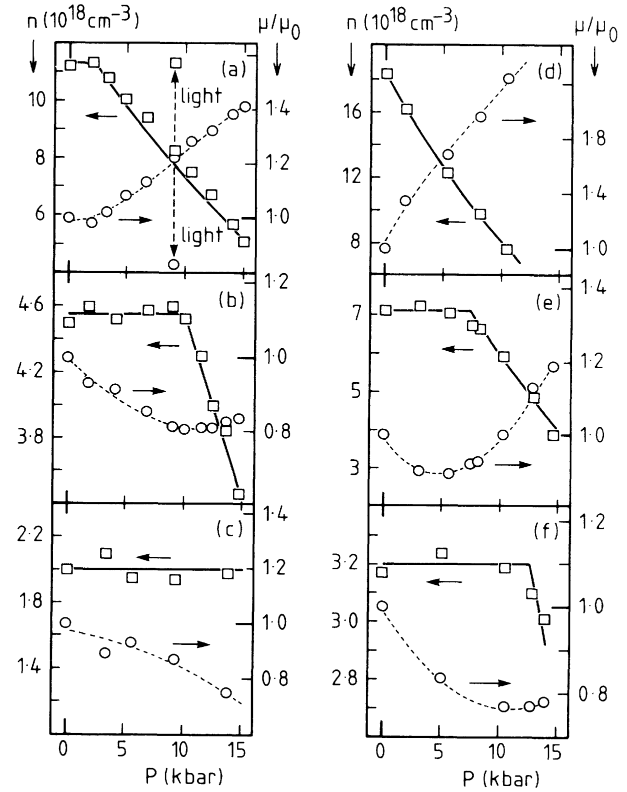

FIG. 2. Carrier concentration n (open squares) and mobility μ (open circles) vs pressure P for a range of Si [(a), (b), and (c)] and Sn [(d), (e), and (f)] -doped samples. The mobility is normalized to its atmospheric pressure value. The solid lines show the expected variation of n with P with use of the fitting procedure described in the text. The effect of illumination on n and μ at 9 kbar is indicated in (a) for the most heavily Si-doped sample. The broken curves through the mobility data are guides to the eye only.

To test if the deep donor level showed the PPC effects which characterize the *DX* center in (Al,Ga)As, we investigated the effect of pulses of light on the carrier concentration and mobility with the sample maintained under pressure at low temperature. Here it is important to note that the pressure in these experiments was initially applied at room temperature and the sample was cooled slowly. Therefore, if the pressure is above the threshold value for trapping out onto the deep donor levels, a fraction of the deep donor states corresponding to thermal equilibrium ($T\simeq120$ K) should be filled with electrons after cooling in the dark to low temperatures. By illuminating the sample with light from a light-emitting diode under pressure at low temperatures, the free-electron concentration, measured by the dHS effect, was restored to its zero-pressure value. The changes in n and μ following illumination at 9 kbar are indicated by broken arrows in Fig. 2(a) for the most heavily Si-doped sample. This increase in n persisted long after switching off the light. It was accompanied by a persistent decrease of μ and of the amplitude of the dHS structure. Such behavior is fully consistent with photoionization of a deep donor level. The PPC indicates that the center involved has the same character as the *DX* center in *n*-type (Al,Ga)As. Note that on illuminating under pressure, the mobility does not fall to its zero-pressure value, but to a somewhat lower value due to the pressure-dependent effective mass.

The role of the hydrostatic pressure in producing the observed trapping out of free electrons from the Γ conduction-band minimum must be related to its effect on the energy of the deep donor level and on the conduction-band structure. It is clear from the measurements that the deep donor responsible for the trapping is present at a concentration comparable to that of the Si or Sn doping level.

The solid lines in Fig. 2 show the expected variation of n with P. For the samples doped at $n \leq 5\times10^{18}$ cm^{-3}, we can fit the variation of n with P by assuming that electrons capture at a donor level whose energy relative to the Γ minimum decreases at a rate of 4.8 meV/kbar. This value is very close to the pressure coefficient of the energy difference between the Γ and L minima,[9] which suggests that the donor level has some of the character of these minima. It is assumed that the Fermi energy ϵ_F of the electrons in the Γ conduction band is pinned at the donor level as the pressure is increased above the critical value at which the measured carrier concentration starts to fall. The decrease of n with P is then governed by the above pressure coefficient and by the density of states of the Γ minimum at ϵ_F. For example, in Fig. 2(b) the donor level (E_D) crosses ϵ_F at around 10 kbar. Taking into account the increasing density of states in the Γ minimum due to the increase of effective mass with pressure,[10] we estimate that the donor level is 43 meV above the Fermi energy in the Γ conduction band at zero pressure. Using this procedure, we can calculate the energy of the donor level above the Γ minimum, $(E_D - E_\Gamma)$, for the samples shown in Figs. 2(a), 2(b), 2(d), 2(e), and 2(f). The corresponding energies of the donor level relative to the L minima can be obtained from the Γ-L energy separation ($E_L - E_\Gamma = 296$ meV at $T=4$ K and $P=0$[9]).

In the fitting procedure, n and ϵ_F are calculated taking into account nonparabolicity and the pressure dependence of the effective mass of the Γ minimum.[10,11] However, for the three most highly doped samples in Figs. 2(a), 2(d), and 2(e), the calculated zero-pressure values of $E_D - E_\Gamma$ (see Table I) indicate that the donor level moves to higher energy as the doping level is increased. At these high doping levels it is possible that this observed reduction of the binding energy of the electron to the donor state arises from Coulomb and screening effects. These effects are known to occur for the much more extended shallow donor states of the Γ minimum at low doping levels ($\simeq 10^{16}$ cm^{-3}).[12] When pressure is applied, the electrons become trapped and neutralize ionized donors, thereby reducing the strength of the Coulomb interactions. Hence, the level should become deeper at a rate, relative to the L minima, of $R = d(E_L - E_D)/dP$. The effect should give rise to an increased rate of shift of the donor level relative to the Γ minimum so that above the critical pressure $d(E_D - E_\Gamma)/dP = -(R+4.8)$ meV/kbar. The final column of Table I gives the values of $d(E_D - E_\Gamma)/dP$ used in the fitting procedure to obtain the fitting curves in Fig. 2.

In the above discussion, we have followed other authors by neglecting the so-called band-gap renormalization. At high doping levels ($\gtrsim 5\times10^{18}$ cm^{-3}) this effect has been estimated to decrease the direct band gap by up to $\Delta E_G \simeq 40$ meV.[13] However, over the range of dopings of interest here, the *change* in direct band gap is small, 10 meV. The uncertainties about the size of the renormalization do not affect our estimates of the energy $(E_D - E_\Gamma)$ of the donor level relative to the Γ minimum. For this reason we have quoted this value in Table I. The pressure dependence of the carrier concentration in

TABLE I. Measured carrier concentration n, at $P=0$, for the samples studied are indicated in column 1. The Fermi energy ϵ_F is calculated taking into account nonparabolicity. P_c is the critical pressure at which n starts to fall. The energy of the deep level above the Γ minimum $E_D - E_\Gamma$ is calculated with use of the procedure described in the text. The final column is the pressure coefficient of the energy of the deep level relative to the Γ minimum used to obtain the fitting curves in Fig. 2.

	Zero-pressure carrier conc. (10^{18} cm^{-3})	$E_F(P=0)$ (meV)	P_c (kbar)	$E_D - E_\Gamma$ (meV)	$d(E_D - E_\Gamma)/dP$ (meV/kbar)
(a)	[Si] 11.3	226	2	234	$-(4.8+2.3)$
(b)	[Si] 4.6	126	10	174	-4.8
(c)	[Si] 2.0	73		Pressure has no effect on n	
(d)	[Sn] 18.0	287	0	287	$-(4.8+6.2)$
(e)	[Sn] 7.1	175	7	204	$-(4.8+2.3)$
(f)	[Sn] 3.2	109	12	159	-4.8

the lighter-doped samples indicates that the level has the same pressure coefficient as the L minimum. The critical pressures at which we observe n to decrease suggest that the energy of the deep level relative to the Γ minimum increases with increasing doping.

To summarize, the measurements reported here show unambiguously that a deep donor level of DX character (i.e., exhibiting PPC) occurs in Si- and Sn-doped GaAs at an energy between the Γ and L minima and at concentrations comparable to the donor doping density (up to 1.8×10^{19} cm^{-3}). Infrared measurements[14] of local vibration modes on sample a[15] indicate that our measured carrier concentration at zero pressure of 1.11×10^{19} cm^{-3} agrees closely with the concentration of Si atoms occupying Ga sites ($[\mathrm{Si_{Ga}}]=1.3\times10^{19}$ cm^{-3}), with the calibrated Si flux employed in the growth (1.3×10^{19} cm^{-3}), and with secondary-ion mass spectrometry measurements (1.4×10^{19} cm^{-3}). The local-vibration-mode measurements[14,15] also show that for sample a $[\mathrm{Si_{As}}]=8\times10^{17}$ cm^{-3}, and that the Si-Si pair and Si complex (Si-X) occur at concentrations of less than 10^{17} cm^{-3}. Note that it is only in the situation when the free-electron carrier concentration is markedly less than the calibrated Si flux that local-vibration-mode measurements reveal compensation due to Si on As sites and to complexing of Si with an unknown defect.[14,15] These observations, coupled with the results reported here, strongly support the conclusion[5-7] that the level causing the pressure-induced trapping and the PPC is associated with the substitutional donor rather than a donor-related complex. Our results are unable to resolve the question concerning the relative importance of lattice relaxation and symmetry in giving rise to the PPC. However, they should encourage further work on this topic.

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