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Electron-paramagnetic-resonance measurements of Si-donor-related levels in $Al_xGa_{1-x}As$

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We report measurements of an EPR signal in indirect-gap Si-doped $Al_xGa_{1-x}As$ whose intensity increases after illumination at low temperature. The data indicate that this signal comes from a hydrogenic level associated with the X valley of the conduction band. Measurements of the spectral dependence of the enhancement of the EPR signal show that electrons are transferred from the DX level, the lowest-energy state of the Si donor, to this higher-lying state. No other signal which might be associated with the DX level was observed. The results are consistent with a large lattice relaxation model of the DX center but do not, at this time, distinguish between positive- and negative-U models.

The so-called DX level is a highly localized deep state associated with both group-IV and group-VI donors in $Al_xGa_{1-x}As$ and other group III-V alloys.[1] In $Al_xGa_{1-x}As$, it is the lowest donor state when $x > 0.22$ (Ref. 2) and thus controls the transport properties of this technologically important semiconductor. Electron capture and emission at the DX level occur by a multiphonon process which is characterized by a temperature-dependent cross section for the thermal capture of electrons[3] which varies with the alloy composition.[4] Electron-capture rates are negligibly small at low temperature resulting in persistent photoconductivity. The photoionization energy is considerably larger (about 1 eV in the case of the Si donor) than the thermal ionization energy indicating that a large relaxation of the crystal lattice occurs when an electron is trapped at the DX level.[5,6] Although the electrical behavior of the DX level is well understood and it is now believed to be a state of the isolated donor atom rather than a defect complex, the microscopic configuration of the relaxed state and the origin of the large lattice relaxation are still controversial.

In addition to the DX level, hydrogenic donor levels associated with the Γ valley in direct-gap $Al_xGa_{1-x}As$ (Ref. 7) and with the X valley in indirect-gap $Al_xGa_{1-x}As$ (Refs. 8 and 9) have been observed after photoionization of the DX level. These levels are associated with the unrelaxed substitutional donor atom and only a small fraction is occupied at low temperature in the dark when $x > 0.22$. In the case of the Si donor, the hydrogenic donor level in indirect-gap material is measured by the Hall effect to lie 70 ± 10 meV below the bottom of the conduction band (X valley) in a sample with $N_D - N_A = 2\times10^{17}$ cm^{-3}.[10] In samples with $N_D - N_A > 1\times10^{18}$ cm^{-3}, values as low as 40 meV were measured. The reduction in activation energy is presumably due to impurity-banding effects in the more heavily doped samples. Figure 1 shows a schematic diagram of the energies of the three conduction-band minima as well as the DX level and the hydrogenic levels for Si-doped $Al_xGa_{1-x}As$ as a function of the alloy composition. Note that the DX level only roughly follows the L valley and that it is the lowest donor state for most alloy compositions.

Recently it has been suggested that the DX center is characterized by negative U, i.e., that capture of a second electron at this level results in a lower-energy configuration than capture of a single electron and that the neutral donor state is therefore unstable.[11,12] Experimental evidence cited to support this model is the failure to observe an electron paramagnetic resonance (EPR) signal which could be associated with the DX level in direct-gap $Al_{0.35}Ga_{0.65}As$ where the DX level is the ground state of the donor.[12]

The first reported EPR measurements made in $Al_xGa_{1-x}As$ were performed in indirect-gap samples with $0.55 < x < 0.8$.[13,14] A nearly isotropic EPR signal with $g \simeq 1.96$ was observed without photoexcitation. It was argued by analogy to the properties of Si-donor states in GaP that this signal should be related to the Si donor and that it is observable without applied stress due to the

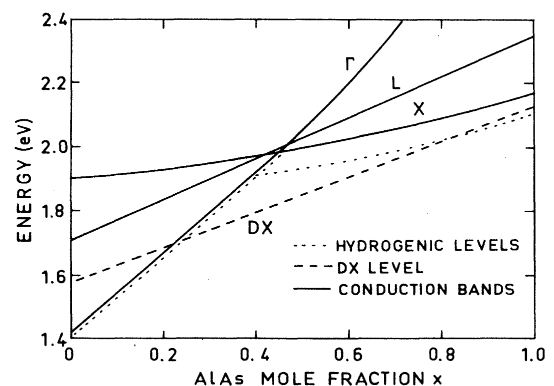

FIG. 1. Schematic diagram of the energy positions of the conduction-band minima, the hydrogenic levels of the Si donor (Refs. 7 and 10), and the DX level as a function of the alloy composition of $Al_xGa_{1-x}As$ (Ref. 2). The effects of intervalley mixing have been neglected.

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breaking of the symmetry in the random alloy. Also, the signal was found to be proportional to the Si concentration in these samples. From later studies of the electrical properties of $Al_xGa_{1-x}As$, it is now known that the *DX* level is the lowest donor state in this alloy composition range. Thus, since this signal was observed without photoexcitation, one could argue that this EPR signal comes from the *DX* level.

This same magnetic resonance has been observed by two different groups who detected it optically as a change in the photoluminescence intensity, a technique known as optically detected magnetic resonance (ODMR).[15-18] One group has argued that this resonance comes from the *DX* level;[16] the other group has suggested that this resonance comes from the hydrogenic donor level associated with the *X* valley, based on their analysis of the *g* values and because they observe the ODMR signal only when $x > 0.35$.[18] In these experiments the sample is exposed to high-intensity laser light which is expected to persistently photoionize the *DX* levels at low temperature. Thus the sample is not in thermal equilibrium and magnetic resonance signals from states other than ground states should be readily observed.

Here we report new EPR measurements of Si-doped $Al_xGa_{1-x}As$ which were motivated by the apparent contradiction in the earlier EPR experiments in direct- and indirect-gap samples. We show that the magnitude of the EPR signal which we observe in the dark in indirect-gap samples increases after exposure to monochromatic light and that therefore the EPR signal does not come from the *DX* level. The spectral dependence of the enhancement of the EPR signal observed here agrees with previous measurements of the photoionization cross section of the *DX* level indicating that electrons are transferred from the *DX* level to an empty higher-lying state. Measurements of the spin concentration after exposure to light confirm that this state is associated with the Si donor, specifically the hydrogenic donor level derived from the *X* valley of the conduction band.

The EPR measurements were performed at 9.4 GHz at temperatures between 4.2 and 20 K. The spin concentration was determined by comparison to a S-doped GaP sample which was measured under similar conditions. Photoexcitation was done with a quartz-tungsten-halogen lamp with interference filters whose bandwidth is about 50 nm. The lamp current was adjusted to maintain a constant photon flux at each wavelength. A mechanical shutter was used to define exposure time as short as 0.5 s.

Two samples of Si-doped $Al_xGa_{1-x}As$ were measured. Both were grown by metallorganic vapor-phase epitaxy (MOVPE) on 500-μm-thick semi-insulating GaAs substrates. A 1-μm-thick undoped spacer layer of $Al_xGa_{1-x}As$ was grown first in order to prevent electron transfer from the doped $Al_xGa_{1-x}As$ layer to the GaAs substrate. The sample characteristics are listed in Table I. The net donor concentration was determined by capacitance-voltage measurements of Schottky-diode structures at 300 K. A stack of six pieces, each 3×20 mm^2, was used for the EPR measurements in both cases.

Figure 2 shows the EPR spectra taken with the magnetic field parallel to the ⟨100⟩ axis of the crystal in the dark and after photoexcitation for the sample with AlAs mole fraction $x=0.60$. A single slightly anisotropic line is observed in the $g=2$ region. Its width is independent of the sample orientation and temperature between 4 and 15 K. Even at 4 K the signal shows almost no saturation. The same signal with slightly different *g* values is observed in the $x=0.41$ sample but only following optical excitation. The linewidth was found to increase as the occupation of the level increased. The values indicated in Table I are the linewidths at the start of the photoexcitation process, i.e., at low occupation. The effective *g* factor variation, as shown in Fig. 3 for both samples, is axial, the symmetry axis being the [001] growth direction. These data agree very well with those reported for indirect-gap $Al_xGa_{1-x}As$:Si (Refs. 14 and 18) where the line in Fig. 2 was identified with the Si shallow-donor resonance in a [001] stressed layer. The spectral dependence of the photoexcitation of the EPR signal in the $x=0.41$ sample has been measured by the initial slope technique. Plotted in Fig. 4 is the initial increase $(\Delta I/\Delta t)_{t=0}$ of the EPR signal at the beginning of the illumination as a function of photon energy. After illumination at each photon energy, the sample was raised to above 150 K to restore the proper initial condition, zero EPR intensity in the dark.

The *DX* level is the lowest donor state in both samples used for this experiment. At room temperature the electrons distribute themselves among the *DX* level, the hydrogenic level associated with the *X* valley, and the bottom of the conduction band (*X* valley) according to Fermi-Dirac statistics. As the sample is cooled to low temperature, fewer electrons are found in the conduction band and one would naively expect that at 6 K virtually all the electrons would lie in the lowest state, the *DX* level. Because of the *DX* level capture barrier, however, longer and longer times are required to reach a thermal equilibrium electron distribution as the sample temperature decreases. Below some critical temperature, the capture of electrons at the *DX* center is effectively stopped and the remaining electrons in the conduction band can only be trapped at the hydrogenic *X*-valley state. With increasing AlAs mole fraction in the indirect-gap region, the *DX* level moves closer to the *X* conduction-band minimum and its capture barrier increases.[4] Therefore, with increasing

TABLE I. Sample characteristics and EPR results.

Sample	AlAs mole fraction	Layer thickness (μm)	N_D-N_A (cm^{-3})	*g* values Parallel	*g* values Perpendicular	ΔH (G)
K_1	0.41	11.0 ± 0.5	2.0×10^{18}	1.947	1.932	60
K_2	0.60	2.5 ± 0.3	2.3×10^{18}	1.966	1.937	31

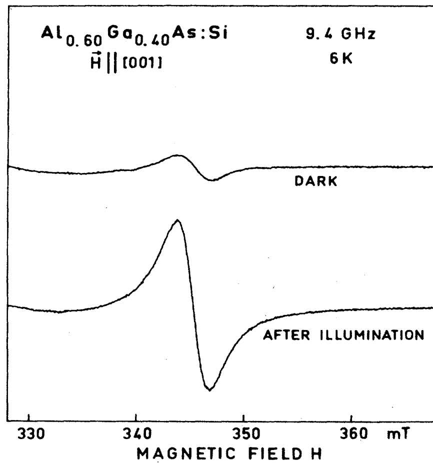

FIG. 2. EPR spectra of $Al_{0.60}Ga_{0.40}As$ taken in the dark and at its maximum intensity after illumination. The magnetic field is parallel to the crystal growth direction [001].

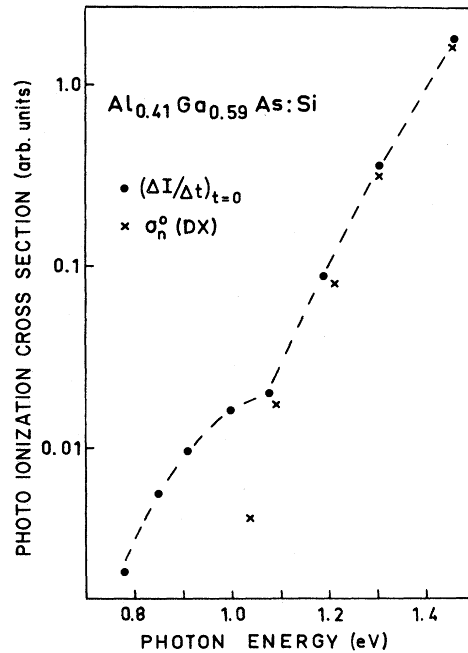

FIG. 4. The spectral dependence of initial increase of the EPR signal of Fig. 2 with illumination in a sample with $x = 0.41$. Data for the photoionization cross section of the DX level from Fig. 6(b) of Ref. 6 are also plotted for comparison.

x more and more electrons are expected to be found in the hydrogenic level after the sample is cooled to 6 K in the dark. Thus the EPR signal measured in the dark is expected to increase with x for $x > 0.40$. This increase with increasing x, is, in fact, seen between the two samples we measured. No EPR signal was observed in the dark in the sample with an alloy composition $x = 0.41$, close to the crossover from direct to indirect gap. However, a signal was observed prior to photoexcitation when $x = 0.60$. We find, as expected, that the magnitude of the dark signal depends on the sample cooling rate. The smallest dark signal we observed in the $x = 0.60$ sample was about 10% of the maximum signal after photoexcitation.

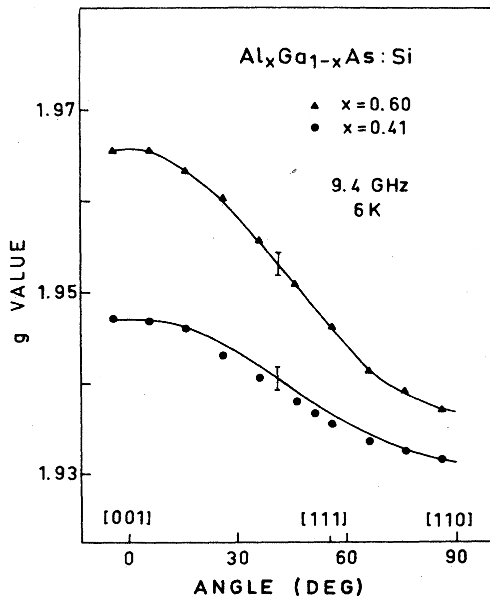

FIG. 3. Angular dependence of the g value of the EPR spectrum in Fig. 2 for $Al_xGa_{1-x}As$ of different alloy compositions. The full lines are fits to the data points with the expression $g^2 = g_{001}^2 \cos^2\theta + g_{110}^2 \sin^2\theta$, where θ is the angle between the [001] direction and the magnetic field.

After exposure to subband-gap monochromatic light, the EPR signal was found to increase and to be persistent when the light was turned off. We interpret this enhancement as the transfer of electrons from the DX level to the hydrogenic X-valley state. This is consistent with the known persistent photoionization of the DX level at low temperature[1] and is confirmed by the spectral shape of the EPR enhancement curve discussed below. At 6 K, electrons excited to the conduction band are rapidly recaptured at the hydrogenic X-valley levels. The hydrogenic states are separated from the DX level by a large energetic barrier related to the lattice relaxation, but themselves exhibit no capture barrier with respect to the conduction-band states as explicitly shown by Hall-effect measurements.[8] The neutral shallow-donor concentration determined from the maximum EPR signal is an order of magnitude lower than the Si concentration in the $Al_xGa_{1-x}As$ layer for both samples. This excludes the possibility that the EPR signal is due to residual impurities and confirms its assignment to the Si dopant.

The photoionization rate of the occupied DX level is given by

$$(\Delta n_{DX}/\Delta t)_{t=0} = \sigma_n^0(h\nu)\phi n_{DX} ,$$

where the left-hand side is the initial change in the concentration of occupied DX centers, $\sigma_n^0(h\nu)$ is the photoionization cross section of the DX level, ϕ is the photon flux, and n_{DX} is the total concentration of the DX center. We expect that electron capture at the shallow-donor level is independent of $h\nu$ and therefore $(\Delta I/\Delta t)_{t=0}$ in Fig. 4 is proportional to $\sigma_n^0(h\nu)$ of the DX center since n_{DX} and ϕ

were held constant. In Fig. 4 the EPR signal enhancement $(\Delta I/\Delta t)_{t=0}$ is compared to the photoionization cross section of the DX level $\sigma_n^0(DX)$, previously measured by photocapacitance techniques in very clean samples grown by molecular-beam epitaxy.[6] At the higher photon energies, the agreement between $(\Delta I/\Delta t)_{t=0}$ and $\sigma_n^0(h\nu)$ is excellent. At $h\nu=1.08$ eV, however, the energy dependence of $(\Delta I/\Delta t)_{t=0}$ changes abruptly, indicating that some other photoionization process occurs at lower photon energies. Similar structure in the photoionization cross section was seen previously for another MOVPE-grown $Al_xGa_{1-x}As$ sample and was found to be due to other deep levels in the sample.[6,19] Thus these measurements of the increase of the EPR signal when the sample is exposed to subband-gap light demonstrate that electrons are indeed photoexcited from the lower-lying DX level, and perhaps from some other deep states in the sample as well, to the hydrogenic X-valley state of the Si donor.

There remains the question of whether the DX level is characterized by negative or positive U. It is clear from the observation of the EPR signal for the X-valley level that the stable state of the unrelaxed donor is the neutral charge state and thus that this level has positive U. However, no EPR signal which can correspond to the DX level has been observed. One possible explanation for this is that the linewidth is so broad that there is not sufficient sensitivity to see it in our samples. In order that the amplitude of a single EPR line would be too small to be observed in our thickest sample at 10 K, the linewidth ΔH would have to be greater than about 1200 G. The EPR linewidths of deep centers in undoped GaAs, for instance, range between 350 and 1200 G.[20] It is known that the DX level is a deep highly localized state. Thus, a broad signal of unobservably small amplitude cannot be ruled out for the DX level and our failure to observe the EPR signal for the DX level does not give conclusive evidence for either a positive- or negative-U model.

In conclusion, we have observed an EPR signal which we attribute to the hydrogenic level derived from the X valley of the conduction band in indirect-gap $Al_xGa_{1-x}As$. Such hydrogenic levels have been observed in indirect-gap $Al_xGa_{1-x}As$ by other experimental techniques. The occupation of this level increases after photoexcitation of electrons from the DX level at low temperature. Our results are completely consistent with a large lattice relaxation model of the DX center. No other EPR signal which might be attributed to the DX level was observed.

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