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LATTICE CONSTANT OF DOPED SEMICONDUCTOR*

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The paper shows an influence of doping on lattice constant of a semiconductor. Three effects are discussed: (i) "size" effect caused by a different ionic radii of dopant and host atoms, (ii) lattice expansion by free electrons proportionally to the deformation potential of the conduction-band minimum occupied by this charge, (iii) different thermal expansion of the undoped and doped samples. The experiments have been performed by using the high resolution X-ray diffraction at 77–770 K on AlGaAs:Te and GaAs:Si.

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1. Introduction

The lattice constant is a basic parameter characterizing every crystal. We can measure it with 1–10 ppm accuracy by using the high-resolution X-ray diffractometry. In the seventies a large number of papers were devoted to factors influencing the lattice constants of semiconductors. Surprisingly, at present we observe much smaller interest in this subject. Such a situation may arise from a common opinion that the lattice constant is dependent on too many factors and it is an extremely difficult task to separate them. However, we have undertaken this problem not only because of interesting physics behind it, but also because of practical reasons as we use lattice constants for scaling a stoichiometry in ternary compounds.

The experiments have been performed in order to evaluate change of the lattice constant caused by three doping-sensitive factors: (i) "size" effect, (ii) electronic effect via the deformation potential of the corresponding conduction band minimum, (iii) doping-induced change of anharmonicity in lattice vibrations at

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295 K (temperature at which lattice constants are usually measured). To achieve our aim we have:

a) investigated AlGaAs layers heavily doped with tellurium in a wide range of Al-content which enabled us to have different electron occupations of various conduction-band minima characterized by different deformation potentials,

b) compared the data obtained on GaAs:Si and on GaAs:Te (different ionic radius of the dopants),

c) performed the X-ray diffractometric measurements at temperatures 77 K and illuminated the samples in order to transfer DX centers (in $Al_xGa_{1-x}As$, $x > 0.2$) into their metastable configurations. The transfer is accompanied by a considerable change of the free-electron concentration and lattice relaxation,

d) performed the measurements at high temperatures up to 670 K. At these temperatures we could induce a redistribution of the free electrons between different band minima. The redistribution depends on the aluminium content in AlGaAs (different positions of Γ, X, L minima).

2. Size effect

An introduction of a dopant of a different ionic radius with respect to the host atoms causes lattice expansion or contraction. For a crystal whose lattice reacts as an elastic medium the Vegard law is obeyed, i.e., change of the lattice constant is proportional to the concentration of the dopant and to the difference between ionic radii of the dopant and substituted host atom. The same happens if we deal with native defects: antisites, vacancies or interstitials. Therefore, if we examine the influence of doping on the lattice constant it is also important to know a concentration of native defects.

A non-trivial example of the size effect is a change of the lattice constant accompanying the transfer of the DX-centers and EL2 defects to their metastable configurations. For DX-centers such a change was observed by Cargill et al. ($Al_{0.22}Ga_{0.78}As$ doped with Si and Sn) [1] and us (AlGaAs doped with Te) [2]. During cooling the samples in dark the dopant atoms capture two electrons and they (Si, Sn) move into the interstitial positions. The illumination below 110–130 K induces a transfer of electrons into the conduction band and the dopant atoms move back into the substitutional sites [3]. This change persists after the light is switched off. Unfortunately, for DX-centers it is impossible to separate effects caused by free-electron concentration changes from the lattice relaxation related to the atomic rearrangements.

The similar rearrangement occurs when the EL2 defects in GaAs are transferred into their metastable configuration. This defect is most probably an antisite arsenic. At low temperature the illumination causes a shift of this antisite into an interstitial position [4]. The shift is not (contrary to DX-centers) accompanied by the change of free-electron concentration and therefore may serve for an evaluation of lattice relaxation caused just by the lattice rearrangement.

In Table we present the lattice constant change accompanying the transfer of DX-centers and EL2-defects into their metastable configurations. For DX-centers we show the estimations of the change related to free-electron concentrations. This problem is discussed further on.

TABLE

Lattice constant change caused by: (A) The transfer of DX (AlGaAs) and EL2-like defects (LT GaAs) into their metastable configurations. The values in parentheses indicate number of electrons transferred into conduction band (AlGaAs) or of EL2-like defects (LT GaAs) transferred into the metastable state; (B) Doping. $\Delta a/a_{\text{size}}$ are estimated from a difference between ionic radii of the dopant and host atoms, $\Delta a/a_{\text{electr}}$ are estimated taking −8.5 eV as a deformation potential of the Γ minimum, $\Delta a/a_{\text{term}}$ is the value measured in the low-temperature study.

Sample Experiment	$\Delta a/a_{\text{exp}}$ (10^{-4})	$\Delta a/a_{\text{size}}$ (10^{-4})	$\Delta a/a_{\text{electr}}$ (10^{-4})	$\Delta a/a_{\text{term}}$ (10^{-4})
	A			
AlGaAs:Si[a] $(0.8 \times 10^{18}$ cm$^{-3})$	0.09	0.02	0.07	–
AlGaAs:Sn[a] $(0.8 \times 10^{18}$ cm$^{-3})$	0.14	0.06	0.08	–
AlGaAs:Te $(8 \times 10^{18}$ cm$^{-3})$	1	0.4	0.6	–
LT GaAs $(10^{20}$ cm$^{-3})$	−4	−4	–	–
	B			
GaAs:Si $(9 \times 10^{18}$ cm$^{-3})$	0.3	−0.5	0.8	?
GaAs:Te $(8 \times 10^{18}$ cm$^{-3})$	0.8	0.1	0.7	0.5
GaAs:Te[b]$(9 \times 10^{18}$ cm$^{-3})$	1.3	0.1	0.8	0.5

[a] Reference [1], [b] Reference [11].

3. Electronic effect

The change of the crystal volume by free charge is a phenomenon reverse to the pressure-induced change of the energy levels and is proportional to the deformation potential of the band minimum occupied by this charge [5]. In the work of Cargill et al. [6] the authors observed the lattice constant decrease in Si implanted with As despite larger ionic radius of arsenic with respect to silicon. The magnitude of this decrease was correlated with a positive value of the deformation potential for the energy gap of silicon. For GaAs, whose gap deformation potential is negative, we observed an increase in lattice constants in the layers doped with silicon (i.e. atoms smaller than arsenic or gallium). The results agreed with calculations which took into account the size effect and electronic effect with a deformation potential of about −8.5 eV (value close to those obtained by other methods). Also for GaAs doped with tellurium (ion larger than As and Ga) it has been observed by many authors that the lattice expansion is much stronger (superdilation phenomenon) than it is predicted by size effect (Vegard's law). When we additionally take into account the lattice expansion by free electrons this phenomenon is explained for some of the experimental results (including ours). However, other data show even stronger lattice expansion than it is predicted by joint size and electronic effects.

The question arises if X-ray methods may be used for a detection of a different lattice-constant change by free charge occupying different band minima of different deformation potentials. This problem is discussed below.

4. Thermal expansion

About ten years ago Bąk-Misiuk et al. [7] performed measurements of thermal expansion of variously doped GaAs and GaAsP samples. For *n*-doped crystals the thermal expansion coefficient was found to be larger than for undoped and *p*-doped crystals. The difference became more pronounced at elevated temperatures. In the time of these experiments the deformation potential of L-minimum was regarded to be ten times larger than of Γ-minimum [8] and the authors interpreted an extra lattice-constant rise by a transfer of free electrons to L-minimum at high temperature. However, further investigations of various authors have pointed out that these two deformation potentials are not much different [9]. Therefore, we decided to re-investigate this problem by using AlGaAs:Te samples with various Al-content (different occupation of the Γ, L, X minima). For higher Al-content the occupation of Γ minimum becomes less probable.

For all doped samples the thermal expansion was found to be greater by about 5% with respect to the undoped samples of the same Al-content. This observation indicates that the temperature-induced redistribution of free electrons between the conduction-band minima is not a main cause of the larger thermal expansion for doped samples. We propose that it is rather a result of an increase in anharmonicity in thermal vibrations. It may be related to a decrease in elastic constants as it was observed for doped germanium [10].

In Table we see that for GaAs:Te examined by us the observed lattice constant change is smaller than a sum of all three factors: size, electronic and thermal. For a similar sample examined by Kuznetsov et al. [11] this sum corresponds well to the experimental value. The difference between these two samples gives an idea of the precision of our estimations and shows that different samples may have other uncontrollable defects changing the lattice constants.

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