NATURE AND SINGULARITIES IN THE BEHAVIOR OF POINT DEFECTS IN DOPED SINGLE CRYSTALS OF A₃B₅ COMPOUNDS

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1. INTRODUCTION

The physical properties of semiconductors are substantially determined by the presence of defects in the crystalline lattice, including the intrinsic. At this time the experimental results (e.g., [1-6]) permit the consideration that doping impurities in A₃B₅ compounds influence the physical properties of not only the impurity atoms directly, which induce appropriate levels and the forbidden band of the semiconductor, but also through the medium of the intrinsic point defects to whose formation doping can contribute and with which the impurity atoms can actively interact. From this aspect, the nature and behavior of singularities of point defects in doped A₃B₅ compounds are discussed in this survey. Selected as the fundamental model material is GaAs doped by different donor impurities.

2. KINDS OF POINT DEFECTS IN A₃B₅ COMPOUNDS

The following fundamental kinds of intrinsic point defects can be present in A₃B₅ compounds: vacancies or their associations, the simplest of which are divacancies, interstitial atoms, and antistructural defects. Until recently it was considered that the prevailing kind of point defects in semiconductor crystals were vacancies upon which relied the explanation of the crystals' physical properties. It was hence noted that the concentration of the above-mentioned intrinsic defects can be quite large (10¹⁸-10¹⁹ cm⁻³) in A₃B₅ compounds since these compounds possess a definite extensiveness of the homogeneity domain and excess superstoichiometric components are dissolved by a kind of subtraction [7]. It has been shown by the use of precision methods of measuring the lattice period and the density that the excess majority component of the III group (Ga and In) in GaAs [8, 8, 57, 58] and InAs [10] crystals actually form subtraction solutions (i.e., vacancies are the predominant kind of point defect) while the components of the V group (As) are simultaneously dissolved both by a kind of insertion and a kind of subtraction (the predominant kind of point defect here is interstitial atoms). Therefore, both vacancies and interstitial atoms can be present simultaneously in the actual crystals of semiconductor compounds. The growth of the GaP lattice period for a deviation of the composition from stoichiometry [11] apparently also indicates the presence of interstitial atoms of the intrinsic component although the authors ascribe the effect observed to vacancies. Preliminary investigations showed that interstitial atoms are also present in GaSb.

The enthalpies of vacancy formation in anion and cation sublattices of semiconductor compounds are distinct. The appropriate value for A₃B₅ compounds determined by one of the authors on the basis of measuring the rms thermal atomic displacements [12] are presented in Table 1. Presented there also are estimated values of the enthalpy of formation of interstitial V group atoms in GaAs [13] and InAs in the elastic-isotropic continuum approximation.

It can be concluded on the basis of the estimates made and from experimental results on the kinds and concentrations of point defects in GaAs [9] and InAs [10] that the following inequality characterizing the enthalpy of point defect formation

\[ \Delta H_v^A < \Delta H_v^B < \Delta H_i^A < \Delta H_i^B \]

(1)

is valid in at least the A₃B₅ compounds investigated (with the apparent exception of GaP and InP).

The vibrational entropy of Schottky defect formation, estimated on the basis of experimental results on the difference concentration of point defects, is ~9.6 k in GaAs [13] and...
### TABLE 1. Enthalpy of Formation of Point Defects in $A_3B_5$ Compounds

<table>
<thead>
<tr>
<th>Compound</th>
<th>$\frac{\Delta H_f}{\Delta H_v}$, eV</th>
<th>$\Delta H_i$, eV</th>
</tr>
</thead>
<tbody>
<tr>
<td>GaP</td>
<td>2.7</td>
<td>1.6</td>
</tr>
<tr>
<td>GaAs</td>
<td>1.6</td>
<td>2.0</td>
</tr>
<tr>
<td>GaSb</td>
<td>1.3</td>
<td>1.7</td>
</tr>
<tr>
<td>InP</td>
<td>1.5</td>
<td>1.3</td>
</tr>
<tr>
<td>InAs</td>
<td>1.4</td>
<td>1.8</td>
</tr>
<tr>
<td>InSb</td>
<td>1.2</td>
<td>1.4</td>
</tr>
</tbody>
</table>

$\approx 11.7k$ in InAs [14], where $k$ is the Boltzmann constant.

The presence of divacancies in GaAs single crystals was confirmed experimentally in an internal friction investigation [15, 16]. According to [17], the temperature spectrum of internal friction in GaAs, InAs, GaP, InSb crystals is analogous in nature, in principle: An internal friction peak is observed in all cases, which is due to the reorientation of the divacancies in the III group element sublattice. This indicates that the kind of point defects in the $A_3B_5$ compounds investigated are identical. Taking account of the energy of vacancy interaction $E_{in} = -0.34$ eV [18], the enthalpy of gallium divacancy formation in GaAs is 2.86 eV [13], while the configuration entropy of divacancy formation is $\Delta S_p = \kappa \ln 6$.

The deduction is made in [19] on the basis of theoretical estimates of the entropy of formation of isolated antistructural defects (appropriate values are presented in Table 2) and of antistructural pairs that the kind of defects mentioned is present in large concentrations in $A_3B_5$ compounds and exerts substantial influence on their electrophysical properties (defects of $B$ type are donors, while $A$ are acceptors). In particular, in the author's opinion the weak influence of the deviation from stoichiometry on the carrier concentration in semiconductor compounds explains the interaction between vacancies and antistructural defects. In the general case, theory [19] predicts that vacancies should predominate in broad-band semiconductors while antistructural defects play a more important role in narrow-band semiconductors. However, although there are indications in the literature on the sufficiently high concentration of antistructural defects in GaAs [21], GaP [22], and GaSb [23, 24], it should be recognized that until now there has not been sufficiently convincing experimental proof of the presence of antistructural defects in $A_3B_5$ compounds obtained by using direct structural methods.

The manifold of levels in the forbidden band of semiconductor $A_3B_5$ compounds, detected by using different physical methods (cf. [25]) is often associated with the presence of intrinsic point defects or complexes with their participation. Nevertheless, a reliable identification of the electrically active centers observed is difficult in the majority of cases. According to [26], $V_{Ga}$ induces a deep acceptor ($E_v + 0.66$ eV), and $V_{As}$ a deep donor ($E_v - 0.85$ eV) level in GaAs. The presence of deep vacancy levels in GaAs also results from an analysis of experimental results [27, 28, 59]. At the same time, there is no information in the literature about the electrical activity of the intrinsic interstitial atoms.

### 3. DOMAIN OF HOMOGENEITY OF SEMICONDUCTOR COMPOUNDS

Knowledge of the phase equilibrium microdiagrams in the domains of the compound, particularly the configurations of the homogeneity domain, as well as of the nature of solutions based on this compound, in principle, permits not only determination of the set (i.e., the kind and concentration) of point defects in the crystal, but can also be the basis for a selection of the heat treatment modes permitting its control.

Hence, the interest manifested in the computed or experimental determination of the homogeneity domain of different semiconductor compounds, especially in recent years, is understandable. The method of quasichemical reactions [29], given here by definite kinds of intrinsic defects and with the assumption that the boundary of compound existence corresponds to the total defect concentration in equilibrium with the vapor phase, is usually used to compute the microdiagram solidus curves.