

# Statistical Thermodynamics of Semiconductor Alloys

VYACHESLAV A. ELYUKHIN



# STATISTICAL THERMODYNAMICS OF SEMICONDUCTOR ALLOYS

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VYACHESLAV A. ELYUKHIN

*Centro de Investigacion y de Estudios Avanzados del  
Instituto Politecnico Nacional, Mexico*



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Elsevier

Radarweg 29, PO Box 211, 1000 AE Amsterdam, Netherlands  
The Boulevard, Langford Lane, Kidlington, Oxford OX5 1GB, UK  
225 Wyman Street, Waltham, MA 02451, USA

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ISBN: 978-0-12-803987-8

### British Library Cataloguing in Publication Data

A catalogue record for this book is available from the British Library

### Library of Congress Cataloging-in-Publication Data

A catalog record for this book is available from the Library of Congress

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STATISTICAL  
THERMODYNAMICS OF  
SEMICONDUCTOR ALLOYS

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# Dedication

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# Preface

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Due to their electronic structure and optical properties, semiconductors are the basic materials of solid-state electronics. Among semiconductor materials, crystalline (polycrystalline) inorganic semiconductor alloys form the majority of the materials used in device applications. The doped elemental semiconductors and doped semiconductor compounds such as, correspondingly, doped Si or doped GaAs, are also substitutional semiconductor alloys. Moreover, a number of the semiconductor compound-rich alloys containing dielectric compounds are semiconducting materials.

Over the last few years, progress in the technologies of epitaxial growth led to significant extension of the class of inorganic semiconductor alloys. It is expected that this extension will be continued in the next years. In connection with this trend, the prediction of the characteristics and properties of possible semiconductor materials becomes very important. In addition, the materials suitable to fabricate solid-state electronic devices should be in the thermodynamically stable or metastable state. Only then can the characteristics of the devices be fixed for a long period of time. Therefore, the development of methods to determine the thermodynamic stability of semiconductor alloys with respect to phase transformations is very important.

The electronic structure and optical properties are considered in great detail in a number of books devoted to the physics of semiconductors. The thermodynamic properties and characteristics (e.g., the thermodynamic stability with respect to the different phase transformations, clustering, and distortions of the crystal structure) are also essential for device fabrication. However, these and other thermodynamic quantities, characteristics, and properties are normally represented only briefly in the available literature. Some models and their applications suitable for the consideration of the thermodynamic properties of semiconductor alloys can be found, for example, in Refs [1–5] and in the books devoted to statistical mechanics and statistical thermodynamics.

This book is for solid-state physicists, semiconductor materials scientists, and specialists who need the application of theoretical methods and models, such as the use of the lattice systems, the cluster variation method, regular solutions, and the valence force field models to analyze the experimental results and to predict the properties and characteristics of possible semiconductor alloys. Both graduate and postgraduate



students of solid-state physics and materials science may use this book to study the methods of statistical physics in solid-state physics as well as the regular solution model and the valence force field model and their applications to the description of semiconductor alloys.

The topics presented in this book include the types of inorganic crystalline semiconductors, the basic concepts and postulates of equilibrium thermodynamics and equilibrium statistical physics, the regular solution model and its applications considered by using the cluster variation method, and the valence force field model with its applications. Elemental semiconductors, semiconductor compounds, and substitutional alloys of such semiconductors are treated in Chapter 1. The most important parts of this chapter are devoted to the alloys of binary semiconductor compounds. The established types of the spontaneously ordered alloys with the zinc blende and wurtzite structures are described. It is shown that in alloys with two mixed sublattices, a one-to-one correspondence is absent between the elemental composition and concentration of chemical bonds. The basic concepts and the mathematical formalism of equilibrium thermodynamics, as well as main elements of statistical physics, are briefly treated in Chapter 2. In addition, the Helmholtz and Gibbs free energies of condensed matter and the separation of the degrees of freedom are presented. The classical regular solution model is in Chapter 3. High accuracy in calculation of configurational entropy may be reached by using this model. The cluster variation method and its different approximations used to describe the properties and characteristics of the semiconductor alloys considered as regular solutions are in Chapter 4. Baker's approach to providing a simple and systematic way to express configurational entropy is introduced and used in this chapter. Chapter 5 is devoted to the modified regular solution model to describe the semiconductor alloys of binary compounds in which the crystal structure consists of two mixed sublattices. A one-to-one correspondence between the elemental composition and concentration of chemical bonds is absent in such alloys. The characteristics of such alloys also represented as regular solutions are treated by using the different approximations of the cluster variation method. It is also shown that the self-assembled identical tetrahedral clusters should be thermodynamically profitable in some semiconductor alloys with the zinc blende structure. The valence force field model and its applications are presented in Chapter 6. This model allows analyzing the distortions of the crystal structure of the mismatched semiconductor alloys at the microscale level. The estimated internal strain energies of the semiconductor alloys with the zinc blende and wurtzite structures demonstrate the tendency to the formation of superstructures. The possible types of superstructures in the ternary alloys with the zinc blende and wurtzite structures are described. The models of the discontinuous and continuous order-disorder phase transitions are presented. The strain energies caused by the

isoelectronic impurities in the semiconductors with the diamond and zinc blende structures are derived.

In this book, the terms in parentheses normally are the synonyms encountered in the literature, and capital and small letters as usual are related to the absolute and molar quantities, respectively.

## References

- [1] R.A. Swalin, *Thermodynamics of Solids*, John Wiley & Sons, New York, 1962, 1972.
- [2] J.C. Phillips, *Bonds and Bands in Semiconductors*, Academic Press, New York, 1973.
- [3] J. Tsao, *Materials Fundamentals of Molecular Beam Epitaxy*, Academic Press, Boston, 1993.
- [4] A.-B. Chen, A. Sher, *Semiconductor Alloys*, Plenum Press, New York, 1995.
- [5] L.A. Girifalco, *Statistical Mechanics of Solids*, Oxford University Press, Oxford, 2000.



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# Semiconductor Materials

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Crystalline inorganic semiconductors are basic materials of solid-state electronics and, therefore, they are considered in this book. An inorganic semiconductor can be an elemental semiconductor, a compound, or an alloy. Elemental semiconductors containing only one chemical element are diamond, Si, Ge, and gray Sn with the diamond structure. Semiconductor compounds consist of two or more chemical elements. The composition of the compound may vary within a composition range called the deviation from stoichiometry or deviation from the ideal ratio between the numbers of the different chemical elements. Normally, such deviations in semiconductor compounds are small, and they are the results of the presence of atoms located at the interstitials or the absence of atoms over the lattice sites. Semiconductor alloys are mainly substitution alloys in which atoms are arranged over the lattice sites. Interstitials and the absence of atoms over the lattice sites also may occur in semiconductor alloys as defects of the crystal structure. The importance of the consideration of substitutional semiconductor alloys results from the fact that they are basic materials in the device applications.

The compressibility of crystalline semiconductor alloys is normally very small. Therefore, the changes of the lattice parameters of semiconductors are significant only at high pressures. The high-pressure effects are not considered in this book. Hence, through the book it is supposed that the lattice parameters of semiconductors do not depend on pressure. Moreover, it is supposed also that the stiffness coefficients of semiconductors do not depend on temperature and the coefficients of thermal expansion are equal to zero for the majority of considerations.

## 1.1 ELEMENTAL SEMICONDUCTORS

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Carbon (diamond, C), silicon (Si), germanium (Ge), and gray tin ( $\alpha$ -Sn) are the elemental semiconductors belonging to Group IV of the periodic

FIGURE 1.1 Elemental semiconductors  $A^{IV}$  with the diamond structure.

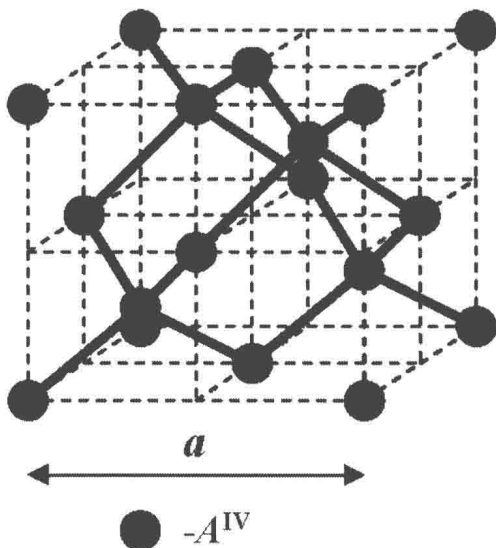


table. They have the diamond structure (cubic structure). The elementary cell (unit cell) of the diamond structure is shown in Figure 1.1.

The diamond structure is composed of two equivalent face-centered cubic lattices displaced from each other by one-quarter of a body diagonal. Also, the diamond structure can be represented as a set of regular tetrahedrons (tetrahedral cells) with atoms in their corners, and 50% of such tetrahedrons have atoms in their centers. Other tetrahedrons are empty.

The Bravais lattice of the diamond structure is the face-centered cubic lattice. Each atom in such a structure has the four nearest neighbors with the tetrahedral bonding and the twelve next nearest neighbors (the nearest neighbors in the face-centered cubic lattice). The distance between the nearest atoms is:

$$R = \frac{\sqrt{3}}{4}a,$$

where  $a$  is the lattice parameter or length of the edge of the elementary cell.

## 1.2 SEMICONDUCTOR COMPOUNDS WITH ZINC BLLENDE STRUCTURE

Binary compounds consisting of atoms belonging to Groups III and V of the periodic table ( $A^{III}B^V$  semiconductors) such as BP, BAs, AlP, AlAs, AlSb, GaP, GaAs, GaSb, InP, InAs, and InSb crystallize with the zinc

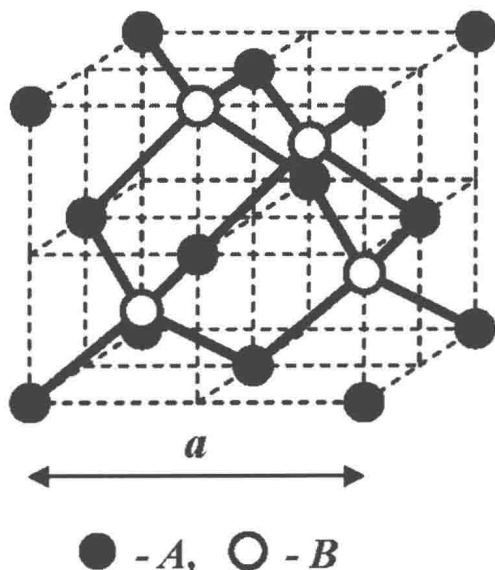


FIGURE 1.2  $AB$  semiconductor compounds with the zinc blende structure.

blende (sphalerite) structure. The elemental cell of the zinc blende structure is shown in Figure 1.2.

The other  $A^{\text{III}}B^{\text{V}}$  semiconductors such as BN, AlN, GaN, and InN can be grown with the zinc blende structure in the thermodynamically metastable state.  $A^{\text{II}}B^{\text{VI}}$  semiconductors BeS, BeSe, BeTe, MgSe, ZnS, ZnSe, ZnTe, CdS, CdTe, HgSe, and HgTe have the zinc blende structure in the thermodynamically stable state. The other  $A^{\text{II}}B^{\text{VI}}$  semiconductors MgS, ZnO, and CdSe can be prepared with the zinc blende structure in the thermodynamically metastable state. The  $A^{\text{IV}}B^{\text{IV}}$  compound SiC also may be grown with the zinc blende structure in the metastable state.

The zinc blende structure is obtained from the diamond structure if cations are placed into one face-centered cubic sublattice and anions are allocated into another face-centered cubic sublattice. There are four atoms of the opposite type placed at the corners of a regular tetrahedron around each atom. Thus, the nearest coordination number  $z_1$  is equal to 4 and the next nearest coordination number  $z_2$  is equal to 12. The next nearest neighbors are the same type atoms as a central atom. The Bravais lattice of the zinc blende structure is the face-centered cubic lattice as well as the Bravais lattice of the diamond structure. All distances between the nearest atoms in the zinc blende structure are the same, and given by:

$$R = \frac{\sqrt{3}}{4}a.$$



where  $a$  is the lattice parameter or length of the edge of the elementary cell. As well as the diamond structure, the zinc blende structure can be represented as a set of regular tetrahedrons (tetrahedral cells) with cations (anions) in their corners and 50% of such tetrahedrons have anions (cations) in their centers. The other tetrahedrons are empty.

### 1.3 SEMICONDUCTOR COMPOUNDS WITH WURTZITE STRUCTURE

$A^{\text{III}}B^{\text{V}}$  semiconductors AlN, GaN, and InN crystallize with the wurtzite structure.  $A^{\text{II}}B^{\text{VI}}$  semiconductors BeO, MgTe, ZnO, CdS, and CdSe also crystallize with the wurtzite structure in the most stable state.  $A^{\text{II}}B^{\text{VI}}$  compounds ZnS and ZnSe can be grown with the wurtzite structure in the thermodynamically metastable state. The  $A^{\text{IV}}B^{\text{IV}}$  semiconductor SiC crystallizes normally with the wurtzite structure.

The ideal wurtzite structure (Figure 1.3) consists of two hexagonal close-packed sublattices filled with cations and anions and displaced from each other by a distance  $\sqrt{\frac{3}{8}}a_0$ , where  $a_0$  is the first lattice parameter of the ideal hexagonal close-packed sublattice or the distance between the nearest neighbors in the hexagonal close-packed sublattice in the (0001)

FIGURE 1.3 AB semiconductor compounds with the wurtzite structure.

