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Publication Date
1988-07-01
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July 1988

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PRESSURE DEPENDENCE OF THE DX CENTER IN Ga_{1-x}Al_{x}As:Te
IN THE VICINITY OF THE $\Gamma$-X CROSS-OVER

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ABSTRACT

The pressure dependence of the DX center in Ga_{1-x}Al_{x}As:Te has been studied in two samples with $x=0.15$ and 0.35 respectively. The pressure coefficients of the activation energies for both emission and capture were found to change sign when the bandgap of GaAlAs changes from direct to indirect. These results together with previous experiments suggested that electrons can be emitted from and capture into the DX centers via both L and X valleys.

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(PACS: 71.55.Eq)
The properties of deep donors known as DX centers in Ga_{1-x}Al_{x}As alloys are known to depend on the Al concentration and on hydrostatic pressure.\textsuperscript{1-5} So far a number of studies have been performed to determine the effect of alloying on the properties of the DX centers. In particular it has been found that the energy of the DX center followed the L conduction valleys as a function of Al concentration\textsuperscript{5} while the activation energy for emission was almost independent of the alloy concentration.\textsuperscript{4} These results have led to the general belief that the DX centers involved the L conduction band wavefunctions only. In particular Theis\textsuperscript{6} has proposed a model in which emission and capture of electrons into the DX center all occurred through the L valleys only. So far there has been relatively few determinations of the pressure dependence of the capture and emission activation energies for the DX centers, especially for pressures sufficient to change the bandgap of GaAlAs alloys from direct to indirect. Pressure has an advantage over changing the Al concentration in that variations in the DX center properties due to different sample histories and effects of alloy fluctuations can be avoided. The pressure dependence of a deep center's ionization energy and capture barrier height can provide important insights into the nature of the deep center. In this Letter we present results on the pressure dependence of the DX center in Ga_{1-x}Al_{x}As:Te samples with two different amounts of Al over a pressure range where the bandgap of Ga_{1-x}Al_{x}As changes from direct to indirect. We found that the pressure coefficients of the activation energies for both emission and capture changed
sign when the bandgap switched from direct to indirect. Our results are inconsistent with the model of Theis and suggest instead that, at least in Te doped samples, when the lowest conduction band minima are at the X points of the Brillouin zone, the X valleys are involved in the emission and capture of electrons into the DX centers. Thus conduction band minima other than the L valleys are also significant in understanding the properties of the DX center. This is what one would expect for a localized center such as the DX center.

The samples used in this study were Schottky diodes fabricated from GaAlAs epilayers grown on GaAs substrate by liquid-phase-epitaxy. GaAlAs layers with Al fractions of 0.35 and 0.15 have been studied. Both types of samples were doped with $5 \times 10^{16}$ cm$^{-3}$ of Te. The Al concentrations were verified by Raman scattering. Ohmic contacts to the samples were prepared by evaporating Au-Ge alloy to the GaAs substrate followed by a 450 °C anneal for one minute. Schottky barriers were formed by evaporating Al onto the epilayer. Samples were loaded into a diamond-anvil high pressure cell surrounded by epoxy and a soft powder CaSO$_4$ as the pressure medium using a technique described by Erskine et al. Although the use of solid powder as the pressure medium would make the pressure quasi-hydrostatic, experiments using powder as the pressure medium inside the Bridgman anvil devices have shown that the nonhydrostatic stress component can be kept negligible in many experiments. In case of the diamond anvil cell we have estimated the pressure inhomogeneity inside the cell by using several ruby chips placed around the sample and determining the pressure at these ruby
chips by the standard ruby fluorescence technique. The variation in the pressure determined from these ruby chips was typically ±1 kbar. Although uniaxial stress may lift the degeneracy of degenerate conduction band valleys such as those at the L and X points of the Brillouin zone in GaAlAs, we did not observe splitting of the DX centers when the X valleys were the lowest conduction band minima. This suggests that any splitting of the degenerate valleys caused by an uniaxial stress component of the order of 1 kbar was too small to be detected within experimental uncertainty.

Deep level transient spectroscopy (DLTS) were performed on the samples using a capacitance meter and a dual-channel boxcar integrator. From the DLTS spectra the emission rates ($e_n$) of the deep center were determined. The capture rates ($\tau_c^{-1}$) were measured by a standard majority-carrier pulse method at constant temperatures. The transient capacitance signal amplitudes were recorded as a function of the width of the pulses used to fill the traps. The capture rate was determined in a way analogous to the method of Lang. Because of the nonexponential dependence of the signal on pulse width we have determined $\tau_c^{-1}$ from the 1/3-signal points rather than the 1/2-signal points used by Lang.

In the inset of Fig.1 a typical DLTS spectrum of the 35% Al sample at atmospheric pressure is shown. In the 15% Al sample no peaks were observed in the DLTS spectra for pressures below 15 kbar. In all our samples both $e_n$ and $\tau_c^{-1}$ were found to have activated temperature dependence:
\[ \frac{e_n}{T^2} = A_e \exp\left(-\frac{E_e}{kT}\right) \quad (1) \]
\[ (\tau_c)^{-1} = A_c \exp\left(-\frac{E_c}{kT}\right) \quad (2) \]

where \( E_e \) and \( E_c \) denote respectively the activation energies for emission and capture of the electron. Some plots of \( \frac{e_n}{T^2} \) vs \( T^{-1} \) in the 35% Al sample at different pressures are shown in Fig. 1. The changes in \( E_e \) and \( E_c \) induced by pressure for both the 15% and 35% Al samples are shown in Fig. 2. For the 35% Al samples two sets of results obtained from two different chips cut from the same wafer are shown. It should be noted that the DLTS spectra of the DX center showed slight variations from sample to sample.

In sample #1 of the 35% Al alloy, we obtained the values of \( E_e = 0.27 \pm 0.01 \) eV and \( E_c = 0.235 \pm 0.01 \) eV at 1 bar. The corresponding values were 0.28 eV and 0.225 eV in sample #2. These values are to be compared with the values 0.33 \( \pm \) 0.03 eV and 0.26 \( \pm \) 0.03 eV reported by Lang et al.\(^{11}\) in a Te doped sample with 36% of Al.

In spite of this difference of about 0.01 eV in the absolute values of \( E_c \) and \( E_e \) in these two samples, their pressure dependences are quite similar. The values of \( E_e \) and \( E_c \) in the 15% sample at 16 kbar are 0.26 and 0.235 eV respectively.

Because of sample to sample variations, changes smaller than 50 meV in \( E_e \) of DX centers due to alloy variations cannot be determined.\(^4\) On the other hand changes in \( E_e \) induced by pressure for a sample with a fixed Al concentration can be determined with the precision of a few meV (see Fig. 1).

An interesting result in Fig. 2 is the change in the sign of the pressure coefficients of both \( E_e \) and \( E_c \) near the pressures at which the bandgap of GaAlAs changes from direct to indirect. In Figure 2 the arrows indicate the predicted pressures at which the
different conduction minima in GaAlAs cross each other. These cross-over pressures have been calculated from these band edge pressure coefficients: \( \frac{dE_r}{dP} = 11.8 \text{ meV/kbar}; \frac{dE_L}{dP} = 5.5 \text{ meV/kbar} \) and \( \frac{dE_X}{dP} = -1.5 \text{ meV} \) in conjunction with the alloy dependence of the band edges given in Ref. 5. In addition to abrupt changes in the pressure dependences of the activation energies we also found that the DLTS signal strength reached a maximum at the pressure when \( E_e \) was maximum.

Although changes in the dependence of \( E_c \) with Al concentration have been reported by Mooney et al. in Ga\(_{1-x}\)Al\(_x\)As:Si at \( x = 0.4 \) where the bandgap changed from direct to indirect, no variations beyond experimental uncertainty, was found in \( E_e \) with Al concentration. This independence of \( E_e \) on Al concentration was one factor cited by Theis for proposing that electrons could be captured into the DX center only via the L valleys even when the X conduction minima were lowest in energy. We should point out that our results are not inconsistent with those of Mooney et al. Beside any possible difference between varying the Al concentration and pressure and between the dopants used in the two experiments (Si versus Te), our accuracy in determining the variation of \( E_e \) with pressure is significantly higher than that with alloy concentration. The variation in \( E_e \) with pressure is slightly less than 20 meV over the pressure range of our experiment. The uncertainty in our determination of the pressure induced change in \( E_e \) is about 3 meV. On the other hand the variation in \( E_e \) of the DX center from sample to sample with nominally the same alloy concentration is often larger than
20 meV thus it is not surprising that Mooney et al.4 found no dependence of $E_e$ on Al concentration.

We have analyzed our results with the model proposed by Theis.6 By assuming that electrons are captured always through the L valleys, we obtained an equation for calculating the thermal ionization energy ($E_T$) as: $E_T = E_e - E_C + E_{LD}$, where $E_{LD}$ is the energy difference between the L valleys and the lowest conduction minimum, whether at $\Gamma$ or at X. Using this equation and our experimental pressure coefficients we deduced the pressure coefficient $dE_T/dP$ in the direct gap region to be -0.3 and -1.2±1 meV/kbar for the 35% and 15% Al samples respectively. This implies that in the direct gap region the DX center follows the L valleys as a function of pressure consistent with previous work2 and with the Theis model. However, in the indirect gap region we found that $dE_T/dP$ increased to 4.2 and 2.5 meV/kbar respectively for the 35% and 15% Al samples. Such a sudden change in $dE_T/dP$ at the direct to indirect bandgap cross-over would be difficult to explain in the Theis model. Our results suggest that the DX center energy no longer follows the L valley in the indirect gap region. On the other hand, such a sudden change in $dE_T/dP$ can be explained if the symmetry of the final states changes from L to X near the bandgap cross-over. If we assume that in the indirect gap region the X valleys are low enough in energy compared to the L valleys to make emission to the X valleys more likely, $E_T$ would be given simply by $E_e - E_C$. In this case $dE_T/dP$ decreases to -2.8 meV/Kbar and -4.5 meV/kbar respectively in the indirect gap region for the 35% and 15% Al samples. We note that the value of $dE_T/dP$ for the 35% sample is then quite consistent with the value
of -3.0 meV/Kbar obtained by Saxena\textsuperscript{1} in Ga\textsubscript{0.67}Al\textsubscript{0.23}As in the indirect bandgap region. One possible explanation of the breakdown in the Theis model in the indirect bandgap region is that the DX center has significant contribution from the X valleys. Saxena\textsuperscript{1} has arrived at the same conclusion based on the pressure dependence of $E_T$. He has gone one step further in using the experimental pressure coefficient of $E_T$ to express the wavefunction of the DX center as a linear combination of the X and L valley conduction band wavefunctions.

Based on the pressure results we suggested a modification of the Theis model for the capture and emission of electrons from the DX centers. In this model electrons can be captured into the DX centers or emitted from the DX centers to both X and L valleys. In the region when the L valleys are lower than the X valleys, which is the case at low pressures or for low Al concentrations, the DX center wavefunction is dominated by the L valleys and as a result both capture and emission are predominantly to the L valleys. In this region the DX center follows the L valleys both as a function of pressure and alloy concentration as have been noted by many authors. However, when the X valleys become lower in energy relative to the L valleys due to increase in either pressure or Al concentration, it becomes energetically more favorable to emit and capture electrons from the X valleys. Because the separation between the X and L valleys is dependent on pressure and Al concentration, we expect the DX center wavefunction and hence the capture cross-section to vary also with these parameters. We note that this
model is consistent with the properties of the DX centers in indirect bandgap GaAlP alloys where it has been proposed that electrons are predominantly captured from and emitted to the X valleys.\textsuperscript{12}

In conclusion we have presented new results on the pressure dependence of the DX center in GaAlAs alloys doped with Te. The pressure dependence of the emission activation energy changes sign when the bandgap switches from direct to indirect, in disagreement with a recent model proposed by Theis. Based on these results we suggest a modified model which includes the contribution of the X valleys to the DX centers. In addition the pressure coefficients of the capture and emission activation energies reported here are important parameters which characterize a deep center within the multiphonon emission capture theory.\textsuperscript{3,13}

ACKNOWLEDGMENTS

We wish to thank J. Beeman, T. Pederson and J. Kant for their valuable technical assistances, Yihe Huang for performing the Raman scattering to determine the Al concentration and Dr. G. Martinez for helpful discussions. This work is supported by the Director, Office of Basic Energy Sciences, Materials Science Division of the U.S. Department of Energy under contract no. DE-AC03-76SF00098.
REFERENCES

8. See, for example, A. S. Balchan and H. G. Drickamer, Rev. of Sci. Instruments, 32, 308 (1961) and references to earlier work by P. W. Bridgman cited in this article.
10. In our case where the concentration of DX centers is comparable to the carrier concentration, it is more reasonable to determine C from the initial filling time when most of the electrons are still in the conduction band and most of the DX centers are empty.


FIGURE CAPTIONS

Fig. 1: Plot of $e_n/T^2$ versus $1/T$ for the DX center in a Ga$_{0.65}$Al$_{0.35}$As:Te sample under four different pressures. The inset shows a DLTS spectra in the same sample at 1 bar. Window times: $t_1=1$ sec, $t_2=2$ sec. Filling pulse width: 200 ms.

Fig. 2: Pressure induced changes in (a) the emission activation energy ($E_e$) and (b) the capture activation energy ($E_c$) in Ga$_{1-x}$Al$_x$As:Te. The closed circles and open circles denote respectively the results for samples #1 and #2 of the $x=0.35$ alloy while the crosses are the results for the $x=0.15$ sample. The vertical and horizontal bars around the experimental points represent the estimated experimental errors. The lines are drawn to guide the eyes. The arrows represent the calculated pressures at which the $\Gamma$, L and X conduction band minima are expected to cross each other.
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