

Non-stoichiometry and problem of heavy doping in semiconductor phases

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Abstract

The experimental results on the influence of non-stoichiometry on defect structure, band structure and physical properties of the IV–VI and I–III–VI₂ semiconductor compounds with wide homogeneity regions were analyzed. It was shown that compositions at which peculiarities in the concentration dependences of properties in the homogeneity region are observed, correspond to the maximum in the melting curves. Using the approach of percolation theory, the transition from weak to heavy self-doping within the homogeneity region was considered, and the percolation threshold under the introduction of non-stoichiometric defects was estimated. Compositions optimal for long-range ordering were determined.

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1. Introduction

According to modern views, all semiconductor compounds have homogeneity regions (HR) and represent phases of variable composition [1,2]. The existence of thermodynamically equilibrium deviation from stoichiometry in a chemical compound is determined by a decrease in free energy under introduction of intrinsic defects whose appearance leads to a sharp growth in configurational entropy [1,2]. The location and size of HR depends on the ratio of formation energies for different types of defects. The stoichiometric composition may lie inside or outside HR. In the latter case, a phase of variable composition represents a berthollide phase.

Deviation from stoichiometry in semiconductor compounds results in the appearance of intrinsic defects, whose concentration depends on the degree of deviation

from stoichiometry. Changing properties through deviation from stoichiometry is one of the most important methods of controlling properties of semiconductors.

An intermediate character of chemical bond in semiconductors, the appearance of free charge carriers induced by deviation from stoichiometry, and a significant contribution of electron energy determine a great variety of possible mechanisms of non-stoichiometry.

A large group of phases of variable composition is constituted by the so-called heavily non-stoichiometric phases with wide HRs and high concentrations of non-stoichiometric defects. Studying of these phases raises a number of fundamental questions related to the defect interaction and its effect on crystal structure, energy band spectrum, physical properties, etc. Properties of such phases cannot be interpreted in terms of point defects. The fundamental concepts of statistical thermodynamics of point defects are valid on the condition that defects can be considered as non-interacting particles and their distribution has purely statistical character. That is why the Wagner–Schottky theory [1] can provide

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satisfactory description only to semiconductor compounds with very narrow HRs.

If charged defects of a certain type are introduced into a crystal, interactions between them (Coulomb, deformational) can lead to their long-range ordering. Under the simultaneous introduction of intrinsic defects of both donor and acceptor type, the most probable processes are the formation of donor–acceptor pairs or neutral complexes, resulting in short-range ordering of the structure. For example, under the introduction of excess VI element into a IV–VI compound, it is charged cation vacancies that appear with the highest probability and their ordering can lead to the formation of superstructure. At present, there is extensive experimental material proving the possibility of short- and long-range ordering of non-stoichiometric defects [1,2]. It was found out that many compounds with wide HRs are dissolved into a number of ordered phases, each phase having its own narrower HR. In metallic phases and phases with ionic–covalent chemical bonding, an important role in the existence of non-stoichiometry is played by the electron factor, stabilization of structure resulting from a change in the degree of filling of energy bands and, consequently, a shift of the Fermi level.

It is quite clear that physical phenomena accompanying significant deviations from stoichiometry are similar, to a great extent, to phenomena taking place under heavy doping. The difference lies in the fact that under deviation from stoichiometry, a compound is doped with its own constituents, intrinsic defects playing the role of impurity atoms. However, problems related to properties of heavily non-stoichiometric phases, order–disorder processes of the semiconductor phases practically have not been studied.

Binary IV–VI and ternary I–III–VI₂ semiconductor compounds are very convenient objects for studying

fundamental problems of non-stoichiometry because these compounds include phases whose properties can change in a wide range.

The goal of this paper is to overview and analyze our works on the influence of non-stoichiometry on defect structure and physical properties of IV–VI (SnTe) and I–III–VI₂ (CuInSe₂, CuInTe₂, CuGaTe₂) semiconductor compounds with wide homogeneity regions.

2. Results

The analysis of the results on experimental determination of HRs of these compounds and studying of their crystal structure, mechanical, thermal, galvanomagnetic, and thermoelectric properties within HRs, we obtained [3–12], shows that there are common features in the behavior of their properties.

In Fig. 1, the boundaries of the SnTe HR in the Sn–Te system [6] and of the CuInTe₂ HR's in the CuInTe₂–Te [9] and CuInTe₂–InTe systems [10] are shown. It is seen that these compounds are typical berthollide phases and the maximum in the melting curves is shifted relative to the stoichiometric composition.

In Fig. 2, the concentration dependences of the microhardness *H* in the HR of SnTe, CuGaTe₂ and CuInSe₂ compounds are presented. One can see that the peculiarities are observed at the composition corresponding to the maximum in the melting curves, which is shifted relative to the stoichiometric composition. As is seen from Fig. 2, the similar anomaly of *H* in the vicinity of 50.4 at% Se is also observed for the two-sided phase CuInSe₂ which changes the sign of its conductivity near the stoichiometric composition. Perhaps, it is this effect that accounts for a shift of the maximum in the

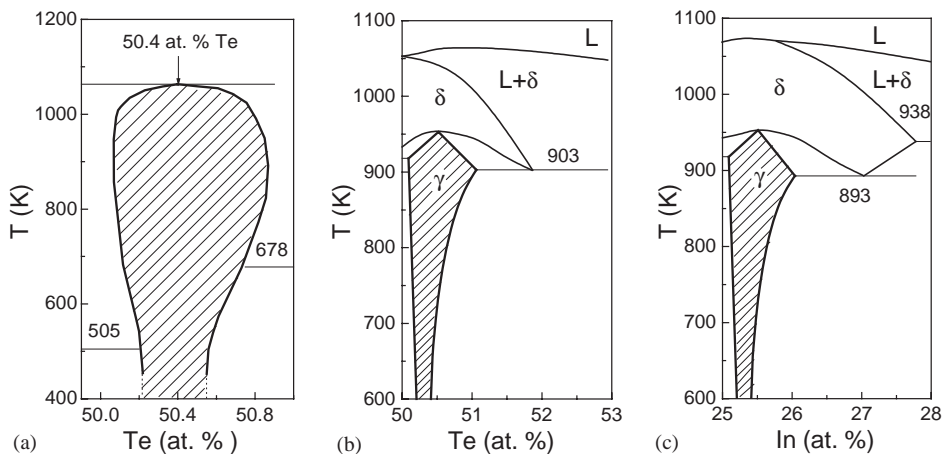


Fig. 1. Homogeneity regions of SnTe (a) and CuInTe₂ (b,c) berthollide semiconductor phases in Sn–Te (a), CuInTe₂–Te (b) and CuInTe₂–InTe (c) systems.

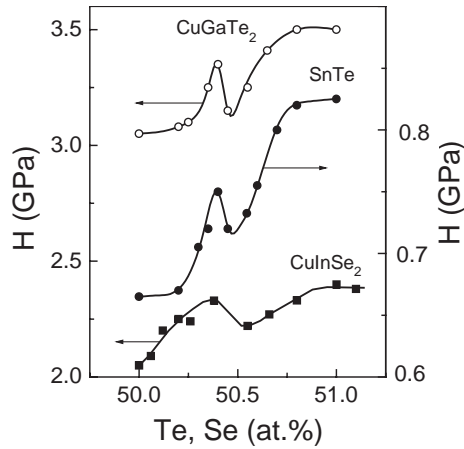


Fig. 2. Microhardness of SnTe, CuGaTe₂ and CuInSe₂ compounds vs. Te (Se) concentration.

melting curve from the stoichiometric composition in the Cu–In–Se system [13–15].

In Fig. 3a, the concentration dependences of the X-ray diffraction line width, the linear expansion coefficient and the Seebeck coefficient in the SnTe HR are given. Fig. 3b and c shows the concentration dependences of H , the Seebeck coefficient S and the electrical conductivity σ in the CuInTe₂ HR in the CuInTe₂–Te [9] and CuInTe₂–InTe systems [10]. It is seen that in all the cases the location of peculiarities corresponds to the maximum in the melting curves, which is shifted relative to the stoichiometric composition.

3. Discussion

1. It is usually assumed that within the HR of a berthollide phase, properties change continuously. However, it can be suggested that peculiarities in the concentration dependences of properties must correspond to maximal thermal and thermodynamic stability of a phase with variable composition, and the composition corresponding to the maximum in the melting curves must be somehow marked in these dependences. As is seen from the presented results, in all the cases considered, peculiarities in the concentration dependences of properties indeed correspond to the maximum in the melting curves within the HRs of semiconductor compounds.

2. In accordance with our views [8], in any solid solution there is a critical concentration (a percolation threshold, in the approach of percolation theory [16]), at which a qualitative change of solid solution takes place. This change is associated with the formation of “an infinite cluster” and percolation channels in the crystal, or, in other words, with the transition from impurity

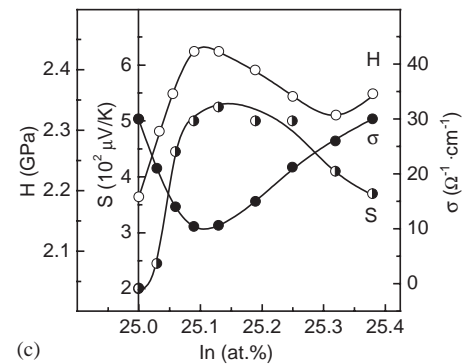
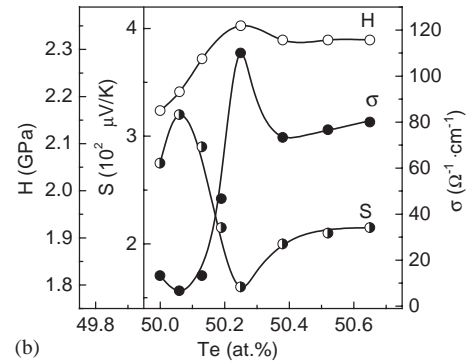
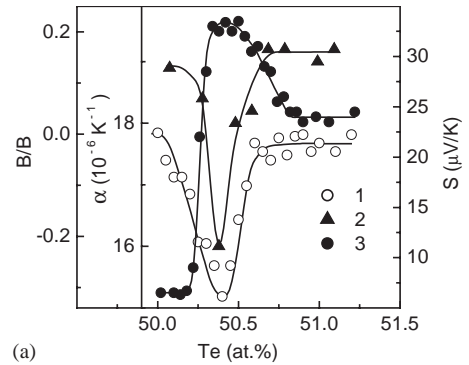


Fig. 3. Concentration dependences of properties in the homogeneity regions of SnTe (a) and CuInTe₂ (b,c) compounds in the Sn–Te (a), CuInTe₂–Te (b) and CuInTe₂–InTe (c) systems. a: (1) X-ray diffraction linewidth $\Delta B/B$; (2) thermal expansion coefficient α ; (3) Seebeck coefficient S . (b, c) H—microhardness; S—Seebeck coefficient; σ —electrical conductivity.

discontinuum to impurity continuum. In the vicinity of this composition, critical phenomena are observed. Reaching the percolation threshold like any critical phenomenon usually manifests itself through the appearance of anomalies in the concentration dependences of properties.

Systematic investigations of property vs composition dependences for solid solutions based on IV–VI binary and I–III–VI₂ ternary compounds have shown that in

the region of small impurity contents, in the concentration dependences of properties, anomalies are observed (see, for example, [17–20]). In all studied systems, the region of small impurity concentrations (up to ~ 1 at%) is clearly distinguished from regions of higher impurity contents due to the difference in the behavior of the concentration dependences of properties. The introduction of a dopant into a crystal leads first to crystal disordering by non-interacting impurity atoms, but then condensation of the “impurity vapor” induces ordering processes.

If one treats non-stoichiometric defects as an impurity, then again there must exist a critical concentration corresponding to the transition from defect discontinuum to defect continuum. In the approach of percolation theory, the transition from weak self-doping to heavy self-doping within the HRs of binary and ternary phases under the introduction of different types of non-stoichiometric defects (cation vacancies, substitution atoms, etc.) can be determined from the experimentally obtained concentration dependences of different physical properties. Due to a short-range character of the impurity potential in IV–VI compounds [21,22], the percolation threshold is reached at a rather high level of doping and can be registered relatively easily in the concentration dependences of properties. A similar phenomenon can take place in I–III–VI₂ ternary compounds.

Considering the observed critical phenomenon in the framework of percolation theory [16] and assuming that peculiarities in the concentration dependences of properties within HR correspond to the percolation threshold, it is possible to calculate the radius of the nonstoichiometric defect “action sphere” R_0 from the composition, at which peculiarities are observed, using the equation [16,23]

$$4/3\pi N_c(2R_0)^3 \approx 2.7,$$

where N_c is the average number of sphere centers per volume unit. The calculation shows that for SnTe, CuGaTe₂ and CuInSe₂

$$R_0 \approx 1.4 a_0,$$

where a_0 is the unit cell parameter.

3. The formation of continuous chains of non-stoichiometric defects upon reaching the percolation threshold can stimulate such redistribution of impurity atoms in the crystal lattice, which would lead to the realization of their configuration corresponding to a minimum of the thermodynamic potential. Ordering of impurity atoms becomes possible only after reaching the percolation threshold. Possible self-organization processes may include a long-range ordering of impurity atoms (“crystallization of impurity liquid”), the formation of complexes, a change in the localization of impurity atoms in the crystal lattice, etc.

For the realization of a long-range ordering of impurity atoms the following conditions must be satisfied: (1) $x \geq x_c$, where x_c is the percolation threshold; (2) the energy of ordering is much higher than kT ; (3) the average distance between impurity atoms corresponds to their regular distribution over the sites of the crystal lattice ($d = na_0$ and $na_0/4^{1/3}$, respectively, for cubic simple and fcc lattices formed by impurity atoms, n is integer, a_0 denotes the unit-cell parameter of the matrix). The formation of a superstructure is expected to cause the appearance of extremum points in the dependences of different properties. In the absence of ordering, the anomalies in the concentration dependences of properties in the vicinity of the percolation threshold will not be so pronounced. For sufficiently wide HRs, different variants of ordering can be realized as concentration of non-stoichiometric defects increases.

The fact that at the same composition (50.4 at% Te), we observed minima of the X-ray diffraction line width, the linear expansion coefficient and a maximum of the Moessbauer effect probability [3–7] is an evidence in favor of non-stoichiometric defects ordering in SnTe. As temperature decreases, the boundaries of SnTe HR shift towards the composition which represents an optimum composition of ordering (Fig. 1). The peculiarities are observed at 50.4 at% Te (Se) in CuInSe₂ and CuGaTe₂ HRs. A simple calculation carried out for Sn–Te, CuInSe₂–Se, and CuGaTe₂–Te systems showed that at 50.4 at% Te (Se), corresponding to the appearance of ~ 1.6 mol% of cation vacancies, a superstructure of nonstoichiometric defects with a fcc lattice and unit cell parameter of $a = 4 a_0$ (where a_0 is the unit cell parameter of the given compound) can be formed.

As was pointed out above, in semiconductor phases, in contrast with, for example, metallic phases, defects are charged, which stimulates both short- and long-range ordering. Since SnTe, CuInTe₂ and CuGaTe₂ phases always exhibit p -type conductivity, it is logical to assume that predominant intrinsic defects are cation vacancies, which can order at their high concentrations. It is concluded that in one-sided semiconductor phases (e.g. SnTe, CuGaTe₂), the maximum in the solidus and liquidus curves corresponds, with a high probability, to an optimal ordering composition.

Elastic interactions between non-stoichiometric defects, similar to Coulomb interactions, can lead to the formation of certain configurations of impurity atoms corresponding to minima of the elastic energy. Non-stoichiometric defects are centers of local distortions of crystal lattice, sources of internal stresses and strains decreasing in an inverse proportion to the cube of the distance. Since noticeable displacements of atoms are created within one or two interatomic distances from an impurity atom, one can consider elastic fields to be short-range and introduce the radius of deformational interactions R_0 . At small impurity concentrations, when

distances between impurity atoms are much larger than R_0 , elastic fields created by separate atoms practically do not overlap. As the impurity concentration increases, elastic fields of neighboring atoms begin to overlap, which leads to a partial compensation of elastic stresses of opposite signs. After percolation channels via deformational fields of separate atoms are formed, the process of the microstress compensation intensifies, spreading over the entire crystal and leading to a sharp decrease in the overall level of elastic strains in the crystal lattice, which, in turn, results in a decrease in H and X-ray diffraction line width B . Further introduction of non-stoichiometric defects into this new medium (“defect liquid”) causes new distortions of the crystal lattice and, consequently leads to a broadening B and increasing H .

One can assume that possible reasons for the existence of one-sided phases, such as SnTe, GeTe, CuGaTe₂ and CuInTe₂ are: (1) the possibility of defect ordering resulting in diminishing internal energy of crystal; (2) the appearance under deviation from stoichiometry of charge carriers, whose electron energy also makes a contribution into overall decrease in internal energy. Both factors stabilize the state with a high concentration of non-stoichiometric defects. The similarity of the concentration dependences of properties in binary and ternary compounds is connected with similarity of processes of defects interactions.

Taking into consideration the above said, one can distinguish so-called “genuine non-stoichiometric phases”, i.e. phases that remain one sided in the entire temperature range, even at $T \rightarrow 0$. The formation of such phases can be connected with a decrease in the crystal free energy under deviation from stoichiometry due to such factors as a sharply increasing contribution of the electron subsystem to the crystal total energy (for example, in SnTe), a long-range ordering, etc.

4. Conclusions

Phases with wide homogeneity regions represent a specific group of semiconductor phases. It is fruitful to use the percolation theory approach to the studying of properties of such phases as well as properties of heavily doped semiconductors. On the basis of the analysis of the experimentally obtained concentration dependences of properties within homogeneity regions of non-stoichiometric phases, such as SnTe, CuInSe₂ and CuGaTe₂, the existence of peculiarities in these dependences corresponding to the maximum in the melting curves is established. It is suggested that with the highest probability the maximum in the melting curves corresponds to a composition optimal for ordering and is close to the percolation threshold. Percolation phenomena can be accompanied by self-organization processes.

The results obtained in this work represent another evidence to the proposition [8] about the universal character of critical phenomena accompanying the transition from impurity discontinuum to impurity continuum. The role of impurities in the case considered in this work was played by non-stoichiometric defects.

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