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Strain splitting of the X-conduction-band valleys and quenching of spin-valley interaction in indirect GaAs/$Al_xGa_{1-x}As$:Si heterostructures

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We report electron-paramagnetic-resonance results for the shallow effective-mass $1s(T_2)$ state of the Si donor associated with the X valleys in indirect-band-gap ($x \geq 0.4$) $Al_xGa_{1-x}As$:Si layers grown on GaAs. The data confirm definitely that the heteroepitaxial strain splits the three X valleys such that the X_z valley lies above the X_x and X_y valleys. An independent-valley model perfectly accounts for the properties of the donor resonance over the full indirect-band-gap range of the alloy *without* inclusion of the spin-valley interaction. This effect is attributed to small local, random in-plane strains which quench the first-order spin-valley splitting.

The GaAs/$Al_xGa_{1-x}As$ heterostructure is often considered as an ideally lattice-matched system since the mismatch is less than 6×10^{-4}.[1] However, the consequences of this small misfit have not been fully appreciated until recently. Because of the residual mismatch, the $Al_xGa_{1-x}As$ layer is strained along the growth direction and thus cannot be considered as a cubic zinc-blende structure. Rather, the layer, when grown on (001) GaAs substrate, behaves as a tetragonal crystal, and this symmetry lowering has measurable consequences on its band structure. For instance, very recently it has been reported[1] that the tetragonal strain leads to a heavy-hole–light-hole splitting of the uppermost valence band, varying from zero for GaAs ($x=0$ to about 12 meV for AlAs layers ($x=1$).

The built-in strain also modifies the lowest conduction-band minima of the indirect-band-gap semiconductor $Al_xGa_{1-x}As$ ($0.4<x\leq1$) (Ref. 2) and the neglect of this effect has led to a considerable controversy about the relative ordering of the three conduction-band X-point valleys (constant-energy ellipsoids) in GaAs/AlAs superlattices.[3,4] The reason for this controversy is that in these structures both confinement and strain (in the AlAs) remove the threefold degeneracy of the X valleys, but the sign of the (X_x,X_y), X_z splitting (z is taken along the growth direction, x and y along [100] and [010], respectively) is opposite for the two effects.[4] Thus, there is a need to investigate the strain splitting of the X valleys without interfering complications due to confinement. This has been done recently on Si-doped GaAs/$Al_xGa_{1-x}As$ heterostructures using optically detected magnetic resonance (ODMR). From an analysis of the Si *shallow* donor resonance it was concluded that the in-plane X_x,X_y valleys are energetically below the X_z valley.[5–7] The ODMR conclusions are based on the splitting *and* the relative intensities of the donor resonance lines. Since ODMR is a nonequilibrium technique, relative intensities of resonance lines can differ from those expected for conventional EPR (electron paramagnetic resonance).[8] It is therefore desirable to confirm and supplement the ODMR results by conventional EPR since this technique probes the shallow-donor ground state in thermal equilibrium.

In this Brief Report we present conventional EPR results for the Si shallow donor in [001]-strained $Al_xGa_{1-x}As$ layers. They confirm the sign of the strain splitting of the X valleys but they also show that for medium AlAs mole fractions ($x=0.4$ and 0.6) the X valleys remain uncoupled. Together with the corresponding result for AlAs (Refs. 6 and 7) this suggests that over the entire indirect-band-gap range, the spin-valley (SV) mixing is unexpectedly small (apparent coupling constant $|\lambda| \ll 0.3\ \mathrm{cm}^{-1}$) such that an independent-valley model is applicable. This finding is surprising since $|\lambda|$ is expected to be near $1\ \mathrm{cm}^{-1}$ for the samples studied here and for AlAs. We attribute this fact to random, local in-plane strains that dominate the SV interaction, thereby "quenching" the first-order SV splitting.

The two samples used for this study were the same as those in our previous photo-EPR work.[9] Both were grown by metal-organic vapor-phase epitaxy on (001)-oriented undoped semi-insulating GaAs and were doped with Si to a level of $2\times10^{18}\ \mathrm{cm}^{-3}$. Sample 1 has an AlAs mole fraction $x=0.4$ and a thickness of 11 μm. The corresponding values for sample 2 are $x=0.6$ and 2.5 μm. Up to 30 layers were stacked for the 9.5-GHz EPR measurements.

In our previous EPR study of the Si shallow-donor resonance in samples 1 and 2, the angular dependence of the resonance line was measured for a rotation of the magnetic field **H** in the (110) plane containing the [001] growth direction.[9] Under this geometry the magnetic field does not destroy the equivalence between the X_x and X_y valleys, and a splitting of the donor line due to the inequivalence of X_z and the X_x,X_y pair could result only if all three valleys were populated at low temperatures.

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This has not been observed and thus implies that either the X_x,X_y pair or X_z is depopulated. To discriminate between these two possibilities a rotation of the **H** field in the (001) plane (x,y) normal to the growth direction is required.

Figure 1 shows EPR spectra for sample 2 for two field directions in the (001) plane. For **H** along [110] a single donor line at 352 mT is observed, whereas for **H**‖[100] the line is split into two components of equal intensity. The association of these lines with the shallow effective-mass Si donor is firmly established[5,6,9,10] and speculations[11] that they may be due to the deep DX state of Si have been ruled out. (The sharp line at 340 mT and the broad feature at lower field are due to the sample holder.) The two split donor lines for **H**‖[100] could be followed up to 25 K with an acceptable signal-to-noise ratio. Their intensities were equal within experimental error even at 25 K. The full angular dependence of the two lines, when rotating **H** in the (001) plane, is shown in Fig. 2. Each of the two branches shows a 180° periodicity and they are equivalent except for a 90° phase shift. Taken together this reveals a fourfold symmetry around the [001] axis.

For sample 1 the Si donor resonance does not split but remains centered at $g=1.937\pm0.004$ when **H** is rotated in the (001) plane. The linewidth, however, is broadened from 6.0 mT for **H**‖[110] to 7.0 mT for **H**‖[100], which could indicate an unresolved splitting.

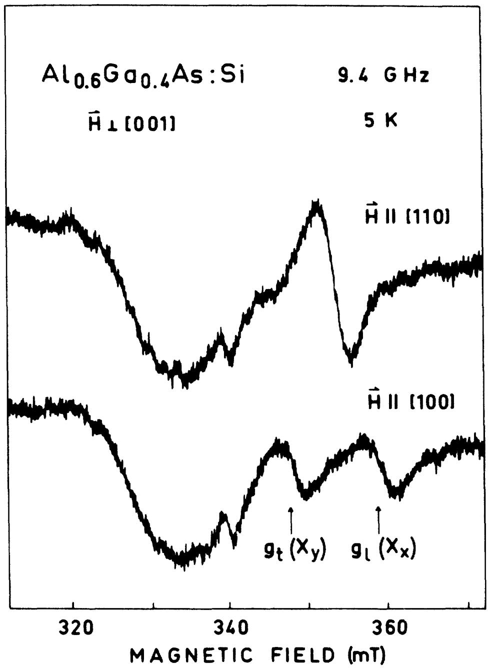

FIG. 1. EPR spectrum of the shallow Si donor $1s(T_2)$ ground state in GaAs/Al$_x$Ga$_{1-x}$As:Si for two orientations of the magnetic field in the (001) plane. The actual sample is a stack of thirty 2×2 mm^2 layers. The sharp line at 340 mT and the broad feature at lower fields arise from the sample holder.

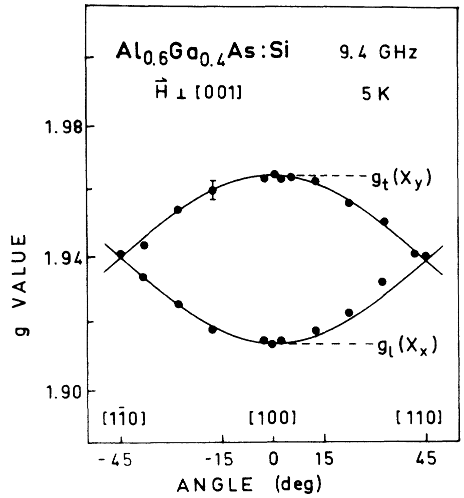

FIG. 2. Angular dependence of the Si donor lines from Fig. 1 upon rotating the magnetic field in the (001) plane. The solid curve is a fit with the analytical dependence quoted in the text and with g_t and g_l as fitting parameters.

Neglecting the heteroepitaxial strain, alloy disorder and spin, for the moment, the lowest conduction-band minimum in indirect Al$_x$Ga$_{1-x}$As is at the X point of the Brillouin zone. It transforms as the irreducible representation X_3 of the wave-vector point group D_{2d} provided that the origin of the coordinate system is chosen at a group-III-atom site. This choice of origin is the proper one for the Si donor. There are three equivalent X points and accordingly three X valleys: X_x, X_y, and X_z. They induce a triply degenerate state transforming as T_2 in the point group T_d of the group-III-atom site.[12–14] A $1s$ donor ground state is tied to each component (valley) of the T_2 state (see Fig. 3). According to effective-mass theory each of these states, in the present case, is a simple product of a hydrogenic envelope function $F_{1s,i}$ and a Bloch function X_i transforming as the component $T_2 i$ ($i=x,y,z$) of T_2 and in an obvious notation we write for the ith donor ground state $|T_2 i\rangle=|1s_i\rangle|X_i\rangle$. The impurity central-cell potential (intervalley or valley-orbit interaction) has cubic symmetry and therefore neither mixes nor splits the $|T_2 i\rangle$ states. When a tetragonal strain of the form $\delta\mathcal{L}_z^2$ ($\mathcal{L}_z$ is the z component of a vector operator $\mathcal{L}$ that transforms as the orbital angular momentum operator **L** and acts on the valley functions $|X_i\rangle$) along the growth direction is present, the X_z valley is split off from X_x and X_y which remain degenerate. The $|T_2 i\rangle$ donor states are split accordingly but are not mixed by this perturbation and remain independent.

At low temperatures the donor electrons are frozen out in the three $1s$ ground states $|T_2 i\rangle$. In thermal equilibrium their occupation is determined by a Boltzmann distribution that fixes the relative intensities of the three individual donor lines. Thus, the multiplicity of donor resonances, their angular dependence, and their relative intensities allow direct and unambiguous conclusions about the symmetries of the valleys and their relative ordering. With spin included, the eigenfunctions of the donor ground states become $|T_2 i\rangle\,|\pm\frac{1}{2}\rangle$. Since the valleys have axial character, two g factors, g_l and g_t for **H** fields along

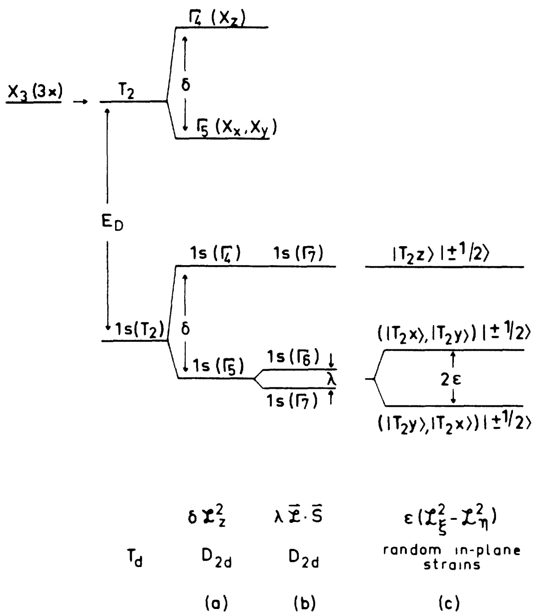

FIG. 3. Splitting of the $1s(T_2)$ ground state of a group-III-site donor tied to the three X_3 minima in indirect-band-gap $\mathrm{Al}_x\mathrm{Ga}_{1-x}\mathrm{As}$ under the action of various perturbations: (a) heteroepitaxial-uniaxial strain along the [001] growth direction, (b) spin-valley splitting, neglecting random in-plane ϵ-type strains, and (c) in-plane ϵ-type strains larger than the spin-valley splitting λ. Here the local donor symmetry can be any subgroup of D_{2d} but the overall layer symmetry remains D_{2d}. The labeling of the irreducible D_{2d} representations is that of Ref. 18. Splittings are not drawn to scale.

and perpendicular to the long valley axis, are required to describe the Zeeman splittings of the $1s$ donor ground states. Both g factors are close to the free-spin value $g_s = 2.0023$ and differ from this value only by small spin-orbit corrections of the order $\Lambda(X)/[E_c(X) - E_v(X)] \sim 0.1/5 = 0.02$, $\Lambda(X)$ being the spin-orbit splitting of the valence band at X.

For a rotation of **H** in the (001) plane, one expects, in this independent-valley model, a single *isotropic* resonance line if the X_z valley (and therefore $|T_2 z\rangle$) is lower but two *anisotropic* lines varying as $g^2 = g_l^2\cos^2\theta + g_t^2\sin^2\theta$, with a 90° phase shift if X_x and X_y are lower. The latter case is exactly that which was observed for sample 2 (see Figs. 1 and 2). Therefore, X_z must be depopulated at low temperatures. The g factor and valley assignments in Figs. 1 and 2 now follow from a comparison of the $\mathbf{H}\|[001]$ spectrum of our previous work[9] with the $\mathbf{H}\|[100]$ spectrum in Fig. 1. In the former spectrum **H** is parallel to the short axes of X_x and X_y. Therefore, $g_{[001]} = 1.966$ (Ref. 9) has to be identified with g_t. The lower-field line in the $\mathbf{H}\|[100]$ spectrum of Fig. 1 occurs at the same g factor. Therefore, this line is associated with g_t of the X_y valley and the upper line with g_l of X_x.

The failure to observe a splitting of the donor resonance for sample 1 ($x = 0.4$) when rotating **H** in the (001) plane is obvious from our previous work.[9] First, the linewidth in sample 1 (6 mT) is twice as large as that in sample 2. Second, the expected splitting for $\mathbf{H}\|[100]$ is only ≈ 3 mT, which is a factor of 3.5 less than for sample 2. Nevertheless, it is clear that also in sample 1, the donor resonance arises from $|T_2 x\rangle$ and $|T_2 y\rangle$ and not from $|T_2 z\rangle$. The line occurs at $g = 1.938 = \frac{1}{2}(g_l + g_t)$, for $x = 0.4$, and not at $g_t = 1.947$, which would be the expected position in the latter case, according to our previous results.[9]

The fact that the two lines for $\mathbf{H}\|[100]$ in Fig. 1 have equal intensities even at 25 K allows one to estimate a lower limit for the strain splitting δ. One obtains $\delta \gg 3$ meV. For GaAs/AlAs, δ has been estimated as ≈ 26 meV (Ref. 2 and 4). Since δ is proportional to the strain and since the strain varies, approximately, linearly with x,[1] one expects δ values of 10 and 15 meV for $x = 0.4$ and 0.6, respectively, consistent with the lower bound inferred from EPR. A significant repopulation of the X_z valley and its associated donor ground state should therefore not occur up to temperatures above 100 K even for $\mathrm{Al}_{0.4}\mathrm{Ga}_{0.6}\mathrm{As{:}Si}$.

We now point out why the success of the independent-valley model, as demonstrated earlier, is not obvious at first sight. When spin-valley coupling ($\lambda\mathcal{L}\cdot\mathbf{S}$) is introduced but alloy disorder and random strains are still neglected, such that the layer can be considered as a crystal having effective tetragonal symmetry, this interaction splits X_x and X_y in first order into SV states having Γ_6 and Γ_7 symmetry. This splitting is equal to λ, (see Fig. 3). The SV interaction can inextricably mix the X_x and X_y valleys depending on the magnitude of λ, which we have to estimate first. A general theory to calculate the SV coupling constant λ, to our knowledge, does not exist. However, it has been suggested[15] that λ scales with the *difference* between the atomic spin-orbit coupling constants of the impurity and that of the host atom it replaces. Typically λ is reduced from this difference by 2–3 orders of magnitude.[15–17] The experimental values of λ for $\mathrm{Si}_{\mathrm{Ga}}$ in GaP (Ref. 15) and $\mathrm{Sn}_{\mathrm{Ga}}$ in GaP (Refs. 16 and 17) are 2.7 and 11.3 cm^{-1}, respectively, corresponding to a reduction of the aforementioned specified difference by a factor of ≈ 350 in both cases. We use this factor to scale the appropriate atomic spin-orbit constant differences for $\mathrm{Al}_x\mathrm{Ga}_{1-x}\mathrm{As{:}Si}$ and obtain $\lambda \approx -1.6\ \mathrm{cm}^{-1}$ for $x = 0.4$, $\lambda \approx -0.8\ \mathrm{cm}^{-1}$ for $x = 0.6$, and $\lambda \approx 0.5\ \mathrm{cm}^{-1}$ for $x = 1$. Thus for $x = 0.4$ and $x = 0.6$, $|\lambda|$ is close to 1 cm^{-1}.

This is a small splitting for most optical experiments but a large one for X-band EPR, where $g\mu_B H \approx 0.3\ \mathrm{cm}^{-1}$. To calculate Zeeman splittings (g factors) one now has to use eigenfunctions that diagonalize the SV interaction and these are no longer the simple $|T_2 i\rangle\,|\pm\frac{1}{2}\rangle$ donor ground-state functions appropriate in the independent-valley model. The proper SV functions are, however, readily obtained from tables of coupling coefficients[18] and are given by $|\Gamma_6 \mp \frac{1}{2}\rangle = |X_\mp\rangle\,|\pm\frac{1}{2}\rangle$ and $|\Gamma_7 \mp \frac{1}{2}\rangle = |X_\pm\rangle\,|\pm\frac{1}{2}\rangle$, where the complex "valleys" $|X_\pm\rangle = 1/\sqrt{2}(i|X_x\rangle \pm |X_y\rangle)$ have been introduced. The very different magnetic behavior of the SV states Γ_6 and Γ_7 are easily demonstrated for the realistic case where $g\mu_B H \ll \lambda$ such that g-factor corrections of the order

$g\mu_B H/\lambda$ are small but $\lambda \ll \delta$ such that second-order SV coupling is negligible. In this case one finds for the g factors of *both* Γ_6 and Γ_7, $g_\parallel = g_t$ (**H** along the tetragonal strain z axis) but $g_\perp = 0$ [**H** in the (001) plane], in obvious disagreement with observation. The g factors differ drastically from the independent-valley model, and actually, no donor resonance would be observable for a rotation of **H** in the (001) plane since the lines would occur at infinite fields. That such a behavior is *not* observed, could be thought to result from an accidental cancellation of the SV coupling constant ($\lambda = 0$) in the case of GaAs/AlAs:Si.[6,7] However, the results presented here, show that SV interaction effects are negligible over the full indirect alloy range and this must have a more fundamental origin.

We attribute the aforementioned quenching of the SV interaction to the presence of local, random in-plane strains of the form $\epsilon(\mathcal{L}_\xi^2 - \mathcal{L}_\eta^2)$ [ξ and η are local, orthogonal axes in the (001) plane], which override the first-order SV splitting and thus completely remove the donor ground-state valley degeneracy, see the right-hand side of Fig. 3. These strains, however, conserve the overall tetragonal symmetry of the layers, as Fig. 2 proves. Of course, ϵ will follow a distribution with both positive and negative values such that a $|T_2x\rangle$ and a $|T_2y\rangle$ ground state are equally probable. This situation is schematically illustrated in the right-hand side of Fig. 3 for two particular Si donors with opposite signs of ϵ but with the same absolute magnitude. In such a case, the relative intensities of the two donor lines in Fig. 1 for **H**$\|$[100] will not change even when $kT \ll \epsilon$ and this is what we observe down to 2 K. For the alloy, the natural origin of ϵ-type strains is alloy disorder. However, the case of AlAs:Si (Ref. 7) suggests that conventional random ϵ-type strains are also important. A reasonable guess for the order of magnitude of ϵ is $\epsilon \sim 10\ \text{cm}^{-1}$ since one must have $\epsilon \gg \lambda$ and $\epsilon \ll \delta$ to explain the data presented.

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