

# Properties of Group-IV, III-V and II-VI Semiconductors

**Sadao Adachi**

*Department of Electronic Engineering  
Gunma University  
Japan*



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# **Properties of Group-IV, III-V and II-VI Semiconductors**

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Japan*



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# Contents

<b>Series Preface</b>	<b>xiii</b>
<b>Preface</b>	<b>xv</b>
<b>Acknowledgments/Dedication</b>	<b>xvii</b>
<b>1 Structural Properties</b>	<b>1</b>
1.1 Ionicity	1
1.1.1 Definition	1
(a) Phillips ionicity	2
(b) Pauling ionicity	2
(c) Harrison ionicity	2
1.1.2 Ionicity Value	3
1.2 Elemental Isotopic Abundance and Molecular Weight	3
1.2.1 Elemental Isotopic Abundance	3
1.2.2 Molecular Weight	4
1.3 Crystal Structure and Space Group	4
1.3.1 Crystal Structure	4
(a) Diamond, zinc-blende and wurtzite structures	4
(b) Hexagonal and rhombohedral structures	7
(c) Rocksalt structure	9
1.3.2 Space Group	10
1.4 Lattice Constant and Related Parameters	12
1.4.1 Lattice Constant	12
(a) Room-temperature value	12
(b) Near-neighbor distance	12
(c) External perturbation effect	13
1.4.2 Molecular and Crystal Densities	13
1.5 Structural Phase Transitions	14
1.6 Cleavage	15
1.6.1 Cleavage Plane	15
1.6.2 Surface Energy	18
(a) Theoretical value	18
(b) Experimental value	20
References	20

<b>2 Thermal Properties</b>	<b>23</b>
2.1 Melting Point and Related Parameters	23
2.1.1 Phase Diagram	23
2.1.2 Melting Point	23
2.2 Specific Heat	26
2.3 Debye Temperature	28
2.4 Thermal Expansion Coefficient	30
2.5 Thermal Conductivity and Diffusivity	33
2.5.1 Thermal Conductivity	33
2.5.2 Thermal Diffusivity	39
References	39
<b>3 Elastic Properties</b>	<b>41</b>
3.1 Elastic Constant	41
3.1.1 General Remarks	41
3.1.2 Room-temperature Value	42
3.1.3 External Perturbation Effect	48
(a) Temperature effect	48
(b) Pressure effect	50
3.2 Third-order Elastic Constant	51
3.3 Young's Modulus, Poisson's Ratio and Similar Properties	53
3.3.1 Young's Modulus and Poisson's Ratio: Cubic Lattice	53
3.3.2 Bulk Modulus, Shear Modulus and Similar Properties: Cubic Lattice	56
3.3.3 Young's Modulus and Poisson's Ratio: Hexagonal Lattice	60
3.3.4 Bulk Modulus, Shear Modulus and Similar Properties: Hexagonal Lattice	61
3.4 Microhardness	62
3.5 Sound Velocity	68
References	72
<b>4 Lattice Dynamic Properties</b>	<b>73</b>
4.1 Phonon Dispersion Relation	73
4.1.1 Brillouin Zone	73
(a) Face-centered cubic lattice	74
(b) Hexagonal lattice	74
(c) Rhombohedral lattice	75
4.1.2 Phonon Dispersion Curve	75
(a) Cubic lattice	75
(b) Hexagonal lattice	77
4.1.3 Phonon Density of States	79
4.2 Phonon Frequency	80
4.2.1 Room-temperature Value	80
4.2.2 External Perturbation Effect	84
(a) Temperature effect	84
(b) Pressure effect	86
4.3 Mode Grüneisen Parameter	87

4.4 Phonon Deformation Potential	88
4.4.1 Cubic Lattice	88
4.4.2 Hexagonal Lattice	91
References	92
<b>5 Collective Effects and Some Response Characteristics</b>	<b>95</b>
5.1 Piezoelectric and Electromechanical Constants	95
5.1.1 Piezoelectric Constant	95
(a) Piezoelectric stress constant	95
(b) Piezoelectric strain constant	98
5.1.2 Electromechanical Coupling Constant	99
5.2 Fröhlich Coupling Constant	99
References	101
<b>6 Energy-band Structure: Energy-band Gaps</b>	<b>103</b>
6.1 Basic Properties	103
6.1.1 Energy-band Structure	103
(a) Diamond-type semiconductor	104
(b) Zinc-blende-type semiconductor	106
(c) Wurtzite-type semiconductor	108
6.1.2 Electronic Density of States	111
6.2 $E_0$ -gap Region	114
6.2.1 Effective $\Gamma$ -point Hamiltonian	114
6.2.2 Room-temperature Value	115
6.2.3 External Perturbation Effect	120
(a) Temperature effect	120
(b) Pressure effect	124
(c) Temperature and pressure coefficients	124
6.2.4 Doping Effect	126
6.3 Higher-lying Direct Gap	130
6.3.1 Cubic Semiconductor	130
(a) Room-temperature value	130
(b) External perturbation effect	133
6.3.2 Hexagonal and Rhombohedral Semiconductors	137
6.4 Lowest Indirect Gap	137
6.4.1 Room-temperature Value	137
6.4.2 External Perturbation Effect	138
(a) Temperature effect	138
(b) Pressure effect	139
(c) Temperature and pressure coefficients	142
6.5 Conduction-valley Energy Separation	142
6.6 Direct–Indirect-gap Transition Pressure	142
References	143
<b>7 Energy-band Structure: Effective Masses</b>	<b>147</b>
7.1 Electron Effective Mass: $\Gamma$ Valley	147
7.1.1 General Remarks	147

7.1.2 Numerical Value	149
7.1.3 Polaron Effect	151
7.1.4 External Perturbation and Doping Effects	152
(a) Temperature effect	152
(b) Pressure effect	153
(c) Doping effect	155
7.2 Electron Effective Mass: Satellite Valley	158
7.2.1 Camel's Back Structure	158
7.2.2 Numerical Value	159
7.3 Hole Effective Mass	159
7.3.1 Effective $\Gamma$ -valence-band Hamiltonian and Luttinger Parameter	159
7.3.2 Numerical Value	164
(a) Cubic semiconductor	164
(b) Hexagonal and rhombohedral semiconductors	167
7.3.3 Polaron Effect	168
7.3.4 External Perturbation and Doping Effects	170
(a) Temperature effect	170
(b) Pressure effect	170
(c) Doping effect	170
References	171
<b>8 Deformation Potentials</b>	<b>173</b>
8.1 Intravalley Deformation Potential: $\Gamma$ Point	173
8.1.1 Conduction Band	173
8.1.2 Valence Band	175
8.1.3 $E_0$ Gap	179
8.1.4 Optical Phonon Deformation Potential	181
8.2 Intravalley Deformation Potential: High-symmetry Points	183
8.2.1 L Point	183
(a) Hydrostatic and shear deformation potentials: conduction band	183
(b) Optical phonon deformation potential	185
(c) Valence-band deformation potential	186
(d) Hydrostatic and interband deformation potentials: $E_1$ and $E_1 + \Delta_1$ gaps	186
8.2.2 X Point	188
(a) Hydrostatic and shear deformation potentials: conduction band	188
(b) Hydrostatic and interband deformation potentials: $E_2$ gap	189
8.3 Intervalley Deformation Potential	189
8.3.1 General Remarks	189
8.3.2 Numerical Value	192
References	192
<b>9 Electron Affinity and Schottky Barrier Height</b>	<b>195</b>
9.1 Electron Affinity	195
9.1.1 An Overview	195
9.1.2 Numerical Value	196

9.2 Schottky Barrier Height	198
9.2.1 An Ideal Schottky–Mott Contact	198
9.2.2 Case Study: Au/Semiconductor Contact	202
9.2.3 Surface Reconstruction and External Perturbation Effect	204
(a) Surface reconstruction	204
(b) Temperature effect	205
(c) Pressure effect	205
9.2.4 Breakdown Voltage	206
References	208
<b>10 Optical Properties</b>	<b>211</b>
10.1 Summary of Optical Dispersion Relations	211
10.1.1 Dielectric Permittivity	211
10.1.2 Optical Dispersion Relation	213
10.1.3 Optical Sum Rule	214
10.1.4 Optical Spectra	216
10.2 The Reststrahlen Region	217
10.2.1 Static and High-frequency Dielectric Constants	217
(a) Room-temperature value	217
(b) External perturbation effect	219
10.2.2 Reststrahlen Spectra	222
(a) Zinc-blende-type and rocksalt-type semiconductors	222
(b) Hexagonal semiconductor	226
(c) External perturbation effect	227
10.2.3 Multiphonon Optical Absorption Spectra	228
10.3 At or Near the Fundamental Absorption Edge	230
10.3.1 Free-exciton Binding Energy and Related Parameters	230
(a) Exciton states: direct exciton	230
(b) Exciton states: indirect exciton	232
(c) Exciton binding energy and related parameters	233
(d) Spin-exchange interaction constant	236
10.3.2 Refractive Index	236
(a) Theoretical dispersion model	236
(b) Long-wavelength $n$ value: empirical formula	240
(c) External perturbation effect	241
10.3.3 Optical Absorption at the Fundamental Absorption Edge	244
(a) Critical point: definition	244
(b) Free electron–hole pair transition	245
(c) Excitonic transition	251
(d) Experimental	253
10.3.4 Urbach Tail	256
10.4 The Interband Transition Region	258
10.4.1 Model Dielectric Function	258
(a) Fundamental absorption edge	259
(b) $E_1$ and $E_1 + \Delta_1$ transitions	259
(c) $E_0'$ , $E_2$ and $E_1'$ transitions	260
(d) Plasma and $d$ -band effects	262

10.4.2 Fundamental Optical Spectra	263
(a) Si	263
(b) GaAs	265
(c) <i>w</i> -CdS	265
10.4.3 External Perturbation and Doping Effects	268
(a) Temperature effect	268
(b) Pressure effect	268
(c) Doping effect	269
10.5 Free-carrier Absorption and Related Phenomena	270
10.5.1 Free-carrier Absorption	270
10.5.2 Interconduction-band and Intervalence-band Absorption	274
(a) Interconduction-band absorption	274
(b) Intervalence-band absorption	275
10.5.3 Free-carrier-induced Change in Refractive Index	278
References	278
<b>11 Elasto-optic, Electro-optic and Nonlinear Optical Properties</b>	<b>283</b>
11.1 Elasto-optic Effect	283
11.1.1 Theoretical Expression	283
11.1.2 Experimental Value	285
11.2 Linear Electro-optic Constant	291
11.2.1 Theoretical Expression	291
11.2.2 Experimental Value	294
11.3 Quadratic Electro-optic Constant	295
11.3.1 Theoretical Expression	295
11.3.2 Experimental Value	298
11.4 Franz–Keldysh Effect	300
11.4.1 Theoretical Expression	300
11.4.2 Experimental Value	301
11.5 Nonlinear Optical Constant	302
11.5.1 Second-order Nonlinear Optical Susceptibility	302
11.5.2 Third-order Nonlinear Optical Susceptibility	308
11.5.3 Two-photon Absorption	309
References	311
<b>12 Carrier Transport Properties</b>	<b>315</b>
12.1 Low-field Mobility: Electrons	315
12.1.1 Electron Scattering Mechanism	315
(a) Intervalley scattering	317
(b) Polar optical scattering	317
(c) Nonpolar optical scattering	318
(d) Piezoelectric scattering	318
(e) Deformation potential scattering	318
(f) Ionized impurity scattering	319
(g) Neutral impurity scattering	319
(h) Space-charge scattering	319

(i) Alloy scattering	320
(j) Carrier–carrier scattering	320
12.1.2 Three-valley Model	320
12.1.3 Room-temperature Value	321
12.1.4 External Perturbation and Doping Effects	324
(a) Temperature effect	324
(b) Pressure effect	325
(c) Doping effect	326
12.1.5 Hall Factor	328
12.2 Low-field Mobility: Holes	331
12.2.1 Hole Scattering Mechanism	331
12.2.2 Room-temperature Value	333
12.2.3 External Perturbation and Doping Effects	333
(a) Temperature effect	333
(b) Pressure effect	337
(c) Doping effect	337
12.3 High-field Transport: Electrons	339
12.3.1 Electron Drift Velocity–Field Characteristic	339
12.3.2 Electron Saturation Drift Velocity	347
(a) Temperature dependence	347
(b) LO phonon scattering-limited electron saturation drift velocity	348
12.4 High-field Transport: Holes	349
12.4.1 Hole Drift Velocity–Field Characteristic	349
12.4.2 Hole Saturation Drift Velocity	352
12.5 Minority-carrier Transport: Electrons in <i>p</i> -type Materials	353
12.5.1 Minority-electron Mobility	353
12.5.2 Minority-electron Drift Velocity	356
12.5.3 Minority-electron Lifetime and Diffusion Length	356
12.6 Minority-carrier Transport: Holes in <i>n</i> -type Materials	359
12.6.1 Minority-hole Mobility	359
12.6.2 Minority-hole Lifetime and Diffusion Length	360
12.7 Impact Ionization Coefficient	362
12.7.1 Theoretical Consideration	362
12.7.2 Experimental Value	365
(a) Electric-field dependence	365
(b) Temperature dependence	366
(c) Crystallographic direction dependence	368
References	369
<b>Index</b>	<b>373</b>



# Series Preface

## 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 topics as electrical conduction in solids, optical properties, thermal properties, etc., 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

Almost all the semiconductors of practical interest are the group-IV, III-V and II-VI semiconductors and the range of technical applications of such semiconductors is extremely wide. All such semiconductor devices can be characterized to a greater or lesser degree. Many scientific papers, review papers, book chapters and specialized books exist that discuss the various semiconductor properties, but no one has integrated such topics on the group-IV, III-V and II-VI semiconductors into one volume.

The purpose of this book is twofold: (i) to discuss key properties of the group-IV, III-V and II-VI semiconductors; and (ii) to systemize these properties from a solid-state physics aspect. The bulk of the text is devoted to the comprehensive description of the lattice structural, thermal, elastic, lattice dynamic, electronic energy-band structural, optical and carrier transport properties of these semiconductors. Some corrective effects and related properties, such as piezoelectric, elasto-optic and electro-optic properties, have also been discussed.

The book contains convenient tables summarizing the various material parameters and the definitions of important semiconductor properties. The book also contains graphs in order to make the information more quantitative and intuitive. I felt that these have not been adequately covered in existing books.

The book is intended not only for semiconductor device engineers, but also physicists and physical chemists, and particularly students specializing in the fields of semiconductor synthesis, crystal growth, semiconductor device physics and technology.

SADAo ADACHI  
*Gunma, Japan*



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# 1 Structural Properties

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1.1 Ionicity	1
1.1.1 Definition	1
1.1.2 Ionicity value	3
1.2 Elemental isotopic abundance and molecular weight	3
1.2.1 Elemental isotopic abundance	3
1.2.2 Molecular weight	4
1.3 Crystal structure and space group	4
1.3.1 Crystal structure	4
1.3.2 Space group	10
1.4 Lattice constant and related parameters	12
1.4.1 Lattice constant	12
1.4.2 Molecular and crystal densities	13
1.5 Structural phase transitions	14
1.6 Cleavage	15
1.6.1 Cleavage plane	15
1.6.2 Surface energy	18
References	20

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## 1.1 IONICITY

### 1.1.1 Definition

All tetrahedrally coordinated  $A^N B^{8-N}$  semiconductors can be treated within the framework of a simple model. The success of this approach requires a careful choice of parameters entering in the model. The most important of these is the ionicity of the bond [1.1].

The ionicity of a bond can be defined as the fraction  $f_i^\alpha$  of ionic or heteropolar character in the bond compared with the fraction  $f_h^\alpha$  of covalent or homopolar character. By definition, these fractions satisfy the relation

$$f_i^\alpha + f_h^\alpha = 1 \quad (1.1)$$

In an elemental semiconductor such as Si, we must have  $f_h^\alpha = 1$  and  $f_i^\alpha = 0$ . In contrast, we shall find that some alkali halides (NaCl, KCl, etc.) are more than 90% ionic.

### (a) Phillips ionicity

Phillips studied the connection between the chemical bonding properties of the  $A^N B^{8-N}$  family of crystals and their electronic energy-band structures [1.1]. His concept evolves from a molecular picture in terms of bonding and antibonding states separated by an energy gap  $E_g$ . His ionicity scale  $f_i$  is defined in terms of average quantities such as the homopolar  $E_h$  and heteropolar parts  $C$  of the complex energy gap  $E_g$  associated with the A–B bond in the crystal

$$E_g = E_h + iC \quad (1.2)$$

Ionicity is then introduced via the relation

$$f_i = \frac{C^2}{E_g^2} = \frac{C^2}{E_h^2 + C^2} \quad (1.3)$$

Some numerical examples of  $E_g$  ( $f_i$ ) are:  $E_g = 4.70 + i0$  ( $f_i = 0$ ) for Si;  $E_g = 4.32 + i2.90$  ( $f_i = 0.310$ ) for GaAs;  $E_g = 4.29 + i5.60$  ( $f_i = 0.630$ ) for ZnSe, where  $E_g$  are in eV.

### (b) Pauling ionicity

Pauling based his definition of ionicity scale  $f_i^P$  not on the total energy of the bond, but on empirical heats of formation [1.2]. Denote the power of an atom A to attract electrons to itself by a dimensionless number called its electronegativity  $X_A$ . The Coulomb interaction between the ionic charge left behind and the valence charge transferred is proportional to  $(X_A - X_B)^2$ , and this is the origin of the extra ionic energy (i.e.,  $f_i^P$ ). By definition  $f_i^P$  never exceeds one, and as  $X_A - X_B$  becomes large  $f_i^P$  tends to one. Moreover, the ionicity of an A–B bond should be the same as ionicity of a B–A bond. Pauling then defined ionicity of a single bond

$$f_i^P = 1 - \exp\left(-\frac{(X_A - X_B)^2}{4}\right) \quad (1.4)$$

### (c) Harrison ionicity

In Harrison's model [1.3], the ionicity parameter  $f_i^H$  can be given in terms of two of the parameters of the electronic structure, by

$$f_i^H = \frac{V_3}{\sqrt{V_2^2 + V_3^2}} \quad (1.5)$$

Here,  $V_2$  is half the splitting between bonding and antibonding states;  $V_3$  is half the energy change in transferring an electron from anion to cation. This parameter  $f_i^H$  can be defined as the excess number of electrons placed on the anion from each bond, called the polarity. Thus, each anion in a tetrahedral structure contains a charge of  $Z^* = 4f_i^H - \Delta Z$ ,

**Table 1.1** Phillips ( $f_i$ ), Pauling ( $f_i^P$ ) and Harrison ionicities ( $f_i^H$ ) for a number of group-IV, III–V and II–VI semiconductors

System	Material	$f_i$	$f_i^P$	$f_i^H$	System	Material	$f_i$	$f_i^P$	$f_i^H$
IV	Diamond	0	0	0	II–VI	MgO	0.841	0.88	
	Si	0	0	0		MgS	0.786		
	Ge	0	0	0		MgSe	0.790		
	Sn	0	0	0		MgTe	0.554		
	SiC	0.177	0.11	0.35		ZnO	0.616	0.80	0.69
III–V	BN	0.221	0.42	0.43	III–V	ZnS	0.623	0.59	0.69
	BP	0.032				ZnSe	0.630	0.57	0.70
	BA <sub>3</sub>	0.044				ZnTe	0.609	0.53	0.68
	AlN	0.449	0.56	0.57		CdS	0.685	0.59	0.74
	AlP	0.307	0.25	0.47		CdSe	0.699	0.58	0.74
	AlAs	0.274	0.27	0.44		CdTe	0.717	0.52	0.76
	AlSb	0.250	0.26	0.56	IV	HgS	0.790		
	GaN	0.500	0.55	0.61		HgSe	0.680		
	GaP	0.327	0.27	0.48		HgTe	0.650		0.78
	GaAs	0.310	0.26	0.47					
	GaSb	0.261	0.26	0.43					
	InN	0.578			II–VI				
	InP	0.421	0.26	0.55					
	InAs	0.357	0.26	0.51					
	InSb	0.321	0.25	0.48					

where  $\Delta Z$  is the difference in valence from 4 ( $\Delta Z = 1$  for nitrogen, 2 for oxygen, etc.). Similarly, then, each bond provides an electronic dipole moment of  $\mathbf{P} = \gamma f_i^H (-e\mathbf{d})$ , where  $\mathbf{d}$  is vector distance from cation to anion and  $\gamma$  is a scale parameter to take into account local fields and charge symmetries; a value of  $\sqrt{2}$  gave a good fit to experiment.

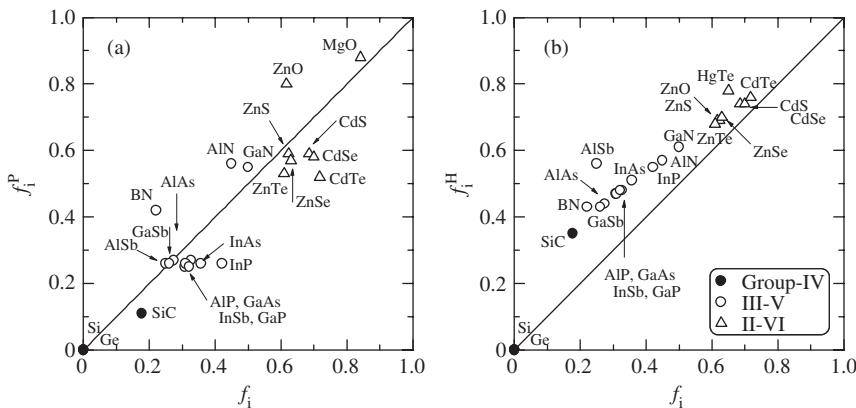
### 1.1.2 Ionicity value

Table 1.1 summarizes the values of Phillips ( $f_i$ ) [1.1], Pauling ( $f_i^P$ ) [1.2] and Harrison ionicities ( $f_i^H$ ) [1.3] for a number of group-IV, III–V and II–VI semiconductors. We also show in Figure 1.1 Phillips ionicity  $f_i$  versus (a) Pauling ( $f_i^P$ ) and (b) Harrison ionicities ( $f_i^H$ ) for these semiconductors.

## 1.2 ELEMENTAL ISOTOPIC ABUNDANCE AND MOLECULAR WEIGHT

### 1.2.1 Elemental isotopic abundance

There are a great many semiconductor materials. We list in Table 1.2 the elements which form at least one tetrahedrally coordinated  $A^N B^{8-N}$  semiconductor, together with their



**Figure 1.1** Phillips ionicity  $f_i$  versus (a) Pauling ( $f_i^P$ ) and (b) Harrison ionicities ( $f_i^H$ ) for some group-IV, III-V and II-VI semiconductors. The solid lines in (a) and (b) indicate the relations of  $f_i = f_i^P$  and  $f_i = f_i^H$ , respectively

natural isotopic abundance in percent [1.4]. Table 1.3 also lists the standard atomic weight for some group IV, III, V, II and VI elements [1.4].

### 1.2.2 Molecular weight

The molecular weight  $M$  for an  $A^N B^{8-N}$  semiconductor ( $N \neq 4$ ) can be simply given by the sum of the atomic weights of atoms A and B. For an elemental semiconductor ( $N = 4$ ), it is given by the atomic weight of the element atom A = B. Tables 1.4 and 1.5 list the values of  $M$  for a number of group-IV, III-V and II-VI semiconductors with cubic and hexagonal (rhombohedral) structures, respectively.

## 1.3 CRYSTAL STRUCTURE AND SPACE GROUP

### 1.3.1 Crystal structure

#### (a) Diamond, zinc-blende and wurtzite structures

The atoms of certain elements are held together in the solid by strongly covalent bonds at tetrahedral angles of  $109.5^\circ$ . Each atom has four nearest neighbors and twelve next nearest neighbors, which is a consequence of each atom sharing one of its outer electrons with each of four neighbors. The typical structure so formed is that of *diamond*, as shown in Figure 1.2(a). The space lattice is face-centered cubic with pairs of atoms at  $(0, 0, 0)$  and  $(1/4, 1/4, 1/4)$  forming a pattern unit.

The atomic orbitals that are used to form hybridized bonding orbitals are usually not the same ones that are occupied in the ground state of the atom. For example, in silicon the ground valence configuration of the atom is  $3s^2 3p^2$ , whereas the hybridized configuration appropriate for the diamond-type crystal structure is  $3s^1 3p^3$  (tetrahedral coordination).

**Table 1.2** Natural isotopic abundance in percent for some group IV, III, V, II and VI elements

Group	Isotope	Natural abundance (%)	Group	Isotope	Natural abundance (%)
IV	<sup>12</sup> C	98.90	IV	<sup>112</sup> Sn	0.97
	<sup>13</sup> C	1.10		<sup>114</sup> Sn	0.65
	<sup>28</sup> Si	92.23		<sup>115</sup> Sn	0.34
	<sup>29</sup> Si	4.67		<sup>116</sup> Sn	14.53
	<sup>30</sup> Si	3.10		<sup>117</sup> Sn	7.68
	<sup>70</sup> Ge	21.23		<sup>118</sup> Sn	24.23
	<sup>72</sup> Ge	27.66		<sup>119</sup> Sn	8.59
	<sup>73</sup> Ge	7.73		<sup>120</sup> Sn	32.59
	<sup>74</sup> Ge	35.94		<sup>122</sup> Sn	4.63
	<sup>76</sup> Ge	7.44		<sup>124</sup> Sn	5.79
III	<sup>10</sup> B	19.9	V	<sup>14</sup> N	99.634
	<sup>11</sup> B	80.1		<sup>15</sup> N	0.366
	<sup>27</sup> Al	100		<sup>31</sup> P	100
	<sup>69</sup> Ga	60.108		<sup>75</sup> As	100
	<sup>71</sup> Ga	39.892		<sup>121</sup> Sb	57.36
	<sup>113</sup> In	4.3		<sup>123</sup> Sb	42.64
II	<sup>115</sup> In	95.7	VI	<sup>16</sup> O	99.762
	<sup>24</sup> Mg	78.99		<sup>17</sup> O	0.038
	<sup>25</sup> Mg	10.00		<sup>32</sup> S	95.02
	<sup>26</sup> Mg	11.01		<sup>33</sup> S	0.75
	<sup>64</sup> Zn	48.6		<sup>34</sup> S	4.21
	<sup>66</sup> Zn	27.9		<sup>36</sup> S	0.02
	<sup>67</sup> Zn	4.1		<sup>74</sup> Se	0.89
	<sup>68</sup> Zn	18.8		<sup>76</sup> Se	9.36
	<sup>70</sup> Zn	0.6		<sup>77</sup> Se	7.63
	<sup>106</sup> Cd	1.25		<sup>78</sup> Se	23.78
	<sup>108</sup> Cd	0.89		<sup>80</sup> Se	49.61
	<sup>110</sup> Cd	12.49		<sup>82</sup> Se	8.73
	<sup>111</sup> Cd	12.80		<sup>120</sup> Te	0.096
	<sup>112</sup> Cd	24.13		<sup>122</sup> Te	2.603
	<sup>113</sup> Cd	12.22		<sup>123</sup> Te	0.908
	<sup>114</sup> Cd	28.73		<sup>124</sup> Te	4.816
	<sup>116</sup> Cd	7.49		<sup>125</sup> Te	7.139
	<sup>196</sup> Hg	0.15		<sup>126</sup> Te	18.95
	<sup>198</sup> Hg	9.97		<sup>128</sup> Te	31.69
	<sup>199</sup> Hg	16.87		<sup>130</sup> Te	33.80
	<sup>200</sup> Hg	23.10			
	<sup>201</sup> Hg	13.18			
	<sup>202</sup> Hg	29.86			
	<sup>204</sup> Hg	6.87			

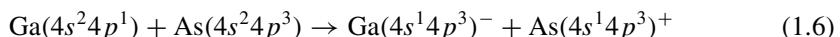
**Table 1.3** Standard atomic weight for some group IV, III, V, II and VI elements. Numbers in parentheses give the uncertainty in the last digit of the stated values

Group	Symbol	Atomic weight	Group	Symbol	Atomic weight
IV	C	12.0107(8)			
	Si	28.0855(3)			
	Ge	72.61(2)			
	Sn	118.710(7)			
III	B	10.811(7)	V	N	14.00674(7)
	Al	26.981538(2)		P	30.973761(2)
	Ga	69.723(1)		As	74.921560(2)
	In	114.818(3)		Sb	121.760(1)
II	Mg	24.3050(6)	VI	O	15.9994(3)
	Zn	65.39(2)		S	32.066(6)
	Cd	112.411(8)		Se	78.96(3)
	Hg	200.59(2)		Te	127.60(3)

The diamond cubic lattice is a consequence of the carbon valency of four. We can expect to find the same structure in compounds where one atom has more than four electrons and the other the same number less than four, so that a total of four valency electrons to each atom is maintained. If the compound is of the form of AB, this structure can be produced in two ways. The first is the cubic, *zinc-blende* structure as shown in Figure 1.2(b), with four A (Ga) and four B (As) atoms per conventional unit cell.

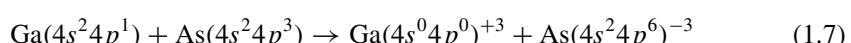
The second method by which a structure is formed where each atom of one kind is surrounded by four of another is shown in Figure 1.2(c). This is the hexagonal CdS (*w*-CdS or  $\beta$ -CdS) or *wurtzite* lattice, which differs only from the zinc-blende structure in the stacking sequence of the sulfur layers. Ideally, the wurtzite structure has the axial ratio  $c/a = (8/3)^{1/2} = 1.633$  (hexagonal close-packed structure). Most III-V semiconductors crystallize in the zinc-blende structure, however, many II-VI and some III-V semiconductors crystallize in the wurtzite structure.

In III-V compounds, group III atoms have three electrons with an  $s^2 p^1$ -configuration outside a core of closed shells and group V atoms five electrons in a  $s^2 p^3$ -configuration. The III and V atoms have, therefore, an average of four valence electrons per atom available for bonding. We might then expect that the covalent bonds are formed between tetrahedral  $s^1 p^3$ -hybrid orbitals, e.g., for GaAs:



For such a covalent bonding each V atom donates an electron to a III atom, so that  $\text{V}^+$  and  $\text{III}^-$  ions are formed, each with four valence electrons.

An ionic bond is due to Coulomb attraction between the excess positive and negative charges on ions formed by transfer of electrons from the metallic to the nonmetallic atom in the scheme:



**Table 1.4** Molecular weight  $M$ , lattice constant  $a$  and crystal density  $g$  for a number of cubic group-IV, III–V and II–VI semiconductors at 300 K

System	Material	$M$ (amu)	$a$ (Å)	$g$ (g/cm <sup>3</sup> )
IV	Diamond	12.0107	3.5670	3.5156
	Si	28.0855	5.4310	2.3291
	Ge	72.61	5.6579	5.3256
	$\alpha$ -Sn	118.710	6.4892	5.7710
	3C-SiC	40.0962	4.3596	3.2142
III–V	<i>c</i> -BN	24.818	3.6155	3.4880
	BP	41.785	4.5383	2.9693
	BAs	85.733	4.777	5.224
	<i>c</i> -AlN	40.98828	4.38	3.24
	AlP	57.955299	5.4635	2.3604
	AlAs	101.903098	5.66139	3.73016
	AlSb	148.742	6.1355	4.2775
	$\beta$ -GaN	83.730	4.52	6.02
	GaP	100.696	5.4508	4.1299
	GaAs	144.645	5.65330	5.31749
	GaSb	191.483	6.09593	5.61461
	InP	145.792	5.8690	4.7902
	InAs	189.740	6.0583	5.6678
	InSb	236.578	6.47937	5.77677
II–VI	MgO	40.3044	4.203	3.606
	$\beta$ -MgS	56.371	5.62	2.11
	$\beta$ -MgSe	103.27	5.91	3.32
	$\beta$ -MgTe	151.91	6.42	3.81
	$\beta$ -ZnS	97.46	5.4102	4.0879
	ZnSe	144.35	5.6692	5.2621
	ZnTe	192.99	6.009	5.908
	<i>c</i> -CdS	144.477	5.825	4.855
	<i>c</i> -CdSe	191.37	6.077	5.664
	CdTe	240.01	6.481	5.856
	$\beta$ -HgS	232.66	5.8514	7.7135
	HgSe	279.55	6.084	8.245
	HgTe	328.19	6.4603	8.0849

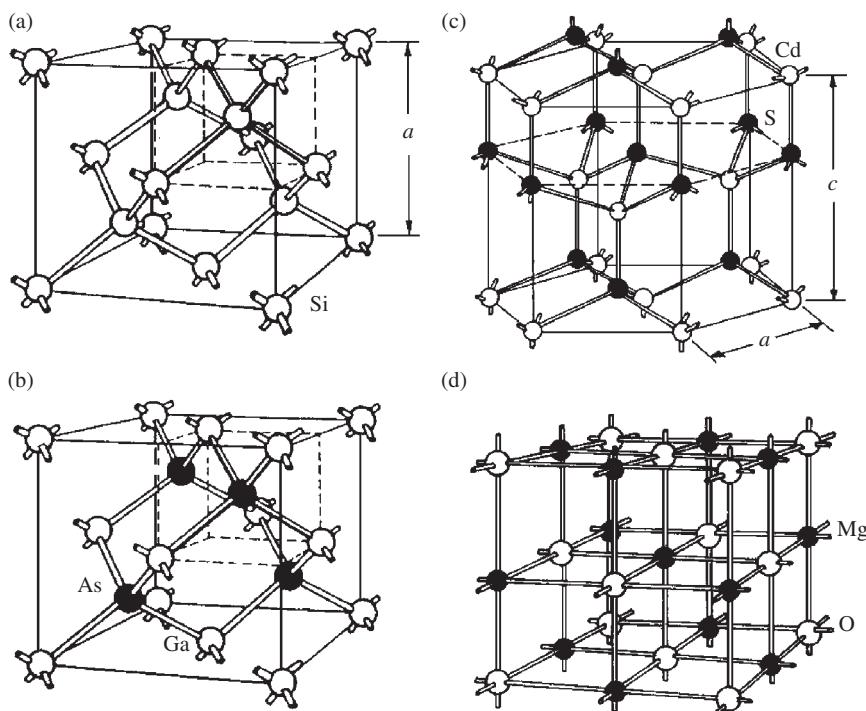
The bonds in most III–V or II–VI semiconductors are not adequately described by any of these extreme types, but have characteristics intermediate to those usually associated with the terms covalent (Equation (1.6)) and ionic (Equation (1.7)).

### (b) Hexagonal and rhombohedral structures

It is well known that silicon carbide (SiC) is a semiconductor crystallizing in a large number of polytypes [1.5]. The various types of SiC differ one from another only by the

**Table 1.5** Molecular weight  $M$ , lattice constants  $a$  and  $c$  and crystal density  $g$  for a number of hexagonal and rhombohedral group-IV, III-V and II-VI semiconductors at 300 K

System	Material	$M$ (amu)	Lattice constant (Å)		$g$ (g/cm <sup>3</sup> )
			$a$	$c$	
IV	6H-SiC	40.0962	3.0806	15.1173	3.2153
	15R-SiC	40.0962	3.079	37.78 ( $\alpha = 13^\circ 54.5'$ )	
III-V	<i>h</i> -BN	24.818	2.5040	6.6612	2.2787
	<i>w</i> -AlN	40.98828	3.112	4.982	3.258
	$\alpha$ -GaN	83.730	3.1896	5.1855	6.0865
	InN	128.825	3.548	5.760	6.813
II-VI	ZnO	81.39	3.2495	5.2069	5.6768
	$\alpha$ -ZnS	97.46	3.8226	6.2605	4.0855
	<i>w</i> -CdS	144.477	4.1367	6.7161	4.8208
	<i>w</i> -CdSe	191.37	4.2999	7.0109	5.6615



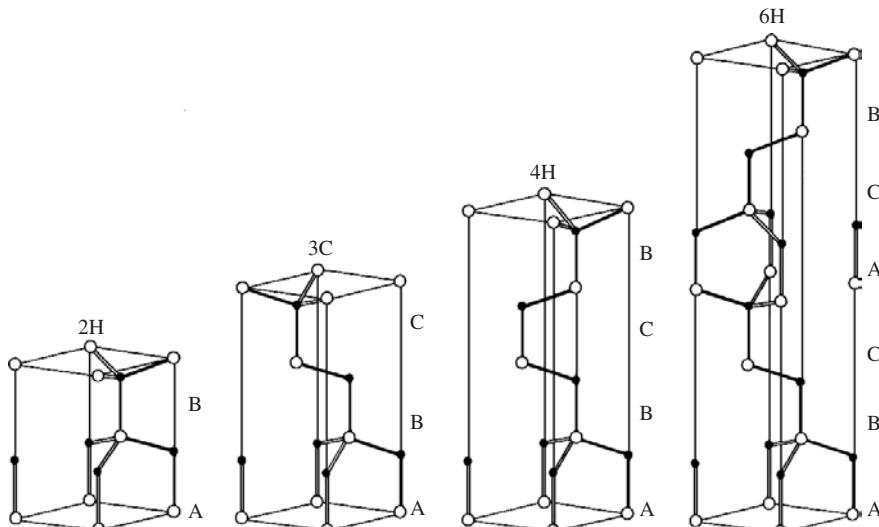
**Figure 1.2** Some important crystal lattice structures. (a) diamond lattice (Si); (b) zinc-blende lattice (GaAs); (c) wurtzite lattice (*w*-CdS); and (d) rocksalt lattice (MgO)

order in which successive planes of Si (or C) atoms are stacked along the  $c$  axis; one polytype is cubic (3C-SiC) while the remainder, including two of the more frequently occurring forms, 6H and 15R, possess uniaxial symmetry. Note that in the polytype name, the integer refers to the number of Si (C) layers in the unit cell, and C, H and R indicate cubic, hexagonal and rhombohedral (trigonal) symmetry, respectively. Of all the polytypes, 6H is by far the most commonly occurring modification in commercial SiC. The next most common types are 15R and 4H, respectively. Silicon carbide can also crystallize in the wurtzite structure (2H-SiC).

Figure 1.3 shows the stacking sequences in 3C-SiC, 2H-SiC and 6H-SiC [1.6]. In the zinc-blende (3C) structure, the sequence involves three layers which are repeated periodically (ABC ABC ...). All the Si–C bond lengths are the same, and the angles are exactly tetrahedral ( $109.5^\circ$ ). In the wurtzite (2H) structure, only two layers are repeated (AB AB ...). The Si–C bond length along the stacking direction is not equal to that which is approximately perpendicular to it, and the angles are not exactly tetrahedral. In the 6H polytype, the basic sequence involves six layers (ABCACB ABCACB ...). Similarly, in the 15R polytype the basic sequence involves fifteen layers (ABCACBCABCABC ...). The II–VI semiconductor,  $\alpha$ -HgS, can also crystallize in the rhombohedral (red cinnabar) structure.

### (c) Rocksalt structure

The II–VI compound MgO crystallizes in the rocksalt (NaCl) structure. The rocksalt structure shown in Figure 1.2(d) is typical of ionic bonding. The Bravais lattice is face-centered



**Figure 1.3** Three-dimensional perspective view of the 2H-SiC, 3C-SiC, 4H-SiC and 6H-SiC polytypes. The characteristic chain structures are represented by the heavy solid lines in the  $(11\bar{2})$  plane. The stacking sequences AB (2H), ABC (3C), ABCB (4H) and ABCACB (6H) are also indicated. [From P. Käckell, B. Wenzien, and F. Bechstedt, *Phys. Rev. B* **50**, 17037 (1994), reproduced by permission from the American Physical Society]

cubic with the unit cell of atomic pattern consisting of one Mg and one O ion separated by one-half the body diagonal of the cube. Since each ion has six nearest neighbors of the opposite kind, the coordination number is six.

We summarize in Table 1.6 the crystal classes for easily or normally grown: (a) group-IV, (b) III-V and (c) II-VI binaries. Table 1.7 also lists the crystal structure for a number of group-IV, III-V and II-VI semiconductors.

### 1.3.2 Space group

A self-consistent arrangement of symmetry elements in a crystal lattice is known as a space group. The operation of any element of the group must have the pattern of symmetry elements unaltered. By inspection of the 230 space groups, or from first principles, there are just 32 different point groups. Crystals are, therefore, divided into 32 crystal classes according to the point-group symmetry they possess. In Table 1.7, we list the space (point) group for a number of group-IV, III-V and II-VI semiconductors.

**Table 1.6** Summary of easily or normally grown crystal structure for: (a) group-IV; (b) III-V and; (c) II-VI semiconductors. d = diamond; zb = zinc-blende; h = hexagonal (wurtzite); rh = rhombohedral (trigonal); rs = rocksalt; or = orthorhombic

(a)

IV/IV	Si	C
Si	d	zb, h, rh
C	zb, h, rh	d

(b)

III/V	N	P	As	Sb
B	zb, h	zb	zb	
Al	h	zb	zb	zb
Ga	h	zb	zb	zb
In	h	zb	zb	zb

(c)

II/VI	O	S	Se	Te
Mg	rs	rs	zb	h
Zn	h	zb, h	zb	zb
Cd	rs	h	h	zb
Hg	rh, or	rh, zb	zb	zb