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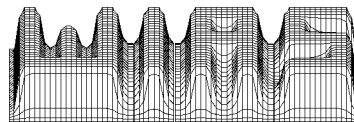# für Angewandte Analysis und Stochastik

Towards thermodynamic modeling of nucleation and growth of droplets in crystals

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Abstract

Stress assisted diffusion in single crystal Gallium Arsenide (GaAs) leads to the formation and growth of unwanted liquid arsenic droplets in a solid matrix. This process happens during the heat treatment of single crystal GaAs, which is needed for its application in opto-electronic devices, and it is of crucial importance to pose and answer the question if the appearance of droplets can be avoided. To this end we start a thermodynamic simulation of this process. Special emphasis is given to the influence of mechanical effects on chemistry, diffusion and interface motion in GaAs.

1 Introduction of the complete problem

Stress assisted diffusion in single crystal Gallium Arsenide (GaAs) leads to the formation and growth of unwanted liquid droplets in a solid surrounding, [14], [15], [4], [5]. This is an elaborate thermodynamic process involving chemical reactions, diffusion, motion of phase boundaries, and all these phenomena are strongly influenced by local mechanical stress fields. The resulting model consists of a coupled system of algebraic equations, partial differential equations and conditions at the appearing liquid/solid interfaces. The variables are the mole fractions of various constituents, which appear in semi-conducting GaAs, the mechanical strain, and a phase density, indicating the size distribution of droplets.

Single crystal GaAs contains the major elements gallium and arsen, and additionally various trace elements, which are of most importance in order to fabricate semi-conducting or semi-insolating GaAs, respectively. All constituents occupy three sublattices of face-centered cubic (fcc) symmetry. The sublattices are indicated by three greek letters: α, β, γ. The lattice α is dominantly occupied by gallium, while the arsenic is the major substance on the lattice sites of sublattice β. The sublattice γ indicates an interstitial lattice, where the dominant elements are vacancies. For a proper application of single crystal semi-conducting or semi-insolating GaAs as a wafer material, it is crucial that the trace elements are distributed homogeneously on the lattice sites of the three sublattices. In order to remove dislocations, which appear during the process of crystal growth, a special heat treatment of the wafer becomes necessary. However, the heat treatment might start a diffusion process, where the trace elements move preferably towards the vicinity of the dislocations, where the trace elements find thermodynamic conditions so that the formation of liquid droplets, dominantly formed by the arsenic, sets in. However, also in regions, which are free of dislocations, the arsenic precipitates appear.

The first Figure shows two graphs, which represent the morphology of single crystal Gallium Arsenide on the mm-scale.
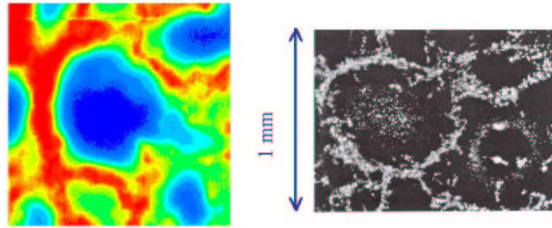

Figure 1: Distribution of dislocations (left), Distribution of droplets (right)

The graph on the left hand side Figure 1 is a photo-luminescence mapping, and shows the distribution of dislocations. The cellular structure is typical for Gallium Arsenide: The dislocations are dominantly arranged in rings, with an inner region, which is free of dislocations. The graph on the right hand side of Figure 1 shows the distribution of droplets. A careful study of this graph reveals that large droplets appear in the cell wall, i.e. in the vicinity of the dislocations. Adjacent to this ring of droplets, there is a region without droplets, and the center of the dislocation ring is occupied by small droplets. The number densities of small and large droplets are of the same order.

We are thus confronted with the problem to describe the thermodynamic nucleation and growth conditions of liquid droplets within a solid matrix. In particular we will study the influence of local mechanical stresses on chemistry, diffusion and interface motion. Stress fields arise due to dislocations, eigenstrains due to point defects and due to misfit strain that describes the phenomenon that the arsenic liquid phase, which appears as inclusions has a larger specific volume than the solid phase.

2 Some physical and chemical properties of semi-insulating/semi-conducting GaAs

2.1 The phase diagram

The phase diagram of GaAs, which is shown in Figure 2, indicates the various phases and their boundaries. Below the liquidus line, we find, left and right of the stoichiometric line, i.e. (arsenic) composition $y = 0.5$, two regions where the solid GaAs crystal may coexist with the liquid. Right and left from $y = 0.5$, the crystal is As-rich and Ga-rich, respectively. These regions are bounded from below by the two eutectic lines at $29.5°C$ and $810°C$, respectively. The two regions below the eutectic lines indicate mixtures consisting of the solid GaAs crystal as matrix material containing solid Ga-rich and As-rich precipitates, respectively. In this study, we are exclusively concerned with thermodynamic processes in the two-phase region right from the stoichiometric line and above the $810°C$ eutectic.
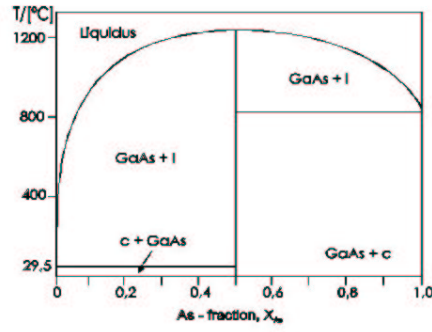
Figure 2: Equilibrium phase diagram of GaAs

The GaAs crystal at the stoichiometric composition consists of two fcc sublattices that are displaced along the diagonal of the elementary cube, i.e. the crystal has the symmetry of Zinkblende. However, the ideal crystal at $y = 0.5$ is neither a semi-conductor nor a semi-insulator. The latter one may form if the crystal composition is slightly on the As-rich side. Moreover there are further constituents appearing in GaAs. These are Oxygen (O), Silicon (Si), Bor (B) and Carbon (C) in very small quantities, but nevertheless these trace elements induce very important phenomena. Above the $810°C$ eutectic there is a region, which is called region of homogeneity, where the excess amount of As and the just mentioned trace elements behave like point defects that are homogenously distributed over the two already mentioned sublattices and on a further sublattice, which is formed by interstitial lattice sites.

Figure 3 shows the region of homogeneity (H) as it was calculated on demand for Freiberg Compound Materials (FCM) by H. Wenzl and G. Erikson. For details of the underlying model see [15]. During a heat treatment of the crystal, the boundary of the region H may be crossed, as it is indicated in the Figure. If this happens, unwanted liquid As-rich precipitates appear. Thus the knowledge of the boundary of the region H is of crucial importance for the proper application of GaAs as a wafer material.
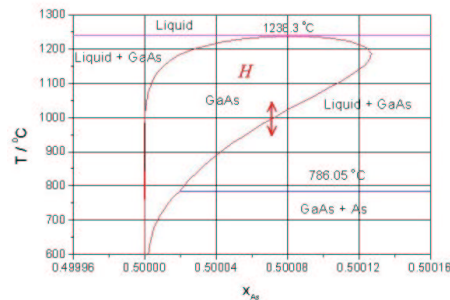

Figure 3: Zoom of the homogeneity sector of the GaAs phase diagram

The calculated region of homogeneity depends sensitively on the assumed chemistry, i.e. on the chemical reaction that are taken into account.

One of the objectives of this study is the determination of the mechanical influence on the region of homogeneity. The mechanical influence arises due eigenstrains, which are induced by point defects and dislocations, and due to misfit strain, which is induced by a volume change during the solid/liquid phase transition. Regarding the non-mechanical parts of the thermodynamic theory, we rely on the chemical model given by Wenzl et. al.,[15], in collaboration with the wafer manufacturer FCM, and which will be discussed in detail in the following Section.

2.2 The chemical constitution of semi-insulating As-rich GaAs

The chemical model of Wenzl et. al. [15] is suited to describe the behaviour of semi-insulating As-rich GaAs that is fabricated by Freiberg Compound Materials (FCM).

The GaAs crystal is assumed to consist of three sublattices, indexed by $\{\alpha, \beta, \gamma\}$. Among them there are the already introduced two *fcc* sublattices, which are mainly occupied by Ga- and As-atoms, respectively, and the fcc interstitial sublattice, whose lattice sites are mostly occupied by vacancies.
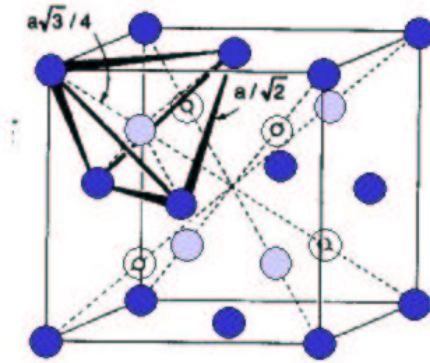

Figure 4: Elemtary cell of the GaAs crystal

Figure 3 gives a scetch of the elementary cell of the crystal. The lattice sites at the corners and faces of the cube form the sublattice α, which is mainly occupied by Ga atoms, indicatet by solid balls. In the interior of the elementary cell of the sublattice α there are further lattice sites, viz. four octahedral and eight tetrahedral lattice sites. Four lattice sites of the tetrahedral sites forme the elementary cell of the β sublattice, indicated in the Figure by light balls. The remaining four tetrahedral sites form the sublattice γ. It is important to know that the available space of a lattice site of the β sublattice is equal to the corresponding space in the γ sublattice. The available space for octahedral sites is too small for an occupation by atoms, and thus the octahedral lattice remains empty.

The number densities of sublattice sites are denoted by n_α, n_β, n_γ. There holds

$n_\alpha = n_\beta = n_\gamma = n_{SL}$. The free electrons and free holes do not need lattice sites, rather the form the electronic gas.

The constituents of the GaAs crystal are the chemical elements Ga, As, O, Si, B, C, and vacancies V, free electrons e and holes h, which are also treated like chemical elements. For a proper description of semi-conducting/semi-insulating GaAs, the list of constituents must be extended because the elements As, O, Si, C and the vacancies V may also occur as charge carriers, which is indicated by a superscript. In addition, when the constituents occur on different sublattices they are considered as different constituents, and this is indicated by a subscript. There are thus 17 constituents: free electrons and holes, which do not occupy lattice sites, and 15 constituents on the three sublattices according to the following table.

Sublattice α	Ga_α	$As_\alpha^{(0)}$	$As_\alpha^{(+)}$	$V_\alpha^{(0)}$	$V_\alpha^{(3-)}$	$B_\alpha^{(0)}$	$Si_\alpha^{(+)}$
Sublattice β	As_β	$O_\beta^{(0)}$	$O_\beta^{(-)}$	$O_\beta^{(+)}$	$C_\beta^{(-)}$	$V_\beta^{(0)}$	
Sublattice γ	$As_\gamma^{(0)}$	$V_\gamma^{(0)}$					

The constituents Ga_α and As_β form the major portions on their privileged sublattices which determine the symmetry of the crystal. The other constituents are called (point) defects, which thus consist of antisite atoms, interstitial atoms, trace elements and vacancies.

The special choice of constituents, and in particular the assumption that Ga is exclusively without charge on the sublattice α, has been suggested by FCM and is called Freiberger model. The underlying reasoning of the Freiberger model relies on experimental hints, and in particular on the objective to calculate a quite realistic homogeneity region that fits to the properties of FCM made semi-insulating GaAs. For different choices and resulting consequences we refer the reader to [15].

3   A list of simplified problems with increasing complexity

The last section has revealed that we have a quite complex thermochemical process under consideration. For this reason it is appropriate to consider at first only very simple initial and boundary value problems that serves especially to design the mathematical model and to calibrate its parameters.

In particular we consider the two situations that are scetched in the following Figure. The two pressure vessels, which are closed by a movable piston, set two thermodynamic systems with prescribed outer pressure, p_0 and temperature T_0. The inner temperature is assumed to be homogeneous and equal to the outer temperature.

The example on the left hand side considers a liquid and a solid phase separated by a planar interface. This example is designed to study the influence of mechanical stresses to the chemical and interfacial equilibrium condition and on the diffusion process in the solid.
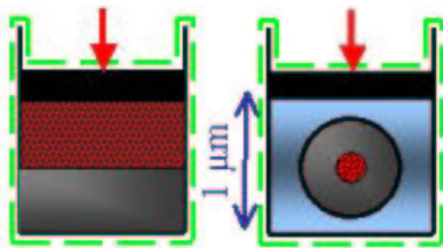
Figure 5: Two example problems: liquid/solid plane interface (left), liquid single droplet in contact with a solid (right)

In particular, the example on the right hand side considers a solid ball on μm scale in contact with a gas consisting of the four arsenic constituents As, As_2, As_3, As_4. The solid ball contains at its center a liquid droplet, made exclusively from As and Ga, that can grow or shrink. The outer interface of the ball is in equilibrium with the gas, and we consider the case that only As_2 may cross the interface and becomes an interstitial As in the solid.

4 Thermodynamics of mixtures, Part 1: Variables

We consider a body B whose volume $V(t)$ may depend on time t. A space point, which is at some time t occupied by a *material point* P of B, is indicated by its cartesian coordinates $x = (x^i) = (x^1, x^2, x^3)$. The notion *material point* means the smallest units of B that cannot further be resolved on the chosen space scale.

The body B may consist of coexisting fluid and solid phases, both are mixtures of various chemically different constituents.

The thermodynamic state of the fluid phase is described by the variables

$$
\begin{aligned}
&n_a = n_a(t, x), \quad a \in \{1, 2, ..., a_L\}, && \text{number densities of constituents,} \\
&v^i = v^i(t, x), && \text{barycentric velocity of the mixture,} \\
&T = T(t), && \text{(absolute) temperature.} && (1)
\end{aligned}
$$

The total mass density of the mixture, ρ, is given by the sum over the number densities $\times$ molecular weights, M_a, and for some purposes it is useful to calculate the mixture velocity, v, from the velocities of the constituents, v_a^i. Thus we write

$$
\rho = \sum_{a=1}^{a_L} M_a n_a \quad \text{and} \quad v^i = \sum_{a=1}^{a_L} \frac{M_a n_a}{\rho} v_a^i. \tag{2}
$$

In order to describe the deformation of the solid phase we must at first introduce a reference configuration. To this end we indicate at a fixed reference time t_0 any

material point P of the solid phase by its cartesian coordinates $X = (X^1, X^2, X^3)$. The motion of P, is described by the field $\chi^i(t, X) = (\chi^1(t, X), \chi^2(t, X), \chi^3(t, X))$, which gives the coordinates of P at time $t > t_0$:

$$x^i = \chi^i(t, X). \tag{3}$$

The field χ^i is called *motion*, and its first derivatives

$$\hat{v}^i = \frac{\partial \chi^i}{\partial t} \qquad \text{and} \qquad F^{ij} = \frac{\partial \chi^i}{\partial X^j} \qquad \text{with} \qquad J = \det(F^{ij}) \neq 0 \tag{4}$$

are the *velocity* and the *deformation gradient*, respectively. The condition on the Jacobian J guarantees that (3) is invertible.

It is well known that the Jacobian is related to the total mass density by

$$J = \frac{\rho_R}{\rho}, \tag{5}$$

where ρ_R is the mass density in the reference configuration.

The solid phase may consist of a mixture with a_S constituents, and thus the thermodynamic state of the solid phase is described by the variables

$$x^i = \chi^i(t, X), \quad n_a = n_a(t, x), \quad T = T(t). \tag{6}$$

5 Thermodynamics of mixtures, Part 2: General Constitutive Model

We consider a GaAs crystal consisting of two coexisting phases, which are formed by a nonviscous mixture of liquids and a thermoelastic solid mixture, respectively. There are eigenstrains due to the presence of point defects, misfit strain and dislocations. However, dislocations are not considered in the current paper.

Beyond the variables, further important quantities are needed to describe properties of mixtures. These are: specific internal energy, u, specific entropy, s, specific free energy, $\psi = u - Ts$, and the chemical potentials of the constituents, μ_a, [10], [11].

Furthermore there are three measures of stress, viz. the Cauchy stress, σ^{ik}, and the first and second Piola Kirchhoff stress, respectively, $\hat{\sigma}^{ik}$ and t^{ik}:

$$\sigma^{ik} = \sigma^{ki}, \quad \hat{\sigma}^{ik} = J\sigma^{ij}\overset{-1}{F}{}^{kj}, \quad t^{ik} = J\overset{-1}{F}{}^{ij}\overset{-1}{F}{}^{kl}\sigma^{jl}. \tag{7}$$

The Cauchy stress appears naturally in a thermodynamic description where the reference configuration of the solid phase does not explicitly appear. The first Piola Kirchhoff stress is a simply measurable quantity, and appears naturally in the description that relies on the reference configuration. Finally the second Piola Kirchhoff stress is needed to formulate constitutive laws, which relate the stress to the variables, [13].

Let us decompose the Cauchy stress into its trace and the traceless part, the latter one is indicated by angle brackets around the indices, for example we write

$$\sigma^{ik} = -p\delta^{ik} + \sigma^{<ik>} \quad \text{with} \quad p = -\frac{1}{3}\sigma^{nn}. \tag{8}$$

The quantity p is called pressure.

There are also various measures of the deformation of a body. The most important one is the right Cauchy Green tensor, C^{ik}, and its unimodular restriction, which we denote by c^{ik}:

$$C^{ik} = F^{mi}F^{mk} \quad \text{and} \quad c^{ik} = J^{-2/3}C^{ik} \quad \text{so that} \quad \det(c^{ik}) = 1. \tag{9}$$

All these quantities are related to each other by the Gibbs equation, which reads in fluids as well as in thermoelastic solids

$$d\rho\psi = -\rho s dT + \frac{1}{2}J^{-1/3}t^{ik}dc^{ik} + \sum_a \mu_a dn_a. \tag{10}$$

The Gibbs equation implies

$$\rho s = -\frac{\partial\rho\psi}{\partial T}, \quad t^{ik} = 2J^{1/3}\frac{\partial\rho\psi}{\partial c^{ik}}, \quad \text{and} \quad \mu_a = \frac{\partial\rho\psi}{\partial n_a}. \tag{11}$$

Furthermore, there holds the Gibbs/Duhem equation

$$\rho\psi + p = \sum_{a=1}\mu_a n_a. \tag{12}$$

For the solid phase the knowledge of the free energy density $\rho_s\psi_s(T, n_1, ..., n_{a_s}, c^{ik})$ is sufficient to relate the introduced quantities to the variables.

In a mixture of isotropic fluids the free energy does not depende on c^{ik}, and the second Piola/Kirchhoff stress drops out of the Gibbs equation. Thus for the liquid phase the knowledge of the free energy density $\rho_L\psi_L(T, n_1, \ldots, n_{a_L})$ is sufficient to relate the introduced quantities to the variables.

The proof of the Gibbs equation for fluid mixtures and for those solids that only consists of a single substance can be found in [10]. The generalization to a solid mixture, viz. eqn. (10), has not been published elsewhere, but it can be derived along the strategies that are outlined by I. Müller in [10].

6 Thermodynamics of mixtures, Part 3: Explicit representations of free energies, chemical potentials, pressure and stresses

In general there are three competing additive contributions to the free energy of a mixture: (i) entropy, (ii) interaction or mixing energy, and (iii) mechanical energy.

If only the entropic contribution is considered, the mixture is called an *ideal mixture*. In the following we combine the two first contributions in the so called chemical part of the free energy, and we write

$$\rho\psi = \rho\psi^{chem} + \rho\psi^{mech} \qquad \text{and accordingly} \qquad \mu_a = \mu_a^{chem} + \mu_a^{mech}. \qquad (13)$$

6.1 Chemical potentials and pressure of the liquid phase

As a simplification we assume that the liquid phase only consists of Ga and As. We give at once the explicit constitutive laws for the chemical potentials and the pressure. The free energy density can then be calculated by means of the Gibbs/Duhem equation (12).

$$\mu_{Ga}^{chem} = \mu_{Ga}^0(T) + RT\,\mathrm{Log}(1-y) + (L_0 + L_1(3-4y))y^2,$$
$$\mu_{As}^{chem} = \mu_{As}^0(T) + RT\,\mathrm{Log}(y) + (L_0 + L_1(1-4y))(1-y)^2. \qquad (14)$$

The newly introduced quantity $y = n_{As}/n$ is the arsenic mole fraction. The first parts give the standard chemical potentials. The second parts are the entropic contributions, and the third parts give the mixing energy according to the Redlich/Kister model, and L_0, L_1 measure the strength of the mixing energy. R is the universal gas constant. For details, see [12].

The mechanical parts of the chemical potentials are nonclassical contributions. These describe the *interfacial misfit*, which arises because the transition from the solid phase to the liquid phase is accompanied by a change of the specific volume. In fact, arsenic rich liquid needs more space than solid GaAs. In order to describe this phenomenon, let us at first introduce the function

$$\frac{1}{\rho^{therm}(T,y)} =$$
$$\upsilon_{As}(T)\frac{M_{As}y}{M_{As}y + M_{Ga}(1-y)} + \upsilon_{Ga}(T)(1 - \frac{M_{As}y}{M_{As}y + M_{Ga}(1-y)}), \qquad (15)$$

where $\upsilon_{As}(T)$ and $\upsilon_{Ga}(T)$ are the specific volumes of pure As and pure Ga, respectively. Next we choose as a reference density of the liquid $\rho_R = \rho^{therm}(T_R, 1)$, and we set $\rho_*(T) = \rho_s^{therm}(T)$, where ρ_s^{therm} is the density of stoichiometric solid GaAs which can be read off from a table. Finally we measure the interfacial misfit by

$$\frac{\rho_*(T) - \rho_R}{\rho_R}. \qquad (16)$$

There results the mechanical chemical potentials

$$\mu_{Ga}^{mech} = \frac{M_{Ga}}{\rho_R}K_L Log(\frac{\rho}{\rho_*(T)}) \qquad \text{and} \qquad \mu_{As}^{mech} = \frac{M_{As}}{\rho_R}K_L Log(\frac{\rho}{\rho_*(T)}), \qquad (17)$$

which rely on the simple constitutive law for the liquid pressure:

$$p = p_R + K_L(\frac{\rho - \rho_*(T)}{\rho_R}). \qquad (18)$$

Recall that the liquid density is denoted by ρ. K_L is the bulk modulus of the liquid.

6.2 The free energy of the solid phase

The solid phase of GaAs consists of three fcc sublattices α, β, γ which are occupied by seventeen different constituents according the description of Section 2.2. However, there are only fifteen unknown number densities, because the trace elements Si, C and B are prescribed.

The chemical part of the free energy density of the solid phase is given by

$$\rho\psi^{chem} = \sum_{a=1}^{17} n_a \mu_a^0(T) + RT \sum_{a=1}^{17} n_a \log(\frac{n_a}{n_{SL}}) + \frac{q}{2} \sum_{a,b=1}^{17} I_{ab}(T) n_a \frac{n_b}{n_{SL}}. \tag{19}$$

The free energy density $\rho\psi^{chem}$ consists of three contributions, which are the standard chemical potential $\mu_a^0(T)$, consisting of the energy and entropy constants (first term), entropy (second term) and mixing energy (third term). The constant q, ($= 4$ in the current study), is the coordination number and the temperature dependent quantities I_{ab} denote the interaction energies. We take only nearest neighbour interactions into account. Furthermore, we assume that electrons, holes and the other charged constituents have only entropic free energies, which is a fairly good approximation. Examples for numerical values for the nonzero interaction energies can be found in [14] and [15].

The free energy density $\rho\psi^{mech}$ describes elastic energy including eigenstrains and is given by

$$\rho\psi^{mech} = \frac{1}{4J}(J^{2/3} c^{ij} - C_*^{ij}) K^{ijkl} (J^{2/3} c^{kl} - C_*^{kl}) - p_R \sqrt{\det(c^{ij})_{|\det(c^{ij})=1}}. \tag{20}$$

K^{ijkl} is the stiffness matrix and C_*^{ij} is a measure for the eigenstrains. The form of $\rho\psi^{mech}$ has been chosen so that the Gibbs equation implies Hookes law for the second Piola/Kirchhoff stress, viz.

$$t^{ij} = \frac{1}{2} K^{ijkl} (J^{2/3} c^{kl} - C_*^{kl}) - p_R J^{1/3} \overset{-1}{c^{ki}} \tag{21}$$

The matrix C_*^{kl} describes the various eigenstrains due to point defects, see the next Section for details.

Next we calculate from (19) and (20) the chemical and mechanical parts of the chemical potentials. There results

$$\mu_a^{chem} = \mu_a^0(T) + RT \log(\frac{n_a}{n_{SL}}) + q \sum_{b=1}^{17} I_{ab}(T) \frac{n_b}{n_{SL}} - \frac{q}{2} \sum_{a,b=1}^{17} I_{ab}(T) \frac{n_a n_b}{n_{SL}^2}, \tag{22}$$

for the chemical part of the chemical potential, while its mechanical part reads

$$\mu_a^{mech} = -\frac{M_a}{3\rho_S J} (\frac{1}{4}(J^{2/3} c^{ij} - C_*^{ij}) - C_*^{ij}) K^{ijkl} (J^{2/3} c^{kl} - C_*^{kl}). \tag{23}$$

7 Thermodynamics of mixtures, Part 4: Eigenstrains due to point defects

There are three different mechanisms that give rise to eigenstrains, which may appear due to (i) dislocations, (ii) point defects, and (iii) interfacial misfit.

The role of eigenstrains due to dislocations have been discussed in the introduction and will not considered anymore in the current study.

The eigenstrains due to interfacial misfit can be attributed either to the liquid phase or to the solid phase, see for example [7]. In the present study we have chosen the liquid phase in order to incorporate the interfacial misfit, see Section 6.1.

There remains to discuss eigenstrains due to the various point defects on lattice sites of the two sublattices α and β, viz. $As_\alpha^{(0)}$, $As_\alpha^{(+)}$, $V_\alpha^{(0)}$, $V_\alpha^{(3-)}$, $B_\alpha^{(0)}$, $Si_\alpha^{(+)}$ on sublattice α, $O_\beta^{(0)}$, $O_\beta^{(-)}$, $O_\beta^{(+)}$, $C_\beta^{(-)}$ on sublattice β. Note that the Freiberger model does not lead to eigenstrains on sublattice γ, because the defect $As_\gamma^{(0)}$ needs the same space as an As atom on the sublattice β. Uncharged vacancies on interstitials have no effect at all. The defects on sublattices α and β induce eigenstrains, which are different for the neutral and the charged defects. The neutral defects except the vacancies can be fairly well approximated as elastic balls, whereas the charged defects and the vacancies behave as they were rigid balls.

Let us decompose the function C_*^{ij} as a product of thermal eigenstrains and eigenstrains due to defects:

$$C_*^{ij} = C_{therm}^{ik} C_{defects}^{kj}. \tag{24}$$

The thermal part is obviously given by

$$C_{therm}^{ik} = (1 + \alpha(T - T_R))^2 \delta^{ik}, \tag{25}$$

where α denotes the coefficient of thermal expansion.

A simple calculation relying on elastic and rigid balls yields explicit expressions for the corresponding eigenstrains, which can be written as a product of elastic and rigid eigenstrains:

$$C_{defects}^{kj} = \prod_a (1 + \frac{n_a}{3n_{SL}}) Z_a \prod_b (1 + \frac{n_b}{3n_{SL}}) Z_b \delta^{kj}. \tag{26}$$

for $a \in \{As_\alpha^{(0)}, B_\alpha^{(0)}, O_\beta^{(0)}\}$ and $b \in \{As_\alpha^{(+)}, V_\alpha^{(0)}, V_\alpha^{(3-)}, Si_\alpha^{(+)}, O_\beta^{(-)}, O_\beta^{(+)}, C_\beta^{(-)}, V_\beta^{(0)}\}$. The constants Z_a and Z_b are given by

$$Z_a = \frac{\delta_a}{1 + \delta_a} \qquad \text{and} \qquad Z_b = \frac{4\mu}{3K} \delta_b. \tag{27}$$

μ and K are the shear and bulk modulus of the solid phase, and

$$\delta_a = \{-0.055, -0.119, -0.317\} \tag{28}$$

$$\delta_b = \{-0.119, -0.119, -0.119, -0.119, 0.479, -0.317, -0.317, -0.317\}. \tag{29}$$

The difference of the two representations for eigenstrains results, because elastic eigenstrains are characterized by continuous normal stresses at the interface between an elastic ball and the solid phase, while rigid eigenstrains are due to a prescribed normal displacement at the interface between a rigid ball and the solid phase.

8 Thermodynamics of mixtures, Part 5: Field equations

The variables of the thermodynamic model are the five components of the strain field and fourteen number densities of constituents in the solid phase, while in the liquid phase the only variables are the two number densities of Ga and As, because for simplicity we do not allow that the other constituents of the solid may cross the interface.

The field equations for the variables rely on several assumptions:

(i) Mechanical equilibrium is reached immediately, so that the strain field is determined by the quasistatic momentum balance for given number densities.

$$\frac{\partial \sigma^{ik}}{\partial x^k} = 0. \tag{30}$$

(ii) Local chemical equilibrium in the solid phase is reached much faster than diffusional equilibrium, so that for given total number densities of Ga and As, the other number densities are determined by the 14 nonlinear algebraic equations representing the laws of mass actions. These equations will be derived in Section 9 and are given by (40), (41), and (44) / (49). They have the generic form

$$F_A(n_1, n_2, ... n_{14}; T, n_{Ga}^S, n_{As}^S) = 0, \qquad A \in \{1, ..14\}. \tag{31}$$

We write the solution of these equations as

$$n_a = \tilde{n}_a(T, n_{Ga}^S, n_{As}^S). \tag{32}$$

(iii) Thus only a single diffusion equation in the solid is needed. Furthermore, this equation simplifies due to the fact that only the mobility of the interstitial arsenic is of importance. The diffusion equation reads

$$\frac{\partial n_{As}^S}{\partial t} = M \Delta (\tilde{\mu}_{As_\gamma^{(o)}} - \tilde{\mu}_{Ga_\alpha}), \tag{33}$$

where M denotes the mobility of the interstitial $As_\gamma^{(o)}$ and n_{As}^S denotes total number density of the As content of the solid. $\tilde{\mu}_{As_\gamma^{(o)}}$ and $\tilde{\mu}_{Ga_\alpha}$ are chemical potentials of the indicated substances. However, the equations (32) has been used to eliminate those constituents that are in thermal equilibrium with n_{Ga}^S, n_{As}^S, and this procedure is

indicated by the tilde. The exploitation of the diffusion equation is carried out in [4].

(iv) The liquid is assumed to be in equilibrium and its number densities can be read off from the liquidus line of the phase diagram.

(v) The form of the interfacial jump conditions depend on the interfacial mobilities. If the interfacial mobilities are much larger than the bulk mobility of $As_\gamma^{(o)}$, local equilibrium at the interface can be assumed, and the jump conditions are those that will be derived in the next two sections, see equations $(43)_2$, (51) and (52). However, currently the magnitude of the interfacial mobilities are not known, and it may happen that they have the same order as the bulk mobility. In this case the interfacial jump conditions result from the Becker/Döring theory of nucleation, for details see [5].

9   Thermodynamics of mixtures, Part 6: The Global Laws of Energy and Entropy

In this Section we derive the equilibrium conditions for two coexisting phases. We consider the systems, which is shown in Figure 5, consisting of a container, which is closed by a piston. At time t, the volume $V(t)$ include either the liquid/solid or the liquid-droplet/solid/gas. We assume that the outer pressure p_0 is given. Furthermore we prescribe the outer temperature T_0 and assume that T_0 is constant throughout $V(t)$. The dashed closed line indicate a control volume which we introduce in order to apply the global balance laws of energy E and entropy S to the described system:

$$\frac{dE}{dt} + p_0 \frac{dV}{dt} = \dot{Q}, \quad \text{and} \quad \frac{dS}{dt} \geq \frac{\dot{Q}}{T_0}. \tag{34}$$

The quantity $\dot{Q}$ denotes the heat power, which may enter, $\dot{Q} > 0$, or leave, $\dot{Q} < 0$, the system, so that a constant temperature T_0 is guaranteed. The equality sign holds in equilibrium, whereas in nonequilibrium, the variation of the entropy is greater than the ratio of supplied heat and temperature. This statement expresses CLAUSIUS version of the second law of thermodynamics, [2].

Elimination of the heat power leads to the main inequality

$$\frac{dA}{dt} \leq 0 \quad \text{with the definition} \quad A = E - T_0 S + p_0 V. \tag{35}$$

The newly defined quantity, A, is called the available free energy or availability. We conclude that in dynamic processes that run at constant outer pressure, constant temperature and constant total mass, the availability must decrease and assumes its minimum in equilibrium.

The availability contains the combination $\Psi = E - T_0 S$ denoting the Helmholtz free energy, whereas $A = \Psi + p_0 V$ give the Gibbs free energy G only if there is an overall

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constant pressure $p = p_0$ in the interior of the volume V. However, we will not meet this situation in the two considered examples.

The evaluation of the main inequality requires an explicit knowledge of the functional dependence of energy, entropy and volume on those variables that may change in the process under consideration. In the next sections we will introduce and discuss the needed functions.

The two considered systems, which is shown in Figure 5, consist of solid, S, liquid,L, and gas, G, phases, which occupy different regions, so that the total volume at time t is given by

$$V(t) = V_S(t) + V_L(t), \qquad V(t) = V_S(t) + V_L(t) + V_G(t), \qquad (36)$$

for the left and right example, respectively. The total free energies of the two examples can be additively decomposed into the free energies of the phases and the surface free energy of the interface boundaries

$$\Psi = \Psi_S(t) + \Psi_L(t) + \Psi_G(t) + \sigma O_L. \qquad (37)$$

The surface energy, which is also called surface tension is denoted by σ and the liquid/solid interface area is O_L.

The free energies of the phases can be represented by the volume integrals

$$\Psi_S(t) = \int_{V_S} \rho\psi dV \qquad \Psi_L(t) = \int_{V_L} \rho\psi dV \qquad \Psi_G(t) = \int_{V_G} \rho\psi dV, \qquad (38)$$

where ψ is the specific free energy and ρ is the mass density of the mixture.

10 The laws of mass action and interface conditions

We consider the left problem in Figure 5, where a liquid phase is connected to a solid phase by a plane interface. We assume that both phases are in equilibrium and we pose the problem to determine the corresponding equilibrium conditions by means of the exploitation of the minimum condition for the availability.

Thus we determine the minimum of the function

$$A = \rho_S\psi_S V_S + \rho_L\psi_L V_L + p_0(V_S + V_L) \qquad (39)$$

under several side conditions.

Conservation of atoms

$$N_{Ga} = n_{Ga_\alpha}V_S + n_{Ga}^L V_L,$$
$$N_{As} = (n_{As_\beta} + n_{As_\alpha^{(0)}} + n_{As_\alpha^{(+)}} + n_{As_\gamma^{(0)}})V_S + n_{As}^L V_L,$$
$$N_O = (n_{O_\beta^{(0)}} + n_{O_\beta^{(-)}} + n_{O_\beta^{(+)}})V_S, \qquad N_{Si} = n_{Si_\alpha^{(+)}}V_S,$$
$$N_B = n_{B_\alpha^{(0)}}V_S, \qquad N_C = n_{C_\beta^{(-)}}V_S. \qquad (40)$$

The three sublattices have the same number of lattice sites:

$$n_{As_\beta} + n_{O_\beta^{(0)}} + n_{O_\beta^{(-)}} + n_{O_\beta^{(+)}} + n_{C_\beta^{(-)}} -$$
$$(n_{Ga_\alpha} + n_{As_\alpha^{(0)}} + n_{As_\alpha^{(+)}} + n_{V_\alpha^{(0)}} + 3n_{V_\alpha^{(3-)}} + n_{B_\alpha^{(0)}} + n_{Si_\alpha^{(+)}}) = 0 \qquad (41)$$
$$n_{As_\beta} + n_{V_\beta^{(0)}} + n_{O_\beta^{(0)}} + n_{O_\beta^{(-)}} + n_{O_\beta^{(+)}} + n_{C_\beta^{(-)}} - (n_{V_\gamma^{(0)}} + n_{As_\gamma^{(0)}}) = 0.$$

Conservation of charges

$$n_{O_\beta^{(-)}} + n_{C_\beta^{(-)}} + 3n_{V_\alpha^{(3-)}} + n_e - (n_{As_\alpha^{(+)}} + n_{Si_\alpha^{(+)}} + n_{O_\beta^{(+)}} + n_h) = 0. \qquad (42)$$

We get rid of these nine constraints by introducing Lagrange multipliers. The variables are the volumes V_S and V_L of the solid and liquid phase, respectively, the number densities n_{Ga}^L, n_{As}^L of the liquid, and fourteen number densities, n_{Ga_β}, $n_{As_\alpha^{(0)}}$, n_{As_β}, $n_{As_\gamma^{(0)}}$, $n_{As_\alpha^{(+)}}$, $n_{O_\beta^{(0)}}$, $n_{O_\beta^{(-)}}$, $n_{O_\beta^{(+)}}$, $n_{V_\alpha^{(0)}}$, $n_{V_\alpha^{(3-)}}$, $n_{V_\beta^{(0)}}$, $n_{V_\gamma^{(0)}}$, n_e, n_h, of the solid.

The minimization with respect to V_S and V_L yield the conditions for mechanical equilibrium, which obviously read

$$p_L = p_0, \qquad \sigma^{33} = -p_L. \qquad (43)$$

Furthermore there result two groups of algebraic equations: The first group contains the so called laws of mass action that determine the number densities of the solid phase for given $(n_{Ga}^S, n_{As}^S, n_O, n_C, n_{Si}, n_B)$. The laws of mass action read

$$\mu_{As_\beta} - \mu_{As_\gamma^{(0)}} - \mu_{V_\beta^{(0)}} + \mu_{V_\gamma^{(0)}} = 0, \qquad (44)$$

$$\mu_{As_\alpha^{(0)}} - \mu_{As_\gamma^{(0)}} - \mu_{V_\alpha^{(0)}} + \mu_{V_\gamma^{(0)}} = 0, \qquad (45)$$

$$\mu_{V_\alpha^{(0)}} + \mu_{V_\beta^{(0)}} + \mu_{V_\gamma^{(0)}} = 0, \qquad (46)$$

$$\mu_{O_\beta^{(+)}} - \mu_{O_\beta^{(0)}} + \mu_e - \frac{M_e}{\rho_S}\sigma^{<33>} = 0, \qquad \mu_{O_\beta^{(-)}} - \mu_{O_\beta^{(0)}} - \mu_e + \frac{M_e}{\rho_S}\sigma^{<33>} = 0, \quad (47)$$

$$\mu_{V_\beta^{(3-)}} - \mu_{V_\alpha^{(0)}} - 3\mu_e + 3\frac{M_e}{\rho_S}\sigma^{<33>} = 0,$$

$$\mu_{As_\alpha^{(+)}} - \mu_{As_\alpha^{(0)}} + \mu_e - \frac{M_e}{\rho_S}\sigma^{<33>} = 0, \qquad (48)$$

$$\mu_e + \mu_h - 2\frac{M_e}{\rho_S}\sigma^{<33>} = 0. \qquad (49)$$

The equations of the second group are jump conditions at the interface that relate the solid densities to the number densities of the liquid. The jump conditions read

$$\mu_{Ga_\alpha} - \frac{M_{Ga}}{\rho_S}\sigma^{<33>} - \mu_{V_\alpha} - \mu_{Ga}^L = 0, \qquad \frac{1}{3}(\mu_{As_\alpha^{(0)}} + \mu_{As_\beta} + \mu_{As_\gamma^{(0)}}) - \frac{M_{As}}{\rho_S}\sigma^{<33>} - \mu_{As}^L = 0.$$
$$(50)$$

11 Interfacial conditions at curved interfaces

In this section we generalize the interfacial jump condition to the case where the liquid and the solid phase are separated by a curved interface. The following results can be obtained for spherical droplets by minimizing (37) or for nonspherical droplets by methods that are introduced in [3]. The mechanical equilibrium condition (43) now read

$$-(\sigma^{ik}\nu^i\nu^k + p_L) = 2\sigma K_M, \tag{51}$$

where σ denotes the surface tension, and is the mean curvature K_M with $K_M = -1/r$ for the spherical liquid droplet discussed in Section 3. The jump conditions regarding the chemical potential at a curved interface read

$$\mu_{Ga_\alpha} - \frac{M_{Ga}}{\rho_S}\sigma^{<ik>}\nu^i\nu^k - \mu_{V_\alpha} - \mu_{Ga}^L = 0,$$

$$\frac{1}{3}(\mu_{As_\alpha^{(0)}} + \mu_{As_\beta} + \mu_{As_\gamma^{(0)}}) - \frac{M_{As}}{\rho_S}\sigma^{<ik>}\nu^i\nu^k - \mu_{As}^L = 0. \tag{52}$$

12 On the influence of misfit strain on the phase diagram

The equilibrium conditions that were derived in the last section can now be used to calculate the liquidus line and the homogeneiity region of the phase diagram. In particular we will determine the influence of mechanical effects on these parts of the phase diagram. To this end we need to know values for the standard chemical potentials, the interaction coefficients and the Redlich/Kister coefficients. Furthermore we need the elastic constants and thermal expansion coefficients. The parameters that are needed for the liquidus line are taken from [12]. The parameters that are needed for the determination of chemical equilibrium of the solid phase are read off from different sources: Data for (49) are from [14]. Data for (44), (45),(46) and (48) are from [15] but have been slightly modified. Data regarding the oxygen were reported from [9]. The elastic and thermal expansion parameters can be calculated from the data given in [1]. The temperature dependent data for liquid arsenic are read off from [8]. The misfit parameter were calculated from atomic radii data, where some information regarding the vacancy misfit were given by [6]. The details of the exploitation of the equilibrium conditions are found to be in [4].

The two graphs were calculated from the solutions of the algebraic system (40) through (50). The graph on the left side shows the liquidus line of the GaAs phase diagram, and turns out to be almost independent of mechanical effects. The graph on the left side represents the homogeneiity region of the phase diagram, where the defects are homogeneously distributed over the lattice sides. The smaller region results if mechanical effects are ignored. If mechanical effects are taken into account, the homogeneity region is affected by the outer pressure and increases if the outer pressure is increased. The graph corresponds to an outer pressure of 500 bar. A
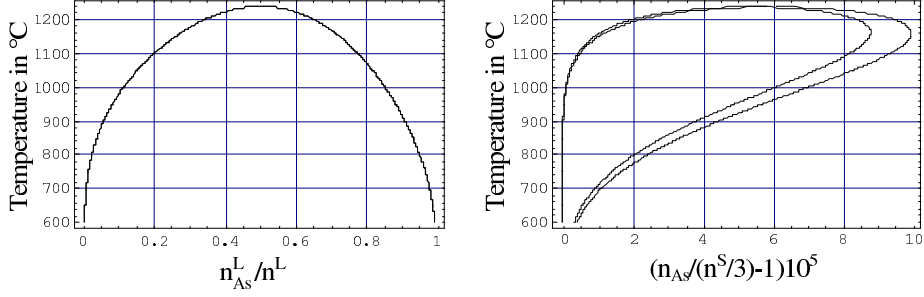
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Figure 6: Calculated liquidus line (left), calculated boundaries of the region of homogeneity (right)

similar calculation for the situation with a spherical droplet within a solid matrix, which is shown in Figure 5 (right), has exhibited a much more drastic mechanical effect that does not need such high external pressure as in the current case with a plane interface, see [4].

The concentration of the charged antisite $As_\alpha^{(+)}$ is of most importance regarding the semi-insulating behaviour of GaAs. The next Figure shows the influence of mechanical effects on the concentration of $As_\alpha^{(+)}$.
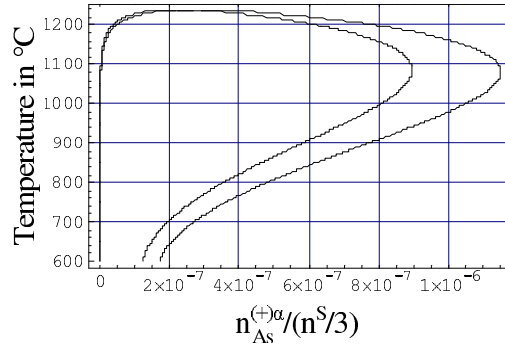

Figure 7: Mechanical influence on the temperature dependence of the charged antisite mole fraction

Right from the melting point, the concentration of $As_\alpha^{(+)}$ increases drastically with increasing outer pressure.

13   Synopsis and outlook

The current paper is the start of a series of studies on the formation and growth of liquid arsenic droplets in solid GaAs. In the first paper we have developed a thermodynamic model that takes in particular local mechanical stress fields into

account. Some simple examples shows their significance on the laws of mass action and on interfacial equilibrium conditions.

The next step of our investigations will be the study of the diffusion problem including the coupling of the Becker/Döring theory to the liquid/solid interface conditions.

References

[1] Brice, J.C. Physical and Thermal Properties, Properties of Gallium Arsenide, EMIS Datareviews Serie No. 2, (1990).

[2] Clausius, R., Über eine veränderte Form des zweiten Hauptsatzes der mechanischen Wärmetheorie, Poggendorf's Annalen der Physik, 93, (1850).

[3] Dreyer,W., On jump conditions of moving interfaces in crystals, WIAS Preprint, (2003).

[4] Dreyer,W & F. Duderstadt, Modeling of the appearance of arsenic droplets in galliumarsenide, WIAS Preprint (2003).

[5] Dreyer,W. & F. Duderstadt, On the Becker/Döring Theory of nucleation of liquid droplets in solids, WIAS Preprint (2003).

[6] Eichler, St., private Communication, Freiberg, (2002).

[7] Eshelby, J.D., The Elastic Energy Momentum Tensor, Journal of Elasticity, 5 (1975).

[8] Gokcen, N. A., The Arsenic System, Boulletin of Alloy Phase Diagrams Vol. !0, No 1, (1989).

[9] Jurisch, M., private Communication, Freiberg, (2001).

[10] Müller, I., Thermodynamics, Interaction of Mechanics and Mathematics Series, Pitman Advanced Publishing Program, Boston, (1985).

[11] Müller, I., Grundzüge der Thermodynamik, 3. Auflage, Springer Berlin, (2001).

[12] Oates, W. A., Erikson, G. & H. Wenzl, Thermodynamic modelling of solid gallium arsenide, Journal of Alloys and Compounds 220, Elsevier, (1995).

[13] Truesdell,C. & R. Toupin, The Classical Field Theories, Handbuch der Physik, III/1, Springer, Berlin, Göttingen, Heidelberg, (1960).

[14] Wenzl, H., Mika, K. & D. Henkel, Thermochemical Analysis of Native Point Defects ans Substitutional Carbon and Baron in GaAs Crystal Growth, Cryst. Res. Technol., (1990).

[15] Wenzl, H., Oates, W. A. & K. Mika, Defect Thermodynamics and Phase Diagrams in Compound Crystal Growth Process, Handbook of Crystal Growth, Vol 1, Elsevier, (1993).

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