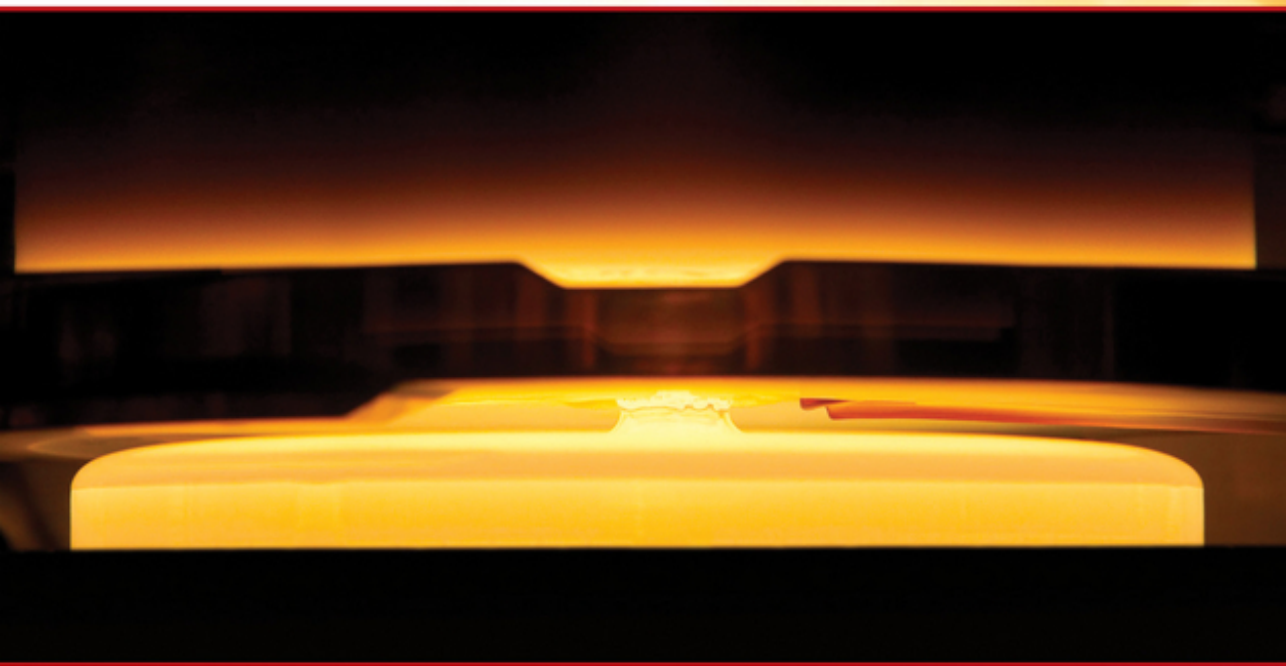


Physical Chemistry

of Semiconductor
Materials and Processes

SERGIO PIZZINI



WILEY

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Preface

Sunt igitur solida ac sine inani corpora prima. Preaterea quoniam genities in rebus inanest, materiam circum solidam constare necessesit, nec res ulla potest vera ratione probari corpore inane suo celare atque intus habere, si non, quod cohibet, solidum constare reliquas.

Lucretius (56-95 BEC) 'De rerum natura'.

Physical chemistry today plays a critical role in our basic understanding, modelling, diagnostics and theoretical forecast of semiconductor materials' properties, albeit some of Lucretius's concepts remain alive, such as the concept of vacuum/vacancies (materia inane) in solid materials.

Their mechanical, electrical and optical properties depend not only on their structure and composition, but also on their defects and impurities content and on their deviations from stoichiometry, when compound semiconductors are considered. We have learned how to manage their properties by doping and defect engineering processes.

Physical chemistry is behind most of these processes and is crucial in the growth, purification and post-growth treatments of semiconductors, such as impurity gettering and passivation. In this respect, this book represents the first attempt to treat semiconductor materials and processes from a purely physico-chemical viewpoint.

This subject is treated at a tutorial level, for students and specialists having a background knowledge in solid-state physics. For this reason the book starts with some elementary thermodynamic concepts, then continues by dealing with issues concerning point and extended defects in elemental and compound semiconductors, having in mind the thermodynamics and kinetics at the base of their behaviour. The physico-chemical aspects of growth-and post-growth processes of semiconductor materials are the final issues considered, giving substantial attention to the majority of semiconductors of industrial interest, but also to semiconductor nanowires and thin film semiconductors for photovoltaic and optoelectronic applications.

This book is dedicated to Professor Giovanni (Nanni) Giacometti, Academician, who stimulated in me a strong interest for the physico-chemical aspects of material science when he was my teacher, and who became a colleague and a close friend in the subsequent years.

This book is dedicated also to the hundreds of masters and doctoral degree students whom I taught, while not having the time to write a book for them.

I express my gratitude to a number of friends and colleagues worldwide who have supported my work during the preparation of this book with advice and delivery

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1

Thermodynamics of Homogeneous and Heterogeneous Semiconductor Systems

1.1 Introduction

Elemental and compound semiconductors represent a vast family of materials of strategic interest for a variety of mature and advanced applications in micro- and opto-electronics, solid state lighting (SSL), solid state physical and chemical sensors, high efficiency solar cells and nanodevices. The materials themselves have always been technology enablers and their role today is even more significant in view of the increasing demand for sustainable development applications and high temperature, high pressure technologies.

The semiconductors family includes elemental solids such as silicon, the material of choice for the microelectronic and photovoltaic industry, binary alloys such as the Si-Ge alloys used for their elevated carrier mobilities, and compound semiconductors, of which SiC is used for high power, high frequency devices and phosphides, arsenides and nitrides for the most advanced optoelectronic applications.

Their preparation under defined limits of stoichiometry (in the case of compounds) and purity requires a deep knowledge of the chemistry and physics of liquid-, solid-, vapour- and plasma-growth and post-growth processes.

Semiconductors, like other inorganic and organic solids, may be stable in different structural configurations, depending on the composition, temperature, hydrostatic pressure and strain. Their chemical, physical and mechanical properties under different environmental conditions (temperature, pressure, strain) depend on their elemental composition, stoichiometry, impurity contamination, and also on their point- and extended-defects content. In fact, although solids are a typical class of materials characterized by microscopic order, most of their electronic and optoelectronic properties depend on or are influenced by impurities and point and extended defects.

Knowledge of their macroscopic features, such as their structural, thermodynamic, chemical, electrical and mechanical properties over a broad range of temperatures and pressures, is critical for their practical use. These properties, when not already available, should be experimentally or computationally determined.

This objective, addressed at metals, metal alloys and non-metallic solids, has been in the last few decades the traditional goal of physical metallurgy and physical chemistry. It is also the subject of several excellent textbooks and monographs [1–4], where emphasis is mainly given to structure–property relationships, solution- and defect-theories and nonstoichiometry of non-metallic solids [5], devoting, until very recently [6], only limited attention to elemental and compound semiconductors.

The aim of this chapter, and of the entire book, is to fill this gap and present in the most concise and critical manner possible the application of thermodynamics and physical chemistry to elemental and compound semiconductors, assuming knowledge of the fundamental laws of thermodynamics [7] and the basic principles of solid state and semiconductor physics [8, 9].

The intent is also to show that physical chemistry applied to semiconductors has been, and still is, of unique value for the practical and theoretical understanding of their environmental compliance and for the optimization of their growth and post-growth processes, all having a strong impact on the final properties of the material.

As impurities have a significant role in the optical and electronic properties of semiconductors, their thermodynamic behaviour will be considered in terms of their solubility and distribution among neighbouring phases as well as in terms of formation of complex species with other impurities and point defects.

For elemental semiconductors the main interest will be devoted to Group IV and VI elements (carbon, germanium, silicon, selenium and tellurium), the first of which being characterized by a number of stable phases, some of these of extreme scientific and technological interest, as is the case for diamond and graphene. For compound semiconductors we will consider the II–VI and the III–V compounds, such as the arsenides, phosphides, selenides, sulfides, tellurides and nitrides, all of which are of crucial interest for optoelectronic applications, SSL and radiation detection.

The most up to date physical and structural data of the different systems will be used: the reader interested in thermodynamic databases and phase diagram computation is referred to the Scientific Group Thermodata Europe (SGTE) Solution database, NSM Archive, www.ioffe.rssi.ru/SVA/NSM/Semicond/ and to Gibbs [10].

1.2 Basic Principles

A semiconductor is a *thermodynamic system* for which one has to define the equilibrium state and the nature of the transformations which occur when it is subjected to external thermal, mechanical, chemical, magnetic or electromagnetic forces during its preparation and further processing.

This system may consist of a homogeneous elemental or multicomponent *phase* or a heterogeneous mixture of several phases, depending on the temperature, pressure and composition.

A phase is conventionally defined as a portion of matter, having the property of being chemically and physically homogeneous at the microscopic level and of being confined within a surface which embeds it entirely.

The surface itself may be an external surface if it separates a phase from vacuum or from a gaseous environment. It is an internal surface, or an interface, when it separates a phase from another identical or different phase. According to Gibbs, the surface itself may be considered a phase of reduced (2D) dimensionality.

When one is concerned with microscopic or nanoscopic phases, such as nanodots, nanowires and nanotubes, the surface area to volume ratio, A_s/V increases considerably, as does the ratio R of the number of atoms at the surface to those in the bulk (see Table 1.1), with reduction in size of the crystallite phase. This has a significant impact on the physical and chemical properties of the phase itself and of its surface, enhancing in particular its chemical reactivity, but also other properties of relevant importance in semiconductor physics, such as the distribution and electrical activity of dopant impurities.

A phase may be gaseous, liquid or solid. In extreme conditions it could be stable in a plasma configuration, consisting of a mixture of electrons and ionized atoms/molecules. A phase is *condensed* when its aggregation state is that of a liquid or a solid material.

The thermodynamic state of a system is defined by specifying the minimum set of measurable properties needed for all the remaining properties to be fully determined. Properties which do not depend on mass (e.g. P , T) are called intensive. Those depending on mass (i.e. on composition) are called extensive.

A critical thermodynamic state of a system is its equilibrium state. It represents the condition where the system sits in a state of minimum energy and there are no spontaneous changes in any of its properties.

For a system consisting of a single, homogeneous multicomponent phase it is possible to define its thermodynamic state using thermodynamic functions (e.g. the internal energy U , the Helmholtz free energy F , the Gibbs free energy G , the entropy S and the chemical potential μ), whose values depend on macroscopic parameters, such as the hydrostatic pressure P , the absolute temperature T and the composition, this last given conventionally in terms of the atomic fraction of the components $x_i = \frac{n_i}{\sum_i n_i}$, n_i being the number of atoms of i -type.

Table 1.1 Cell size dependence of the surface to volume ratio (A_s/V) and of the ratio R of atoms sitting at the surface vs those sitting in the volume, for a cubic crystal having an atomic density of 10^{21} cm^{-3}

Cell edge length (nm)	Volume (nm^3)	Surface area (nm^2)	A_s/V (nm^{-1})	Atoms in the volume (N_V)	Atoms at the surface (N_s)	$R = N_s/N_V$
10^7	10^{21}	$6 \cdot 10^{14}$	$6 \cdot 10^{-7}$	10^{21}	$6 \cdot 10^{14}$	$6 \cdot 10^{-7}$
10^5	10^{15}	$6 \cdot 10^{10}$	$6 \cdot 10^{-5}$	10^{15}	$6 \cdot 10^{10}$	$6 \cdot 10^{-5}$
10^4	10^{12}	$6 \cdot 10^8$	$6 \cdot 10^{-4}$	10^{12}	$6 \cdot 10^8$	$6 \cdot 10^{-4}$
10^3	10^9	$6 \cdot 10^6$	$6 \cdot 10^{-3}$	10^9	$6 \cdot 10^6$	$6 \cdot 10^{-3}$
10^2	10^6	$6 \cdot 10^4$	$6 \cdot 10^{-2}$	10^6	$6 \cdot 10^4$	$6 \cdot 10^{-2}$

For Ge and Si the actual values of atomic densities are $4.42 \cdot 10^{22}$ and $5 \cdot 10^{22} \text{ (cm}^{-3}\text{)}$.

A system is said to be in *mechanical equilibrium* when there are no unbalanced mechanical forces within the system and between the system and its surrounding. The system is also said to be in mechanical equilibrium when the pressure P throughout the system and between the system and the environment is the same. This condition is typical of the liquid state but not of the solid state unless internal mechanical stresses are fully relaxed.

Two systems are said to be in mechanical equilibrium with each other when their pressures are the same.

A system is said to be in chemical equilibrium when there are no chemical reactions going on within the system or they are fully balanced, such that there is no transfer of matter from one part of the system to another due to a composition gradient. Two systems are said to be in chemical equilibrium with each other when the chemical potentials of their components are the same. A definition of the chemical potential will be given below.

When the temperature T of the system is uniform and not changing inside the system, the system is said to be in thermal equilibrium. Two systems are said to be in thermal equilibrium with each other when their temperatures are the same. By convention, the temperature is expressed in degrees Kelvin.

Mechanical equilibrium conditions in a solid phase may be modified by an imbalance of mechanical forces arising from the presence of thermal or composition gradients and of lattice misfits. This imbalance is the driving force for the migration of point defects and for the formation of extended defects during crystallization processes from a liquid phase or a vapour phase and during heteroepitaxial depositions, as will be shown in Chapter 4.

We call *transformation* any change of the structural, physical and chemical properties of a system and, therefore, of its thermodynamic state, induced by the work w carried out on it by external mechanical, thermal, chemical, magnetic or electromagnetic forces, that is as the result of interaction of the system with the ambient.

To deal properly with the properties of a transformation it is necessary to know whether it is uniquely driven by mechanical forces, or by thermal, chemical, magnetic or electromagnetic ones.

The definition of a *thermally insulated system*, originally associated to a system impervious to any exchange of heat, should be extended to the case of systems impervious to exchanges of any kind of energy of non-mechanical nature with an external system (its environment), which behaves as the source or the sink of non-mechanical energy.

In the rest of this chapter heat is identified with the electromagnetic energy emitted by a specific radiation source (the flame of a combustion process, the hot filament of a light bulb, the surface of a star, a light emitting diode (LED) or a laser), which emits a broad- or line-like spectrum of radiations, depending on the physics of the emission process. Thermal sources behave as black bodies and the property of their spectrum is described by Planck's radiation law

$$E_{\lambda} = \frac{8\pi hc}{\lambda^5 (e^{(hc/\lambda kT)} - 1)} \quad (1.1)$$

where E_{λ} is the emitted energy per unit volume, h is the Planck constant (6.626×10^{-34} J s), λ is the wavelength and c is the speed of light (3×10^8 m s⁻¹).

The black body radiation spectra for different black body temperatures are displayed in Figure 1.1.

As conventional hot filament light bulbs operate with a maximum colour temperature around 3500 K, their emission occurs almost entirely in the infrared, with a

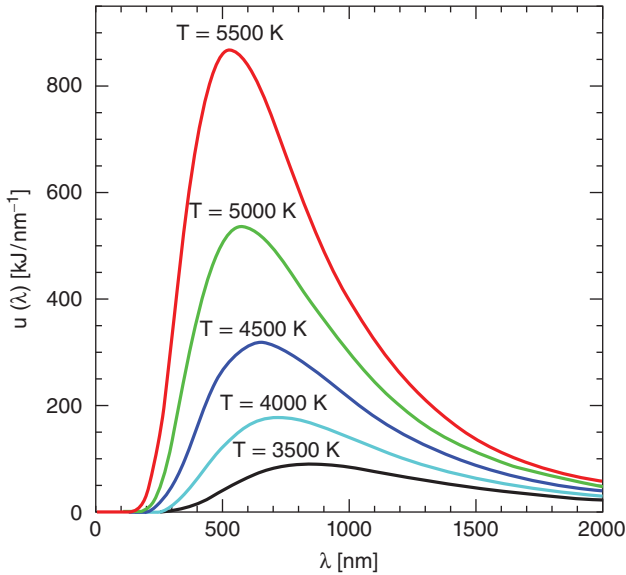


Figure 1.1 Black body radiation curves. earthguide.ucsd.edu

fraction not larger than 5% in the visible. This condition grants huge advantages to semiconductor-based SSL devices, whose monochromatic light emission depends on the energy gap E_g of the semiconductor used as the active substrate for quantum device applications which will be discussed later in this section.

By definition, a transformation which occurs without any input or output of heat is defined as *adiabatic*.

In this context, the work carried out by the system or supplied to the system is directly related to the variation in its internal energy U

$$\Delta U = \pm w \quad (1.2)$$

An *isothermal transformation*, however, occurs when the temperature of the system remains constant during the transformation.

Important examples of isothermal transformations are the changes of phase associated with solidification, melting, vaporization and sublimation or phase transitions of systems crystallizing in phases of different structure, as we will see later in this chapter.

In this last case, the system consists of two phases in thermodynamic equilibrium at the transformation temperature, any heat exchange from/with an external source/sink merely serves to modify the mass ratio of the two phases.

For a generic process involving a system that adsorbs heat from an external source and delivers work, the following equation holds for the variation of the internal energy U of the system

$$\Delta U = -w + q \quad (1.3)$$

where q is the energy absorbed as heat, w is the supplied work and $\Delta U = U_2 - U_1$ is the difference in the internal energy of the system.

Heat can be converted to mechanical work using a transfer fluid (liquid, gas or vapour) and operating a thermodynamic cycle (e.g. a Carnot cycle), whose maximum efficiency η is given by the second law of thermodynamics

$$\eta = \frac{W_{\text{out}}}{W_{\text{in}}} = \frac{T_s - T_a}{T_s} \quad (1.4)$$

where W_{out} and W_{in} are the output and input power, respectively, T_s is the temperature of the source and T_a is the temperature of a sink which dissipates the excess heat not converted to work.

As semiconductor-based devices play a crucial role in harvesting light and transforming it into electrical energy or emitting light as a result of a supply of electrical work, it is interesting to examine here these processes from the viewpoint of thermodynamics.

The electromagnetic energy of a radiation can be directly transformed into energy/work without making use of a transfer fluid using, for example, a semiconductor-based single- or multiple-junction device, where light is converted into electrical work qV , where q is the charge and V is the tension.¹

Conversely, the electrical work qV supplied by polarizing an n-p junction fabricated on a direct gap semiconductor can be converted into the energy of a beam of monochromatic light. In fact, upon excitation, a fraction $\varepsilon = \frac{\hbar\nu}{kT}\eta_{\text{EQE}}$ of the generated free electrons and holes, where η_{EQE} is the quantum efficiency of the process, relaxes by radiative recombination and generates a beam of photons with energy $\hbar\nu = E_g$, where E_g is the energy gap of the semiconductor. In principle, this process could occur with a theoretical 100% efficiency, as it is submitted only to the restrictions of the first principle of thermodynamics [11]. The second law of thermodynamics provides, instead, an upper limit to the theoretical efficiency of a direct transformation of the light adsorbed by a semiconducting material into electrical work qV , occurring through the recombination of the generated free electrons and holes in an external circuit.

In this case, if the radiation is that of a black body at a temperature T , as is the case of the light emitted by the sun, the efficiency of a solar cell is again ruled by the temperature of the source T_s and that of the substrate T_a , which behaves as a selective light absorber for light photons with energy $\hbar\nu \geq E_g$ and dissipates the light not converted into energy as heat.

This upper theoretical limit cannot be reached by a single junction solar cell because only the photons of the incident light beam having an energy $\hbar\nu \geq E_g$ are absorbed and excite electrons from the valence to the conduction band.

According to Shockley and Queisser [12], the variables on which the efficiency of a single junction semiconductor-based light converter depends are: the temperature of the sun T_s

$$kT_s = qV_s \quad (1.5)$$

the temperature of the solar cell T_c

$$kT_c = qV_c \quad (1.6)$$

¹ It is not the author's intention to deal here with the physics of solar cells or of solid state light emitters, but only to discuss the behaviour of these devices with respect to the second law of thermodynamics.

and the energy gap of the absorber

$$E_g = \hbar\nu_g = qV_g \quad (1.7)$$

so that the efficiency of the device involves only the two ratios

$$x_g = \frac{E_g}{kT_s} \quad (1.8)$$

$$\text{and } x_c = \frac{T_c}{T_s} \quad (1.9)$$

but depends also on the probability t_s that a photon of energy $\hbar\nu \geq E_g$ would produce an electron–hole pair and on a geometrical factor ζ related to the angle of incidence of the light on the surface of the device.

The ultimate efficiency is given by the equation

$$\eta(x_g, x_a, t_s, \xi) = \frac{qV}{W_{\text{in}}} \quad (1.10)$$

where the product qV is the maximum electrical power output of the device and W_{in} is the power (in watts) of the incident radiation. If the light source emits, instead, a beam of monochromatic light of energy $\hbar\nu'$ and the absorber has an energy gap $E_g = \hbar\nu'$, the system obeys only the first law and the maximum theoretical conversion efficiency should be 100%, as the electrical work qV corresponds to the variation of the internal energy of the system.

Other important kinds of transformation involve chemical forces, which drive matter fluxes among neighbouring phases of different structure and chemical composition. These transformations may be reversible or irreversible, and the latter ones are the concern of the thermodynamics of irreversible processes [13]. Most of the modern growth processes, such as physical vapour deposition (PVD), the chemical vapour deposition (CVD), atomic layer deposition (ALD) and metal-organic chemical vapour deposition (MO-CVD), which will be discussed in Chapter 4, belong to this kind of chemical processes. The systems involved in these processes are *open* systems.

1.3 Phases and Their Properties

1.3.1 Structural Order of a Phase

The properties of a phase are determined by its short- and long-range order and by its macroscopic and microscopic composition. While only short-range order is present in liquid phases, short- and long-range order is present in crystalline phases. In liquid and solid phases the short-range order can be investigated by extended X-ray absorption fine structure (EXAFS) spectroscopy [14–19].

Long-range order is investigated by diffraction experiments using X-rays, electrons or neutrons of adequate energy $h\nu$ or wavelength λ , while high resolution transmission electron microscopy (HRTEM) directly reveals short- and long-range order with sub-nanometric resolution.

Today, knowledge of local composition is an additional, crucial requirement in mesoscopic and nanoscopic applications of semiconductors. Depending on the detection range and on the chemical sensitivity required, X-ray fluorescence (XRF), infrared spectroscopy (IRS), Scanning Ion mass spectroscopy (SIMS, both time of flight (TOF)-SIMS and dynamic SIMS), Raman spectroscopy, energy dispersive X-ray spectroscopy (EDS), field-emission Auger electron spectroscopy (FE-AES), electron energy loss spectroscopy (EELS) and atom probe tomography (APT) may be used [20–24], with local resolutions ranging from a few micrometres for Fourier transform infrared (FTIR) to sub-nanometres for APT and a detection sensitivity down to 100 ppt for dynamic SIMS.

To get information simultaneously on local structure and composition, APT is particularly suited, as it allows both atomic range structural resolution and excellent chemical selectivity for the study of local order [25]. Figure 1.2 shows an interesting example of the application of APT to Ge-Sn alloys which will be discussed in Section 1.7.

A phase may consist of a single crystal or a polycrystalline aggregate. The crystalline materials found in nature, with several exceptions, consist mainly of polycrystalline aggregates, where the single crystallite size may vary from a few micrometres to several centimetres. The size- and orientation-distribution of the crystallites in a natural polycrystalline matrix is generally disordered. The interfaces between crystallites are called grain boundaries (GBs).

Synthetic crystals can be grown as single-crystalline or polycrystalline ingots, or as thick or thin polycrystalline or amorphous films, as will be shown in Chapter 4. Synthetic polycrystalline ingots can present a disordered or an ordered microstructure, depending on the growth process adopted.

GBs in natural and synthetic polycrystalline semiconductor materials (see Figure 1.3) are characterized by conditions of local disorder and electrical activity, associated with the

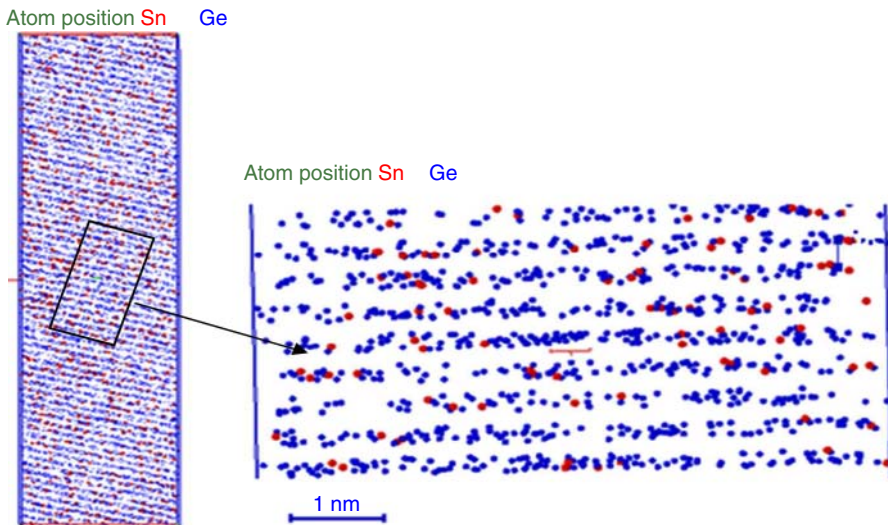


Figure 1.2 Atom probe tomography of a Ge-Sn alloy sample: lattice planes lie in the $\langle 111 \rangle$ direction. Distance between the $\langle 111 \rangle$ planes for this sample is 0.377 nm. Kumar et al., 2012, [24]. Reproduced with permission from John Wiley & Sons, Ltd

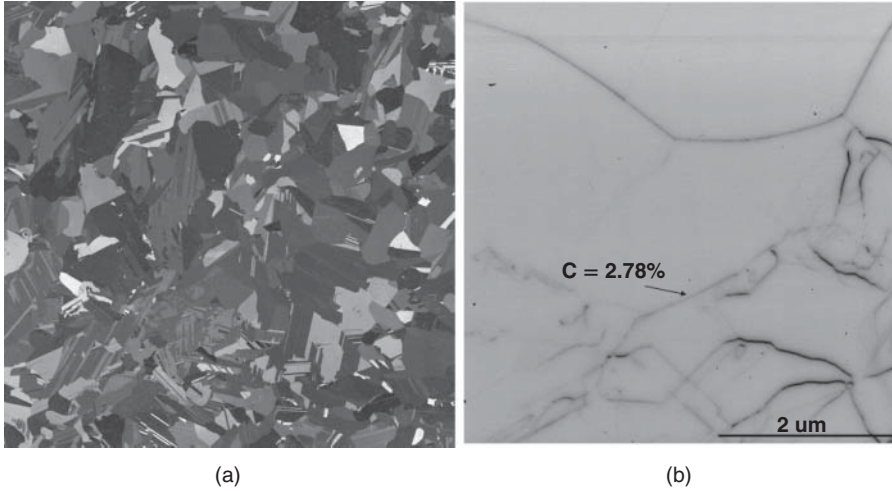


Figure 1.3 (a) Scanning electron microscopy (SEM) micrograph of a multicrystalline silicon sample. (b) Light beam induced current (LBIC) image of the electrical activity of GBs associated with recombination of minority carriers

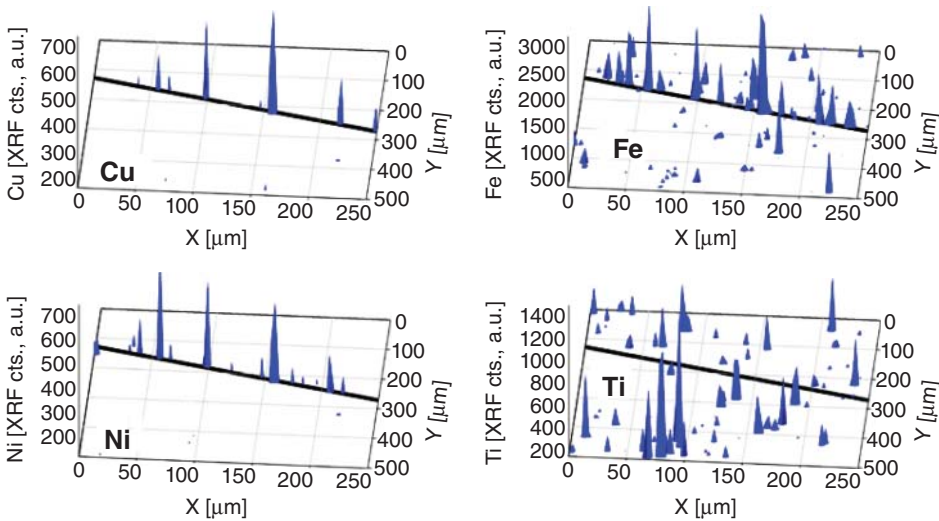


Figure 1.4 Impurity segregation patterns in multicrystalline silicon, localized by synchrotron X-ray measurements. Buonassisi et al., 2006, [28] Reproduced with permission from John Wiley & Sons, Ltd

presence of dislocations, distorted or broken (dangling) bonds and impurities segregated on them as individual species, precipitates or microprecipitates. SIMS, APT [26], X-ray absorption microspectroscopy (μ -XAS) [27] and X-rays microfluorescence (Figure 1.4) [28–31] are the main tools for direct impurity localization on GBs in semiconductors.

One can see in Figure 1.4 that Ni and Cu impurities segregate in correspondence to a GB (the solid line in the figure), Fe segregates both at the GB and in the bulk and Ti segregates

elsewhere rather than at the GB. This is already an indication that segregation of impurities at a GB is dominated by selective interactions depending on the chemical nature of the impurity. This will be discussed further in Chapters 2 and 3.

A phase may consist of a single or multiple components. Homogeneous multicomponent solid phases may be stable as a *solution* or consist of stoichiometric or non-stoichiometric compounds. In both cases, the chemical composition of a phase in thermodynamic equilibrium should be microscopically, or at least mesoscopically, homogeneous. Solid solutions of semiconductors are conventionally called *alloys*, as in the case of metallic alloys.

The *solvent* and the *solutes*, respectively, are the components which are present in larger and smaller amount, respectively, in a homogeneous solution. Solutions are discussed in terms of ideality or non-ideality of their thermodynamic behaviour.

Ideal solution behaviour, which will be discussed in Section 1.6 and occurs very rarely in semiconductor alloys, is accomplished when the components do not interact chemically with each other and distribute randomly in the condensed phase, giving rise to a compositional disorder. Deviations from the ideal behaviour are also discussed in Section 1.6 in the frame of the most recent applications of the regular solution approach [32] and of the generalized quasichemical approximations (QCAs) [33, 34].

The solution is of the substitutional-type when the solute atoms replace the solvent atoms in their stable lattice positions, as is the case for the solution of Ge, Al, B, Ga, P in Si.

The solution is of the interstitial-type when the solutes enter in interstitial positions of the lattice. This is the case for transition metals (TMs), carbon and oxygen in Si and Ge.

Several impurities in elemental or compound semiconductors, however, may enter in both lattice and interstitial positions, behaving as substitutional and interstitial species. An additional possibility is present in compound semiconductors, where impurities may share occupancy in both sublattices.

Solutes which, added in trace amounts, as is the case of B, P, Sb, Ga, As in Si, modify the carrier concentration in the semiconductor are conventionally called dopants. The impurity/dopant content is generally reported in terms of atoms cm^{-3} , parts per million by weight (ppmw) or in parts per million atoms (ppma). As the concentration of dopants and impurities in semiconductors is directly correlated with the concentration of the corresponding shallow and deep levels, the best concentration notation is that expressed in atoms cm^{-3} .

Solutions of two different compounds, such as the solutions of alkali halides, alkali earth oxides or the III–V and II–VI compounds, could be considered pseudo-binary when the content of one of the components is invariant towards the composition changes of the other components.

A solution may be stable and homogeneous in a limited range of concentration or in a continuous range of compositions. A solution of different elemental or compound semiconductors is called a multicomponent alloy.

In the case of ionic solids forming a continuous series of substitutional solid solutions, Vegard [35] observed that often the effective lattice constants change linearly with the solute concentration, expressed in terms of atomic fraction, with a law which took his name

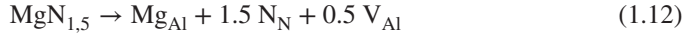
$$a_{\text{A}_x\text{B}_{(1-x)}}^{\circ} = xa_{\text{A}}^{\circ} + (1-x)a_{\text{B}}^{\circ} \quad (1.11)$$

(where $a_{\text{A}_x\text{B}_{(1-x)}}^{\circ}$ is the lattice constant of the solution for a certain value of x and a_{A}° and a_{B}° are the lattice constants of the pure components). In spite of many experimental and

theoretical proofs which show that this empirical law is very rarely followed, ideal solid solution formation in semiconductors has often been correlated in the literature on their accomplishment with Vegard's law.

As will be discussed in detail in Chapter 2, solid solution formation may involve the additional presence of point defects [36–39].

This is the case for ionic and compound semiconductors, when aliovalent dopants are added to favour the ionic conductivity or to induce a p-type or n-type carrier excess, as occurs when AlN is doped with Mg_2N_3



where Mg_{Al} is a Mg atom in an Al-lattice site, behaving as an acceptor, N_N is a nitrogen atom in a regular lattice position and V_{Al} is an aluminium vacancy.²

Amorphous solids (and glasses) exhibit the absence of long-range order and the presence of distorted and broken bonds: they might be conceived as metastable phases because they transform spontaneously in crystalline phases under suitable activation of the transformation.

1.4 Equations of State of Thermodynamic Systems

1.4.1 Thermodynamic Transformations and Functions of State

The properties of a thermodynamic system are described using equations of state that account for the dependence of a specific property of the system, such as its internal energy U , on the external variables and take the general form

$$f(P, V, \dots T) = 0 \quad (1.13)$$

A well known equation of state is that of ideal gases, written as

$$PV = RT \quad (1.14)$$

where R is the gas constant

Any transformation of a thermodynamic system from a generic state 1 to a generic state 2 is quantitatively accounted for by the corresponding changes in the function of state X which better describes the thermodynamic state of that system in the state 1 and in the state 2.

A specific character of a function of state X is that its change ΔX_{1-2} when the system passes from a state 1 to a state 2 must be independent of the path followed passing from 1 to 2.

Figure 1.5 shows such a change of state in a PV diagram, where $X_1 = P_1V_1$ and $X_2 = P_2V_2$.

A is well known, the functions which have this property are the internal energy U , the enthalpy H , the entropy S , the Helmholtz free energy F and the Gibbs free energy G .

² The Kröger and Vink notation [40] for defects in solids will be used throughout this book.

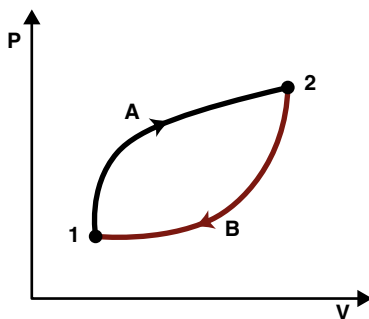


Figure 1.5 Two possible paths for the transformation of the system from state 1 to state 2 and vice versa

As it is experimentally impossible, although theoretically feasible, to define the absolute value of a function of state, it is common practice to define an arbitrary standard reference state, to which all changes associated with a transformation refer.

Thermodynamic transformations may be carried out reversibly or irreversibly. Reversible transformations are carried out along a continuous, formally infinite series of intermediate equilibrium states, each of them presenting a negligible energy difference from the neighbouring ones. Such types of transformations are invariant with respect to time and are fully deterministic. This condition allows one to bring a system from its initial state 1 to the final state 2, and to bring it back to the initial state 1 without hysteresis effects.

It should be noted that the transformations of real systems seldom follow full reversibility conditions, for various chemical, physical and structural reasons. The value of this procedure, however, rests in the fact that it allows calculation of the maximum work done by a transformation or the minimum work needed to induce the transformation.

1.4.2 Work Associated with a Transformation, Entropy and Free Energy

Every change in the thermodynamic state of a system is associated with an exchange of energy, and in particular of heat q and work w with the environment or with a neighbouring phase.

Like work, heat is not a function of state, because the amount of heat exchanged or supplied in any kind of transformation depends on the path followed in the transformation.

The infinitesimal change of internal energy dU associated with a reversible stage of a transformation is the sum of a mechanical work term and a heat term

$$dU = \delta w + \delta q \quad (1.15)$$

where the partial derivative notation for the heat and work terms shows that the values of δq and δw in the transformation depend on the route followed along the transformation.

In a closed cycle $\oint dU = 0$ and thus $\delta q = -\delta w$.

The work, here, is formally associated with a volumetric expansion or contraction of the system and is given by the integral

$$w = \int_1^2 p dV \quad (1.16)$$

Thus, the total variation of internal energy of the system is given by the sum

$$\Delta U = \int_1^2 dq \pm \int_1^2 pdV = T \int_1^2 \frac{dq}{T} \pm \int_1^2 pdV \quad (1.17)$$

where T is the absolute temperature.

The value of the integral $\int_1^2 pdV$, for an isothermal expansion/compression of an ideal gas

$$\int_1^2 pdV = RT \int_1^2 \frac{dV}{V} = RT \ln \frac{V_2}{V_1} \quad (1.18)$$

depends only on the values V_2 and V_1 of the final and initial states and represents the maximum work done by the system or, changing the sign, the minimum work needed to carry out the transformation.

Furthermore, the value of the integral $\int_1^2 \frac{dq}{T}$ relative to a reversible transformation from state 1 to 2 at constant temperature T , is independent of the path followed, depending only on the states 1 and 2 and allows definition of a new function of state S

$$\int_1^2 \frac{dq}{T} = \frac{q_2}{T} - \frac{q_1}{T} = S_2 - S_1 = \Delta S \quad (1.19)$$

which is the entropy.

According to Eq. (1.17)

$$\Delta U = T\Delta S + RT \ln \frac{V_2}{V_1} \quad (1.20)$$

It must be emphasized here that only the variation ΔU of the internal energy associated with a transformation is thermodynamically well defined and measurable. The complete definition of U for a specific system would require, in fact, an arbitrary definition of its state of zero energy. Once this reference state is fixed, any other state is univocally determined.

It is then useful to define another function of state, the Helmholtz free energy F , whose change $\Delta F = RT \ln \frac{V_2}{V_1}$ is a measure of the maximum (here mechanical) work done by the system in isothermal conditions.

We have, therefore, for a reversible transformation, that

$$\Delta F = \Delta U - T\Delta S \quad (1.21)$$

It should be mentioned that U , S and F are extensive properties of the system: it is, therefore, common practice to account for them in terms of unit of mass or mole.

Another thermodynamic function is G , the Gibbs free energy, whose variation is defined as the sum

$$\Delta G = \Delta U - T\Delta S + P\Delta V \quad (1.22)$$

where the $P\Delta V$ term is a measure of the work carried out on the system to pass from an initial volume V_0 to the final volume V during a composition change or an isobaric and isothermal transformation. Typical examples of processes involving a volume change are chemical reactions, the sublimation of solids and a number of solid state phase transformations, as is the case of silicon dioxide (i.e. silica) (see Table 1.2)

Table 1.2 Density and crystal structure of silica polymorphs

Phase	Structure	Density (g cm ⁻³)	Temperature (°C)	Pressure (MPa)
β-Cristobalite	Cubic	2.33	>1470	—
β-Tridymite	Hexagonal	2.28	>870	—
β-Quartz	Hexagonal	2.53	>570	—
α-Quartz	Rhombohedral	2.65	<570	—
Coesithe	Monoclinic	2.93	—	>2000
Stishovite	Tetragonal	4.30	—	>8000

The definition of G allows also the definition of enthalpy H , by means of the equation

$$\Delta H = \Delta U + P\Delta V \quad (1.23)$$

Because in semiconductor alloys the volume dependence on composition is often negligible, the Helmholtz free energy F is interchangeable with the Gibbs free energy [33].

The standard thermodynamic properties of inorganic and organic solids³ are tabulated in the CRC Handbook of Chemistry and Physics [41]. An entry value of 0.00 for ΔH or ΔG for an element indicates the reference state of the element.

1.4.3 Chemical Potentials

The transformations discussed so far occur in the absence of matter exchanges. Of special relevance are, however, the transformations, or processes, which involve mass transfer within neighbouring phases of different structure and composition, and which occur in the vast majority of chemical and physical processes used in the technology of materials of current use.

To quantify the variation of the internal energy of a homogeneous phase associated with a defined amount of mass exchange, it is convenient to use a new function, called the chemical potential μ_i

$$\mu_i = \left(\frac{dU}{dn_i} \right)_{S,V,n_i} \quad (1.24)$$

which accounts for the variation of the internal energy of a phase consisting of a solution of j components, when only its i -content changes by an infinitesimal amount dn_i .

Therefore, the total change in the internal energy of a homogeneous phase associated with an infinitesimal composition change dn of all its components is given by:

$$dU = TdS - PdV + \sum_i \mu_i dn_i \quad (1.25)$$

Given the definition of the Gibbs free energy (see Eq. (1.22)), we have also

$$dG = \sum_i \mu_i dn_i \quad (1.26)$$

³ The temperature dependence of thermodynamic functions may be found in the NIST-JANAF Thermochemical Tables, making reference to their standard conditions, corresponding to an absolute temperature of 298.15 K and a pressure of 1 atm or 101.3 kPa.

In a system consisting of only one component, Eq. (1.26) reads

$$\mu_i = \left(\frac{d\tilde{G}}{dn_i} \right)_{T,P} \quad (1.27)$$

and

$$G_i^o = \mu_i \quad (1.28)$$

where the chemical potential μ_i takes the value of the molar free energy G_i^o of the species i .

Let us now denote by $\left(\frac{dG}{dn_i} \right)_{\alpha \rightarrow \beta}$ the work needed to transfer an infinitesimal amount dn_i of the species i from the phase α to the phase β and by $\left(\frac{dG}{dn_i} \right)_{\beta \rightarrow \alpha}$ the work needed to transfer the same infinitesimal amount of mass dn_i from the phase β to the phase α , at the equilibrium coexistence temperature $T_{\alpha,\beta}$ in the absence of any change of the concentration of the other species in both α and β .

To maintain the system in full equilibrium conditions during and after the transformation ($dG = 0$)

$$\left(\frac{dG}{dn_i} \right)_{\alpha \rightarrow \beta} = \left(\frac{dG}{dn_i} \right)_{\beta \rightarrow \alpha} \quad (1.29)$$

and

$$\mu_i^\alpha = \mu_i^\beta \quad (1.30)$$

The equilibrium between phases of different composition is, therefore, given by a set of equations (1.30) for each j component of the solution. The relationship between μ_i and the composition will be given in Section 1.5.

1.4.4 Free Energy and Entropy of Spontaneous Processes

Let us now consider a thermally isolated system consisting, as before, of an intimate mixture of two phases α and β of identical composition in mutual equilibrium.

It holds, therefore, in equilibrium conditions

$$T_\alpha = T_\beta; G_\alpha = G_\beta \quad (1.31)$$

and

$$S = S_\alpha + S_\beta \quad (1.32)$$

if the two phases maintain their original integrity during and after the mass transfer process.

Let us suppose, instead, that the two phases are at different temperatures

$$T_\alpha > T_\beta \quad (1.33)$$

In this case a heat flux⁴ $\Phi_q = \frac{dq}{dt}$ (where t is the time) would spontaneously flow from α to β until $T_\alpha = T_\beta$. Consequently, we will have a change of entropy of each of the two phases

⁴ Heat fluxes may involve conduction, convection and radiation.

$dS_\alpha = -\left(\frac{dq}{T_\alpha}\right)$ and $dS_\beta = \left(\frac{dq}{T_\beta}\right)$ and a variation of entropy dS of the system

$$dS = -\left(\frac{dq}{T_\alpha}\right) + \left(\frac{dq}{T_\beta}\right) = dq\left(\frac{1}{T_\beta} - \frac{1}{T_\alpha}\right) > 0 \quad (1.34)$$

Therefore, $dS > 0$ for a spontaneous process. We expect, similarly, that $dF < 0$ and $dG < 0$ for a spontaneous process.

1.4.5 Effect of Pressure on Phase Transformations, Polymorphs/Polytypes Formation and Their Thermodynamic Stability

Knowledge of the effects of an applied gas or hydrostatic pressure on the properties and the stability of a phase has important technological outcomes, as it may allow, as a not exclusive example, the synthesis of materials outside conventional temperature and pressure conditions, where their preparation would be challenging or impossible.

As an example, the equilibrium vapour pressure or the decomposition pressure of phosphide, arsenide and nitride alloys may be so high at their growth temperatures (even well below the melting point) as to induce partial or full decomposition of the material or/and the onset of non-stoichiometry. This would make their growth as bulk single crystal or single crystalline- or polycrystalline-thin films very challenging, unless the applied gas pressure is sufficiently high to prevent the decomposition.

Meanwhile, an understanding of the effects of a mechanical strain, arising from external or internal sources of stress, on the properties of a material, is important in order to optimize its growth or deposition processes and to accomplish for the presence of extended defects. A typical, but not exclusive example is the dislocation generation induced by lattice mismatch, occurring in the heteroepitaxial deposition processes which will be discussed in Chapter 4.

As a further example, the combined effect of temperature and applied pressure may induce a sequence of phase transformations in elemental or compound semiconductors. In this section we will deal with the effects of an externally applied hydrostatic pressure on the equilibrium transformation temperatures of liquid/solid systems and of solid/solid systems, leaving the analysis of the effects of internal mechanical stresses on defect generation to later chapters.

The effect of the applied pressure on the melting temperature T_f and the molar volume of a number of model systems, including Ge and Si, is reported in Table 1.3 [42, 43], while Table 1.4 reports the value of the critical pressure at which typical phase transformations of alkali halides and oxides occur.

Pressure-induced phase transformations in silicon and germanium were studied by Bundy [44], who showed a transition from semiconductor to metallic character in both cases, although the silicon transition was more sluggish. In the case of silicon this transition occurs at 10–13 GPa and is associated with a volume decrease of 22%. Diamond anvil cell and micro- and nano-indentation experiments showed the formation of at least 12 different silicon polymorphs following the application of increasing pressures [45]. Other examples can be found within compound semiconductors (see Section 1.7), as is the case of GaAs, which crystallizes in the cubic zinc blende structure at ambient pressures but undergoes a transition to at least two orthorhombic structures, the first of which occurs at 12 ± 1.5 GPa at 300 K [46]. CdS, CdSe and ZnS, eventually, show unique behaviour

Table 1.3 Effect of the applied hydrostatic pressure on the melting temperature of model systems

Material	T_f (K)	$\Delta_f H$ (kJ mol ⁻¹)	ΔV_m (cm ³ mol ⁻¹)	ΔT_{calc} (0.9 GPa)	ΔT_{exp} (0.9 GPa)
H ₂ O	273.2	6.012	-1.6308	-7.5	-7.4
Sn	505	7.03 (white tin)	+0.4617	+3.4	3.28
Bi	544.7	11.3	-0.7147	-3.56	-3.10
Si [42]	1687	50.21	-6.767	-20.46	900 (10 GPa)
Ge	1211.4	34.7	-20.121	-78.048	—
Al [43]	933.47	10.71	+7.473	+58.62	1500 (10 GPa)

Adapted from Soma and Matsuo, 1982, [42] and from Hänström and Lazor, 2000, [43].

Table 1.4 Critical phase transformation pressures for a number of model systems

Material	Phase transformation	P_c (GPa)	$\Delta V_{m\alpha\rightarrow\beta}$ (cm ³ mol ⁻¹)	$\Delta H_{\alpha\rightarrow\beta}$ (kJ mol ⁻¹)
KCl	NaCl → CsCl	1.96	-4.11	8.03
KBr	NaCl → CsCl	1.80	-4.17	7.65
RbCl	NaCl → CsCl	0.57	-6.95	3.39
ZnO	Wurtzite → NaCl	8.86	-2.55	19.23
SiO ₂	Quartz → coesite	1.88	-2.0	2.93
SiO ₂	Coesite → stishovite	9.31	-6.6	52.27

in view of their wurtzite–zinc blende transformations which resemble quasi-equilibrium conditions.

An even more important case of polymorphism for its relevance to material applications is that exhibited by carbon and silicon carbide, which will be discussed in Section 1.7. The polymorphism of silicon carbide, with its more than 200 different polymorphs, falls into the category of polytypism, as each different polymorph can be regarded as built up by stacking layers of (nearly) identical structure and composition, and the difference lies only in their stacking sequence. Polytypism is, therefore, a special case of polymorphism where the two-dimensional translations within the layers are essentially preserved [47].

While the evaluation of the critical pressure at which a structural phase transformation occurs may be obtained by *ab initio* or molecular dynamics (MD) computations, the effect of the pressure on the phase transformation temperature $T_{\alpha\rightarrow\beta}$ of a generic material may be deduced by the Clausius–Clapeyron equation

$$\frac{dP}{dT} = \frac{\Delta H_{\alpha\rightarrow\beta}}{T_{\alpha\rightarrow\beta}\Delta V_{\alpha\rightarrow\beta}} \quad (1.35)$$

where $\Delta H_{\alpha\rightarrow\beta}$ is the enthalpy of the $\alpha \rightarrow \beta$ transformation, $T_{\alpha\rightarrow\beta}$ is the equilibrium transformation temperature and $\Delta V_{\alpha\rightarrow\beta}$ is the volume change associated with the $\alpha \rightarrow \beta$ transformation.

Equation (1.35) could also be written

$$dT_{\alpha\rightarrow\beta} = \frac{T_{\alpha\rightarrow\beta}\Delta V_{\alpha\rightarrow\beta}}{\Delta H_{\alpha\rightarrow\beta}}dP \quad (1.36)$$

for the change in the transformation temperature as a function of pressure.

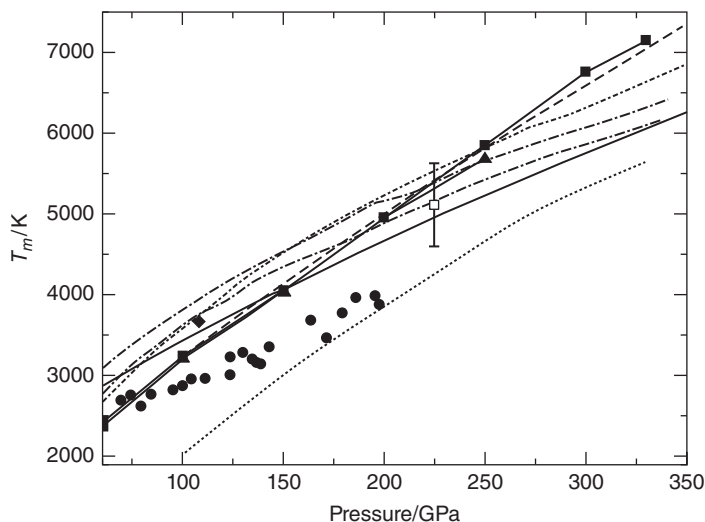


Figure 1.6 Effect of the pressure on the melting point of iron. Luo et al., 2011, [48]. Reproduced with permission from American Chemical Society

If both the $\Delta H_{\alpha-\beta}$ and $\Delta V_{\alpha-\beta}$ terms are taken as independent of both temperature and pressure, a linear increase or decrease of the melting temperature is expected with increase in the applied pressure, depending on whether there is a volume contraction or expansion on melting, as shown in Table 1.3.

The melting temperature, therefore, increases with the applied pressure in the case of metals, see Figures 1.6 and 1.7, and decreases in semiconductors, see Figure 1.8 for the typical case of silicon, because, almost systematically, there is, on freezing, a volume contraction in metals and a volume expansion in elemental semiconductors [43, 48–50]. As the Clapeyron equation has been deduced for conditions very close to the equilibrium melting temperature $T_{\alpha-\beta}^0$, we might expect sensible deviations from the linearity at elevated pressures, as is, in fact, shown in Figures 1.6–1.8.

The validity of the Clapeyron equation may be, however, extended to a wider pressure and temperature range once the pressure and temperature dependence of the $\Delta H_{\alpha-\beta}$ and $\Delta V_{\alpha-\beta}$ terms are known or could be calculated.

A critical role is expected to be played by the $\Delta V_{\alpha-\beta}$ term in Eqs. (1.35) and (1.36), which is related to the effect of the applied pressure on the density of the two phases in equilibrium. Density should decrease in absolute value with increase in the applied pressure, that is with increase in the mechanical deformation. Figure 1.9 shows, as an example, the calculated strong decrease of the atomic volume of hexagonal close packed (HCP) solid iron with increase in pressure, which is associated with a decrease in the $\Delta V_{\alpha-\beta}$ term value from $0.16 \text{ cm}^3 \text{ mol}^{-1}$ at atmospheric pressure to $0.10 \text{ cm}^3 \text{ mol}^{-1}$ at 250 GPa [48].

The effect of volume changes on the melting temperature is phenomenologically taken into account by the Lindeman equation [51] in its integrated form [43]

$$T_m = T_m^0 \left(\frac{V_{T_m}}{V_{T_m}^0} \right)^{\frac{2}{3}} \exp \left[\frac{2\gamma^0}{q} \left(1 - \frac{V_{T_m}}{V_{T_m}^0} \right)^q \right] \quad (1.37)$$