Thermodynamics of extrinsic semiconductors with dislocations

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In this paper we construct a geometric model for the thermodynamics of deformable semiconductors with impurities defective by dislocations, using a nonconventional model based on the extended irreversible thermodynamics with internal variables developed in [1], in which a dislocation density tensor à la Maruszewski (see Fig.1, 2 and 3) and its flux are introduced as internal variables. The dislocation lines disturb the periodicity of the lattice of the crystal and their structure resembles a network of infinitesimally thin pores or capillary tubes. Following [2], we introduce the concepts of processes and transformations and we derive the entropy function. The models for semiconductors defective by dislocations may have relevance in many fundamentals technological sectors: in applied computer science, in the technology for integrated circuits VLSI (Very Large Scale Integration), in the field of electronic microscopy, in the nanotechnology. The defects acquired during the process of fabrication can provoke a premature fracture because they can self propagate because of changed conditions and surrounding conditions that are favorable. Now, we recall the model developed in [1], where it was assumed that in anelastic and defective semiconductor the following fields interact with each other: the elastic field described by the stress tensor $T_{ij}$ and the small-strain tensor $\varepsilon_{ij}$; the thermal field described by the temperature $\theta$ and the heat flux $q_i$; the electromagnetic field described by the electromotive intensity $\mathcal{E}_i$ and the magnetic induction $\mathcal{B}_i$; the charge carrier fields described by the densities of electrons $n$ and holes $p$ and their fluxes $j^n_i$ and $j^p_i$, respectively; the dislocation field described by the dislocation density tensor $a_{ij}$ and the dislocation flux $\mathcal{V}_{ijk}$. The independent constitutive variables are represented by the set

$$ C = \{ \varepsilon_{ij}, \mathcal{E}_i, B_i, n, p, \theta, a_{ij}, \mathcal{V}_{ijk}, j^n_i, j^p_i, q_i, n, p, \theta, a_{ij, k} \}. $$

All the processes occurring in the body considered are governed by the following laws:

the continuity equation: $\dot{\rho} + \rho v_i, i = 0$,

where $\rho$ denotes the mass density, the superimposed dot denotes the material derivative and the mass charge carriers have been neglected compared to $\rho$;

the momentum balance: $\rho \dot{v}_i - T_{ji,j} - p Z \varepsilon_i - \varepsilon_{ijk} \left( j^n_j + j^p_j + \Phi_j \right) B_k - P_j \varepsilon_{i,j} - f_i = 0$,
Further, we have the take that \( \hat{P}_i = P_i + P_i v_{k,k} - P_k v_{i,k} \), the total charge and current as follows: \( Z = n + p - n_0 + p_0 - p_0 \), \( j_i = j_i^n + j_i^p \), \( T_{ij} \) denotes the total stress tensor, \( P_i \) is the body force (neglected in the following), \( n < 0, n_0 < 0, p > 0, p_0 > 0 \) denote mass densities of nonequilibrium and equilibrium electrons and holes, respectively; \( \hat{n} < 0 \) and \( \hat{p} > 0 \) denote fixed charges of ionized impurities; the momentum of momentum balance: \( \varepsilon_{ijk} T_{jk} + c_i = 0 \).

In [1] it was demonstrated that the coupled \( c_i \) for unit volume is vanishing;

the internal energy balance

\[
\rho \dot{e} - T_{ji} v_{i,j} - (j_j^n + j_j^p) E_j - \rho \varepsilon_i \hat{P}_i + q_{i,i} - \rho r = 0
\]  
(2)

Here \( e \) is the internal energy density, \( r \) is the heat source distribution neglected in the follows, \( P_i = \rho P_i, v_{i,j} = L_{ij} = L_{(ij)} + L_{[ij]} \) (where \( L_{(ij)} \) and \( L_{[ij]} \) are respectively the symmetric and antisymmetric part of the velocity gradient and \( L_{[ij]} = \Omega_{ij} = \frac{1}{2} (v_{ij} - v_{ji}) \)). Introducing the deformation gradient \( F \), also we have \( L = \nabla v = \tilde{F} \tilde{F}^{-1} \).

The electromagnetic field is governed by the following Maxwell’s equations:

\[
\varepsilon_{ijk} E_{k,j} + \frac{\partial B_i}{\partial t} = 0, \quad D_{i,j} - \rho Z = 0, \quad \varepsilon_{ijk} H_{k,j} - j_i - \rho Z v_i - \frac{\partial D_i}{\partial t} = 0, \quad +B_{i,i} = 0,
\]

where \( H_i = \frac{1}{\mu_0} B_i, E_i = \frac{1}{\varepsilon_0} (D_i - P_i) \), and \( \varepsilon_0, \mu_0 \) denote the permittivity and permeability of vacuum. \( H \) and \( D \) are respectively the magnetic field and the electric displacement field.

The evolution equations of charge carriers read: \( \rho \dot{n} + j_{i,i}^n - g^n = 0, \rho \dot{p} + j_{i,i}^p - g^p = 0 \), then the equations for the ionized impurities are as follows: \( \rho \dot{\hat{n}} + \hat{g}^n, \rho \dot{\hat{p}} = \hat{g}^p, g^n \) and \( g^p \) describe the recombination of electrons and holes and together with the ionization of impurities \( \hat{g}^n \) and \( \hat{g}^p \) satisfy the equation \( g^n + g^p + \hat{g}^n + \hat{g}^p = 0 \). Following [1], we take that \( \hat{n} = \hat{p} = 0 \) and \( \hat{g}^n = \hat{g}^p = 0 \).

Further, we have the evolution equation for the dislocation density:

\[
\dot{a}_{ij} + \nabla_{ijk,k} - A_{ij} (C) = 0, \quad \text{where} \quad \dot{a}_{ij} = a_{ij} - \Omega_{ik} a_{kj} - \Omega_{jk} a_{ik};
\]

the evolution equation for the dislocation flux:

\[
\dot{\nabla}_{ijk} - \nabla_{ijk} (C) = 0, \quad \text{where} \quad \dot{\nabla}_{ijk} = \dot{\nabla}_{ijk} - \Omega_{ij} \nabla_{ijk} - \Omega_{ji} \nabla_{ik} - \Omega_{ij} \nabla_{ij}
\]

and the evolution equations concerning heat, electron and hole fluxes:

\[
\dot{j}_i - j_i^n (C) = 0, \quad \dot{j}_i - j_i^p (C) = 0, \quad \dot{q}_i = q_i (C),
\]

where

\[
\dot{j}_i = j_i^n - \Omega_{ik} j_k^n, \quad \dot{j}_i = j_i^p - \Omega_{ik} j_k^p, \quad \dot{q}_i = q_i - \Omega_{ij} q_j.
\]

In the above equations a superimposed asterisk indicates the Zaremba-Jaumann time derivative. All the admissible solutions of the proposed evolution equations should be restricted by the following entropy inequality:

\[
\rho \dot{S} + J_{S,k} - \frac{\partial F}{\partial t} \geq 0,
\]

where \( S \) denotes the entropy per unit mass and \( J_S \) is the entropy flux associated with the fields of the set \( C \) given by

\[
J_S = \frac{1}{\rho} q + k,
\]  
(3)

2
with \( k \) an additional term called extra entropy flux density.

In [1] all the following constitutive functions \( \mathbf{Z} = \mathbf{Z}(\mathbf{C}) \) with

\[
Z = \{ T_{ij}, P_i, e_i, g^n, g^p, A_{ij}, V_{ijk}, J^n_i, J^p_i, Q_i, S, \Phi_i, \mu^n, \mu^p, \tau_{ij} \}
\]

were obtained by analyzing the entropy inequality by Liu's theorem and (using Smith theorem) with the help of the isotropic polynomial representations of the proper constitutive functions, satisfying the objectivity principle. Now, we construct a geometric model for the thermodynamics of extrinsic defective semiconductors (following [2]) and we derive the expressions for the existence of an entropy function. We assume that the body \( \mathcal{B} \) having a regular boundary \( \partial \mathcal{B} \), is regularly embedded into Euclidean space \( \mathbb{R}^3 \) by a regular family of instantaneous time-dependent configurations \( \mathbf{B}_t \).

We treat the time on equal footing as the other state variables entering explicitly the state functions. Then, we consider a material element and we define the state space at time \( t \) as the set \( \mathcal{B}_t \) of all state variables which "fit" the configuration of the element at time \( t \). \( \mathcal{B}_t \) is assumed to have the structure of a finite dimensional manifold. The "total state space" is the disjoint union \( \mathcal{B} = \bigcup_t \{ t \} \times \mathcal{B}_t \) with a given natural structure of fibre bundle over \( \mathbb{R} \) where time flows [2]; if the instantaneous state space \( \mathcal{B}_t \) does not vary in time the state space \( \mathcal{B} \) reduces to a Cartesian product \( \mathbb{R} \times \mathcal{B} \).

Moreover we consider an abstract space of processes [2], i.e. a set \( \Pi \) of functions \( P^t_i : [0, t] \rightarrow \mathcal{G} \), where \([0, t]\) is any time interval, the space \( \mathcal{G} \) being a suitable target space defined by the problem under consideration, \( i \) a label ranging in an unspecified index set for all allowed processes and \( t \in \mathbb{R} \) the so called duration of the process. A continuous function then is defined \( \rho : \mathbb{R} \times \Pi \rightarrow C^0(\mathcal{B}_0, \mathcal{B}_t) \) so that for any instant of time \( t \) and for any process \( P^t_i \in \Pi \) a continuous mapping called transformation (induced by the process) is generated. Now, we assume that the behavior of defective thermoelastic semiconductors is described by the following state variables:

\[
\mathbf{C} = \{ F_{ij}, D_{ij}, B_i, n, p, e, a_{ij}, V_{ijk}, J^n_i, J^p_i, q_i, n_i, p_i, \theta_i, a_{ij,k} \}. \]

The full state space is then

\[
\Sigma = \text{Lin}(\mathcal{V}) \oplus \mathcal{V} \oplus \mathbb{R} \oplus \mathbb{R} \oplus \mathcal{W}_1 \oplus \mathcal{W}_2 \oplus \mathcal{V} \oplus \mathcal{V} \oplus \mathcal{V} \oplus \mathcal{V} \oplus \mathcal{V} \oplus \text{Lin}(\mathcal{W}_1),
\]

where \( \mathcal{V} \cong \mathbb{R}^3 \), \( \mathcal{W}_1 \) and \( \mathcal{W}_2 \) are vector spaces accounting for the internal variables \( \mathbf{a} \) and \( \mathcal{V} \) respectively. The process \( P^t_i \) is described by the following functions

\[
P^t_i = [ L, \mathbf{H}, \Xi, G^n, G^p, h, \gamma, \Lambda, J^n, J^p, Q, N, \mathcal{P}, \Theta, \Gamma ], \]

where \( \mathbf{H}_i = e_{ijk}H_{kj} - (j^n_i + j^p_i) - \rho \Xi v_i; \quad \Xi_i = -\epsilon_{ijk}E_{kj}; \)

\( G^n = g^n - j^n_i; \quad G^p = g^p - j^p_i; \quad h = (j^n_i + j^p_i)E_i - \frac{p}{2}E_i P_i + E_i P_i - q_i + \rho r; \quad \gamma_{ij} = \Omega_{ik}a_{kj} - a_{ik} \Omega_{kj} - V_{ijk,k} + A_{ijk}; \)

\( \Lambda_{ijk} = \Omega_{ik}V_{ijk} + \Omega_{jl}V_{ljk} + \Omega_{il}V_{jlk} + V_{ijk}; \quad J^n_i = J^n_i + \Omega_{ik}j^n_k; \quad J^p_i = J^p_i + \Omega_{ik}j^p_k; \quad Q_i = Q_i + \Omega_{ik}q_k. \)

Following standard procedures in this geometrical structure we are able to introduce an "entropy function", which is related to a transformation between the initial and the actual states \( \sigma_0 \) and \( \sigma_t \), by setting [2]:

\[
s(t) = - \int_0^t \frac{1}{\rho} \nabla \cdot \mathbf{J}_S d\tau,
\]

where \( \mathbf{J}_S \) is defined according to equation (3). We assume that the transformations
induced by the process are governed by the following dynamical system

$$
\begin{align*}
\dot{\mathbf{F}} &= \mathbf{L}(\tau)\mathbf{F}(\tau) \\
\dot{\mathbf{D}} &= \mathbf{H}(\tau) \\
\dot{\mathbf{B}} &= \mathbf{\Xi}(\tau) \\
\rho\dot{\mathbf{\mu}} &= \mathbf{G}^\mu(\tau) \\
\rho\dot{\mathbf{\pi}} &= \mathbf{G}^\pi(\tau) \\
\rho\dot{\mathbf{e}} &= \mathbf{T}(\sigma) \cdot \mathbf{L}(\tau) + h(\tau) \\
\dot{\mathbf{a}} &= \gamma(\tau) \\
\dot{\mathbf{V}} &= \Lambda(\tau) \\
\dot{\mathbf{j}}^n &= \mathbf{\mathcal{J}}^n(\tau) \\
\dot{\mathbf{j}}^p &= \mathbf{\mathcal{J}}^p(\tau) \\
\dot{\mathbf{q}} &= \mathbf{Q}(\tau) \\
\dot{\mathbf{n}} &= \mathbf{N}(\tau) \\
\dot{\mathbf{p}} &= \mathbf{P}(\tau) \\
\dot{\mathbf{\theta}} &= \mathbf{\Theta}(\tau) \\
\dot{\mathbf{a}} &= \mathbf{\Gamma}(\tau)
\end{align*}
$$

(7)

Then we get an expression for s(t) which in turn defines a 1-form \( \Omega \) in \( \mathbb{R} \times \mathbb{B} \) called the entropy 1-form in the following way: \( s = \int_{\sigma} \Omega \). Using Eqs. (7)\(_6\), (3) we obtain

$$
\Omega = -\frac{1}{\rho \theta} \mathbf{T} \mathbf{F}^T d\mathbf{F} - \frac{1}{\rho \theta} (\mathbf{E} + \mathbf{v} \wedge \mathbf{B}) \cdot d\mathbf{D} + \frac{1}{\rho} d\mathbf{e} + \frac{1}{\rho \theta} \mathbf{q} \cdot \nabla \mathbf{\theta} - \frac{1}{\rho \theta} (\mathbf{j}^n + \mathbf{j}^p) \cdot (\mathbf{E} + \mathbf{v} \wedge \mathbf{B}) + \frac{1}{\rho \theta} \bar{\rho} (\mathbf{E} + \mathbf{v} \wedge \mathbf{B}) \cdot \mathbf{P} + \varepsilon_0 \frac{\rho \theta}{\rho^2} (\mathbf{E} + \mathbf{v} \wedge \mathbf{B}) \cdot \dot{\mathbf{E}} - \frac{1}{\rho} \nabla \cdot \mathbf{k} \right] d\tau,
$$

(8)

where the expressions for \( \mathbf{T}, \mathbf{P}, \mathbf{k}, \mathbf{j}^n, \mathbf{j}^p \) and \( \mathbf{q} \) have been calculated in [1] in a suitable form. Thus the entropy function is now calculated as an integral along a path into the space \( \mathbb{R} \times \mathbb{B} \) of all thermodynamic variables together with the independent time variable. Finally, by applying the closure conditions for the 1-form we give the necessary conditions for the existence of the entropy function during analyzed processes.

References


Fig. 1 An edge dislocation structure (see [1]).

Fig. 2 The perfect crystal in (a) is cut and an extra plane of atoms is inserted; in (b) the bottom edge of the extra plane is an edge dislocation; in (c) a Burgers vector is required to close a loop of equal atom spacings around the edge dislocation (see [1]).

Fig. 3 Characteristics of the pore-core structure ($\bar{h} \ll R$) (see [1]).