

Influence of boron on the point defect equilibrium in highly n-doped gallium arsenide single crystals

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Abstract

High n-type conductivity of melt-grown gallium arsenide single crystals is usually achieved by doping with tellurium or silicon. The lower carrier concentration and Hall mobility in silicon-doped crystals is attributed to the formation of acceptor defects, in particular Si_{As}^- , the isolated gallium vacancy $\text{V}_{\text{Ga}}^{3-}$ and the $(\text{Si}_{\text{Ga}} - \text{V}_{\text{Ga}})^{2-}$ complex. We show that the contamination of the crystals with boron, which is unavoidable in growing techniques using a boron oxide encapsulant, is decisive for the degree of compensation. In highly n-doped gallium arsenide crystals boron is not only incorporated as the isoelectronic defect B_{Ga}^0 . Additionally, high concentrations of $\text{B}_{\text{As}}^{2-}$ and the negatively charged B_{As} -donor complex are formed. These acceptors can dominate the equilibrium of point defects depending on the concentration ratio of the n-dopant and boron.

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PACS: 71.55.-i; 71.55.Eq; 72.10.Fk; 72.20.Jv

Keywords: Gallium arsenide; Silicon doping; Electrical compensation; Fermi level effect

1. Introduction

Highly n-doped gallium arsenide substrates are used for the fabrication of opto-electronic devices such as high brightness LED and laser diodes. These applications require substrates of low dislocation density and high conductivity. In melt-grown gallium arsenide crystals grown by the vertical Bridgman (VB) and the vertical gradient freeze (VGF) techniques, mainly silicon is used as an n-dopant. The low dislocation density achieved in this material is attributed to lattice hardening by silicon point defects [1]. Crystals doped with tellurium show a cellular dislocation network which is also typical for undoped crystals. Although Si is the favorable n-dopant from the dislocation density point of view Te-doped crystals show better electrical properties. The doping efficiency η_d , which can be defined as the ratio of carrier concentration n to the concentration of the n-dopant N_d , is substantially higher in the range of $N_d = (10^{17} \dots 10^{19}) \text{cm}^{-3}$ than in the case of

Si-doping. This means, that for a given N_d carrier concentration n is higher for Te-doped than for Si-doped crystals. In Fig. 1 this is illustrated on experimental data of about 500 Si-doped and 40 Te-doped GaAs crystals. Moreover, in Si-doped material a limitation of carrier concentration to values below $(3 \dots 4) \times 10^{18} \text{cm}^{-3}$ is observed. Fig. 2 shows that the Hall mobility μ_H of Si-doped crystals is lower than of Te-doped crystals for a given n . Similar results, especially for Si-doped material can be found in numerous publications [2–7].

The observed differences in the electrical parameters are attributed mainly to a different incorporation of the dopants into the GaAs lattice. Besides the Si_{Ga}^+ donor, Si can form also the acceptor Si_{As}^- [8], the donor–acceptor complex $(\text{Si}_{\text{Ga}} - \text{Si}_{\text{As}})^0$ [9] and the donor–vacancy complex $(\text{Si}_{\text{Ga}} - \text{V}_{\text{Ga}})^{2-}$ [10]. Tellurium is only incorporated in the As sublattice, forming the donor Te_{As}^+ and the acceptoric donor-vacancy defect $(\text{Te}_{\text{As}} - \text{V}_{\text{Ga}})^{2-}$ [11]. The formation of further types of defects containing donor atoms, as in Si-doped crystals, was not observed. Therefore, the lower η_d in Si-doped crystals should be due to the amphoteric behavior of silicon, leading to a higher concentration of

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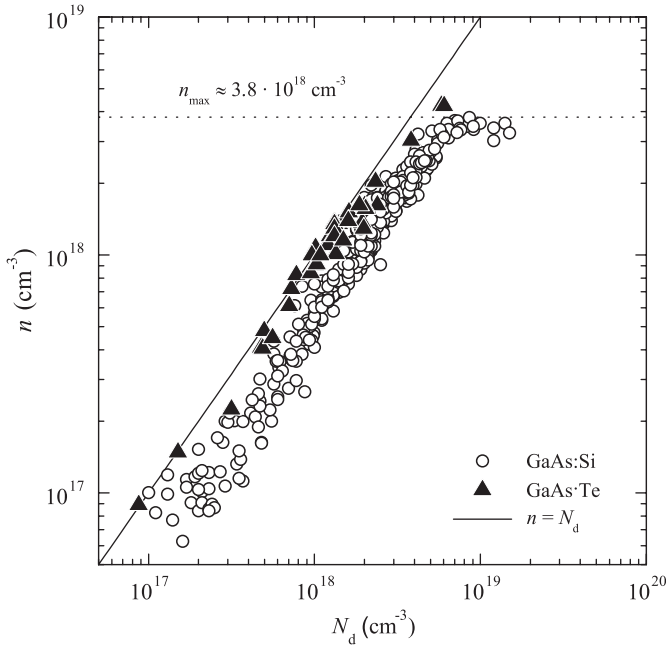


Fig. 1. Hall carrier concentration n of VGF-grown GaAs:Si and LEC-grown GaAs:Te crystals vs. concentration of the n-dopant. For GaAs:Si n is limited to about $3.8 \times 10^{18} \text{ cm}^{-3}$ (dotted line). The solid line illustrates the case of $\eta_d = 1$.

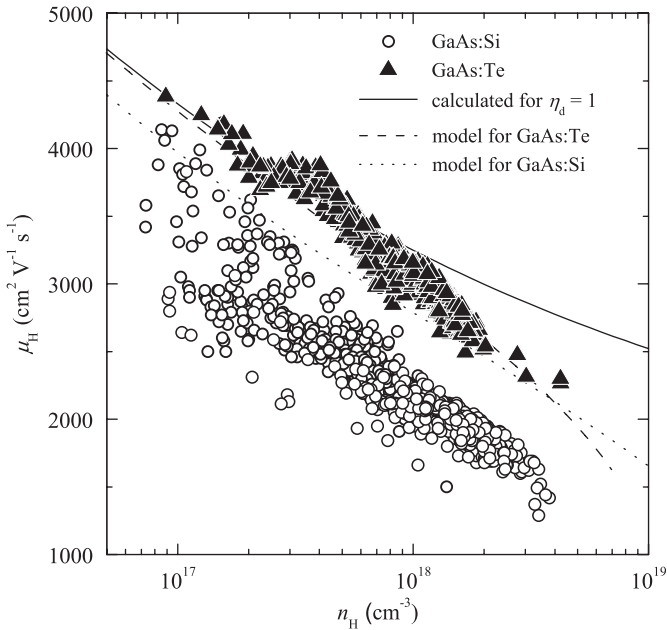


Fig. 2. Hall mobility μ_H of VGF-grown GaAs:Si and LEC-grown GaAs:Te crystals vs. carrier concentration n . The lines show the calculated Hall mobility for the cases of $\eta_d = 1$ and for models for GaAs:Te and GaAs:Si, respectively, valid for material with low boron content. For details of the calculation see Section 3.

acceptoric or electrical inactive defects, respectively [4,7]. We will show, however, by a comparison of experimental data and results from calculations of the $\mu_H(n)$ dependency, that for crystals, which contain boron in a concentration

comparable to that of the n-dopant, this model cannot describe the observed differences.

2. Experiments

The experimental data shown in Figs. 1 and 2 have been measured by the van-der-Pauw/Hall method at samples taken from Si-doped VGF-grown and Te-doped LEC-grown GaAs crystals. The diameter of the crystals was 100 mm in the case of Si-doping and 3 inch in the case of Te-doping. Details of the growing conditions can be found in Refs. [12,13]. In both growing techniques an encapsulation of the GaAs melt by liquid boron oxide was used to prevent a decomposition of the melt. The B_2O_3 melt undergoes complex physical and chemical interactions with the GaAs melt and the dissolved dopants and impurities as well as with the ambient gas atmosphere [14,15]. The reaction



leads to a loss of Si dopant. The GaAs melt and the grown crystals are contaminated with boron [16]. It becomes clear from Eq. (1) that the concentration of boron in the GaAs melt can even exceed the Si concentration. Tellurium shows a much lower chemical activity, so that in Te-doped crystals a contamination of boron in the concentration range of only 10^{16} cm^{-3} is found, which arises from thermal decomposition of B_2O_3 . In semi-insulating GaAs boron is incorporated nearly completely as the isoelectronic defect B_{Ga}^0 . For Si-doped crystals the existence of B_{As} and $(\text{Si}_{Ga} - B_{As})$ defects has been proved by localized vibrational modes (LVM) spectroscopy [17]. It can be assumed that also in Te-doped crystals the donor- B_{As} complex is formed, provided a sufficiently high boron concentration. For a systematic investigation of the formation of boron acceptors in GaAs two special VGF crystals have been grown. One crystal was obtained from a melt containing an initial Te concentration of $3.75 \times 10^{19} \text{ cm}^{-3}$ and a B concentration of $1.3 \times 10^{19} \text{ cm}^{-3}$. For the growth of the other crystal the same amount of Te has been added to the melt. The second dopant was Si instead of boron, with an initial concentration of $1.1 \times 10^{19} \text{ cm}^{-3}$. The crystals have been sliced into wafers. A selection of wafers from different axial positions has been characterized by van-der-Pauw/Hall measurements and chemical analysis by glow discharge mass spectrometry (GDMS).

In Fig. 3 the $\mu_H(n)$ dependency for these samples is plotted by analogy with Fig. 2. In contrast to Te-doped crystals not intentionally doped with B, the Hall mobility in the Te-B-doped samples drops by more than $1000 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ while n increases from 1.0 to $1.6 \times 10^{18} \text{ cm}^{-3}$. A similar decrease of μ_H is observed for the crystal doubly doped with Te and Si. Although no boron has been added to the melt in this case, a high concentration of B was expected because of Eq. (1). This was proved by chemical analysis. The boron content amounts to $1.1 \times 10^{18} \text{ cm}^{-3}$ at the seed end and $7.2 \times$

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