Explicit constitutive model for semi-insulating GaAs including surface tension and bulk stresses

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Abstract

The necessary heat treatment of single-crystal semi-insulating gallium arsenide (GaAs), which is deployed in micro- and optoelectronic devices, generates undesirable liquid precipitates in the solid phase. The appearance of precipitates is influenced by surface tension at the liquid–solid interface and deviatoric stresses in the solid. The central quantity for the description of the various aspects of phase transitions is the chemical potential, which can be additively decomposed into a chemical and a mechanical part. In particular, the calculation of the mechanical part of the chemical potential is of crucial importance. We determine the chemical potential in the framework of the St. Venant–Kirchhoff law, which gives an appropriate stress–strain relation for many solids in the small-strain regime. We calculate non-standard phase diagrams for GaAs above 1059 K, i.e. those that take into account surface tension and deviatoric stresses, and we compare the results with classical phase diagrams without these phenomena.

Keywords: phase transitions; phase diagrams; surface tension; deviatoric stress; chemical potentials; GaAs

Introduction

Phase transitions in solids are usually strongly influenced by surface tension and non-isotropic stresses that give rise to non-zero stress deviators. An important example regards the nucleation and the growth of liquid droplets in semi-insulating gallium arsenide. These processes are accompanied by deviatoric stresses resulting from the liquid–solid misfit. In the classical treatment, the nucleation barrier is determined by the surface tension of the droplet. However, due to deviatoric stresses in the neighbourhood of the droplet, and in particular at the liquid–solid interface, the nucleation barrier may be decreased. A further mechanism that controls the evolution of liquid droplets in semi insulating GaAs is diffusion in the vicinity of the droplet. The diffusion flux results from a competition of chemical and mechanical driving forces. The quantity of central importance for the description of all these phenomena is the chemical

potential. Its calculation in the presence of mechanical stresses is among the subjects of this study. We determine the chemical potential in the framework of the St. Venant–Kirchhoff law, which gives an appropriate stress–strain relation for many solids in the small-strain regime. In a series of studies, we develop a thermodynamical model for the description of liquid–solid phase transitions that are accompanied by deviatoric stresses, diffusion and chemical reactions. The model is especially designed to describe phenomena that arise during heat treatments of GaAs wafers at elevated temperatures above the right eutectic line. However, a generalization of the model to other materials with dynamic precipitation phenomena may be undertaken. An example is the formation of cementite in steel. This paper we address the special constitutive laws that we will use for the description of semi-insulating GaAs. We decompose the constitutive quantities into chemical and mechanical parts. The chemical parts rely on the well-established sublattice model that was formulated by Oates et al. (1995) and Wenzl et al. (1990, 1993). The mechanical parts rely on the St. Venant–Kirchhoff law that relates the Green strain tensor to the second Piola–Kirchhoff stress tensor.

Explicit constitutive model for GaAs

In this section, we will formulate explicit constitutive laws for solid and liquid GaAs. These laws regard the dependence of Helmholtz energy densities, chemical potentials and stresses to the variables and on temperature-dependent quantities that refer to special reference states, which will be introduced next.

(a) Reference systems and reference configurations

We consider at first the situation a solid phase is in contact with a liquid phase and a gas. The order of the phases ought to indicate that the solid is under hydrostatic pressure. Moreover, there are no curved interfaces, so that no capillary forces appear and the three phases live under the same common pressure, which is equal to the outer pressure p_0 established. In this case, we call the system the reference standard. If the gas is an inert gas, which does not take part during phase changes between the liquid and solid phases, we call this system the standard system. If the gas consists of Ga and As constituents, which may cross the interfaces, a triple phase equilibrium under the vapour pressure $p_0 = \bar{p}(T)$ may be established. In this case, we call the system the reference standard system. In this study, the Helmholtz energy densities and the chemical

potentials will be given with respect to the reference standard system. On the other hand, the stress–strain relations will be formulated with respect to a reference configuration, which is defined as follows. A liquid–solid body of GaAs is free of strain, i.e. $C^{ij} = C_R^{ij} = \delta^{ij}, n_G = n_G^R = \bar{n}_G$ in the solid and $\rho_L = \rho_L^R = \bar{\rho}_L$ in the liquid, if the body (i) is under uniform pressure $\bar{p}(T)$ and (ii) has the composition $\bar{Y}_{bs}$ in the solid and $\bar{X}_L$ in the liquid. The bar indicates that the corresponding quantity is measured in the reference standard system. For the solid and liquid mass densities, we define –

$$\bar{\rho}_S = 2\bar{n}_G m(\bar{Y}_{Ga}, \bar{Y}_{As})$$

$$\bar{\rho}_L = \bar{n}_L M(\bar{X}_L) \quad \text{.... (1)}$$

The changes of mass densities due to elastic deformations are thus given by –

$$J_S = \frac{\bar{\rho}_S}{\rho_S} = \tilde{J}_S(Y_{Ga}, Y_{As}, n_G)$$

$$J_L = \frac{\bar{\rho}_L}{\rho_L} = \tilde{J}_L(X_L, n_L) \quad \text{.... (2)}$$

The mole densities in the reference configuration may be read off from the corresponding data tables that can be found in the literature.

(b) Constitutive model: the chemical parts of the chemical potentials for the solid and liquid phases of GaAs

The modeling of the solid phase relies on the sublattice model, which was introduced and described by Wenzl et al. (1990, 1993), Oates et al. (1995), Hurle (1999, 2004). Furthermore, we assume that there are exclusively entropic contributions to the chemical potentials. Owing to the sublattice structure, these are not given in terms of the mole fractions X_a but by lattice occupancies Y_a. Recall that the three sublattices have an equal number of lattice sites, so that the Y_a give the mole densities per sublattice site. The reason to consider only entropic contributions is the fact that currently no data are available for the material constants of the energetic contributions. In this case, we write –

$$\mu_a^{chem} = \bar{\mu}_a(T) + RT \ln\left(\frac{Ya}{\bar{Y}_a(T)}\right) \quad \text{.... (3)}$$

The quantities $\bar{\mu}_a(T)$ refer to the equilibrium of the triple-phase system, where surface tension is ignored and exclusively hydrostatic stresses may appear. We have called this system the

reference standard system, and we have chosen the thermodynamic equilibrium states of this system as the reference states of the chemical parts. Accordingly, we denote the minimizers of the available free energy for the reference standard system by $\overline{Y}_a(T)$. In the liquid phase, we consider entropic and energetic contributions to the chemical potentials of the two constituents As_L and Ga_L. We use the arsenic mole fraction X_L, to represent the chemical potentials of the two constituents of the liquid phase. These read, for Ga_L –

$$\mu_{GaL}^{chem}(T, X_L) = \bar{\mu}_{GaL}(T) + RT\ In\left(\frac{1-X_L}{1-\overline{X}_L(T)}\right) + (L_0(T) + L_1(T)(3-4X_L))X_L^2$$
$$-(L_0(T) + L_1(T)(3-4\overline{X}_L(T)))\overline{X}_L(T)^2 \quad .... (4)$$

and for As_L

$$\mu_{AS_L}^{chem}(T, X_L) = \bar{\mu}_{As_L}(T) + RT\ In\left(\frac{X_L}{\overline{X}_L(T)}\right)$$
$$+(L_0(T) + L_1(T)(1-4X_L))(1-X_L)^2$$
$$-(L_0(T) + L_1(T)(1-4\overline{X}_L)))\,(1-\overline{X}_L(T))^2. \quad ....$$

(5)

As above, the functions $\bar{\mu}_{GaL}$ (T) and $\bar{\mu}$ As_L(T) refer to the reference standard system, and $\overline{X}_L$(T) represents the arsenic mole fraction, which minimizes the available free energy of the reference standard system.

(c) Constitutive model: the St. Venant–Kirchhoff law for stresses and mechanical parts of the Helmholtz energy and the chemical potentials of the solid phase

While the chemical parts of the chemical potentials for the solid phase rely on the well-established sublattice model, their mechanical parts are introduced here in order to model and simulate the problem of the appearance and evolution of As-rich droplets in solid GaAs. The procedure is as follows – We first formulate the stress–strain relation according to the St.

Venant–Kirchhoff law, see for example Truesdell & Noll (1965). Next, we calculate the Helmholtz energy density by integration. Finally, we obtain the mechanical parts of the chemical potentials by differentiation of the Helmholtz energy density with respect to the mole densities. The St. Venant–Kirchhoff law assumes that the stress that results for small elastic strains, (C^{ij} – $J^{*(2/3)}\delta^{ij}$)/2, is given by a linear representation for the second Piola–Kirchhoff stress. The special form of this representation, which will be given below, is suited to describe the response of GaAs to elastic deformations.

$$t^{ij} = \frac{1}{2} k^{ijkl} \left(\left(\frac{\bar{n}_G}{n_G} \right)^{2/3} c^{kl} - \delta^{kl} \right) - \bar{p}(C^{-1})^{ij} J. \quad \text{.... (6)}$$

This version of the St. Venant–Kirchhoff law relies on the assumption that elastic deformations describe here exclusive deformations of the crystal lattice, so that the volumetric part, in particular, is given by the ratio $\bar{n}_G/n_G$. Furthermore, there is no misfit strain due to a rearrangement of the Ga and As atoms on the lattice sites. If we were to allow that Ga atoms may occupy the b and g sublattices, such a misfit strain would appear because the lattice sites of both sublattices offer less space than the lattice sites of the a lattice. Finally, we mention that the absence of misfit strain due to thermal expansion results from the chosen reference state. In other words, thermal expansion is already included in $\bar{p}$(T) and the temperature-dependent stiffness matrix k^{ijkl}. By means of above equation we may rewrite as –

$$t^{ij} = \frac{1}{2j^{*(2/3)}} k^{ijkl} (C^{kl} - j^{*(2/3)} \delta^{kl}) - \bar{p}(C^{-1})^{ij} J. \quad \text{.... (7)}$$

The St. Venant–Kirchhoff law is appropriate in the small-strain regime. The reference pressure is introduced here, so that the homogeneous deformation $F^{ij} = J^{*(1/3)}\delta^{ij}$ leads to δ^{ij} = - $\bar{p}$ (T)δij . The complete linearization of the St. Venant–Kirchhoff law with respect to the spatial displacement gradient h^{ij} gives the spatial version of the classical Hooke law. The linearization of the Green

strain (c^{ij} - δ^{ij})/2 gives the strain (e^{ij} = (h^{ij} + h^{ij})/2. We now calculate the Helmholtz energy density e^{ij} = (h^{ij} + h^{ji}) /2. by integration. Next, obtain the following representation of the mechanical part of the Helmholtz energy density – a

$$p\hat{\psi}^{mech}(T, Y_{bs}, J, c)$$

$$= \frac{1}{8(\tilde{J}\ (Y_{bs}))^{2/3} J} \left(J^{2/3}c^{ij} - (\tilde{J}^{*}(Y_{bs}))^{2/3}\delta^{ij}\right) k^{ijkl}(T) \left(J^{2/3}c^{kl} - (\tilde{J}*(Y_{bs}))^{2/3}\delta^{kl}\right)$$

$$-\bar{p}(T)\left(1 - \frac{(\tilde{J}(UY_{bs}))}{J}\right). \quad .... (8)$$

We add this function to the chemical part of the Helmholtz energy density in order to calculate the chemical potentials by differentiating with respect to the mole densities. We start the calculation of the chemical potentials with the Gibbs–Duhem equation, which reads, in the elastic strain free configuration $C^{ij} = J*^{(2/3)}\delta^{ij}$.

$$\psi^{chem} = -\frac{\bar{p}}{p*} + \frac{1}{p*}\sum_{a}\mu_a^{chem} n_a^R \quad .... (9)$$

Multiplying this equation by p and with and the first equation of we obtain.

$$p\psi = \frac{1}{8J^{*2/3}J}(J^{2/3}c^{ij} - J^{*2/3}\delta^{ij})K^{ijkl}\ (T)(J^{2/3}c^{kl} - J^{*2/3}\delta^{ij}) - \bar{p} + \sum_{a}\mu_a^{chem} n_a. \quad .... (10)$$

Next we obtain the chemical potentials by differentiation.

$$\mu_a = \frac{\partial(p\psi)}{\partial n_a}$$

$$= \mu_a^{chem} + \frac{1}{24J^{*2/3}} k^{ijkl}(C^{kl} - J^{*2/3}\delta^{kl})$$

$$\times\left(2\frac{J*}{J}(C^{ij} + J^{*2/3}\ \delta^{ij})\frac{\partial J^{*-1}}{\partial n_a} - (c^{ij} + 3J^{*2/3}\ \delta^{ij})\frac{\partial J^{-1}}{\partial n_a}\right) \quad .... (11)$$

and

$$\mu_a^{mech} = \frac{K^{ijkl}(C^{kl} - J^{*(2/3)}\ \delta^{kl})}{24J^{*2/3}}$$

$$\times\left(2\frac{J^*}{J}(C^{ij} + J^{*2/3}\ \delta^{ij})\frac{\partial J^{*-1}}{\partial n_a} - (c^{ij} + 3J^{*2/3}\ \delta^{ij})\frac{\partial J^{-1}}{\partial n_a}\right). \quad \text{.... (12)}$$

The calculation of $\frac{\partial J^{-1}}{\partial n_a}$ relies on where n_G is given by and with $\bar{n}_G(T)$. We finally obtain And

We finally obtain

$$\mu_a^{chem} = -\frac{K^{ijkl}(C^{kl} - J^{*(2/3)}\ \delta^{kl})}{72J^{*2/3}}$$

$$\times\left(2J^{*-1}(C^{ij} + J^{*2/3}\delta^{ij}) - \frac{3}{2}(C^{ij} - J^{*2/3}\ \delta^{ij})\frac{M_a}{m(\bar{Y}_{Ga}, \bar{Y}_{As})}\right)\frac{1}{\bar{n}_G} \quad \text{.... (13)}$$

(d) Constitutive model: pressure and mechanical parts of the Helmholtz energy and the chemical potentials for the liquid phase

We describe the liquid phase as a compressible liquid that is linear in $J_L^{-1} = \rho_L / \bar{\rho}_L$ and whose strain-free state is realized under the pressure $\bar{\rho}(T)$. We write

$$p = \bar{p}(T) + \frac{\bar{\ell}_L(T, \bar{X}_L)}{l_L^*}\tilde{k}k(T, X_L)\left(\frac{\ell_L}{\bar{\ell}_L(T, \bar{X}_L)} - \frac{\ell_L^*}{\bar{\ell}_L(T, X_L)}\right). \quad \text{.... (14)}$$

The newly introduced function $\bar{k}_L$(T, XL) > 0 denotes the bulk modulus of the liquid. The problem that we consider exclusively in this study regards the formation and evolution of liquid droplets in semi-insulating GaAs. Owing to this application, we may restrict ourselves to liquid GaAs mixtures with an arsenic mole fraction X_L>0.9. Thus, for simplification and due to lack of data for the function $\tilde{k}_L$ (T,X_L), we set X_L=1 within $\tilde{k}_L$ and write.

$$p_L = \bar{p}(T) + k_L(T)\frac{M(\bar{X}_L)}{M(\bar{X}_L)}\left(\frac{\rho_L}{\rho_L^R(T, \bar{X}_L)} - \frac{M(X_L)}{M(\bar{X}_L)}\right) = \hat{p}_L(T, X_L, \rho_L)$$

$$= \bar{p}(T) + \tilde{J}_L^*(X_L)k_L(T)(J_L^{-1} - \tilde{J}_L^{*-1}(X_L)) = \tilde{p}_L(T, X_L, J_L). \quad \text{... (15)}$$

The thermal expansion of the liquid is included in this law and represented by means of the dependence of nR L and kL on temperature. The chemical part of the chemical potentials of the liquid phase is now calculated in a manner analogous to the solid phase. We obtain

$$\mu_a^{mech}(T, X_L, J_L) = \frac{k_L(T)}{\bar{n}_L(T)} 1n\left(\frac{J_L^*(X_L)}{J_L}\right) \quad .....$$

(16)

Summary and outlook

In this study, we have proposed a model that is designed to simulate the appearance of liquid droplets in semi-insulating GaAs. The main part of the study regards the incorporation of mechanical stresses in the thermodynamic equations that describe phase transitions without surface tension and deviatoric stresses. Further applications of the model regard (i) the diffusion problem of an evolving liquid droplet within a solid matrix and (ii) the evolution of a many droplet system and, in particular, the determination of the size distributions of the droplets. These tasks have been described in Dreyer & Duderstadt (2006) and Dreyer et al. (2006).

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