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ELECTRON PARAMAGNETIC RESONANCE OF THE SHALLOW Si DONOR IN INDIRECT GaAs/$Al_xGa_{1-x}As$ HETEROSTRUCTURES

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ABSTRACT

We report electron paramagnetic resonance (EPR) results for the shallow effective mass ground state $1s(T_2)$ of the Si donor associated with the X valleys in indirect (x > 0.4) $Al_xGa_{1-x}As$:Si layers grown on GaAs. EPR data taken in thermal equilibrium 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 symmetry properties of the donor resonance over the full indirect gap range of the alloy <u>without</u> inclusion of spin-valley interaction. This unexpected result is attributed to local, random in-plane strains which quench the first order spin-valley splitting. Photo EPR and low temperature annealing studies of the photo-enhanced shallow donor signal provide also information on the deep DX state of Si. In particular the data confirm the increase of the DX capture barrier height with increasing Al content within the indirect alloy range.

INTRODUCTION

In $Al_xGa_{1-x}As$ the Si donor creates both a shallow and a deep level. The deep, highly localized state is called DX center [1]. DX is the lowest lying donor level over a wide composition range. In contrast, the shallow, hydrogenic state introduces a shallow level 40-70 meV below the conduction band edge [2]. In indirect $Al_xGa_{1-x}As$ (x>0.4) it derives from the X conduction band minima. Performing EPR we use this hydrogenic state of the Si donor to probe the symmetry properties of the X valleys in strained $Al_xGa_{1-x}As$. The EPR data demonstrate that the uniaxial strain produced by the small residual lattice mismatch [3] splits the X valleys such that the X_z valley (z along the growth axis) is higher in energy than X_x and X_y [4]. This result is obtained under thermal equilibrium conditions for the first time. It confirms previous ODMR interpretations [5,6]. An independent valley model perfectly accounts for the symmetry properties of the donor resonance. This unexpected result is attributed to the presence of random in-plane strains which suppress the first order spin-valley splitting.

In addition, the shallow donor EPR when combined with optical excitation and low temperature annealing provides information about the properties of the DX level. Electron capture into this level is thermally activated [7], compare figure 1. The EPR data show that within the indirect alloy range the capture barrier height increases with increasing AlAs mole fraction x.

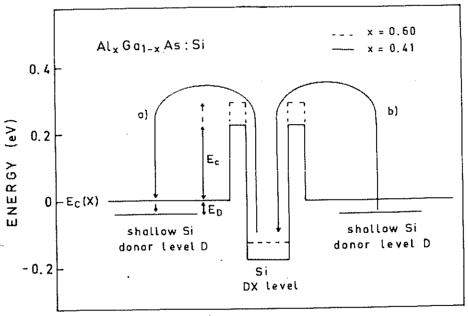

Figure 1. Schematic diagram of the shallow Si donor level and of the deep DX level for two different AlAs mole fractions. The capture barrier that separates the DX level from the conduction band is shown too. Barrier heights are taken from ref. [7]. Process a) corresponds to electron transfer from the filled DX level to the empty shallow donor level and therefore to the optical enhancement of the shallow donor EPR, process b) to its thermal quenching.

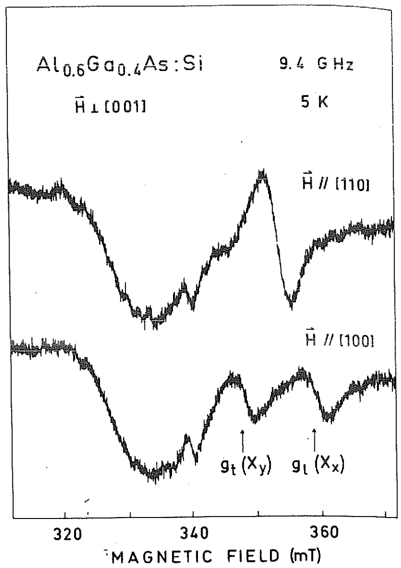

Figure 2. EPR spectra of the shallow Si donor $1s(\Gamma_5)$ ground state in the dark for two orientations with the magnetic field in the (001) plane. The sharp line at 340 mT and the broad feature at lower fields arise from the sample holder.

EXPERIMENTAL

We investigated two samples. Both were grown by metal-organic vapor phase epitaxy on (001) oriented undoped semi-insulating GaAs. The layers were doped with Si to a level of $2 \cdot 10^{18}$ cm^{-3}. Sample 1 had an AlAs mole fraction of x = 0.41 and a thickness of 11 μm. The corresponding values for sample 2 were x = 0.6 and 2.5 μm. A 1 μm thick undoped $Al_xGa_{1-x}As$ buffer layer separated the doped layers from the substrate.

RESULTS

Figure 2 shows 9.5 GHz EPR spectra of sample 2 taken in the dark. Both spectra were taken for orientations of the magnetic field H perpendicular to the growth direction. At an orientation of H along [110] we observe a single donor line at g = 1.940 ± 0.003. For H along [100] the line is split into two components of equal intensity. The relative intensities did not change over the full temperature range that allowed detection of these two lines from 2 K to 25 K. Figure 3 shows the full angular dependence of the two lines when rotating H in the (001) plane. We observe two branches, each with a 180 degree periodicity. Both are equivalent except for a 90 degree 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= 1.936 ± 0.004 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 indicates an unresolved splitting.

To study the low temperature annealing behavior of the shallow donor EPR we first enhanced the signal optically as decribed in ref. [8] and then heated the layer to temperatures between 40 K and 140 K. These annealing temperatures were hold constant within 2 K for 12 minutes. Eventually we cooled the layers to 5 K and finally

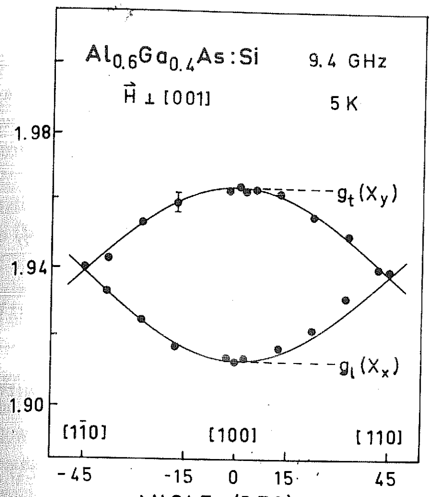

Figure 3. Angular dependence of the Si donor resonance from figure 2 upon rotating the magnetic field in the (001) plane. The full curve is a fit to $g^2 = g_l^2\cos^2\theta + g_t^2\sin^2\theta$ with g_l and g_t used as fitting parameters.

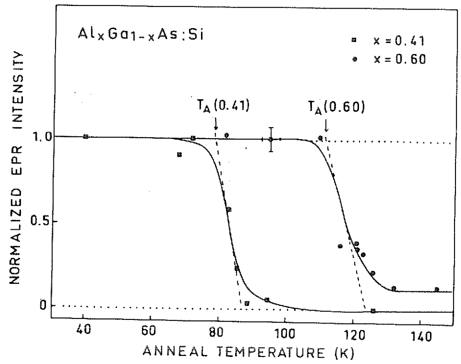

Figure 4. Isochronal annealing of the photo-enhanced shallow donor EPR for two samples with different alloy compositions. The full curves are guide to the eye. The annealing temperature T_A is defined by the intersect between the 100 percent line and the tangent at the point where the photo-enhanced part of the signal has decayed to 50 percent.

recorded the EPR spectrum. Figure 4 depicts the relative signal intensities as a function of annealing temperatures. The temperature range where the signal decays from its photo-enhanced value to the dark value depends strongly on x. Defining an annealing temperature T_A as shown in figure 4 one finds T_A values of (78 ± 3) K and (111 ± 3) K for x = 0.41 and x = 0.60, respectively.

DISCUSSION

In indirect AlGaAs the conduction band minimum is at the X point of the Brillouin zone. A shallow donor 1s ground state derives from each of the three X valleys, X_x, X_y and X_z. These are degenerate in cubic symmetry. The origin of the proper coordinate system is fixed by the Si impurity which occupies a group III site at the doping levels of our samples. Therefore each X valley transforms as the irreducible representation X_3 of the wavevector point group D_{2d}. This band symmetry X_3 induces the bound state representation T_2 of the point group T_d [9,10]. This valley triplet in cubic symmetry is split by a tetragonal strain , $\delta\mathscr{L}_z^2$, into a valley doublet $\Gamma_5(X_x,X_y)$ and a valley singlet $\Gamma_4(X_z)$, see figure 5, the irreducible representations of D_{2d} being labelled according to ref. [11].

The observation that the shallow donor resonance splits under thermal equilibrium conditions, see figures 2 and 3, proves that the 1s state deriving from the valley doublet, $\Gamma_5(X_x,X_y)$, is thermally occupied. For a rotation in the (001) plane one expects for these two states two anisotropic lines with g factors varying as $g^2 = g_l^2\cos^2\theta + g_t^2\sin^2\theta$ with a relative phase shift of 90 degree if X_x und X_y are decoupled. Here, g_l and g_t are the single valley g factors and θ is the angle between the [100] crystal axis and the magnetic field for X_x. The resulting fourfold symmetry is exactly what we observe. If the 1s singlet deriving from X_z were occupied one would expect a single isotropic resonance which we do not detect from 2 K to 25 K. Therefore, X_z is thermally depopulated at these temperatures and is raised in energy more than 3 meV above the ground state.

The g factor assignments given in figures 2 and 3 now follow from a comparison of these figures with the angular dependence in our previous work [8]. One obtains g_l = 1.917 ± 0.004, g_t = 1.947 ± 0.004 for x = 0.41 and g_l = 1.908 ± 0.003, g_t = 1.966 ± 0.003 for x = 0.60.

The single valley g factors g_l and g_t, in first order, are equal to the free electon g factor, g_e. Theoretical expressions including second order corrections are available [12]. If only spin-orbit coupling between the X_3 conduction band and the uppermost valence band at X is condsidered they simplify to

$$g_l \approx g_e - \Delta_2/E_2(m_e/m_t - 1) \qquad (1)$$
$$g_t \approx g_e - \Delta_2/E_2(m_e/m_l - 1) \qquad (2)$$

where m_l, m_t are the longitudinal and transverse effective masses of the X_3 conduction band, Δ_2 is the spin-orbit splitting of the uppermost valence band and E_2 is the energy gap at X. All four parameters are known from independent experiments as a function of alloy composition [13,14] and it is possible to plot g_l and g_t as a function of x. While g_l drops nearly linearly from $\approx$ 1.94 at x = 0.4 to $\approx$ 1.92 at x = 1.0, g_t is almost constant at 2.00. Thus, equation 1 for g_l reasonably reproduces the experimental values for x = 0.4 and x = 0.6, see above, and for x = 1.0 [5,15]. In particular it predicts the decrease in g_l with increasing x. On the other hand the expression for g_t reasonably accounts for the measured g_t of AlAs [5,15], but does not predict the increase from g_t = 1.947 at x = 0.4 to g_t = 1.99 at x = 1.0. It appears that this failure is due to intervalley mixing of the $T_2(X)$ donor ground state with the $T_2(L)$ donor state, see also ref. [16]. This mixing should be small for AlAs where the X-L separation is about 200 meV but will become significant for x $\approx$ 0.4 where the X and L conduction band minima are nearly degenerate. In this case g_t is not simply $g_t(X)$, but contains also contributions from $g_l(L)$. Since $g_l(L) < 2$ [12] g_t values near 1.95 seem plausible for x $\approx$ 0.4.

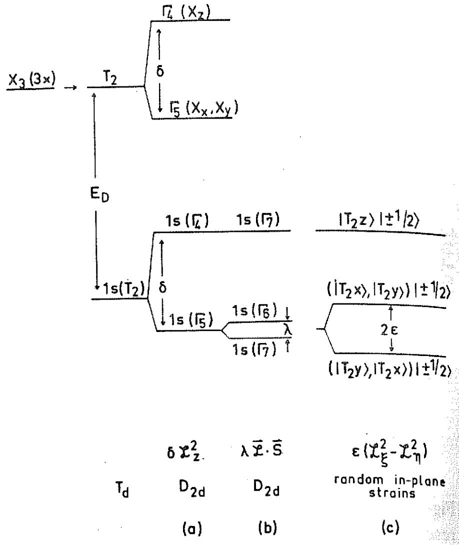

Figure 5. Splitting of the $1s(T_2)$ state of a group III site donor tied to the three X_3 minima in indirect AlGaAs due to a) heteroepitaxial uniaxial strain along the [001] growth direction b) spin-valley interaction, neglecting random in-plane ϵ-type strains c) in-plane ϵ-type strains larger than the spin-valley splitting λ.

The fact that the donor resonance can be understood in an independent valley model is not obvious at first sight, since spin-valley (sv) coupling, $\lambda\mathcal{L}\cdot S$, is expected to split the $1s(\Gamma_5)$ donor ground state into sv states having Γ_6 and Γ_7 symmetry, see figure 5. For the samples studied here one estimates that $|\lambda| \approx 1$ cm^{-1} [10] which is considerably larger than the Zeeman splitting of 0.3 cm^{-1} in our experiment. In this case both Γ_6 and Γ_7 have g_L $\approx$ 0 (H perpendicular to [001]) in obvious contradiction with experiment. Therefore the sv interaction must be quenched. This quenching can not be accidental since the results presented here together with those reported for AlAs [5,15] show that sv interaction effects are negligible over the full indirect alloy range and this must have a more fundamental origin.

We attribute the quenching of the sv interaction to the presence of local, random in-plane strains of the form $\epsilon(\mathcal{L}_\xi^2-\mathcal{L}_\eta^2)$ which override the first order sv splitting leading to purely spin degenerate states, see the right of figure 5, for which g_l and g_t are the appropriate g factors. These ϵ-type strains lower the local symmetry of a donor atom to any subgroup of D_{2d}. The global symmetry, however, remains tetragonal because of the random distribution of ϵ. This distribution of ϵ with both positive and negative values gives equal probabilities for $|T_2x\rangle$ and $|T_2y\rangle$ to be the ground state for each particular Si donor. For the alloy, a natural origin of ϵ-type strains is alloy disorder. However, the case of AlAs:Si suggests that conventional random ϵ-type strains are also important. A reasonable guess for the order of magnitude is $\epsilon \sim 10$ cm^{-1} which fullfills the assumptions, $\epsilon >> \lambda$ and $\epsilon << \delta$, made to explain the data presented.

We now proceed to discuss the annealing results presented in figure 4. When the samples are slowly cooled to liquid helium temperatures in the dark a free electron can be captured into both the shallow Si donor level or the DX level. The relative equilibrium occupation can now be changed by optical excitation of the samples. According to our previous interpretation [8] the photo-enhancement of the shallow donor EPR is due to the transfer of an electron from the DX level into an empty shallow donor level, see process a) in figure 1. At low temperatures the electron remains captured in the shallow level. Therefore the photo-enhanced part of the signal is stable when the excitation light is switched off. However, if the temperature is raised thermal retransfer of the electron into the deep DX level will occur, see process b) in figure 1, and the shallow donor EPR intensity will finally drop to the dark equilibrium value. This model is used to analyse the annealing data shown in figure 4. Since our samples contain $2 \cdot 10^{18} cm^{-3}$ Si donors the DX level can be assumed to be the dominant deep level in the material. In this case practically all electrons thermally released from the shallow donor level are trapped at the DX level if their energy is sufficient to overcome the DX capture barrier. Therefore the temperature range in which the enhanced portion of the EPR signal decays is directly related to the DX barrier height E_c. In that range thermal retransfer of the electrons from DX to the shallow level is negligible since the DX level is considerably deeper than the shallow one. Thus the decay of the EPR signal, $\Delta I/\Delta t$, occurs at a rate proportional to $\exp(E_a/kT)$ where the activation energy E_a is given by $E_a = E_c + E_D$, E_D being the shallow donor binding energy. Determination of E_a would require measurements of the decay rate as a function of temperature. Unfortunately this is not possible since the EPR signal is not observable at the temperatures where it decays. However, we can determine the relative activation energies of the two samples in figure 4. At the annealing temperatures T_A we can write

$$\frac{(\Delta I/\Delta t)_{0.41}}{(\Delta I/\Delta t)_{0.60}} = \frac{\exp(E_a/kT_A)_{0.41}}{\exp(E_a/kT_A)_{0.60}} \qquad (3)$$

From the curves in figure 4 one infers that the left hand side of equation 3 is close to unity which leads to the approximate relation

$$\frac{E_a(0.41)}{E_a(0.60)} \simeq \frac{T_A(0.41)}{T_A(0.60)} \qquad (4)$$

With the T_A values quoted before we get $E_a(0.41)/E_a(0.60) \simeq 0.71 \pm 0.03$. Since $E_D \simeq 40$ meV for both x values the capture barrier height E_c must increase with increasing x in the indirect alloy range. This provides independent confirmation of previous DLTS measurements [7] which gave $E_c(0.4) = 230$ meV and $E_c(0.6) = 300$ meV. The E_a ratio calculated with these values is 0.79 ± 0.07, in remarkable agreement with the value inferred from EPR.

CONCLUSION

In conclusion, we presented experimental evidence that strains severely modify the electronic structure of the shallow Si donor ground state in indirect GaAs/AlGaAs layers. Heteroepitaxial uniaxial strain raises the X_z valley relative to the X_x and X_y valleys. For the $1s(\Gamma_5)$ Si donor ground states tied to this valley doublet the sv splitting is quenched. This unexpected observation is explained by the presence of local, random in-plain strains. A thermal annealing study of the photo-enhanced shallow donor EPR demonstrates that in the indirect alloy range the DX capture barrier height increases with increasing Al content.

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