Title

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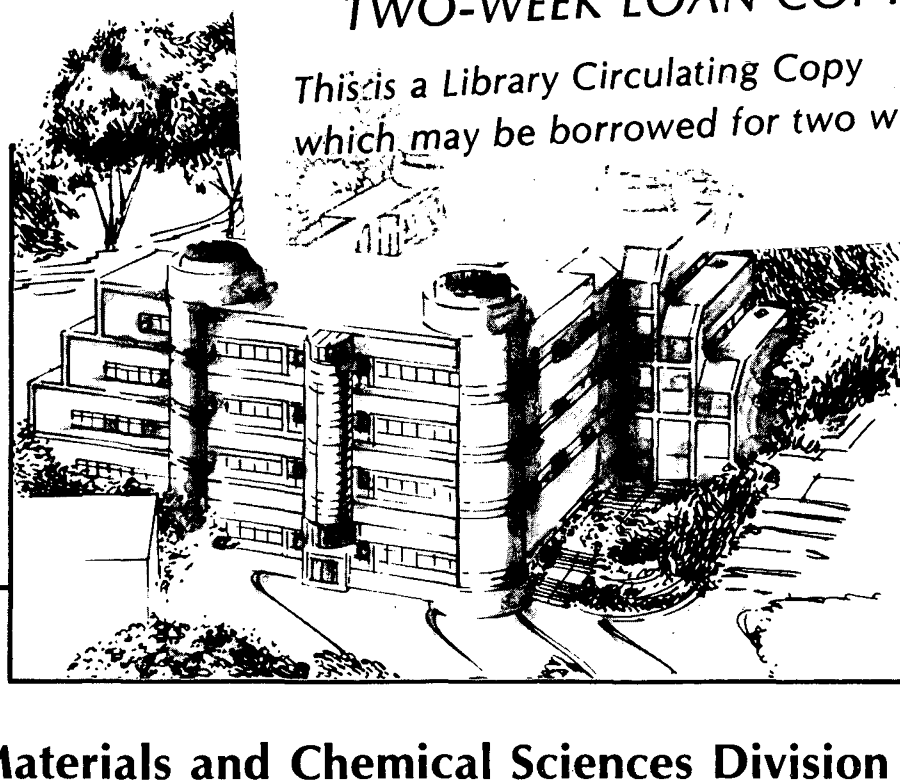

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REDUCTION OF CAPTURE BARRIER HEIGHT OF PRESSURE-INDUCED DEEP DONORS (DX CENTER) IN GaAs:Si

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ABSTRACT

When boron was introduced into GaAs:Si, the DX-like deep donors which appeared in GaAs under pressure were found to disappear while new centers with reduced capture barrier heights appeared. It is proposed that B atoms paired up with Si donor atoms. The reduction in the capture barrier height is interpreted in terms of a recent model proposed by Chadi and Chang.

INTRODUCTION

Recently several experiments[1-3] have shown that hydrostatic pressure above 20 kbar can transform shallow donors in GaAs, such as Si and Te, into deep donors with many of the properties of the DX centers in GaAlAs.[4,5] Some of these characteristics are: (a) thermal depth from the conduction band of ~0.1 eV and optical depth of ~1 eV; and (b) a very small thermally activated electron capture cross section at low temperatures giving rise to persistent photoconductivity (PPC). In this paper we present new and interesting results on the effect of boron in reducing the capture barrier height of these pressure-induced deep donors (PIDD) in GaAs:Si. Significance of our result in controlling PPC due to DX centers in devices will also be discussed.

EXPERIMENTAL DETAILS AND RESULTS

The effect of B on PIDD was first discovered in bulk GaAs grown by liquid encapsulated Czochralski (LEC) method and doped with Si. The concentration of B and Si in these samples was determined by SIMS analysis to be $2x10^{17}$ cm^{-3} and $9x10^{16}$ cm^{-3} respectively. The carrier concentration as supplied by the vendor was $4x10^{16}$ cm^{-3}. Subsequently the effect was reproduced in bulk GaAs:Si grown by the horizontal Bridgman (HB) technique and implanted with B ions. The starting HB GaAs contained Si (N_D-N_A=$2x10^{17}$ cm^{-3}) but no Boron. The GaAs wafer was then ion-implanted with B at 25-180 KeV to form a ~0.5 micron thick top layer containing about $2x10^{18}$ cm^{-3} of B. This was followed by one hour of annealing at 500 C in a nitrogen atmosphere. After implantation and anneal

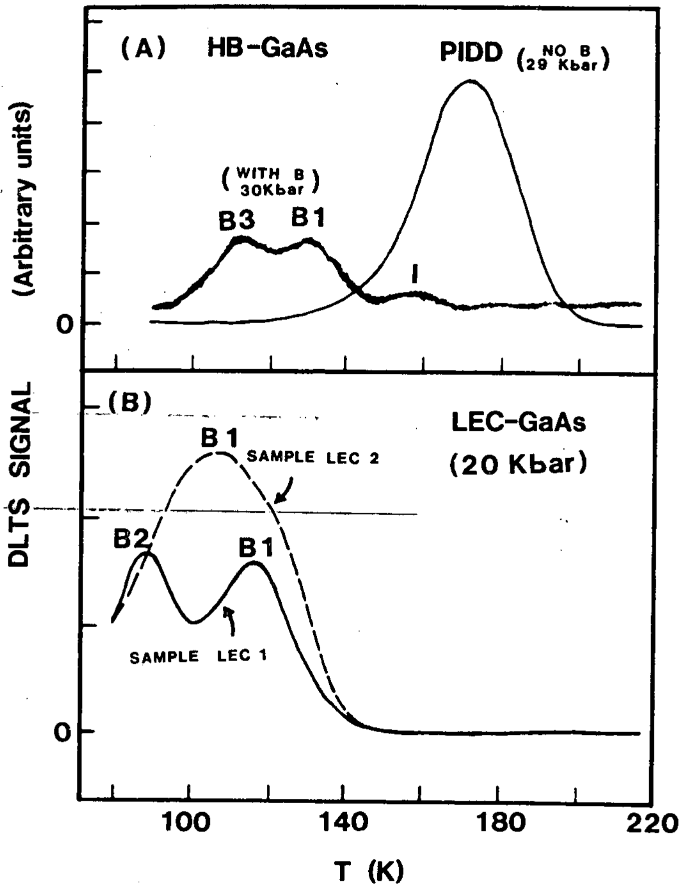

Figure 1. DLTS spectra of (A) HB GaAs:Si sample with and without B; and (B) LEC GaAs containing B and Si. The window times used in obtaining these DLTS spectra were t_1=1 ms and t_2=0.5 ms and the filling pulse width was 0.5 ms.

the sample carrier concentration was estimated from C-V measurements and was found to have been reduced by a factor of ~4. Schottky diodes were fabricated from both kinds of samples in exactly the same way as described in Ref. 2. The pressure medium and the technique for loading the samples into the diamond anvil high pressure cell have already been described elsewhere [2,3]. Pressure inside the cell was determined by the standard ruby flourescence technique. Pressure inhomogeneity, as deduced from the pressure at several ruby chips surrounding the sample, was typically ±0.5 kbar.

The presence of PIDD in these samples was detected by standard deep level transient spectroscopy (DLTS) and constant temperature capacitance transient measurements [2]. Figure 1 shows the DLTS spectra of two LEC GaAs samples containing B under pressure. We found that diodes fabricated from the same LEC GaAs wafer show slight variations in their DLTS peaks under pressure. In one LEC GaAs:Si sample (labelled as LEC1) there are two peaks (B1 and B2 in Fig. 1(B)) while in the other sample (denoted as LEC2) there is only one broad peak centered around 110 K. From the emission and capture behavior of the 110 K peak we conclude that it corresponds to peak B1 in LEC1. This broad peak in LEC2 actually contained another unresolved peak with a much faster capture rate. Quantitative measurements on the other peak was not possible since it was overshadowed by the larger peak B1. For comparison, the spectrum of the PIDD in a HB GaAs without B is shown in Fig. 1(A).

Although there are many similarities between the DLTS peaks in the LEC GaAs samples and the PIDD in the HB GaAs sample, there are also significant differences. For example, in the LEC samples DLTS peaks started to appear above 16 kbar, whereas in the HB samples without B, peaks typically did not appear until above 24 kbar. In addition the peaks B1 and B2 occurred at temperatures much lower than that of the PIDD in the HB GaAs:Si samples[2]. Finally their capture rates were also significantly *larger* than that of the PIDD in HB GaAs:Si. A detailed SIMS analysis of the LEC samples showed no significant amount of impurities besides B and Si. To verify that the new peaks B1 and B2 in the LEC GaAs:Si are related to B we compare the DLTS spectra of HB GaAs:Si before and after B ion implantation. The results are shown in Fig. 1(A). Indeed we found that the PIDD peak disappeared after B implantation while new peaks, labelled B1 and B3, appeared at temperatures comparable to those found in LEC samples. These results provide very strong evidence that B is responsible for the difference in the behaviors of the deep donors in the LEC and HB GaAs samples under pressure. The small peak labelled I in Fig. 1(A) was observable at atmospheric pressure and did not

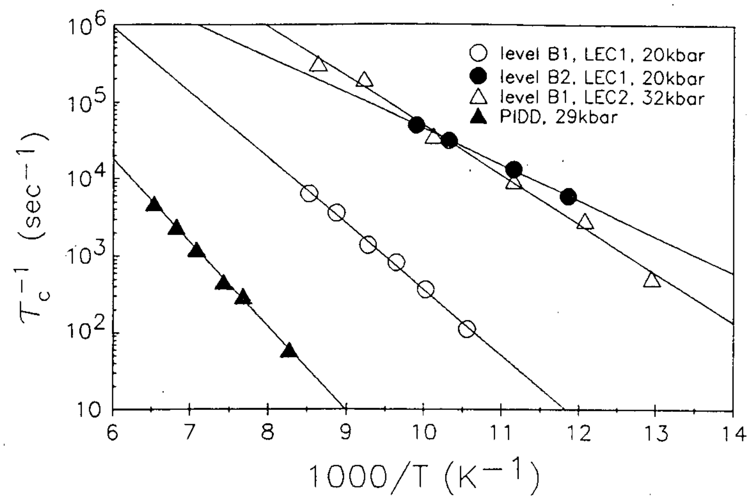

Figure 2. A comparion of the Arrhenius plots of the capture rates for the PIDD in GaAs and for the deep levels in LEC GaAs containing B.

show much pressure dependence so it has been attributed to deep levels associated with defects induced by ion implantation.

Both emission and capture processes in these new centers in GaAs containing B are found to be thermally activated according to the equations:[2]

$$e_n/T^2 = A_e \exp-(E_e/kT) \quad (1)$$

and

$$(\tau_c)^{-1} = A_c \exp-(E_c/kT) \quad (2)$$

where e_n is the emission rate, E_e is the emission activation energy, E_c is the capture barrier height, τ_c is the capture time constant, T is the sample temperature and k is the Boltzmann constant. E_e and E_c are related to each other via the equation: $E_e=E_c+E_t$ (3)
where E_t is the thermal depth of the center relative to the conduction band. Some Arrhenius plots of the capture rate for B1 and B2 are compared with those of the PIDD in Fig. 2. The values of E_e, E_c, the prefactors A_e, and A_c deduced from these plots for the PIDD and the peaks B1 and B2 in LEC1 are summarized in Table 1. Note that the values for the peaks correspond to different pressures.

Table 1 Capture barrier height and emission activation energy of the PIDD in HB and LEC GaAs.

Sample	HB	LEC1	
Peak	PIDD (29 kbar)	B1 (20 kbar)	B2 (20 kbar)
E_e (eV)	0.30	0.18	0.14
E_c (eV)	0.22	0.16	0.09
A_e ($s^{-1}T^{-2}$)	2.5×10^7	7.9×10^6	1.6×10^7
A_c (s-1)	7.9×10^9	7.9×10^{10}	2×10^9

Figure 3 shows the pressure induced change of E_e and E_c for level B1 and B2 in sample LEC1.

In case of the B implanted HB GaAs:Si sample the peaks B1 and B3 were rather weak and observable only at pressures close to 30 kbar so it was not possible to determine reliably some of their properties. Probably the quality of the Schottky barrier was poorer in this sample because the damages from the implantation were not completely annealed out.[6] However from the values of E_e and A_e we concluded that the peak around 130 K in Fig. 1(A) was essentially the same peak B1 in the LEC samples.

DISCUSSIONS

From Table 1 it is clear that boron changes significantly some of the properties of the PIDD in GaAs:Si. The most striking effect is the reduction of E_c and a factor of ten increase in A_c. Using the pressure coefficient of E_c for the PIDD given in Ref. 2 we deduce a value of 0.24 eV for its E_c at 20

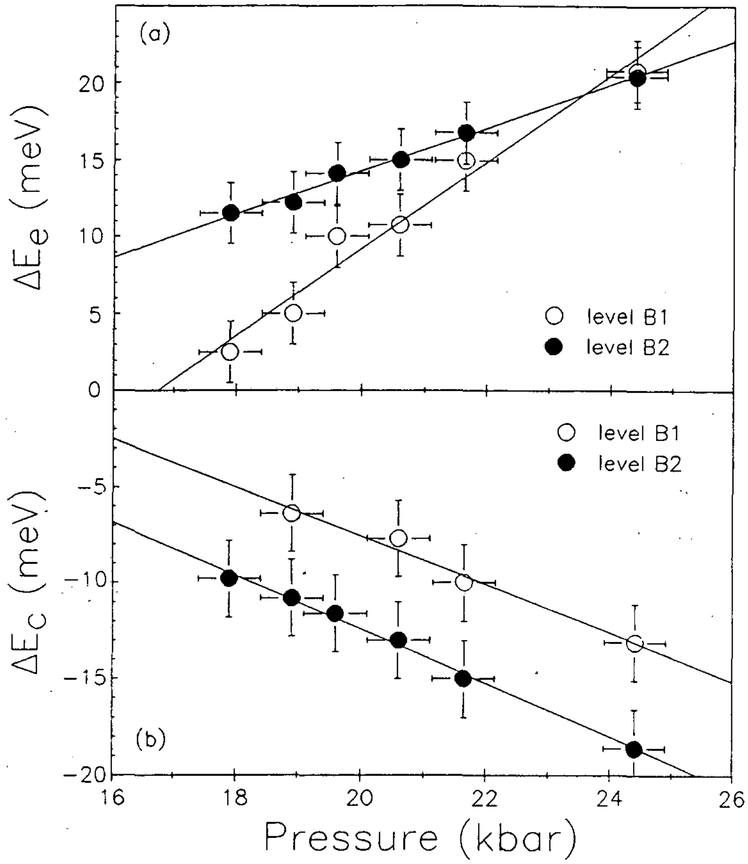

Figure 3. The pressure induced change in the (a) emission and (b) capture activation energies of the level B1 and B1 in the sample LEC1.

kbar. Compared to the value of E_c for peak B1 there is a decrease of about 60 meV as a result of B. Combined with the larger value of A_c for B1, this has pronounced effects on PPC. For example at a pressure of 30 kbar and temperature of 77 K, the capture time constant of the PIDD in the HB GaAs is estimated to be $4x10^4$ s while the corresponding time constant of level B1 in the LEC1 sample would be $7x10^{-2}$ s. The difference in time constant between the two levels is almost six orders in magnitude! Based on the similarity in properties between the PIDD in GaAs under pressure and the DX centers in AlGaAs alloys, this result suggests that PPC in devices, such as modulation-doped field effect transitors, may be controlled by the incorporation of B. A preliminary attempt to introduce B into AlGaAs by ion implantation was not successful because deep centers introduced by implantation were not completely annealed out even at 800 C. Further studies are required to understand the incorporation of B into AlGaAs.

From Table 1 it appeared that E_e and hence E_t was also reduced by B. Using Eq. (3) we deduced the value of E_t to be 80 meV in the HB GaAs at 29 kbar and 20 meV in LEC1 at 20 kbar. Recently Theis [7] has proposed that emission and capture to the DX center could occur only through the L valleys. Within this model,the relevant thermal ionization energy (E_t') is the energy separation between the L conduction valleys and the DX level rather than the Γ valley and the DX level. Taking into consideration that in GaAs the Γ and L valley separation is 110 meV at 29 kbar, we deduce the value of 190 meV for E_t' of the PIDD and a corresponding value of 155 meV for the level B1. Thus, relatively speaking, the effect of B on E_t' is much smaller than its effect on E_c.

The reduction of E_c for PIDD in GaAs:Si by B suggests that there is interaction between B and shallow donors such as Si in GaAs. Pairing of B and shallow donors in GaAs has previously been suggested by Morrison and Newman[8] based on far-infrared absorption measurements and by Rao et al.[9] as a possible explanation of the effect of B on donor enhanced interdiffusion in GaAs-GaAlAs superlattices. Otherwise it is generally assumed that B is electrically inactive in GaAs at atmospheric pressure. It is now generally believed that the PIDD and the DX center both involve a substitutional donor and not a complex as suggested by Lang et al. [4,5]. Recently two groups [10,11] have independently proposed that the DX center is a doubly charged donor (d^{--}). In the model of Chadi and Chang the DX center moves along a bond away from one of its four nearest neighbors until it becomes essentially three-fold coordinated. Thus a clue in understanding the effect of boron on the PIDD in GaAs would lie in the effect of boron on the Si-As bond and on the lattice relaxation of the Si donor. We note that according to Phillip's dielectric electronegativity scale[12] B is more electronegative than even As. Thus it is possible that , when B and Si occupy next nearest neighbor Ga sites, the presence of B will weaken the Si-As bond charge in the B-As-Si triplet because electrons which normally concentrate more on the As atoms will now be attracted towards the B atom. As a result the Si donor has to overcome a smaller barrier in moving from its normally four-fold coordinated site to the three-fold coordinated site. At atmospheric pressure, the d^{--} state is above the conduction band so this effect of B is not observable. Only when the resonant d^{--} state is brought into the gap by high pressure or alloying then this effect of B becomes observable.

CONCLUSIONS & ACKNOWLEDGEMENTS

We have found that boron will reduce the capture barrier height of pressure-induced deep donors in GaAs:Si. Based on a recent theoretical model of the DX center proposed by Chadi and Chang [12] we suggest that, due to its large electronegativity, B will weaken the Si-As bond and hence reduce the barrier between the relaxed doubly charged state and the unrelaxed neutral states of the Si donors.

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REFERENCES

1. Mizuta, M., Tachikawa, M., Kukimoto, H., and Minomura, S.: Jpn. J. Appl. Phys., 1985, 24, L143
2. Li, M.F., Yu, P. Y., Weber, E.R., and Hanson, W.L.: Appl. Phys. Lett., 1987, 51, 349
3. Li, M.F., Yu, P. Y., Weber, E.R., and Hanson, W.L.: Phys. Rev., 1987, B36, 4531
4. Lang, D.V., Logan, R.A., and Jaros, M.: Phys. Rev., 1979, 19, 1015
5. Lang, D. V.: in Deep Centers in Semiconductors, ed. by S. T. Pantelides, 1985, Gordon and Breach, New York, 489
6. Rao, E.V.K., Duhamel, N., Favennec, P.N. and Haridon, H.L.: J. Appl. Phys., 1978, 49, 3898
7. Theis, T.: in Proc. of the 14th International Symposium on GaAs and Related Compounds, 1987, Heraklion, Crete (to be published).
8. Morrison, S.R. and Newman, R.C.: J. Phys., 1974, C7, 633
9. Rao, E.V.K., Ossort, P., Alexander, F. and Thibierge, H.: Appl. Phys. Lett., 1987, 50, 588
10. Chadi, J., and Chang, K.J.: Phys. Rev. Lett., 1988 (in press)
11. Khachaturyan, K., Weber, E.R., and Kaminska, M.: unpublished
12. Phillips, J.C.: in Covalent Bonding in Crystals, Molecules, and Polymers, 1969, University of Chicago Press, Chicago

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