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Symmetry of the Si shallow donor state in AlAs/GaAs and $Al_xGa_{1-x}As/GaAs$ heterostructures

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Optically detected magnetic resonance experiments performed on Si-doped epitaxial layers of AlAs and $Al_xGa_{1-x}As$ with $x \geq 0.4$ grown on (001) GaAs substrates reveal the donor state to have the symmetry of the X point in the conduction band. The heteroepitaxial strain raises the X_z valley relative to the X_x and X_y valleys. The donor g values for the AlAs/GaAs heterostructure are as follows: $g_\perp = 1.976 \pm 0.001$ and $g_\parallel = 1.917 \pm 0.001$ with respect to the long axis of an ellipsoid. The alloy results suggest the importance of spin-orbit interactions in coupling the valley-degenerate shallow-level states.

The doping of $Al_xGa_{1-x}As/GaAs$ heterostructures with group-IV and group-VI impurity atoms is widely employed to control the electrical and optical properties of this technologically important material system. However, the doping of $Al_xGa_{1-x}As$ crystals over a wide range of AlAs mole fraction with donor atoms results in the formation of *both* shallow and deep levels. The phenomenon of persistent photoconductivity at low temperatures, observed strongly in $Al_xGa_{1-x}As$ crystals with $0.22 \leq x \leq 0.42$, is associated with the existence of the deep level commonly referred to as the DX center.[1-4] A theoretical description has been given recently of the effective-mass shallow donor states associated with the Γ, X, and L conduction-band minima in n-doped $Al_xGa_{1-x}As$.[5] Far-infrared absorption measurements of the ground (1s) to first-excited-state (2p) transition associated with the Γ-related shallow bound state have been reported[6] in bulk Si-doped $Al_xGa_{1-x}As$ crystals with low AlAs mole fraction ($x \leq 0.3$). In addition, transport and photo-Hall measurements[7] show the existence of shallow and deep levels in the indirect region of $Al_xGa_{1-x}As$ crystals. Electron-paramagnetic-resonance (EPR) studies[8-10] and photoinduced ir optical-absorption measurements[11] on $Al_xGa_{1-x}As$ layers (≤ 100 μm) with high AlAs mole fraction ($0.35 \leq x \leq 0.8$) reveal features ascribed to the X-related shallow level. Recent optically detected magnetic-resonance (ODMR) studies performed by our group[12,13] on similar, but much thinner (1-1.5 μm), Si-doped $Al_xGa_{1-x}As$ layers reveal a feature with a similar g value (~ 1.95) as observed in the EPR experiments. Concurrent ODMR studies carried out by another group[14] yield similar results. However, the origin of the resonance feature was ascribed by these workers to a deep donor level that tracks with the L-point conduction-band minima as the AlAs mole fraction is varied from 0.35 to 0.8.

The present optically detected magnetic resonance studies on Si-doped epitaxial layers of $Al_xGa_{1-x}As$ on GaAs with moderate to high AlAs mole fractions ($0.4 \leq x \leq 1$) demonstrate explicitly the symmetry of an effective-mass state derived from the X-point conduction-band minima. The results reveal that heteroepitaxial stress is present in the nearly lattice-matched $GaAs/Al_xGa_{1-x}As$ alloy system. The data for the $Al_xGa_{1-x}As/GaAs$ heterostructures with decreasing Al mole fraction strongly suggest the importance of spin-orbit interactions in coupling the valley-degenerate shallow-level states associated with the X-point conduction-band minima, especially near the direct-indirect crossover region.

The samples investigated in this work were thin (1-1.5 μm) epitaxial layers of $Al_xGa_{1-x}As$ ($0.4 \leq x \leq 0.8$) grown by molecular-beam epitaxy (MBE) on semi-insulating, 500-μm-thick (001) GaAs substrates. In addition, experiments were performed on a 5.5-μm-thick AlAs layer grown by organometallic vapor phase epitaxy on a similar substrate. The samples (2.5×7.5 mm^2) were Si-doped to nominal concentrations of 10^{16} to 10^{18} cm^{-3}. Also, a single, undoped sample grown by liquid-phase epitaxy (LPE) with an AlAs mole fraction of ~ 0.6 was studied before and after Si ion implantation. Double-crystal x-ray measurements were performed in order to determine the aluminum mole fraction (x).

The magnetic resonance was detected synchronously as a change in the total intensity of deep donor-acceptor pair recombination which was coherent with the chopping (77-200 Hz) of 50 mW of microwave power in a K-band (24 GHz) spectrometer. The photoluminescence was excited with above-band-gap radiation provided by a Kr$^+$ laser at 476 nm or an Ar$^+$ laser at 458 nm with power densities between 0.1 and 1 W/cm^2. Light from 1.0-1.8 μm was detected by a liquid-nitrogen-cooled Ge photodiode. The immersed samples were studied under pumped-helium conditions (~ 1.6 K) in a commercial optical cryostat.

Two sample geometries were employed in these studies. In both cases the measurements were carried out in the Voight geometry with the applied magnetic field supplied by a 9-in. pole face electromagnet. When the magnetic field was rotated in the $(1\bar{1}0)$ plane, the sample was mounted at the end of a cylindrical piece of Teflon fixed to a $\frac{1}{16}$-in.-o.d. stainless-steel tube. The excitation light was coupled to the samples in this configuration through the optical windows at the bottom of the cryostat. In order to rotate the magnetic field in the (001) growth plane, the sample was mounted at the end of a 3-mm-o.d. quartz rod. The excitation light was coupled to the sample in this geometry via the quartz rod and fiber optics.

The nature of the Si donor ground state in AlAs and $Al_xGa_{1-x}As$ with high (i.e., $x \geq 0.35$) AlAs mole fraction has been described by Morgan.[5] The conduction-band minima in these crystals are located along the ⟨001⟩ principal axes at the Brillouin-zone edges (X points). The conduction-band constant energy ellipsoids (also referred to as valleys) in momentum space about the X-point minima are depicted schematically in Fig. 1. The wave function of the donor ground state, in the effective-mass approximation, is derived from (i) Bloch functions for the three equivalent X_x, X_y, and X_z valleys, and (ii) 1*s* envelope functions that satisfy the effective-mass equation. Due to the symmetry of the group-III site relative to the X-point minimum, the central cell potential does *not* mix the three 1*s* states. Thus, the ground state of an electron bound to a Si donor, neglecting spin-orbit interactions and random strains due to alloy disorder in the $Al_xGa_{1-x}As$ crystals, is an orbital triplet. However, the degeneracy can be lifted, for example, by a large uniaxial stress applied in a direction that removes the equivalence of the three X-point conduction-band minima. It will be shown below that the heteroepitaxial strain present in the AlAs/GaAs and $Al_xGa_{1-x}As$ heterostructures significantly modifies the nature of the Si-donor ground state.

Representative spectra for the Si-doped AlAs/GaAs heterostructure are shown in Fig. 2. Angular rotation studies were performed with the applied magnetic field in the $(1\bar{1}0)$ and (001) planes of the sample. In the former geometry (top half of Fig. 2), a single line is observed that shifts from $g = 1.945 \pm 0.001$ for $B \parallel [110]$ to $g = 1.978 \pm 0.001$ for $B \parallel [001]$. In the latter geometry (bottom half of Fig. 2), two resonances with approximately equal amplitudes are observed with $g = 1.917 \pm 0.001$ and $g = 1.976 \pm 0.001$ for $B \parallel [100]$. A single line is observed again with $g = 1.947 \pm 0.001$ as the magnetic field is rotated to the [110] direction.

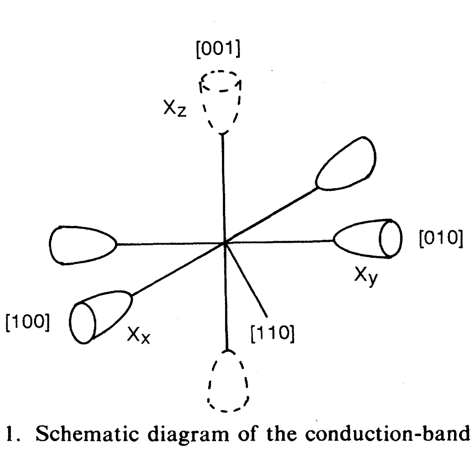

FIG. 1. Schematic diagram of the conduction-band constant energy ellipsoids about the X-point minima in momentum space for the $Al_xGa_{1-x}As$/GaAs samples with high x. The dashed ellipsoids indicate that these valleys lie higher in energy due to the heteroepitaxial stress along the [001] growth axis. The magnetic field (B) in the ODMR experiments is rotated in real space from [001] to [110] and from [100] to [110].

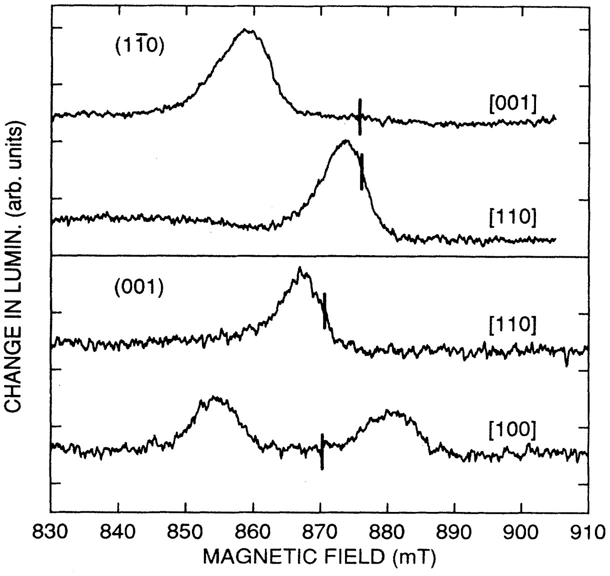

FIG. 2. ODMR spectra obtained for the Si-doped AlAs/GaAs heterostructure with B rotated in the $(1\bar{1}0)$ and (001) planes. Vertical bars indicate $g = 1.94$.

These results can be understood using an independent valley model in the presence of strain. The mismatch of the AlAs and GaAs lattice constants at 1.6 K leads to a biaxial compression in the plane of the epilayer and an elongation (i.e., a tensile strain) along the [001] growth direction of 1.4×10^{-3} due to the Poisson effect.[15] As a result, the X_z valley is raised in energy (depicted by the dashed half-ellipsoids in Fig. 1) relative to the X_x and X_y valleys and is not populated. Two resonances of about equal intensities are observed with the magnetic field along the [100] direction in the (001) plane because the field is oriented parallel to the long axis (g value denoted by $g_{\parallel}$) of the X_x valley, but parallel to the short axis (g value denoted by $g_{\perp}$) of the X_y valley. A single resonance feature is observed as the field is rotated in the $(1\bar{1}0)$ plane since this plane mirrors the X_x and X_y valleys.

The results obtained for the AlAs/GaAs sample indicate that (i) the X_x and X_y valleys are decoupled since the two resonances are so clearly resolved and (ii) the X_z valley is not populated since only one resonance is observed for $B \parallel [001]$. Thus, the Si-donor ground state can be described as a doublet with tetragonal symmetry about the [001] growth direction. The symmetry behavior of the resonance feature with the orientation of the applied magnetic field confirms the states' association with the X-point conduction-band minima and *not* with the Γ or L points.

The nature of the donor state in the $Al_xGa_{1-x}As$/GaAs heterostructures with $x < 1$ will now be discussed. The ODMR spectra obtained on the Si-doped $Al_xGa_{1-x}As$/GaAs samples for several values of aluminum mole fraction (x), with the applied magnetic field parallel to the [100] direction, are shown in Fig. 3. The vertical bars are $g = 1.94$ markers due to the slightly different microwave cavity frequencies associated with each spectrum. The

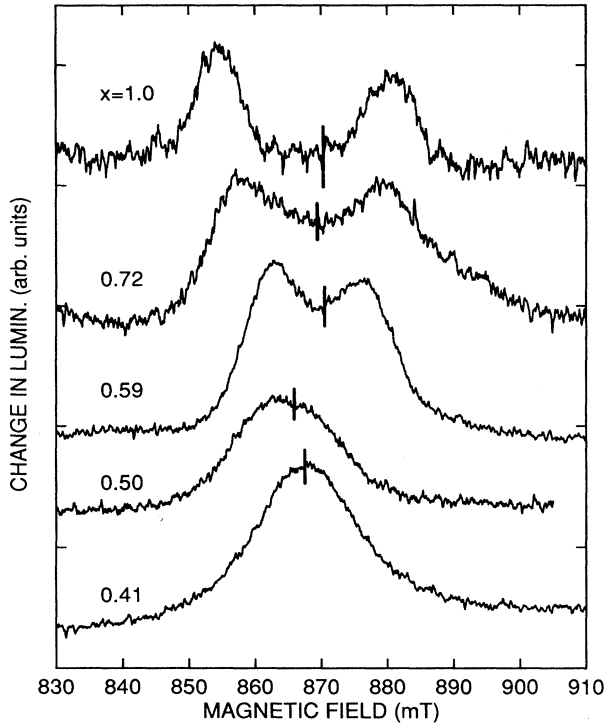

FIG. 3. ODMR spectra obtained for several $Al_xGa_{1-x}As$/GaAs samples with $B \| [100]$. Vertical bars indicate $g = 1.94$.

most dramatic feature of these spectra is the decrease in splitting between the two resonances with decreasing aluminum mole fraction. It is observed that only one resonance peak can be resolved in this geometry for the sample with $x = 0.41$. In addition, the linewidths of the individual resonances increase with decreasing x.

A compilation of the donor g values as a function of AlAs mole fraction (x) determined from the ODMR experiments on the AlAs/GaAs and $Al_xGa_{1-x}As$/GaAs heterostructures is shown in Fig. 4. The donor g values obtained with the external magnetic field rotated in the $(1\bar{1}0)$ and (001) planes are displayed by the open and solid symbols, respectively. Several features of these data are important. First, the donor g values (solid squares) obtained with the magnetic field along the [100] direction shift monotonically towards $g = 1.94$. Second, the average donor g values obtained with the magnetic field along the [110] direction are found to be approximately constant (~ 1.94).

The behavior of the donor g values in the Si-doped $Al_xGa_{1-x}As$/GaAs samples is attributed to the breakdown of the independent valley model that was employed to describe the symmetry of the donor ground state in the Si-doped AlAs/GaAs heterostructure. The spin-orbit interaction in the $Al_xGa_{1-x}As$ epilayers leads to a coupling of the X_x and X_y valleys. The results suggest that the mixing between these valleys becomes stronger with decreasing heteroepitaxial stress (i.e., decreasing AlAs mole fraction). The X_z valley will shift to lower energies with decreasing x and may also begin to couple with the X_x and X_y valleys. However, a finite stress in the [001] direction is still present in the sample with $x = 0.41$ since a donor g-value anisotropy about the [001] growth axis, though small, is observed with the field rotated in the $(1\bar{1}0)$ plane.

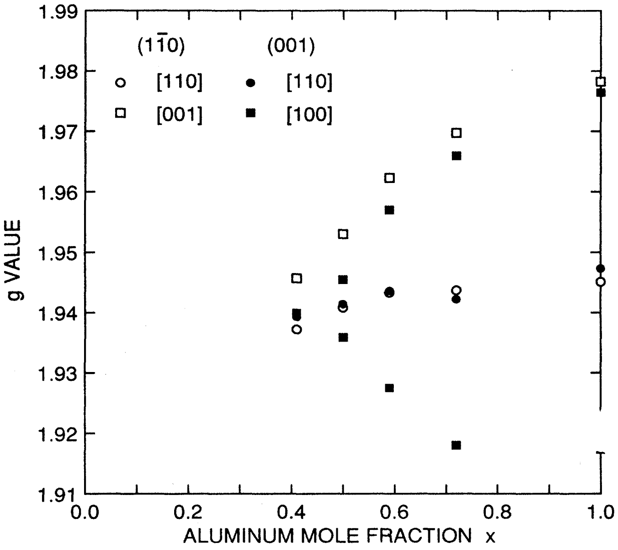

FIG. 4. Compilation of the ODMR g values as a function of the AlAs mole fraction (x) with B rotated in the $(1\bar{1}0)$ and (001) planes.

In addition to spin-orbit coupling, other mechanisms can influence the nature of the Si-donor ground state in the $Al_xGa_{1-x}As$/GaAs samples. These include random strain due to alloy disorder, which reaches maximum strength for $x = 0.5$ and X-L band-mixing effects, especially near the direct-indirect crossover region. However, the present results suggest that these effects are small relative to the spin-orbit interaction for the following reasons. First, the ODMR spectra found in the $Al_xGa_{1-x}As$ epitaxial layers that should have similar alloy disorder (i.e., the samples with $x = 0.4$ and 0.6) are significantly different. Second, the nearly constant average donor g value (~ 1.94) observed in these studies for the entire set of samples is consistent with a diminished X-L interaction, as the donor g values associated with the L-point conduction-band minima[16] are expected to differ significantly from those associated with the X-point conduction-band minima.

In summary, ODMR experiments reveal the X-point symmetry of Si donor states in $Al_xGa_{1-x}As$/GaAs heterostructures with high AlAs mole fraction. The effective-mass states are modified by heteroepitaxial strain and spin-orbit interactions. These ODMR results for X-related states complement the infrared studies of the Γ-related states[6] to demonstrate the shallow character of donors in $Al_xGa_{1-x}As$. Further details will be provided in a later paper.

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