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# ON THE PINNING OF THE FERMI LEVEL BY GERMANIUM $A_1^{0/+}$ DEEP DONOR STATE IN GaAs CODOPED WITH Ge AND Te*

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We present the possibility of GaAs:Ge,Te crystals growth from the melt (liquid encapsulated Czochralski method) with partially occupied, at ambient pressure, the $A_1$ localized electronic state of $Ge_{Ga}$ impurity. In as-grown crystals the amphotericity of Ge and creation of defects (deep acceptor complexes, precipitates etc.) during cooling after growth limit the free electron concentration below the value necessary to populate the $A_1^{0/+}$ level. Special annealing of the samples, which enlarges the free electron concentration, was used. The occupation of $A_1^{0/+}$ level, at ambient pressure, was observed by pressure dependent Hall effect measurements.

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## 1. Introduction

Highly doped $n$-GaAs attracts many interest for fundamental research of the localized electronic states, resonant with conduction band (CB) — the DX centers and $A_1$ states (see e.g. [1]). These states are believed to be of substitutional donor origin, e.g. $Ge_{Ga}$ or $Te_{As}$ [2, 3]. DX state, in contrary to $A_1$ one, exhibits some metastable properties in GaAs, because of the energy barrier for capture and emission of electron. At ambient pressure, in the case of $Ge_{Ga}$, the $A_1$ and DX states give the energy levels at about 80 meV and 100 meV above the bottom of CB [4, 10], respectively, which are the lowest energies amongst all donors in GaAs.

In GaAs:Ge the same $Ge_{Ga}$ center gives the shallow donor, supplying electron to CB and the localized states $A_1$ or DX. Therefore, it is not possible to have the Fermi level above the energy of localized state. The pinning of the Fermi energy should take place [5].

Here we describe the investigations of GaAs:Ge,Te specially designed LEC crystals in order to maximize, at ambient pressure, the occupation of $Ge_{Ga}$ $A_1$ state.

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## 2. Experiment

Several samples were cut along the crystal length. The free electron concentration $n_H$, the concentration of $A_1$ states and its occupation with electrons were determined by measurement of the Hall effect as a function of pressure up to 1.5 GPa (15 kbar) at 77 K and under illumination with LED diode. The $Ge_{Ga}$ concentration was determined as equal to that of $A_1$ states. Some samples were annealed in a small volume closed quartz ampoules under vacuum, without controlled arsenic pressure. The procedure applied, increasing free electron concentration [7], was 1100°C/15 min + rapid cooling of the ampoule in water.

## 3. Results and discussion

In low doping range ($n_H \approx 10^{17}$ cm$^{-3}$) the increase in electron concentration $n_H$ along the crystal length (or fraction solidified $g$) was observed as a consequence of segregation phenomena of impurities during crystal growth [8, 9]. In higher doping range, in crystals #B31 and #B32, in spite of a codoping with Te, the free electron concentration was almost constant as a function of $g$, $n_H \approx 1 \times 10^{18}$ cm$^{-3}$.

TABLE

Results of measurements of samples cut from crystals at a given fraction of liquid solidified $g$. Data in columns show concentration of $Ge_{Ga}$ centers [$Ge_{Ga}$], the Hall electron concentration $n_{77}^H$, initial concentration of Ge and Te in the melt [$Ge_l$] and [$Te_l$]. The increase in [$Te_l$] proportionally decreases [$Ge_{Ga}$] — samples B31/1 and B32X2. Annealing leads to the increase in both $n_{77}^H$ and [$Ge_{Ga}$] — samples B32X2 and B32X2W.

| Sample | $g$ | [$Ge_{Ga}$] [$10^{18}$ cm$^{-3}$] | $n_{77}^H$ [$10^{18}$ cm$^{-3}$] | [$Ge_l$] [ppm at.] | [$Te_l$] [ppm at.] | Remarks |
|---|---|---|---|---|---|---|
| B31/1 | 0.03 | 0.40 | 1.0 | 4000 | 1350 | Fig. 1a |
| B31/13 | 0.60 | 0.45 | 1.0 | 4000 | 1350 | – |
| B32X2 | 0.23 | 0.20 | 1.1 | 3913 | 2641 | – |
| B32X2W | 0.23 | 0.48 | 2.35 | 3913 | 2641 | annealed Fig. 1b |

To clarify the role of $Ge_{Ga}$ $A_1^{0/+}$ level for observed stabilization of electron concentration and to measure $A_1$ states concentration and its occupation we performed the pressure dependent Hall and resistivity measurements. The obtained results were analyzed following the reasoning presented in Ref. [10]. The application of pressure shifts the $A_1^{0/+}$ and $DX^{-/0}$ energy levels downward to the bottom of CB [4, 10]. If these levels cross the Fermi energy at some pressure, the decrease of free electron concentration occurs. When all deep centers are occupied, a plateau in $n_H$ vs. pressure is observed if excess free electrons are present in the sample e.g.

from Te donors. The decrease in $n_H$ due to the electron capture by $A_1$ state is equal to the $A_1$ centers concentration, unoccupied at ambient pressure. Since $A_1$ and DX states can capture one and two electrons respectively [10], the difference between the plateaus related to $A_1$ and DX centers gives directly the concentration of $Ge_{Ga}$ centers. An occupation of $A_1$ level at ambient pressure can also be determined.

The sequence of measurement was the following (Fig. 1a). First, pressure was applied at $T = 300$ K to shift DX and $A_1$ energy levels. Then at 1.4 GPa

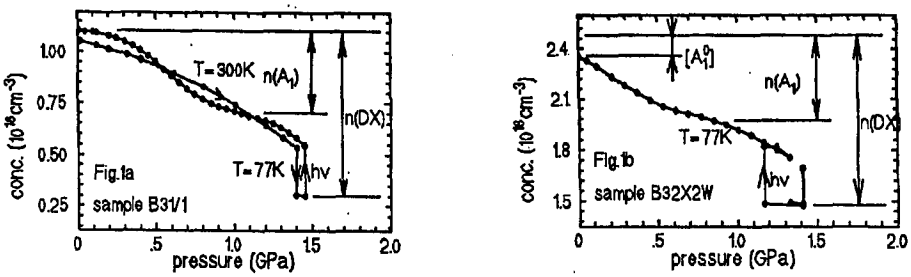


Fig. 1. The Hall electron concentration as a function of hydrostatic pressure. Sequence of measurement is described in the text. Arrows indicate number of electrons captured by $A_1$ state — $n(A_1)$ and by DX state — $n$(DX). The difference gives the concentration of $A_1$ states (and so $Ge_{Ga}$). In part (b) the initial occupation of $A_1^{0/+}$ level is seen for annealed sample B32X2W.

temperature was lowered to $T = 77$ K to make a return of the electrons captured on the DX level to the band impossible due to an energy barrier between DX and CB, and so to populate all DX states. Then at $T = 77$ K and $p = 1.5$ GPa the sample started to be permanently illuminated with an infrared LED, therefore DX levels were depopulated due to optical ionization and passing the electrons over the energy barrier. Turning the light off caused slow capture of electrons back onto DX states because of too high temperature $T = 77$ K for a given energy barrier height, therefore permanent illumination had to be applied during subsequent measurements to keep DX state not populated and to observe the $A_1$-related plateau in $n_H$ during pressure releasing. However, the temperature $T = 77$ K was not low enough to completely depopulate DX states even under illumination and the $A_1$-related plateaus observed for pressures above 0.8 GPa for sample B31/1 and 0.6 GPa for B32X2W were distorted — decreasing $n_H$ for pressures above $p = 1.2$ GPa and 0.9 GPa respectively in Fig. 1.

Results of measurement of the $Ge_{Ga}$ concentration by above method are given in Table. For samples 1, 2, and 3 the measured free electron concentration is not sufficient to put the Fermi energy close to $A_1$ level. This result supports the explanation of constancy of $n_H$ along the crystals #B31 and #B32 length by an increase in amphoteric character of Ge during crystal growth because of Te codoping [9] according to equations: $Ge_I + V_{Ga} \rightarrow Ge_{Ga}^{+} + e^{-}$ and $Ge_I + V_{As} \rightarrow Ge_{As}^{-} + h^{+}$ and their mass action laws. By comparison of measured $Ge_{Ga}$ concentrations in

samples 2 and 3, cut from the two crystals grown from melts with equal Ge contents [Ge$_l$] and Te contents different by a factor of 2 [Te$_l$], one can see the influence of Te doping on incorporation of $Ge_{Ga}$ donors into the crystals in agreement with the above equation. The total compensation $N_a/N_d$ [6] in our crystals increased with $g$ from 0.45 to 0.55 for crystal #B31 and from 0.5 to 0.73 for #B32.

Another phenomenon, which causes a decrease in free electron concentration relatively to predictions from doping amounts and impurities segregation effects during crystal growth, is a creation of various kinds of defects in the crystal during cooling. These can be deep acceptor complexes or precipitates containing Ge and Te atoms. When as-grown sample was annealed at high temperature (about 1100°C), some of these defects were dissolved. Fast cooling to room temperature froze the defect equilibrium from high temperature and the increase in both free electron and $Ge_{Ga}$ donor concentrations was observed — samples B32X2W and B32X2 in Table.

Increase in $n_H$ after annealing of the sample allowed us to partially populate the $A_1^{0/+}$ level to the concentration of about $(1\text{–}1.5)\times10^{17}$ cm$^{-3}$ (Fig. 1b). For unannealed sample B31/1 in Fig. 1a, the $A_1$ states are not occupied at ambient pressure.

## 4. Conclusions

In this paper we have shown that:

1. $Ge_{Ga}$ $A_1$ state can capture the electrons and its energy position in CB limits the maximal free electron concentration in GaAs:Ge crystals to the value of $2.35 \times 10^{18}$ cm$^{-3}$ (the Fermi level pinning) in agreement with papers reporting on crystal growth by bulk or epitaxial methods [4, 8, 11]. To overcome this limit of $n_H$ an additional doping with other donors must be applied, e.g. with Te, S, or Si.

2. In high temperature GaAs:Ge,Te crystal growth (equilibrium conditions), e.g. by LEC method, additional factors limit the free electron concentration below $2 \times 10^{18}$ cm$^{-3}$, these are creation of $Ge_{As}$ compensating acceptors at growth temperature and its enhancement by a codoping [9], creation of acceptor complexes or electrically inactive precipitates during post-growth cooling, etc. Free electron concentration can be increased in such crystals by proper annealing, which can dissolve some of complex defects. We manage to occupy with electrons only 20–30% of $A_1$ centers.

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