Acta Physica Academiae Scientiarum Hungaricae, Tomus 51 (4), pp. 441—448 (1981)

DONOR-GALLIUM VACANCY COMPLEX IN GaP

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Using a thermochemical model for the formation and incorporation of various defects in GaP the behaviour of an electron trap is explained. It can be concluded that the deep level probably comes from a complex involving a donor element and a gallium vacancy.

1. Introduction

Deep levels in the forbidden gap of semiconductors are properly detected by means of the capacitance spectroscopy [1]. These methods allow to measure the low concentration of localized states present in a small volume of a space-charge device but they are not capable of giving data on the chemical composition of the related lattice defects. Hence, most of the deep levels found in A^{III}—B^{V} compounds have not been identified till now. In order to study the role that certain defects play in optoelectronic devices the nature of the defect has, however, to be taken into consideration. Furthermore, theoretical calculations of the electronic structure can only be done if the chemical and the structural composition of the defects are known.

In [2] a deep level was found to be typical of the n-type material GaP. Often an electron trap at about E_C — 0.4 eV in the forbidden gap (labelled alpha) occurs in epitaxial layers (LPE, VPE) as well as in LEC and solution grown crystals. The dominant feature of the electron trap is its strong dependence on the net donor concentration N_d irrespective of the kind of the shallow donor incorporated. Additionally, a linear relationship was observed [3] between the trap concentration N_α and the etch pit density determined directly beneath the contact of the device investigated. To explain this behaviour a defect model was proposed with a complex involving donor element and gallium vacancy on neighbouring lattice sites. It is now widely admitted that such impurity associated complexes are formed during crystal growth and heat treatment of A^{III}—B^{V} compounds [4]. As the crystal cools down the grown-in defects become supersaturated and ionized native defects or impu-

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rities of both charge signs attract each other to form neutral complexes rather than to occur as isolated species. Looking at the alpha centre it demands, however, further explanation that the deep level concentration N_α is equal in both LPE and VPE layers in contrast to the different growth conditions [3].

The complexing of donors with gallium vacancies was demonstrated to be very important in GaAs [5] in order to understand that the fixed compensation ratio does not depend on donor concentration and growth condition. It also gives a possible interpretation for the formation of dislocation loops after heat treatment in tellurium-doped material and the large lattice dilation of n-type GaAs. These effects can be satisfactorily accounted for by assuming partial compensation of the Te donor with the complex $Te_{As}V_{Ga}$ having acceptor-like behaviour in n-type material GaAs. With regard to GaP a donor-gallium vacancy complex containing an antisite defect was postulated to be the dominant nonradiative recombination centre [6]. On the othe1 hand, impurity-gallium vacancy complexes were suggested when discussing deep-level luminescence bands in GaP material [7, 8] and devices [9].

In this paper, a model of point defect equilibria in GaP is employed for explaining the properties of the alpha centre. It is shown that thermochemical considerations may contribute to the identification of a deep electron state. The agreement of the predicted behaviour with the experimental data strongly indicates that this defect is probably a donor-gallium vacancy complex.

2. Point defect model

Essential in the point defect model applied [5] is the formation of the group-VI donor-vacancy complex (Te_PV_{Ga}, S_PV_{Ga}, Se_PV_{Ga}) which is assumed to be the alpha centre. Since the electron trap has a rather low capture cross section for electrons, namely below 10^{-17} cm^2, it may be characterized as an acceptor-like defect, i.e. singly negatively charged if occupied by an electron. Acceptors introduced by other impurities or by antisite defects are neglected. Taking the Te_PV_{Ga} complex as example the reactions for the formation and incorporation of the various defects during crystal growth and heat treatment can be written as follows (notations according to [5]):

$$P_P + V_i = P_i + V_P\,, \tag{1}$$

$$V_P = V_P^+ + e^-\,, \tag{2}$$

$$0 = e^- + h^+\,, \tag{3}$$

$$1/2P_2(g) + V_i = P_i\,, \tag{4}$$

$$Ga_{Ga} + V_i = Ga_i + V_{Ga}\,, \tag{5}$$

$$0 = V_{Ga} + V_P , \tag{6}$$

$$V_{Ga} = V_{Ga}^- + h^+ , \tag{7}$$

$$Te(l) + V_P = Te_P^+ + e^- , \tag{8}$$

$$Te_P^+ + V_{Ga}^- + e^- = (Te_P V_{Ga})^- . \tag{9}$$

Then the following mass-action relations hold for the reactions (1)—(9):

$$K_1 = [P_i]\,[V_P],$$
$$K_2 = [V_P^+]\,n/[V_P],$$
$$K_3 = n[h^+] ,$$
$$K_4 = [P_i]\,p_{P_2}^{-1/2},$$
$$K_5 = [Ga_i]\,[V_{Ga}] ,$$
$$K_6 = [V_{Ga}]\,[V_P] ,$$
$$K_7 = [V_{Ga}^-]\,[h^+]/[V_{Ga}] ,$$
$$K_8 = [Te_P^+]n/[V_P]\,\gamma_{Te}\,[Te_l],$$
$$K_9 = N_\alpha/n\,[Te_P^+]\,[V_{Ga}^-] .$$

The condition of electrical neutrality is:

$$n = [V_{Ga}^-] + N_\alpha = [Te_P^+] + [V_P^+] + [h^+] . \tag{10}$$

The magnitude of the activity coefficients for electrons and holes was set equal to unity. The net donor concentration at room and growth temperature is

$$N_d^r = [Te_P^+] - N_\alpha \tag{11}$$

and

$$N_d^g = N_d^r + [V_P^+] + [h^+] - [V_{Ga}^-] ,$$

respectively. Substitution of

$$[Te_P^+] = \frac{N_\alpha\,[V_P^+]}{N_d^g}\,\frac{K_3}{K_2 K_6 K_7 K_9} = \frac{N_\alpha\,[V_P^+]}{N_d^g\,K_{10}} \tag{12}$$

into (11) gives

$$N_\alpha = N_d^r \frac{1}{\dfrac{[V_P^+]}{K_{10}\,N_d^g} - 1} . \tag{13}$$

Under gallium-rich conditions the dominant donor at growth temperature is the phosphorus vacancy [10] provided that the Te donor concentration is lower. Since $N_d^g = [V_P^+] \gg [Te_P^+]$ holds in this case Eq. (13) becomes

$$N_\alpha = N_d^r K_{10}/(1 - K_{10}) . \qquad (14)$$

A linear relationship is obtained between the trap concentration and the net donor concentration measured at room temperature. The defect density N_α is determined by both the amount of extrinsic donors and the temperature of crystal growth. At higher Te doping level the donor concentration is given by the Te_P^+ concentration at growth temperature. Thus, it follows that $N_d^g \approx N_d^r \gg [V_P^+]$ and because of

$$K_1 K_2 = K_4 N_d^g p_{P_2}^{1/2} [V_P^+] \qquad (15)$$

Eq. (13) now becomes

$$N_\alpha = N_d^r \frac{1}{\dfrac{K_1 K_2}{K_4 K_{10} p_{P_2}^{1/2} (N_d^r)^2} - 1} . \qquad (16)$$

As far as the defect concentration N_α remains below the Te donor density it follows

$$N_\alpha = (N_d^r)^3 \, p_{P_2}^{1/2} \frac{K_{10} K_4}{K_1 K_2} , \qquad (17)$$

i.e. a cubic characteristic holds that depends on both the phosphorus partial pressure and the temperature at growth.

3. Discussion

In what follows results are discussed which were obtained by detecting the deep level in LPE as well as in VPE layers [2, 3]. While the VPE layers were grown in a Ga—HCl—PH_3—H_2 system at 1110 K the growth temperature of the LPE layers was about 1170 K. As donors Te and S were incorporated during crystal growth. In order to avoid effects that could come from different heat treatments of the samples only *p—n* junctions were investigated here. All the *p—n* junctions were formed by sealed-tube zinc diffusion at 1100 K [11] complemented by a subsequent annealing procedure at 1020 K. To separate the influence of the dislocation density special sets of samples were selected having comparable values of the etch pit density.

The data points summarized in Fig. 1 were measured on samples having nearly the same dislocation density and a net donor concentration below

$4 \cdot 10^{17}$ cm^{-3}. A linear relationship between the trap concentration N_α and the net donor concentration N_d^r is cleaıly seen. In spite of the different growth conditions LPE and VPE data points belong to the same line with a regression coefficient of 0.97. For light doping Eq. (14) predicts the linear correlation. Furthermore, the relation (14) does not depend on the phosphorus paıtial pressure at growth. Thus, the trap concentration is equal in both LPE and VPE samples provided that they were subject to similar heat treatment. Using p—n junctions prepared without the annealing procedure mention-

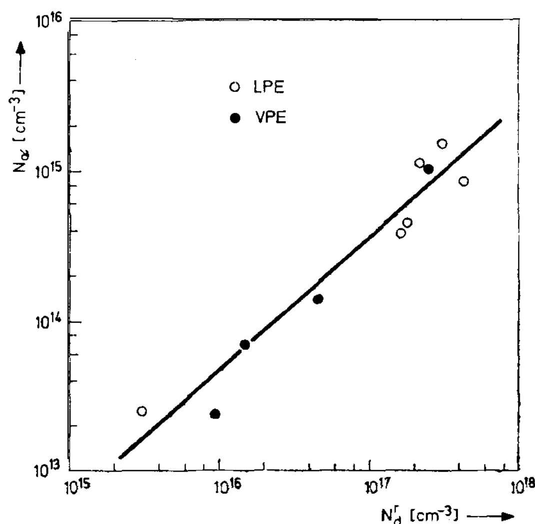

Fig. 1. N_α—N_d^r characteristic of samples having a comparable etch pit density

ed above it was observed that the defect concentration N_α decreases below the detection limit of $5 \cdot 10^{-4}$ N_d^r of the measuring equipment applied. This result compares with the case of $Te_{As}V_{Ga}$ complexes in GaAs. In [5] the mass-action constant K_{10} was evaluated giving an increase of the complex concentration for heat treatment at lower temperature.

At high doping levels the trap concentration considerably increases in accordance with the point defect model proposed Except for the data points of Fig. 1 only LPE layers having different etch pit densities were selected in Fig. 2. From Fig. 2 it can be concluded that the dislocation density plays no role at high donor concentration for forming the alpha centre. The slope of the line is 2.6 with a regression coefficient of 0.87 and agrees very well with the exponent of 3 given by Eq. (17). Hence ,the explanation of such a behaviour should not necessarily include a complex of two (or even three) donor atoms as it was done in [12]. The kink in Fig. 2 is connected with the condition $[Te_P^+] = [V_P^+]$ or $[S_P^+] = [V_P^+]$ so that the V_P^+ concentration in LPE material

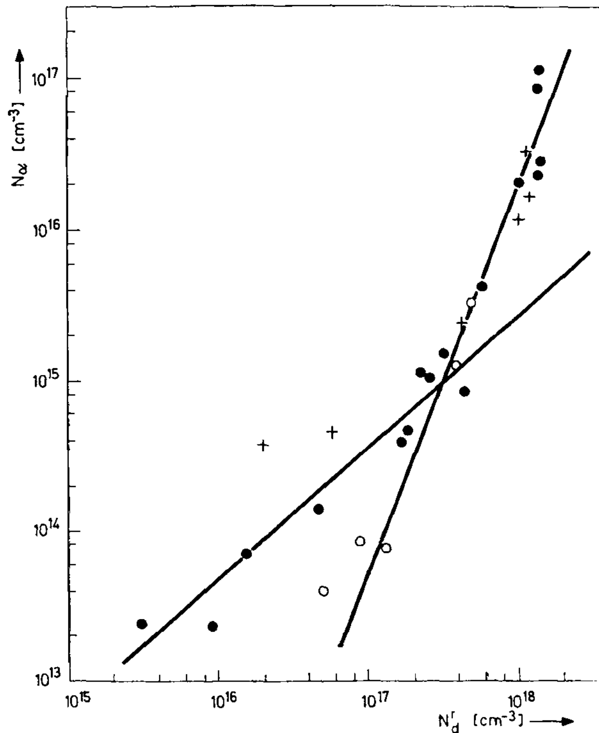

Fig. 2. N_α vs N_d^r curve for LPE material having an etch pit density of about $2 \cdot 10^4$ cm^{-2} (○), $2 \cdot 10^5$ cm^{-2} (●), and $5 \cdot 10^5$ cm^{-2} (+)

GaP can be estimated to be in the 10^{17} cm^{-3} range. However, it must be emphasized that this value reflects not only the crystal growth at 1170 K but also the heat treatment for forming the *p—n* junction. For comparison, the V_P^+ concentration can be roughly estimated from calculations of the GaP solidus [13, 14] to be about 10^{18} cm^{-3} at 1000 K.

As seen in Fig. 2 the trap concentration depends also on the etch pit density in the light doping range. In order to separate the influence of the net donor concentration and the dislocation density the relative defect concentration N_α/N_d^r is plotted vs the etch pit density in Fig. 3. The LPE data points show a clear correlation with a regression coefficient of 0.92. Obviously not only thermochemical reactions but also processes caused by dislocations lead to the formation of the alpha centre at high temperature. It is known [15, 16] that dislocation climb is likely to occur in A^{III}—B^{V} compounds by emitting vacancies. Hence, centres that involve vacancies may be additionally formed at high temperature.

From Fig. 3 the thermodynamic mass-action constant K_{10} can be taken to be below 10^{-3}. Thus, the group-VI donor-V_{Ga} complex in GaP seems to be

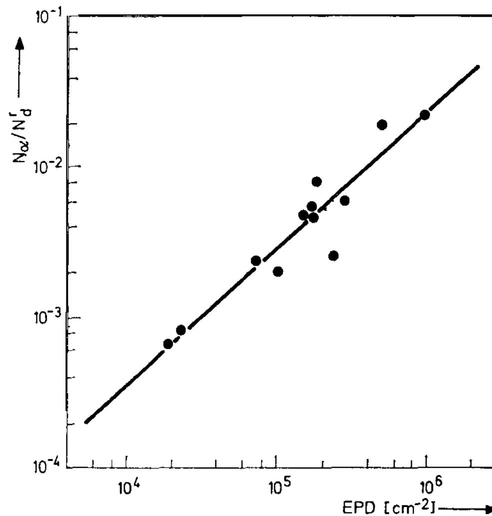

Fig. 3. Relative trap concentration N_α/N_d' as a function of the etch pit density EPD for LPE layers (N_d' below $4 \cdot 10^{17}$ cm^{-3})

the dominant acceptor only above a donor concentration of $5 \cdot 10^{18}$ cm^{-3} (see Fig. 2). For GaAs, a large body of data was explained by the assumption that the dominant acceptor in Te-doped material is the $Te_{As}V_{Ga}$ complex [5]. Particularly, a fixed compensation ratio of about 0.3 was found to be typical of various samples. However, there is some experimental evidence [17] which does not appear to support this model of compensation. In contrast to [5] it should be expected therefore that the mass-action constant K_{10} valid for $Te_{As}V_{Ga}$ defects in GaAs may be considerably lower than 0.3 as in the case of GaP.

Investigating metal contacts on LEC crystals GaP a similar electron trap was detected [12]. A nearly quadratic relationship between the trap concentration and the net donor concentration was observed. It may be possible that the linear part was suppressed because of the higher growth temperature of the samples compared with the epitaxial layers used here.

In conclusion, it was attempted to apply a set of thermochemical defect reactions to the behaviour of a deep level. Regarding the alpha centre in GaP the experimental results confirm the predictions of a model that contains the formation of donor-gallium vacancy complexes. So it is this defect which probably causes the deep level at E_C — 0.4 eV in GaP.

Acknowledgements

The author is indebted to Mr. L. Hildisch and Mr. J. Maege for many stimulating discussions and for providing the samples. The technical assistance of Mrs. C. Dombrowski is very much appreciated.

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