Properties of Semiconductor Alloys: Group-IV, III–V and II–VI Semiconductors

SADAO ADACHI

Gunma University, Gunma, Japan
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      (c) (III, III)–As Alloy
      (d) (III, III)–Sb Alloy
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WILEY SERIES IN MATERIALS FOR ELECTRONIC AND OPTOELECTRONIC APPLICATIONS

This book series is devoted to the rapidly developing class of materials used for electronic and optoelectronic applications. It is designed to provide much-needed information on the fundamental scientific principles of these materials, together with how these are employed in technological applications. The books are aimed at (postgraduate) students, researchers and technologists, engaged in research, development and the study of materials in electronics and photonics, and industrial scientists developing new materials, devices and circuits for the electronic, optoelectronic and communications industries.

The development of new electronic and optoelectronic materials depends not only on materials engineering at a practical level, but also on a clear understanding of the properties of materials, and the fundamental science behind these properties. It is the properties of a material that eventually determine its usefulness in an application. The series therefore also includes such titles as electrical conduction in solids, optical properties, thermal properties, and so on, all with applications and examples of materials in electronics and optoelectronics. The characterization of materials is also covered within the series in as much as it is impossible to develop new materials without the proper characterization of their structure and properties. Structure-property relationships have always been fundamentally and intrinsically important to materials science and engineering.

Materials science is well known for being one of the most interdisciplinary sciences. It is the interdisciplinary aspect of materials science that has led to many exciting discoveries, new materials and new applications. It is not unusual to find scientists with a chemical engineering background working on materials projects with applications in electronics. In selecting titles for the series, we have tried to maintain the interdisciplinary aspect of the field, and hence its excitement to researchers in this field.

Peter Capper
Safa Kasap
Arthur Willoughby
Preface

Semiconductor alloys provide a natural means of tuning the magnitude of the band-gap energy and other material properties so as to optimize and widen the application of semiconductor devices. Current research and development in semiconductor alloys is focused on areas of improved materials growth, development of unique materials characterization and suitable process technologies, fabrication of novel devices using artificially controlled materials structures and better understanding of degradation mechanisms in electronic and optoelectronic devices for improved device reliability.

Even though the basic semiconductor alloy concepts are understood at this time, the determination of some device parameters has been hampered by a lack of definite knowledge of many material parameters. The main purpose of this book is to provide a comprehensive treatment of the materials aspects of group-IV, III–V and II–VI semiconductor alloys used in various electronic and optoelectronic devices. The topics treated in this book include the structural, thermal, mechanical, lattice vibronic, electronic, optical and carrier transport properties of such semiconductor alloys. The book covers not only commonly known alloys (SiGe, AlGaAs, GaInPAs, ZnCdTe, etc.) but also new alloys, such as dilute-carbon alloys (CSiGe, CSiSn, etc.), III–N alloys, dilute-nitride alloys (GaNAs, GaInNAs, etc.) and Mg- or Be-based II–VI semiconductor alloys.

The reader may also find the companion book ‘Properties of Group-IV, III–V and II–VI Semiconductors’ published in this series useful since it emphasizes the endpoint semiconductor principles and properties.

The extensive bibliography is included for those who wish to find additional information if required. It is hoped that the book will attract the attention of not only semiconductor device engineers, but also solid-state physicists and materials scientists, and particularly postgraduate students, R&D staff and teaching and research professionals.

Sadao Adachi,
Gunma University, Japan
<table>
<thead>
<tr>
<th>Abbreviation</th>
<th>Full Form</th>
</tr>
</thead>
<tbody>
<tr>
<td>BAC</td>
<td>band anticrossing</td>
</tr>
<tr>
<td>bct</td>
<td>body-centered tetragonal</td>
</tr>
<tr>
<td>BZ</td>
<td>Brillouin zone</td>
</tr>
<tr>
<td>c-</td>
<td>cubic-</td>
</tr>
<tr>
<td>CB</td>
<td>conduction band</td>
</tr>
<tr>
<td>CL</td>
<td>cathodoluminescence</td>
</tr>
<tr>
<td>Cl-VPE</td>
<td>chloride-transport vapor-phase epitaxy</td>
</tr>
<tr>
<td>CP</td>
<td>critical point</td>
</tr>
<tr>
<td>CR</td>
<td>cyclotron resonance</td>
</tr>
<tr>
<td>C-V</td>
<td>capacitance–voltage</td>
</tr>
<tr>
<td>CVD</td>
<td>chemical vapor deposition</td>
</tr>
<tr>
<td>DLTS</td>
<td>deep-level transient spectroscopy</td>
</tr>
<tr>
<td>DOS</td>
<td>density of states</td>
</tr>
<tr>
<td>DP</td>
<td>deformation potential</td>
</tr>
<tr>
<td>ER</td>
<td>electoreflectance</td>
</tr>
<tr>
<td>EXAFS</td>
<td>extended X-ray absorption fine-structure spectroscopy</td>
</tr>
<tr>
<td>fcc</td>
<td>face-centered cubic</td>
</tr>
<tr>
<td>FET</td>
<td>field effect transistor</td>
</tr>
<tr>
<td>FTIR</td>
<td>Fourier transform infrared</td>
</tr>
<tr>
<td>HBT</td>
<td>heterojunction bipolar transistor</td>
</tr>
<tr>
<td>HH</td>
<td>heavy-hole</td>
</tr>
<tr>
<td>HREELS</td>
<td>high-resolution electron-energy-loss spectroscopy</td>
</tr>
<tr>
<td>HRXRD</td>
<td>high-resolution X-ray diffraction</td>
</tr>
<tr>
<td>HT-VPE</td>
<td>hydride-transport vapor-phase epitaxy</td>
</tr>
<tr>
<td>IR</td>
<td>infrared</td>
</tr>
<tr>
<td>I–V</td>
<td>current–voltage</td>
</tr>
<tr>
<td>LA</td>
<td>longitudinal acoustic</td>
</tr>
<tr>
<td>LH</td>
<td>light-hole</td>
</tr>
<tr>
<td>LO</td>
<td>longitudinal optical</td>
</tr>
<tr>
<td>LPE</td>
<td>liquid-phase epitaxy</td>
</tr>
<tr>
<td>MBE</td>
<td>molecular beam epitaxy</td>
</tr>
<tr>
<td>MDF</td>
<td>model dielectric function</td>
</tr>
<tr>
<td>MOCVD</td>
<td>metalorganic chemical vapor deposition</td>
</tr>
</tbody>
</table>
ABBREVIATIONS AND ACRONYMS

MOMBE  metalorganic molecular beam epitaxy
MQW    multiple quantum well
MREI   modified random-element-isodisplacement
PDP    phonon deformation potential
PIXE   particle-induced X-ray emission
PL     photoluminescence
PLD    pulsed-laser deposition
PLE    photoluminescence excitation
PR     photoreflectance
PzR    piezoreflectance
QW     quantum well
RBS    Rutherford backscattering spectrometry
rf     radio-frequency
RHEED  reflection high-energy electron diffraction
SE     spectroscopic ellipsometry
SL     superlattice
SO     spin–orbit
TA     transverse acoustic
TEM    transmission electron microscopy
THM    traveling heater method
TO     transverse optical
TP     triple-period
TR     thermoreflectance
UHV    ultrahigh vacuum
UV     ultraviolet
VB     valence band
VCA    virtual crystal approximation
VPE    vapor-phase epitaxy
w-     wurtzite
WDXS   wavelength-dispersive X-ray spectroscopy
XPS    X-ray photoelectron spectroscopy
XRD    X-ray diffraction
1D     one-dimensional
2D     two-dimensional
3D     three-dimensional
An alloy is a combination, either in solution or compound, of two or more elements. An alloy with two components is called a binary alloy; one with three is a ternary alloy; one with four is a quaternary alloy; one with five is a pentanary alloy. The resulting alloy substance generally has properties significantly different from those of its components. The proportions of the ingredients are available.

A chemical compound is a substance consisting of two or more chemical elements that are chemically combined in fixed proportions. The ratio of each element is usually expressed by chemical formula. For example, water is a compound consisting of two hydrogen atoms bonded to an oxygen atom (H\textsubscript{2}O). The atoms within a compound can be held together by a variety of interactions, ranging from covalent bonds to electrostatic forces in ionic bonds. A continuum of bond polarities exists between the purely covalent and ionic bonds. For example, H\textsubscript{2}O is held together by polar covalent bonds. NaCl is an example of an ionic compound.

Simply, an alloy is formed from a physical mixture of two or more substances, while a compound is formed from a chemical reaction. An alloy crystal is sometimes called a mixed crystal or a solid solution. For example, GaAs is a compound consisting of Ga atoms bonded to As atoms. It is not an alloy. Al\textsubscript{x}Ga\textsubscript{1-x}As is an alloy compound consisting of AlAs and GaAs with a mole ratio of x:(1 − x). The bonds in GaAs and AlAs are not adequately described by any of these extreme types, but have characteristics intermediate to those usually associated with the covalent and ionic terms. The bonds in diamond, C−C, can be described by the covalent bond term only. It is an elemental semiconductor, not a compound semiconductor. Similarly, Si and Ge are elemental semiconductors. Like Al\textsubscript{x}Ga\textsubscript{1-x}As, Si\textsubscript{x}Ge\textsubscript{1−x} (0 ≤ x ≤ 1.0) is an alloy semiconductor. The bonds Si−Ge, Si−Si and Ge−Ge in Si\textsubscript{x}Ge\textsubscript{1−x} are, therefore, described by the covalent term only. It should be noted, however, that silicon carbide (SiC) is a compound, not an alloy. This is because that the chemical bonds in SiC cannot be described only by the covalent term, but have characteristics intermediate to those associated with the covalent and ionic terms, like GaAs and AlAs.

There is an ordered alloy phase in Si\textsubscript{x}Ge\textsubscript{1−x} binary alloy [1]. This phase exhibits long-range order rather than random arrangement of atoms as expected previously. The ordered phase, as expected, occurs mostly in bulk Si\textsubscript{x}Ge\textsubscript{1−x} layers at x ~ 0.5 and can be explained by the rhombohedral structure. Note that SiC is thought to be an ordered alloy. It crystallizes in a large number of polytypes. The various types of SiC differ one from another only by the order in which successive planes of Si (or C) atoms are stacked along the c axis; one polytype is the cubic, zinc-blende structure (3C) while the reminder, including two of the more frequently occurring forms, 6H (hexagonal) and 15R (rhombohedral), possess uniaxial symmetry [2]. There is no diamond structure in the SiC polytypes. An ordered alloy phase has been found not only in Si\textsubscript{x}Ge\textsubscript{1−x}, but also in many III–V and II–VI semiconductor alloys [3].
A.2 GRIMM–SOMMERFELD RULE

The periodic law is most commonly expressed in chemistry in the form of a periodic table or chart. An important part of this table is shown in Table A.1. The so-called short-form periodic table, based on the Mendeleyev table, with subsequent emendations and additions, is still in widespread use. The elements in this table are arranged in seven horizontal rows, called the periods, in order of increasing atomic weights, and in 18 vertical columns, called the groups. The first period, containing two elements, H and He, and the next two periods, each containing eight elements, are called the short periods. The remaining periods, called the long periods, contain 18 elements, as in periods 4 and 5, or 32 elements, as in period 6. The long period 7 includes the actinide series, which has been filled in by the synthesis of radioactive nuclei through element 103, lawrencium (Lr). Heavier transuranium elements, atomic numbers 104 to 112, have also been synthesized.

<table>
<thead>
<tr>
<th>Period</th>
<th>Groups</th>
<th>Elements</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>IA</td>
<td>H, He</td>
</tr>
<tr>
<td>2</td>
<td>IIA</td>
<td>Li, Be</td>
</tr>
<tr>
<td>3</td>
<td>IIIA</td>
<td>Na, Mg</td>
</tr>
<tr>
<td>4</td>
<td>IIIA</td>
<td>K, Ca, Sr</td>
</tr>
<tr>
<td>5</td>
<td>IIIA</td>
<td>Rb, Ba, Cs</td>
</tr>
<tr>
<td>6</td>
<td>IIIA</td>
<td>Ba, Sr, Ca</td>
</tr>
<tr>
<td>7</td>
<td>IIIA</td>
<td>Ce, Pr, La</td>
</tr>
</tbody>
</table>

The elemental semiconductors in column IVa of the periodic table are diamond, Si and Ge, and they are of some importance in various device applications. Note that gray tin (α-Sn) is a semiconductor (semimetal) and Pb is a metal. SiC is the only compound semiconductor formed by column IVa elements. The III–V and II–VI semiconductors possess a crystal structure similar to either one of the cubic mineral, sphalerite or to hexagonal wurtzite. There are 15 III–V, 18 II–VI and four I–VII compound semiconductors. The four I–VII compound semiconductors are: CuCl, CuBr, CuI and AgI.

A substantial development in the search for semiconducting materials with new combinations of physical and chemical properties was reached when Goryunova using the ideas of Huggins [4] and Grimm and Sommerfeld [5], developed a method of prediction of the composition of chemical compounds with the tetrahedral and octahedral (NaCl-type) coordination of atoms in their crystal lattice [6]. His method is based on consideration of the number of valence electrons in the elements, which is assumed to be equal to the number of the group in...
the periodic table to which they belong (so-called full or normal valency) and can be expressed in the form of the equation system [7]

\[
\begin{align*}
\sum_{i=1}^{A} B_i x_i &= 4 \\
\sum_{i=1}^{n} B_i x_i &= \sum_{i=n+1}^{A} (8-B_i)x_i \\
\sum_{i=1}^{A} x_i &= 1
\end{align*}
\]

(A.1)

for calculating the content of the representatives of different groups of the periodic table in a compound containing \(A\) components, \(n\) of which are considered as cations, where \(B_i\) is the number of the group in the periodic table to which the \(i\)th component of the compounds belongs, and \(x_i\) is its concentration in the compound. The first expression in Equation (A.1) represents the condition that the average number of valence electrons per atom is equal to four (tetrahedral rule). The second equation states that in the compound, the number of valence electrons, which ‘cations’ give to ‘anions’ is equal to the number of electrons the anion needs to form the octet (i.e. the normal valency condition). The quotation marks here are used to remind us that in the solids with dominating covalent bonds, which factually form the class of semiconductor, the ion concept is quite conditional. Based on these criteria, it is possible to obtain all probable types of tetrahedral substances, taking into consideration only the location of their components in one or another group of the periodic table. Table A.2 briefly summarizes these results.

Table A.2  Summary of valence binary compounds and ternary analogs of binary valence compounds which satisfy tetrahedral rule (\(Z=4\)). ch=chalcopyrite; zb=zinc-blende; t=tetragonal; or=orthorhombic; w=wurtzite; h=hexagonal (\(P6_3mc\) (\(C_{6v}\))); rh=rhombohedral

<table>
<thead>
<tr>
<th>Cation</th>
<th>Compound</th>
<th>Typical compound (Crystal structure)</th>
</tr>
</thead>
<tbody>
<tr>
<td>I</td>
<td>I–III–VI2</td>
<td>CuGaSe2 (ch)</td>
</tr>
<tr>
<td></td>
<td>I–IV2–V3</td>
<td>CuGeP2 (zb)</td>
</tr>
<tr>
<td></td>
<td>I2–IV–VI3</td>
<td>Cu2GeSe3 (t)</td>
</tr>
<tr>
<td></td>
<td>I3–V–VI4</td>
<td>Cu3PS4 (or)</td>
</tr>
<tr>
<td></td>
<td>I–VII</td>
<td>(\gamma)-CuCl (w)</td>
</tr>
<tr>
<td>II</td>
<td>II2–III–VII3</td>
<td>ZnSiP2 (ch)</td>
</tr>
<tr>
<td></td>
<td>II–IV–V2</td>
<td></td>
</tr>
<tr>
<td></td>
<td>II3–IV–VII2</td>
<td></td>
</tr>
<tr>
<td></td>
<td>II2–V–VII</td>
<td></td>
</tr>
<tr>
<td></td>
<td>II–VI</td>
<td>CdTe (zb)</td>
</tr>
<tr>
<td>III</td>
<td>III2–IV–VI</td>
<td>Al2CO (w)</td>
</tr>
<tr>
<td></td>
<td>III3–IV2–VII</td>
<td></td>
</tr>
<tr>
<td></td>
<td>III–V</td>
<td>GaAs (zb)</td>
</tr>
<tr>
<td>IV</td>
<td>IV–IV</td>
<td>SiC (zb, w, h, rh)</td>
</tr>
</tbody>
</table>
In analyzing the normal valency compounds, not only tetrahedral phases but all compounds of this category can be grouped, first of all, in accordance with the average valence electron content per atom of a compound, \( Z \). We list in Table A.3 all possible types of the binary valence compounds \(^7\). If \( A \) and \( B \) are the cation valencies in a binary compound, the atomic ratio of components in a valence compound \( A_xB_y \) is given by

\[
\frac{x}{y} = \frac{8 - B}{A} \tag{A.2}
\]

and the valence electron concentration per atom in the corresponding binary compound is

\[
Z = \frac{8A}{8 - (B - A)} = \frac{8A}{8 + (A - B)} \tag{A.3}
\]

as following from Equation (A.1).

In Table A.3, there are 22 types of binary valence compounds. Goryunova \(^6\) concluded from the available experimental data that the phases possessing semiconducting properties are those with \( Z \) between two and six; the phases smaller than two are either metal alloys or the compounds with typical metallic crystal structure and properties. Goryunova also showed that there are 148 types of ternary compounds which are the electron analogs of the binary valence compounds \(^7\). Among them, there are 10 types of ternary compounds which satisfy the tetrarahedral rule \( Z = 4 \), as listed in Table A.2.

### A.3 AN INTERPOLATION SCHEME

The electronic energy-band parameters of semiconductor alloys and their dependence on alloy composition are very important, and so they have received much attention in the past. Investigation
of many device parameters have, however, been hampered by a lack of definite knowledge of
various material parameters. This necessitates the use of some sort of interpolation scheme.
If the linear interpolation scheme is used, the ternary material parameter $T$ for an alloy of the
form $A_xB_{1-x}C$ can be derived from binary parameters ($B$) by

$$T(x) = xB_{AC} + (1-x)B_{BC} \equiv a + bx$$  \hspace{1cm} (A.4)$$

where $a \equiv B_{BC}$ and $b \equiv B_{AC} - B_{BC}$. Some material parameters, however, deviate significantly
from the linear relationship shown in Equation (A.4), and exhibit an approximately quadratic
dependence on $x$. The ternary material parameter in such a case can be very efficiently
approximated by the relationship

$$T(x) = xB_{AC} + (1-x)B_{BC} + x(1-x)C_{AB} \equiv a + bx + cx^2$$  \hspace{1cm} (A.5)$$

where $a \equiv B_{BC}$, $b \equiv B_{AC} - B_{BC} + C_{AB}$ and $c \equiv -C_{AB}$. The parameter $c$ is called a bowing
parameter.

The quaternary material $A_xB_{1-x}C_yD_{1-y}$ is thought to be constructed from four binaries: $AC$, $AD$, $BC$ and $BD$. If the linear interpolation scheme is used, the quaternary material parameter $Q$
can be derived from the binary parameters by

$$Q(x,y) = xB_{AD} + yB_{BD} + (1-x-y)B_{CD}$$  \hspace{1cm} (A.6)$$

If one of the four binary parameters (e.g. $B_{AD}$) is lacking, $Q$ can be estimated from

$$Q(x,y) = xB_{AC} + (1-x)B_{BC} + (1-y)B_{BD}$$  \hspace{1cm} (A.7)$$

The quaternary material $A_xB_yC_{1-x-y}D$ is thought to be constructed from three binaries: $AD$, $BD$ and $CD$. The corresponding linear interpolation is given by

$$Q(x,y) = xB_{AD} + yB_{BD} + (1-x-y)B_{CD}$$  \hspace{1cm} (A.8)$$

If relationships for the ternary parameters are available, the quaternary material parameter $Q$
can be expressed either as $(A_xB_{1-x}C_{y}D_{1-y})$

$$Q(x,y) = \frac{x(1-x)[yT_{ABC}(x) + (1-y)T_{ABD}(x)] + y(1-y)[xT_{ACD}(y) + (1-x)T_{BCD}(y)]}{x(1-x) + y(1-y)}$$  \hspace{1cm} (A.9)$$

or $(A_xB_{y}C_{1-x-y}D)$

$$Q(x,y) = \frac{xyT_{ABD}(u) + y(1-x-y)T_{BCD}(v) + x(1-x-y)T_{ACD}(w)}{xy + y(1-x-y) + x(1-x-y)}$$  \hspace{1cm} (A.10)$$

with

$$u = (1-x-y)/2$$
$$v = (2-x-2y)/2$$
$$w = (2-2x-y)/2$$  \hspace{1cm} (A.11)$$
If a quaternary bowing term $D_{ABCD} = -d$ is considered in Equation (A.9) or Equation (A.10), we can obtain

$$Q(x,y) = \{x(1-x)yT_{ABC}(x) + (1-y)T_{ABD}(x) + y(1-y)D_{ABCD} \} + y(1-y)$$

$$\times [xT_{ACD}(y) + (1-x)T_{BCD}(y) + x(1-x)D_{ABCD}] \times [x(1-x) + y(1-y)]^{-1}$$  \hspace{1cm} (A.12)

for the $A_xB_1-x,C_3D_{1-y}$ quaternary or

$$Q(x,y) = \frac{xyT_{ABD}(u)+y(1-x-y)T_{BCD}(v)+x(1-x-y)T_{ACD}(w)+xy(1-x-y)D_{ABCD}}{xy+y(1-x-y)+x(1-x-y)}$$  \hspace{1cm} (A.13)

for the $A_xB_3,C_{1-x-y},D$ quaternary.

The weighted form of Equation (A.12) can be written as

$$Q(x,y) = y(1-x)B_{BC} + xyB_{AC} + (1-y)xB_{AD} + (1-x)(1-y)B_{CD} + x(1-x)(1-y)C_{AB(D)}$$

$$+ x(1-x)yC_{AB(C)} + (1-x)y(1-y)C_{(B)CD} + xy(1-y)C_{(A)CD}$$

$$+ x(1-x)y(1-y)D_{ABCD}$$  \hspace{1cm} (A.14)

where $C_{AB(D)}$ is the ternary bowing parameter for an alloy $A_xB_{1-x}D$ and so on. Expression (A.14) can be conveniently compacted into an inner product whose $3 \times 3$ matrix includes only the alloy parameters and closely resembles the map of the quaternary alloy in its compositional space [8]

$$Q(x,y) = [y \ y(1-y) \ 1-y] \begin{bmatrix} B_{BC} & C_{AB(C)} & B_{AD} \\ C_{(B)CD} & D_{ABCD} & C_{(A)CD} \\ B_{BD} & C_{AB(D)} & B_{AD} \end{bmatrix} \begin{bmatrix} 1-x \\ x(1-x) \\ x \end{bmatrix}$$  \hspace{1cm} (A.15)

If the bowing parameters $C$ and $D$ in Equation (A.15) are zero, Vegard law is recovered in its bilinear formulation. Equation (A.15) is valid for quaternaries of types $A_xB_{1-x}C_yD_{1-y}$ and $A_xB_3C_{1-x-y}D$ ($ABC_3D_{1-y}$). For the latter, one binary can be assigned twice in the same row or column of the alloy matrix with a zero bowing factor (i.e., $B_{AC} = B_{AD}$ and $C_{(A)CD} = 0$). The composition for such an alloy is given by $(B_{AD})_1[(B_{BD})_1(B_{CD})_{1-y}]_{1-x}$ (e.g., $Al_x(Ga_{1-y}In_{1-y})_{1-x}P$).

The essentially same expressions can be obtained for group-IV semiconductor alloys. The binary material parameter $B$ in the form of $A_xB_{1-x}$ can be written using the elemental material parameters $A$ as

$$B(x) = xA_A + (1-x)A_B \equiv a + bx$$  \hspace{1cm} (A.16)

The bowing effect modifies Equation (A.16) in the form

$$B(x) = xA_A + (1-x)A_B + x(1-x)C_{AB} \equiv a + bx + cx^2$$  \hspace{1cm} (A.17)

Similarly, the ternary material parameter $T$ in $A_xB_3,C_{1-x-y}$ can be expressed as

$$T(x,y) = xA_A + yA_B + (1-x-y)A_C$$  \hspace{1cm} (A.18)