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Unusual behaviour of the Ge DX centre in GaAs: coexistence of two localized donor states

P J van der Wel†, P Wisniewski‡, T Suski‡, J Singleton†§, C Skierbiszewski‡, L J Giling†, R Warburton§, P J Walker§, N J Mason§, R J Nicholas§ and M Eremets¶

† Experimental Solid State Physics III and High Field Magnet Laboratory, University of Nijmegen, Toernooiveld, NL-6525ED Nijmegen, The Netherlands
‡ UNIPRESS, Polish Academy of Sciences, 01-142 Warszawa, Poland
§ The Clarendon Laboratory, Parks Road, Oxford OX1 3PU, UK
¶ High Pressure Institute, Russian Academy of Sciences, Troitsk, Moscow Region, 142092 Russia

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Abstract. Hall measurements have been performed as a function of hydrostatic pressure and temperature to study the effect of deep donor levels on the electron concentration and mobility in bulk GaAs heavily doped with germanium. For the first time, the coexistence of the metastable DX centre and the non-metastable localized deep A1 level has been unambiguously observed in GaAs. Furthermore, we have determined the energy positions and pressure dependences of both resonant levels (0.066 eV and $-6.9\,\mathrm{meV\,kbar^{-1}}$ for the A1 level and 0.105 eV and $-10\,\mathrm{meV\,kbar^{-1}}$ for the DX centre) and the energy barrier for electron emission from the DX centre (0.285 eV). The latter appeared to be pressure independent. From the mobility behaviour during depopulation of DX centres, an elegant proof for the negative-U character of DX centres and the positive-U character of deep A1 levels has been obtained.

1. Introduction

The charge state of the DX centre in heavily doped n-type III–V semiconductors has been the subject of much controversy [1, 2]. Recently, the negative-U model, in which a donor captures two electrons to form a negative centre has been successful in accounting for much of the experimental data [3]. However, the influence of the DX centre on the electron mobility has remained an open question with no one model being able to describe the data unambiguously. Both the negative-U and the positive-U model (in which a donor captures one electron to form a neutral centre) can be used to describe the observed mobility increase if pressure is applied by taking into account spatial correlations between the charged centres in the system [4, 5]. In n-GaAs, DX centres can be occupied by conduction electrons if sufficient hydrostatic pressure is applied [2], causing a decrease in the free-electron concentration which can be measured in magnetotransport experiments. Due to the lattice relaxation which accompanies the occupation of a DX centre, the transfer of electrons to and from DX centres can only occur if the temperature exceeds the equilibrium temperature T_{eq}. Below T_{eq}, electrons are frozen at the DX centres and electron transfer to the conduction band can only take place by means of the persistent photoconductivity (PPC) effect. The energy barrier for this thermal electron emission process is denoted by E_e.

An additional interesting problem is manifested in InSb, where at least one other deep donor level besides the DX centre can be observed [6–8]. This donor level has the same

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symmetry as the crystal lattice (i.e. A1 symmetry) and is resonant with the Γ-conduction band at ambient pressure. This level results in an anticrossing with the well known shallow A1 donor level connected to the Γ conduction-band minimum [8] when pressure is applied. Wasilewski and co-workers [9] also observed these anticrossing effects for the Ge donor in GaAs in far-infrared (FIR) magneto-optical experiments at a pressure of around 9 kbar. Similar, but less explicit, effects have been observed for other donor species [10–13]. These experiments have been performed with pure unintentionally doped samples in which no effects of DX centres could be seen. Although the results for InSb and the FIR results for GaAs indicate that the DX centre and the localized deep A1 level might coexist in GaAs, no direct proof has been found so far. In a paper by Skuras and co-workers [14], the presence of a localized non-metastable resonant Si-donor state was suggested to account for a number of missing electrons in delta doped GaAs under hydrostatic pressure.

In this paper we present low-field magnetotransport measurements on heavily doped GaAs:Ge under hydrostatic pressure. Ge is rarely used as a donor because of its amphoteric character [15] and its rather low solubility [16]; the low-energy position of its DX centre [17] also makes it an unattractive dopant for devices in which heavily n-doped material is needed, since the maximum achievable doping concentration is reached when the Fermi level reaches the DX centre. However, Ge is interesting from a fundamental point of view as it lies between the extensively studied donors Si and Sn in group IV of the periodic table. For the first time, we have observed the coexistence of the deep localized A1 level and the DX centre for germanium in GaAs. Beside the energy positions (E_{DX} and E_{A1}) and pressure dependences (dE_{DX}/dp and dE_{A1}/dp) of both levels we also have determined the energy barrier E_e for the electron emission from the Ge DX centre. From the mobility behaviour during depopulation of the DX centres, we have confirmed the charge states of both levels, thus giving unambiguous support to the negative-U model.

2. Experimental details

The samples were grown in an atmospheric pressure metal organic vapour phase epitaxy (MOVPE) reactor. GeH_4 was used as the Ge source. Germanium incorporated in GaAs by MOVPE is well known to act as a donor [18, 19]. Sample characteristics are given in table 1. The thicknesses of the samples, which have been processed into a Hall-bar shape, were about 2 μm. In order to calibrate the sample thicknesses the Shubnikov–de Haas (SdH) effect was measured in magnetic fields up to 15 T at $p = 0$ and $T = 4.2$ K. Exact thicknesses were determined by comparing electron densities derived from the SdH effect with the Hall densities; DC techniques were used in all cases. Finally, the presence of a shallow donor level which is attributed to the Ge shallow donor level was verified using standard photoluminescence techniques at $T = 4.2$ K [20]. The Hall coefficient R_H and resistivity as a function of pressure up to 10 kbar and temperature between 77–294 K have been measured in a 0.5 T magnet in a He-gas compressor, allowing the pressure to be changed in a hydrostatic way at temperatures down to 77 K. A red LED was used to observe PPC effects.

3. Results and discussion

3.1. Coexistence of DX centre and deep A1 level

Figure 1 shows the carrier concentration behaviour during a high-pressure freeze-out (HPFO) cycle. First, the pressure is increased at $T = 294$ K, then the sample is cooled to $T = 77$ K

Table 1. Sample characteristics. Growth temperature, Hall mobility and electron concentrations of several GaAs:Ge samples at $T = 4.2$, $T = 77$ and $T = 294$ K.

Sample	T_{gr} (°C)	n_H (10^{18}cm^{-3})			μ_H (cm^{2}V^{-1}s^{-1})		
		294 K	77 K	4.2 K	294 K	77 K	4.2 K
1056	600	0.4	0.5	0.5	2330	2626	1913
1053	650	0.6	0.6	0.7	1909	2116	1852
1061	610	1.6	1.9	2.3	1375	1645	1569
1055	620	2.1	2.5	2.8	1261	1560	1544
1057	585	2.9	3.6	3.6	1121	1646	1643

and finally the pressure is released. As will be shown later, $T = 77$ K is smaller than T_{eq} and thus similar plots are expected if even lower temperatures (down to $T = 0$) are used. It can be easily seen that the quasi-reversible decrease of the concentration is due to a non-metastable energy level which must be the deep A1 level. The final carrier concentration at $p = 0$ is even higher than the start value. This indicates that at $p = 0$ the deep A1 level is already very close to the Fermi level. The same effect can be seen in table 1, which shows that the ambient pressure carrier densities increase with decreasing temperature. Due to broadening of the Fermi distribution function at $T = 294$ K, more electrons will occupy the A1 level, leading to a lower free-carrier concentration at $T = 294$ K compared to $T = 77$ K. It must be noted that part of the free electrons will be trapped by DX centres after the HPFO cycle of figure 1.

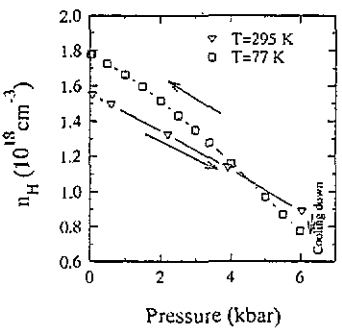

Figure 1. Hall concentration of electrons as a function of hydrostatic pressure applied at 294 K (triangles) for sample 1061. The squares at 77 K were obtained after cooling of the sample at $p = 6$ kbar. The full curves are guides to the eye.

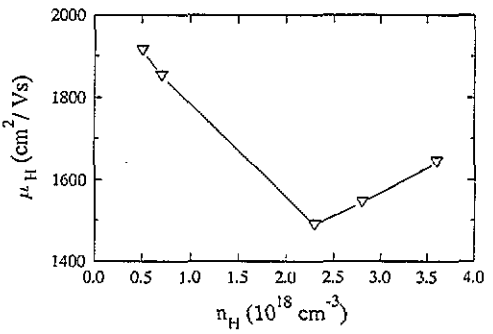

Figure 2. Hall mobility as a function of electron concentration for the samples of table 1; $p = 0$ and $T = 4.2$ K. The full curve is a guide to the eye.

Another proof for the existence of the non-metastable deep A1 level is the absence of PPC effects at 2.2 K and 10 kbar. This temperature is far below T_{eq} and both the DX level and the A1 level lie below the conduction-band minimum at 10 kbar. This means that electrons are transferred from the DX centres, which form the lowest energy level, to the deep A1 level. Further evidence is given by figure 2, which shows the mobilities of all samples from table 1 as a function of their carrier densities at $p = 0$ and $T = 4.2$ K. The increase of mobility for the most heavily doped samples 1055 and 1057 indicates that already at ambient pressure, the deep A1 level starts to be occupied by electrons. In GaAs doped with, for example, Si, no such increase is observed [21] because the deep A1 level

lies at much higher energy and remains unoccupied until pressures of about 30 kbar [10–13]. However, it must be stated that this conclusion is based on the assumption that the compensation ratio is more or less constant with doping concentration, which cannot be verified.

Having shown the existence of the non-metastable A1 centre, we turn to the DX centre, the presence of which is demonstrated by the metastability of the carrier density. Figure 3 shows the effect of the depopulation of DX centres at $p = 0$ and 4 kbar. The first measurement point of figure 3(*a*) follows the HPFO cycle of figure 1. After a HPFO cycle, a temperature increase to $T > 85$ K provides the electrons at the DX centres with sufficient thermal energy to overcome the emission barrier (E_e), resulting in a sudden increase in carrier concentration. The background slopes are caused by the temperature dependence of the A1 occupation. The results shown in figures 1 and 3 are similar for all samples.

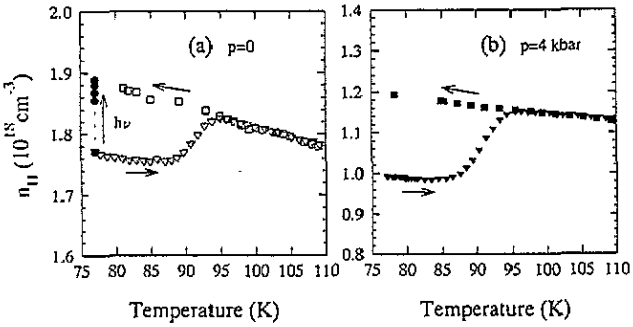

Figure 3. Hall concentration of electrons measured at (*a*) $p = 0$, (*b*) $p = 4$ kbar, during heating of the sample 1061 (triangles). The decrease of n_H was induced by high-pressure freeze-out and the sample was cooled at (*a*) 6 kbar, (*b*) 9 kbar. The squares illustrate the temperature dependence of n_H measured after cooling the sample at (*a*) $p = 0$, (*b*) $p = 4$ kbar. The circles in (*a*) show the effect of subsequent LED pulses after high-pressure freeze-out at $p = 6$ kbar.

3.2. Emission barrier energy

We have used the analysis of the kinetics of this emission process [22] for the two most lightly doped samples 1056 and 1053 in order to reveal E_e. This analysis cannot be used directly for the more heavily doped samples because then the A1 levels are already occupied at ambient pressure. The heating rate used in the experiment was 0.2 K min^{-1} and the pre-exponential factor A obtained from the fit [22] is 5×10^8 s^{-1}K^{-2}, whereas the value obtained for E_e is 0.285 eV. This value is smaller than that for Si in GaAs (0.33 eV [23]) and larger than that for Sn (0.07 eV [23]), hardly surprising considering the positions in the periodic table of these three group IV elements. The depopulation of DX centres after a HPFO cycle measured at 4 kbar starts in the same temperature range as at 0 kbar (figure 2) indicating that E_e does not depend much on pressure. This also explains the good agreement between the value we have found (0.285 eV) and that of [21] at $p = 20$ kbar (0.28 eV). The pressure independence of E_e for the Ge DX centre in GaAs confirms that this feature is specific for group IV donors, whereas the group VI donor-induced DX centres do show a strong pressure dependence of E_e [22]. The fact that T_{eq} for the more heavily doped samples is comparable to those for samples 1056 and 1053 indicates that E_e does not depend much on doping concentration.

3.3. Energy positions and dependences

In order to estimate the energies of the DX level and the A1 level we have performed a series of HPFO cycles at different pressures (all comparable to figure 1) which all induce different DX occupations. The DX centre occupation has been determined by the temperature- or PPC-induced increase of the carrier density after each HPFO cycle. The electron densities at the A1 levels have been derived from the n_H curves measured during pressure release after a HPFO cycle (see, for example, the squares in figure 1). The results are shown in figure 4. From the occupation of the deep A1 level at different freeze-out pressures, its energy position and its pressure dependence can be determined directly from Fermi–Dirac statistics of an energy level occupied by one electron:

$$n_H = N_0 \frac{\exp[-\beta(E_F - E_{A1})]}{2 + \exp[-\beta(E_F - E_{A1})]} - N_A \tag{1}$$

where $\beta = 1/kT$, E_F is the Fermi energy, N_0 is the total number of electrons to be distributed among the conduction band and the deep $A1$ levels and N_A is the number of compensating acceptors. The influence of N_A will be discussed in a forthcoming paper. Again, this procedure can only be performed for the most lightly doped samples 1053 and 1056 because the A1 levels are not occupied at ambient pressure and thus the total number of electrons (which is equal to the number of donors N_D if N_A is neglected) is determined by n_H at $p = 0$ kbar. Obviously N_0 depends on the number of occupied DX centres (n_{DX^-}) and thus on the freeze-out pressure via $N_0 = N_D - 2n_{DX^-}$. Using (1), it is found that E_{A1} and dE_{A1}/dp are 0.066 eV and -6.9 meV kbar^{-1} respectively. These values correspond reasonably well with the values from [9] (0.1 eV and -8.6 meV kbar^{-1}) which were measured for residual Ge donors in very pure GaAs. All energies and pressure dependences are calculated with respect to the bottom of the Γ conduction band and hold for ambient pressure.

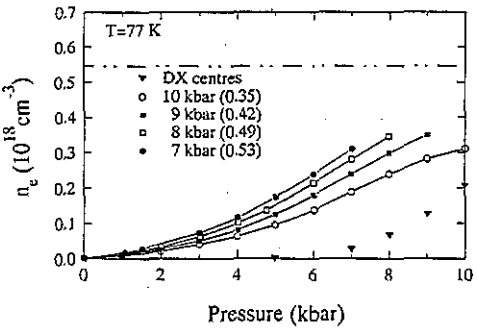

Figure 4. Electron concentrations at the deep A1 levels (full curves) for sample 1056 during pressure release after HPFO at different pressures. The numbers between brackets are the values for N_0 (in 10^{18}cm^{-3}) as used in (1). The triangles indicate the number of electrons at DX centres as a function of pressure. The broken/full curve reflects the total number of electrons in the system.

Once the occupation of the A1 level is known, E_{DX} and dE_{DX}/dp can be determined. To achieve this we used the following expression for the carrier density with two coexisting levels involved [24] and assuming that the DX centre captures two electrons:

$$n_H = N_D \frac{1 - \exp[-2\beta(E_{DX} - E_F)]}{1 + 2\exp[-\beta(E_{A1} - E_F)] + \exp(-2\beta(E_{DX} - E_F)]} - N_A \tag{2}$$

where E_{DX} is the energy per electron. The temperature used in fitting the experimental n_H against p curve to (2) was 95 K, at which point the electrons start to be frozen at the DX centres (see figure 3). As a result we find that E_{DX} and dE_{DX}/dp are 0.105 eV and $-10\,\text{meV kbar}^{-1}$ respectively. The value for E_{DX} is indeed very low compared to those of Si and Sn (0.3 and 0.4 eV [23] respectively) thus confirming the results of [25]. The value for dE_{DX}/dp is comparable to those for Si and Sn (-11 and $-12\,\text{meV kbar}^{-1}$ respectively [23].

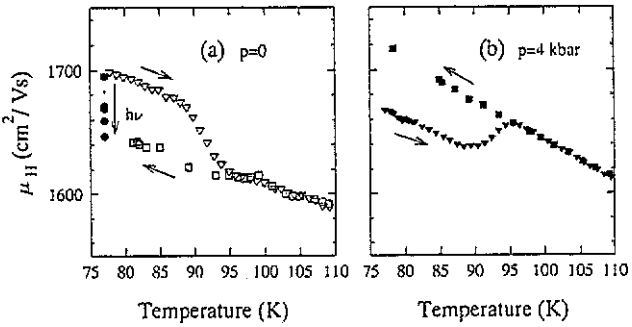

Figure 5. Hall mobility of electrons measured at (*a*) $p = 0$, (*b*) $p = 4$ kbar, during heating of the sample 1061 (triangles). The decrease of μ_H was induced by high-pressure freeze-out and the sample was cooled at (*a*) 6 kbar, (*b*) 9 kbar. The squares illustrate the temperature dependence of μ_H measured after cooling the sample at (*a*) $p = 0$, (*b*) $p = 4$ kbar. The circles in (*a*) show the effect of subsequent LED pulses after high-pressure freeze-out at $p = 6$ kbar.

We now turn to the controversial question of the charge state of the DX centre. The effect of the depopulation of DX centres on the electron concentration is shown in figure 3: the mobilities during the depopulation at $p = 0$ and 4 kbar are plotted in figure 5(*a*) and (*b*). The difference between the two cases is obvious: at $p = 0$, the mobility decreases when the electrons are emitted from the DX centres, whereas at $p = 4$ kbar the mobility increases. This can be explained by the difference in redistribution of the electrons. An electron can be transferred either to the conduction band or to a deep A1 level. The energy of the deep A1 level is much higher at $p = 0$ than at $p = 4$ kbar. Therefore, one can conclude that, in the case shown in figure 5(*a*), electrons are mainly transferred to the conduction band, whereas in figure 5(*b*), electrons are more likely to end up in an A1 level. The mobility decrease seen during depopulation at $p = 0$ kbar is very common for these kind of experiments, when only DX centres are involved. It can be explained by destruction of the correlation between charged centres in the system [4, 5], and holds for the positive-U model, in which the DX centre is uncharged, as well for the negative-U model. However, in our work the mobility increase accompanying the depopulation at 4 kbar (figure 4(*b*)) provides us with an unambiguous proof of the negative-U character of DX centres. In this case, a relatively large number of A1 levels will be occupied before and after the depopulation of the DX centres. This means that the correlation will be dominated by the neutrally charged occupied A1 levels and thus will not change significantly. The increase of the mobility thus can only be explained by a decrease of the number of charged scattering centres. If an electron is transferred from a DX centre to a deep A1 level, this decrease can only be achieved if the DX centre is negatively charged (i.e. negative U) and the deep A1 level is neutral ($d^+ + DX^- \rightarrow 2A_1^0$). If the DX centre had a positive-U character one would expect a decrease in mobility because some of the occupied DX centres (neutral) would be changed into positively charged ionized donors whereas the majority will be replaced

by other neutral particles (occupied A1 levels, $DX^0 \rightarrow A_1^0$). In this case the number of charged particles will be slightly enhanced, leading to a mobility decrease. Therefore, one can conclude that the DX centres really do have a negative-U character, supporting the proposal of Chadi and Chang, which has successfully explained much of the experimental data [3]. It must be noted that from our experiments it is impossible to deduce the exact process of DX centre depopulation. Either it gives both its electrons to two neighbouring donor atoms, or it gives just one electron to become a deep A1 level itself.

4. Summary and conclusions

We have observed the coexistence of DX centres and deep A1 levels in heavily Ge doped n-GaAs. The fact GaAs:Ge exhibits this feature implies that the deep A1 level also exists for other donor species. Therefore, one has to be careful when analysing pressure-induced changes of carrier concentration and mobility. A good criterion for the absence of deep A1 level effects can be obtained from PPC experiments: if one can transfer all the electrons trapped by DX centres back into the conduction band, deep A1 levels are certainly not involved. If, on the other hand, this is not possible (as in [14]), the A1 level is probably involved. The coexistence of both levels also probably resolves the controversy in the literature over the most likely identity of occupied donor states between Chadi and Chang [1], who propose a negative-U DX centre at an interstitial site (for the first time unambiguously proven through its influence on the scattering mechanisms by this work) and Yamaguchi [26], who argues for a strongly localized state of the impurity atom with A1 symmetry (probably the deep A1 level also observed in this work). As it is reasonable to assume that the identity of the donor and the pressure will determine whether the DX centre or the A1 level is lower in energy, the two models are not contradictory [27].

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References

[1] Chadi D J and Chang K J 1989 *Phys. Rev.* B **39** 10063
[2] Maude D K, Portal J C, Dmowski L, Foster T, Eaves L, Nathan M, Heiblum M, Harris J J and Beall R B 1987 *Phys. Rev. Lett.* **59** 815
[3] Mooney P M 1991 *Semicond. Sci. Technol.* **6** B1
[4] Kossut J, Wilamowski Z, Dietl T and Świątek K 1990 *Proc. 20th Int. Conf. on the Physics of Semiconductors* ed E M Anastassakis and J D Joannopoulos (Singapore: World Scientific) p 613
[5] Suski T, Wiśniewski P, Litwin-Staszewska E, Kossut J, Wiłamowski Z, Dietl T, Świątek K, Ploog K and Knecht J 1990 *Semicond. Sci. Technol.* **5** 261
[6] Wasilewski Z, Davidson A M, Stradling R A and Porowski S 1982 *Springer Lecture Notes in Physics* **177** (Berlin: Springer) p 233
[7] Porowski S and Trzeciakowski W 1985 *Phys. Stat. Sol. (b)* **125** 11
[8] Wasilewski Z, Stradling R A and Porowski S 1986 *Solid State Commun.* **57** 123
[9] Wasilewski Z and Stradling R A 1986 *Semicond. Sci. Technol.* **1** 264

[10] Holmes S N, Philips C C, Stradling R A, Wasilewski Z, Droopad R, Parker S D, Yuen W T, Balk P, Brauers A, Heinicke H, Plass C, Weyhers M, Foxon C T, Joyce B A, Smith G W and Whitehouse C R 1989 *Semicond. Sci. Technol.* **4** 782

[11] Dmochowski J E, Wang P D and Stradling R A 1991 *Semicond. Sci. Technol.* **6** 118

[12] Dmochowski J E, Stradling R A, Wang P D, Holmes S N, Li M, McCombe B D and Weinstein B 1991 *Semicond. Sci. Technol.* **6** 476

[13] Dmochowski J E, Wang p D, Stradling R A and Trzeciakowski W 1992 *Mat. Sci. Forum* **83–7** ed G Davies, G G Deleo and M Stavola (Aedermansdorf: Trans Tech)

[14] Skuras E, Kumar R, Williams R L, Stradling R A, Dmochowski J E, Johnson E A, Mackinnon A, Harris J J, Beall R B, Skierbiszewski C, Singleton J, van der Wel P J and Wiśniewski P 1991 *Semicond. Sci. Technol.* **6** 535

[15] Phelan P, Makita Y, Shibata H, Yamada A, Ohnishi N and Beye A C 1990 *Defect Control in Semiconductors* ed K Sumino (Amsterdam: North-Holland) p 1009

[16] Keizer L C, Tang X, van Meerten R Z C and Giling L J 1990 *J. Crystal Growth* **102** 667

[17] Fujisawa T, Yoshino J and Kukimoto K 1989 *J. Crystal Growth* **98** 243

[18] Bass S J 1979 *J. Crystal Growth* **47** 613

[19] Keil G, Le Métayer M, Cuquel A and Le Pollotec D 1982 *Rev. Phys. Appl.* **17** 405

[20] Szmyd D M, Porro P, Majerfeld A and Lagomarsino S 1990 *J. Appl. Phys.* **68** 2367

[21] Tang X, Lochs H G M, Hageman P R, de Croon M H J M, Giling L J and Bons A J 1989 *J. Crystal Growth* **98** 827

[22] Piotrzkowski R, Suski T, Wiśniewski P, Ploog K and Knecht J 1990 *J. Appl. Phys.* **68** 3377

[23] Suski T, Wiśniewski P, Skierbiszewski C, Dmowski L H, van der Wel P J, Singleton J, Giling L J and Harris J J 1991 *J. Appl. Phys.* **69** 3087

[24] Theiss T N, Morgan T N, Parker B D and Wright S L 1989 *Mat. Sci. Forum* **38** 1073

[25] Fujisawa T, Yoshino J and Kukimoto H 1990 *Japan. J. Appl. Phys.* **29** L388

[26] Yamaguchi E and Shiraishi K 1990 *Proc. 20th Int. Conf. on the Physics of Semiconductors* ed E M Anastassakis and J D Joannopoulos (Singapore: World Scientific) p 501

[27] Dąbrowski J, Scheffler M and Strehlow R 1990 *Proc. 20th Int. Conf. on the Physics of Semiconductors* ed E M Anastassakis and J D Joannopoulos (Singapore: World Scientific) p 489