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EFFECT OF BORON ON THE PRESSURE INDUCED DEEP DONORS IN GaAs:Si

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ABSTRACT

We found that when boron was introduced into GaAs:Si the deep level induced by pressure exceeding 20 kbars reported previously by Mizuta et al. (Jpn. J. Appl. Phys. **24**, L143 (1985)) disappeared while new deep donor levels with reduced emission and capture activation energies appeared. It is proposed that B atoms paired up with Si donor atoms and the resultant change in the short range potential of the Si donor atoms depressed the capture activation energy of the pressure induced deep donor.

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Recently several experiments[1-3] have shown that when hydrostatic pressure above 20 kbar was applied to GaAs containing shallow donors such as Si, a deep donor with many of characteristics of the DX centers in GaAlAs appeared.[4,5] Since GaAs under pressure can be better characterized than GaAlAs alloys, these pressure induced deep donors (PIDD) in GaAs are ideal for studying phenomena which are associated with metastable states of deep centers such as persistent photoconductivity. In this Letter we report the discovery of an unexpected effect of boron on the PIDD in GaAs:Si. So far the effect of B in GaAs has been studied by several authors.[6-10] Most of these studies have concluded that B tends to replace Ga atoms and the substitutional B atoms are electrically inactive.[8-10] However, we find that when B is present in GaAs doped with Si the PIDD disappear and new deep donors with significantly reduced binding energies and capture barrier heights appear. We attribute the effect of B on the PIDD to the formation of B-Si pairs which change the lattice relaxation and hence the binding energies and capture barrier heights of the PIDD. The significance of our results on models of the DX center and persistent photoconductivity will also be discussed.

The effect of B on PIDD has been studied in two kinds of GaAs samples. The first kind of samples consist of bulk GaAs grown by the horizontal Bridgman (HB) technique and doped with Si (N_D-N_A=2x10^{17} cm^{-3}) but no detectable amount of B.[11] The GaAs wafer was then implanted with B at 25-180 KeV to form an approximately 0.5 micron thick top layer containing about 2x10^{18} cm^{-3} of B. This was then followed by one hour of annealing at

500 C in a nitrogen atmosphere. After implantation and anneal the sample carrier concentration as determined from the C-V measurement was reduced to about 5×10^{16} cm^{-3}. The second kind of samples consist of liquid encapsulated Czochralski (LEC) grown bulk GaAs doped with Si.[12] The concentration of B and Si in these samples was determined by SIMS analysis to be 2×10^{17} cm^{-3} and 9×10^{16} cm^{-3} respectively. The carrier concentration as supplied by the vendor was 4×10^{16} cm^{-3}. Schottky diodes were fabricated from both kinds of samples in exactly the same way as described in Ref. 2. The carrier concentration in the sample was checked by C-V measurement at ambient pressures. Only diodes with good C-V curves were loaded into a diamond anvil high presure cell. The pressure medium and technique for determining the pressure inside the cell are all similar to those described by Erskine et al.[13] The pressure variation inside the cell as determined by measuring the fluorescence from several ruby chip scattered around the sample was typically ± 1 kbar. The activation energies for emission and capture of any PIDD have been measured up to about 30 kbar by standard methods such as deep level transient spectroscopy (DLTS) and constant temperature capacitance transient measurements.[2]

The effect of boron on the PIDD in GaAs:Si was discovered accidentally when we were studying the effect of pressure on shallow donors in LEC grown GaAs:Si. Figure 1(B) shows the DLTS spectra of two samples fabricated from the same LEC GaAs:Si wafer. We found that in these samples pressure above 16 kbar produced strong deep donor peaks (labelled B1 and B2) in the DLTS spectra at temperatures much lower than those reported by Mizuta et al.[1] and by ourselves in HB GaAs:Si samples[2] (shown in Fig. 1(A)). In addition their capture rates were significantly larger than the PIDD we reported earlier in HB GaAs:Si. A detailed SIMS analysis of the samples showed no significant amount of impurities besides B and Si. To verify that the peaks B1 and B2 in the LEC GaAs:Si are indeed caused by the presence of B we compare the DLTS spectra of HB GaAs:Si before and after B ion implantation. The results are shown in Fig. 1(A). The interesting feature of Fig. 1(A) is the complete disappearance of the PIDD peak after B implantation and the appearance of peaks labelled B1 and B3 at temperatures comparable to those found in the LEC grown GaAs:Si samples. The small peak labelled I in Fig. 1(A) was observable at atmospheric pressure and did not show much pressure dependence so it has been attributed to deep levels associated with defects induced by ion implantation. In contrast the peaks B1, B2 and B3 were not observable at atmospheric pressure and only appeared at pressures above 16 kbar.

To check whether these new pressure induced deep level peaks in the LEC samples and in the B implanted HB samples are related to each other and to the PIDD in GaAs without B, we have determined their capture and emission properties as a function of temperature between 90 and 120 K. We found that their emission and capture properties are qualitatively very similar to each other and to the PIDD in that theses processes are all activated according to the equations:[2]

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

and $$(\tau_e)^{-1} = A_c \exp-(E_c/kT) \qquad (2)$$

where e_n is the emission rate, E_e is the emission activation energy, and E_C is the capture activation energy, τ_e is the capture time constant,[2] T is the sample temperature and k is the Boltzmann constant. The only difference is that the values of E_e, E_C, the prefactors A_e, and A_C and some of their pressure dependences for these new deep donors differ in magnitude from the PIDD in GaAs without B. For comparison purpose the results for these new deep centers are listed in Table 1 with the corresponding values for the PIDD in the HB GaAs:Si sample without B.

In case of the LEC GaAs:Si samples we found that diodes fabricated from the same wafer show slight variations in their DLTS peaks under pressure. Similar small variations from sample to sample have been commonly observed for the DX centers in GaAlAs alloys. In the LEC GaAs:Si sample 2 (to be abbreviated as LEC2) shown in Fig. 1 (B) there is only one broad peak centered around 110 K while sample 1 (to be denoted as LEC1) shows two peaks. From the emission and capture behavior of the peak at 110 K we conclude that it corresponds to peak B1 in sample 1. We also found evidence that this broad peak in LEC2 actually contained another unresolved peak with a much faster capture rate. We were not able to obtain quantitative measurements on the other peak because it was overshadowed by the larger peak B1. In both these samples we estimated that nearly all the shallow donors were converted by pressure into the deep levels. In the case of the B implanted HB GaAs:Si sample the peaks B1 and B3 were quite weak and observable only at pressures close to 30 kbar so it was not possible to determine reliably their E_c nor the pressure coefficients of E_c and E_e. The signals in this sample were relatively weak because of two factors: firstly the carrier concentration is lowered by about a factor of four after B implantation and secondly the quality of the Schottky barrier was poorer in this sample probably because the damage from the implantation was not completely annealed out.[6] As a result of the second factor it was not possible to estimate the concentration of the deep centers responsible for the levels B1 and B3. However from the values of E_e and the prefactor A_e we identify the peak around 130 K as essentially the same as the peak B1 in the LEC samples.

From the above results we conclude that boron is responsible for the disappearance of the PIDD in GaAs:Si reported previously by Mizuta et al. and by ourselves[1,2] and the appearance of new donor peaks with activation energies different from the PIDD. The disappearance of the PIDD suggested 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[14] based on far-infrared absorption measurements and by Rao et al.[10] as a possible explanation of the effect of B on donor enhanced interdiffusion in GaAs-GaAlAs superlattices. Other than this we are not aware of any report on the effect of such pairing on the electrical activity of shallow donors in GaAs at atmospheric pressure. Here we will speculate on some of the reasons why such pairing can have a significant effect on the PIDD.

Although the structure of the PIDD in GaAs and of the related DX center in GaAlAs is still controversial, it is now generally believed that, at least in case of the PIDD, the center involves a substitutional donor and not a complex consisting of a donor and another defect as suggested by Lang et al. [4,5] for the DX center. Under sufficient pressure the donor atom suffers lattice relaxation which results in it having a rather large E_c. There is controversy[2] as to how large is this lattice relaxation but there seems to be general agreement that some lattice relaxation occurs under pressure and is responsible, at least partially, for some of the unusual properties of the PIDD. Also it is generally accepted that the DX center and probably also the PIDD is a localized center with contributions to its wavefunction coming from several critical points of the Brillouin zone.[15] Some authors, such as Saxena,[15] have proposed a phenomenological model for the DX center in which the L and X valleys are coupled by the impurity potential. Others authors have suggested that the lattice relaxation of the PIDD in GaAs and of the DX center in GaAlAs involved displacement of the substitutional donor atom as in a Jahn-Teller distortion.[16,17] While the validity of these models is still debatable the importance of the X and L conduction minima and of their interaction with phonons in determining the properties of the PIDD seems to be certain. Thus a clue in understanding the effect of boron on the PIDD in GaAs would lie in the possible effects boron can have on the local electronic structures and electron-phonon interaction in the vicinity of the Si donor.

First we note that according to Phillip's dielectric electronegativity scale[18] B is more electronegative than even As. Then it is conceivable that in GaAs codoped with B and Si, B and Si will be attracted to each other so that they occupy next nearest neighbor Ga sites. The presence of B may weaken the Si-As bond charge in the B-As-Si triplet because electrons which normally tend to concentrate more on the As atoms will now be attracted towards the B atom. This effect of the B will change the short range potential around Si_{Ga} but will not affect its long range Coulomb potential. As a result,at atmospheric pressure when Si_{Ga} is a shallow donor, boron produces no observable effect. Only under pressure when Si_{Ga} becomes a deep donor does the effect of boron become significant. The weakening of the Si-As bonds will probably reduce the electron-phonon interaction and hence reduce the lattice relaxation. Recently Wentzcovitch and Cohen[19] have calculated the band structure of BAs using ab initio pseudopotential methods. They found that, as a result of the large electronegativity of boron, the ordering of the conduction bands at the X point in BAs was reversed from those of GaAs and other III-V semiconductors. Thus based on Saxena's model of the DX center one may expect that B will influence the DX center through its effect on the X conduction band minima.

The above arguments suggested that boron will affect the Si donor energy levels under pressure when the center is deep. Based on the assumption that B will weaken the electron-phonon interaction we proposed that the peak B1 can be identified with the next nearest neighbor Si-B pair in GaAs. Presumably the other peaks B2 and B3 which vary somewhat from sample to sample can be associated with complexes involving more than one B, such as Si surrounded by two B atoms in the next nearest neighbor sites. That the peaks B2 and B3 both have much larger capture cross sections is consistent with the notion that more B surrounding Si will further reduce the lattice relaxation and hence the capture activation energy.

Perhaps the most significant result of this work is the fact that the deep donor levels in GaAs:Si containing B all have a much smaller capture time constant τ_e than the corresponding PIDD in GaAs:Si. From our data we estimated the capture time constants at 77 K for the levels PIDD, B1 and B2 to be 4×10^4 sec, 7×10^{-2} sec and 10^{-4} sec respectively under an applied pressure of 30 kbar. Thus these results suggested that perhaps persistent photoconductivity in n-GaAlAs and in devices using GaAlAs, such as modulation-doped field effect transitors, can also be eliminated by the introduction of boron. Such possibilities are currently being investigated.

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REFERENCES

1. M. Mizuta, M. Tachikawa, H. Kukimoto and S. Minomura, Jpn. J. Appl. Phys. 24, L143 (1985).
2. M. F. Li, P. Y. Yu, E. R. Weber and W. Hansen, Appl. Phys. Lett. 51, 349 (1987).
3. M. F. Li, P. Y. Yu, E. R. Weber and W. Hansen, Phys. Rev. B36, 4531 (1987).
4. D. V. Lang, R. A. Logan and M. Jaros, Phys. Rev. B19, 1015 (1979).
5. D. V. Lang, in **Deep Centers in Semiconductors**, ed. by S. T. Pantelides (Gordon and Breach, New York, 1985) p.489.
6. E. V. K. Rao, N. Duhamel, P. N. Favennec and H. L. Haridon, J. Appl. Phys. 49, 3898 (1978).
7. L. B. Ta, H. M. Hobgood and R. N. Thomas, Appl. Phys. Lett. 41, 1091 (1982).
8. T. Itoh and M. Nomura, Jpn. J. Appl. Phys. 22, L389 (1983).
9. J. Osaka, F. Hyuga, T. Kobayashi, Y. Yamada and F. Orito, Appl. Phys. Lett. 50, 191 (1987).
10. E. V. K. Rao, P. Ossort, F. Alexander and H. Thibierge, Appl. Phys. Lett. 50, 588 (1987).
11. Obtained from Wacker Chemitronic GmbH.
12. Obtained from Hewlett-Packard Co.
13. D. Erskine, P. Y. Yu and G. Martinez, Rev. of Sci. Instrum. 58, 406 (1987).
14. S. R. Morrison and R. C. Newman, J. Phys. C7, 633 (1974).
15. A. Saxena, Appl. Phys. Lett. 36, 79 (1980).
16. T. Morgan, Phys. Rev. 34, 2664 (1986).

17. K. A. Khachaturyan and E. R. Weber (unpublished).

18. J. C. Phillips, in **Covalent Bonding in Crystals, Molecules, and Polymers** (University of Chicago Press, Chicago, 1969).

19. R. M. Wentzcovitch and M. L. Cohen, J. of Phys. C 19, 6791 (1987).

TABLE CAPTION

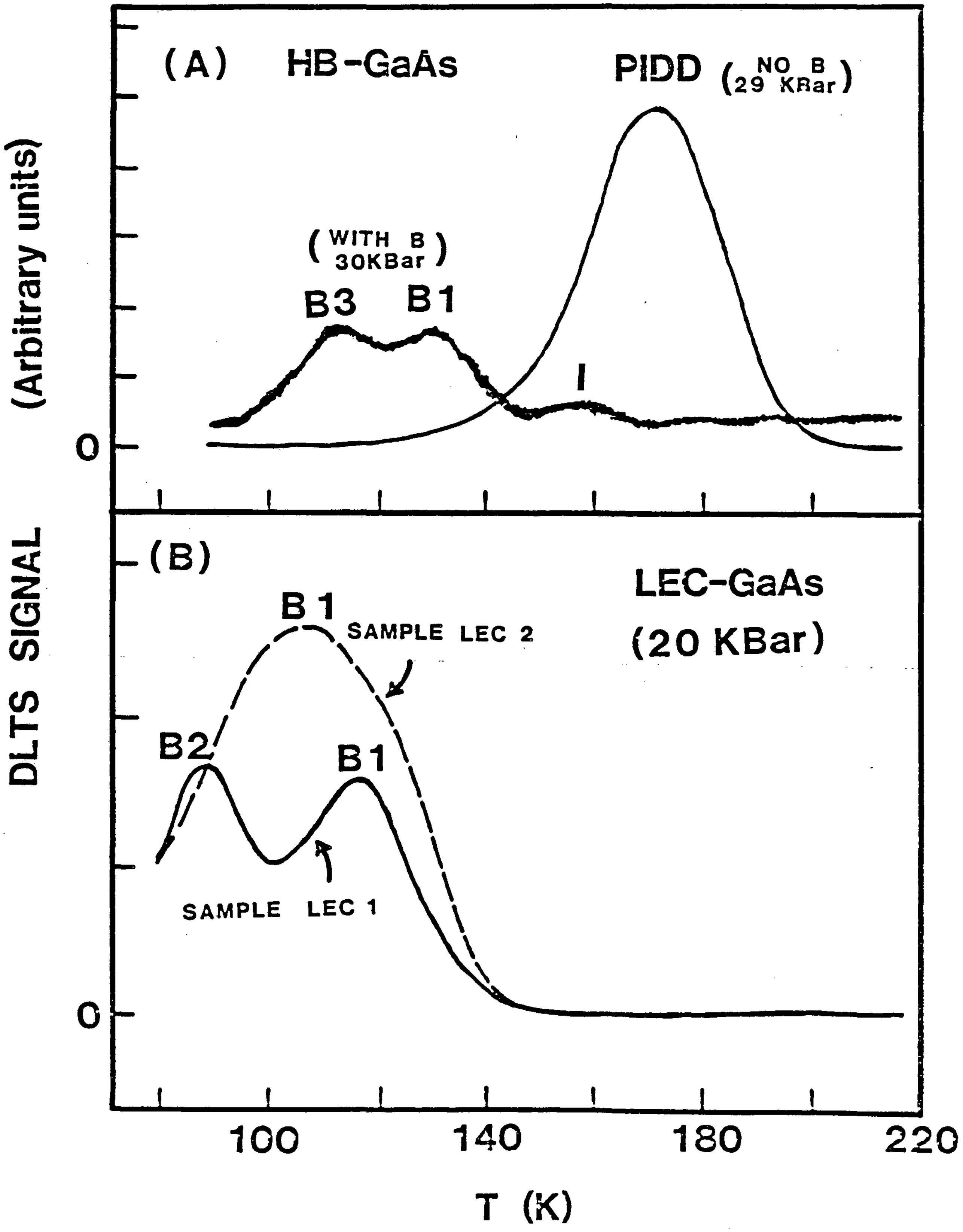
Table 1 A summary of the emission and capture properties of the pressure induced deep donors in GaAs:Si containing boron. The corresponding results in GaAs:Si not containing boron are also presented for comparison.

TABLE 1

PEAK		HB GaAs:Si	HB GaAs:Si,B	LEC GaAs:Si,B	
				SAMPLE 1	SAMPLE 2
		P=29 kbar	P=30 kbar	P=20 kbar	P=20 kbar
PIDD	E_e (eV)	0.30 ± 0.01			
	E_c (eV)	0.22 ± 0.01			
	A_e	2.5×10^7			
	A_c	7.9×10^9			
	$\frac{dE_e}{dP}\left(\frac{meV}{kbar}\right)$	-1.3			
	$\frac{dE_c}{dP}\left(\frac{meV}{kbar}\right)$	-2.1			
B1	E_e (eV)		0.18 ± 0.06	0.18 ± 0.002	0.15 ± 0.03
	E_c (eV)			0.16 ± 0.02	0.13 ± 0.03
	A_e		10^6	7.9×10^6	1.6×10^6
	A_c			7.9×10^{10}	16×10^{10}
	$\frac{dE_e}{dP}\left(\frac{meV}{kbar}\right)$			1.4	
	$\frac{dE_c}{dP}\left(\frac{meV}{kbar}\right)$			-1.4	
B2	E_e (eV)			0.14 ± 0.03	
	E_c (eV)			0.09 ± 0.03	
	A_e			1.6×10^7	
	A_c			2.0×10^9	
	$\frac{dE_e}{dP}\left(\frac{meV}{kbar}\right)$			2.9	
	$\frac{dE_c}{dP}\left(\frac{meV}{kbar}\right)$			-1.3	
B3	E_e (eV)		0.12 ± 0.06		
	A_e		10^3-10^5		

FIGURE CAPTION

Figure 1 (A) DLTS spectra of horizontal Bridgman GaAs:Si with and without B ion implantation. Note that the signal in the B implanted sample has been multiplied by a factor of five. (B) DLTS spectra of two LEC grown GaAs:Si samples. For these DLTS spectra the window times of t_1= 1 ms and t_2= 0.5 ms and filling pulse width of 0.5 ms have been used.



(A) HB-GaAs
PIDD (NO B 29 KBar)
(WITH B 30KBar)
B3
B1
I
0
(B)
LEC-GaAs
(20 KBar)
B1
SAMPLE LEC 2
B2
B1
SAMPLE LEC 1
0
DLTS SIGNAL (Arbitrary units)
100
140
180
220
T (K)

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