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THERMODYNAMICS OF SEMICONDUCTORS WITH IMPURITIES

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ABSTRACT. In this paper we construct a geometric model for the thermodynamics of semiconductors with impurities, using a nonconventional model based on the extended irreversible thermodynamics with internal variables. For this purpose, we derive the transformation induced by the process and the dynamical system for a *simple material element* of extrinsic semiconductors. Finally, we obtain the expressions for the entropy function, the necessary conditions for its existence and the entropy 1-form, starting point to investigate an extended thermodynamical phase space.

1. Introduction

The models for extrinsic semiconductors 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 and in the nanotechnology. Semiconductor crystals, as germanium and silicon, are tetravalent elements [1] with electrical conductivity in between that of a conductor and that of an insulator. In Fig.1_a we have the representation of a germanium crystal that has a behaviour of an

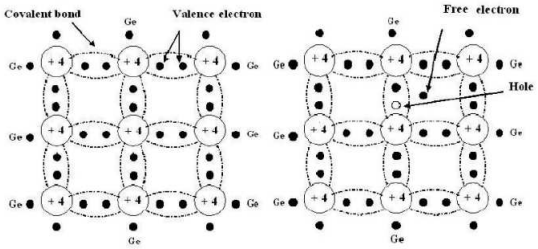

FIGURE 1. A symbolic representation in two dimension of a germanium crystal structure: (a) at $0°K$ and (b) at $300°K$ with a broken covalent bond

insulator at a temperature of $0°K$. But at room temperature, $300°K$ (see Fig.1_b), electrons

of the crystal can gain enough thermal energy to leap the band gap from the valence band to the conduction band and to be available for the electric current conduction.

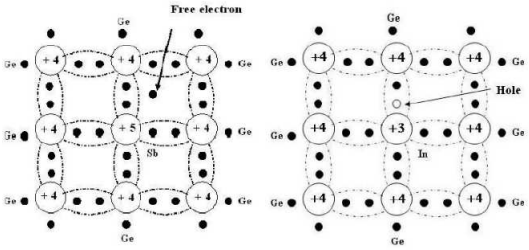

FIGURE 2. (a) A crystal structure with an atom of Germanium replaced with an atom of a pentavalent impurity (Antimony); (b) Crystal structure with an atom of Germanium replaced with an atom of trivalent impurity (Indium)

To modify the electrical properties of intrinsic semiconductors, impurity atoms adding one electron or one hole are introduced inside semiconductor crystals, using different techniques of "doping". By pentavalent impurities, as antimony, dopant in a semiconductor crystal, an n-type extrinsic semiconductor is obtained, having more free electrons that may flow (see Fig.2_a). Using tetravalent impurities dopant, as indium, an p-type extrinsic semiconductor crystal is obtained, having more holes that may flow freely (see Fig.2_b).

In a previous paper [2], taking into account the nonconventional model for extrinsic semiconductors developed in [3]-[7] and [8] (where the effectes due to internal defects were disregarded), we exploited Clausius-Duhem inequality for these media. Following Maugin in [9] (see also Colemann-Noll procedure [10]), we worked out the laws of state and we derived the extra entropy flux (see also [11]), the residual dissipation inequality and the heat equation in the first and second form.

In this paper, taking in account the results obtained in [3]-[8], following [12]-[14] and [15]-[18], using the concepts of process and transformation, we construct a geometrical model for the thermodynamics of semiconductors with impurities within a nonconventional model based on the extended irreversible thermodynamics with internal variables. Finally, we derive the expressions for the entropy function, the entropy 1-form and, applying the closure condition for the entropy 1-form, the necessary conditions for the existence of the entropy function. Starting from the entropy 1-form it is possible to introduce and investigate an extended thermodynamical phase space in a suitable way [23]. Furthermore, from the conditions for the existence of the entropy function, the state laws can be investigated following [24].

In [19]-[22] geometrical models for piezoelectric media with defects, for polarizable media with internal variables, for deformable dielectrics with a non-Euclidean structure and for heterogeneous and anisotropic nonlinear ferroelastic crystals were derived by one of us (L.R.) in the same geometrized framework.

2. A non conventional model for extrinsic semiconductors

In [3]-[7], thermodynamical models of semiconductors with impurities were developed. In [8] the behaviour of defective extrinsic semiconductors was studied. In this paper we use the model developed in [8], disregarding the internal defects of semiconductor crystals. We use the standard Cartesian tensor notation in a rectangular coordinate system. We refer the motion of our material system to a current configuration $\mathcal{K}_t$ and we assume that in thermoelastic semiconductors the following fields interact with each other: *the elastic field* described by the total stress tensor T_{ij} and the small-strain tensor ε_{ij}; *the thermal field* described by the temperature θ, its gradient and the heat flux q_i; *the electromagnetic field* described by the electromotive intensity $\mathcal{E}_i$ and the magnetic induction B_i per unit volume; *the charge carrier fields* described by the densities of electrons *n* and holes *p* and their fluxes j_i^n and j_i^p.

Then, the independent variables are represented by the set

$$C = \{\varepsilon_{ij}, \mathcal{E}_i, B_i, n, p, \theta, j_i^n, j_i^p, q_i, n_{,i}, p_{,i}, \theta_{,i}\}. \tag{1}$$

This specific choice shows that the relaxation properties of the thermal field and charge carrier fields are taken into account. However, we ignore the corresponding effect for the mechanical properties so that T_{ij} is not in the set (1).
All the processes, occurring in the considered body, are governed by the following laws:

the continuity equation:

$$\dot{\rho} + \rho v_{i,i} = 0, \tag{2}$$

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

the momentum balance:

$$\rho \dot{v}_i - T_{ji,j} - \rho Z \mathcal{E}_i - \varepsilon_{ijk} \left(j_j^n + j_j^p + \overset{\triangle}{P}_j \right) B_k - P_j \mathcal{E}_{i,j} - f_i = 0, \tag{3}$$

where

$$\overset{\triangle}{P}_i = \dot{P}_i + P_i v_{k,k} - P_k v_{i,k}, \quad \mathcal{E}_i = E_i + \varepsilon_{ijk} v_j B_k,$$

the total charge Z and the current **j** are as follows:

$$Z = n + \bar{n} - n_0 + p + \bar{p} - p_0 \quad j_i = j_i^n + j_i^p,$$

T_{ij} denotes the total stress tensor, P_i is the polarization vector, f_i is the body force (neglected in the following), E_i is the electric field, $n < 0$, $n_0 < 0$, $p > 0$, $p_0 > 0$ denote mass densities of nonequilibrium and equilibrium electrons and holes, respectively, $\bar{n} < 0$ and $\bar{p} > 0$ denote fixed charges of ionized impurities;

the momentum of momentum balance:

$$\varepsilon_{ijk} T_{jk} + c_i = 0, \tag{4}$$

where c_i is a couple for unit volume;

the internal energy balance

$$\rho\dot{e} - T_{ji}v_{i,j} - \left(j_j^n + j_j^p\right)\mathcal{E}_j - \rho\mathcal{E}_i\dot{\mathcal{P}}_i + q_{i,i} - \rho r = 0. \tag{5}$$

Here e is the internal energy density, r is the heat source distribution neglected in the follows,

$$P_i = \rho\mathcal{P}_i, \qquad v_{i,j} = L_{ij} = L_{(ij)} + L_{[ij]},$$

(where $L_{(ij)}$ and $L_{[ij]}$ are the symmetric and antisymmetric part of the velocity gradient, respectively) and

$$L_{[ij]} = \Omega_{ij} = \frac{1}{2}(v_{i,j} - v_{j,i}).$$

Let $\mathbf{F}$ denote the deformation gradient $\mathbf{F} \equiv \left(F^i_{.K}\right)$, with $F^i_{.K} = \frac{\partial \mathrm{x}^i}{\partial X^K} = \mathrm{x}^i_{,K}$, where $\mathbf{x} \equiv \left(x^i\right)$ are Eulerian coordinates and $\mathbf{X} \equiv \left(X^K\right)$ are the material coordinates of the same material particle P in a current configuration $\mathcal{K}_t$ and in a configurational reference $\mathcal{K}_R$ and at the time t, respectively. Also we have

$$\mathbf{L} = \nabla\mathbf{v} = \dot{\mathbf{F}}\mathbf{F}^{-1}. \tag{6}$$

The electromagnetic field is governed by the following

Maxwell's equations:

$$\varepsilon_{ijk}E_{k,j} + \frac{\partial B_i}{\partial t} = 0, \qquad \varepsilon_{ijk}H_{k,j} - j_i - \rho Z v_i - \frac{\partial D_i}{\partial t} = 0,$$

$$D_{i,i} - \rho Z = 0, \qquad B_{i,i} = 0, \tag{7}$$

where $H_i = \frac{1}{\mu_0}B_i$, $E_i = \frac{1}{\varepsilon_0}\left(D_i - P_i\right)$, and ε_0, μ_0 denote the permittivity and permeability of vacuum. $\mathbf{H}$ and $\mathbf{D}$ are the magnetic field and the electric displacement field, respectively. Moreover, we assume that the magnetic properties of the semiconductor are disregarded so the magnetization of the body is $M_i = 0$.

The *evolution equations of charge carriers* read:

$$\rho\dot{n} + j^n_{i,i} - g^n = 0, \quad \rho\dot{p} + j^p_{i,i} - g^p = 0, \tag{8}$$

the equations for the ionized impurities are as follows:

$$\rho\dot{\bar{n}} = \bar{g}^n, \quad \rho\dot{\bar{p}} = \bar{g}^p, \tag{9}$$

where g^n and g^p describe the recombination of electrons and holes and together with the ionization of impurities $\bar{g}^n$ and $\bar{g}^p$ satisfy the equation $g^n + g^p + \bar{g}^n + \bar{g}^p = 0$. Following [6], we take that $\dot{\bar{n}} = \dot{\bar{p}} = 0$ and $\bar{g}^n = \bar{g}^p = 0$. Further, we have the

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

$$\overset{*}{j}{}^n_i - J^n_i(C) = 0, \qquad \overset{*}{j}{}^p_i - J^p_i(C) = 0, \qquad \overset{*}{q}_i = Q_i(C),$$

where J^n, J^p and Q are the electron, hole and heat flux sources, respectively, and

$$\overset{*}{j}{}^n_i = \dot{j}^n_i - \Omega_{ik}j^n_k, \qquad \overset{*}{j}{}^p_i = \dot{j}^p_i - \Omega_{ik}j^p_k, \qquad \overset{*}{q}_i = \dot{q}_i - \Omega_{ij}q_j.$$

In the above equations a superimposed asterisk indicates the Zaremba-Jaumann time derivative (see [25]-[27] for the form of these equations).

All the admissible solutions of the proposed evolution equations should be restricted by the following *entropy inequality*:

$$\rho\dot{S} + J_{S_{k,k}} - \frac{\rho r}{\theta} \geq 0, \tag{10}$$

where S denotes the entropy per unit mass and $\mathbf{J}_S$ is the entropy flux associated with the fields of the set C given by

$$\mathbf{J}_S = \frac{1}{\theta}\mathbf{q} + \mathbf{k}, \tag{11}$$

with $\mathbf{k}$ an additional term called *extra entropy flux density*.

In [3]-[7] all the following constitutive functions $\mathbf{Z} = \tilde{\mathbf{Z}}(C)$, with

$$\mathbf{Z} = \{T_{ij}, P_i, c_i, e, g^n, g^p, J_i^n, J_i^p, Q_i, S, J_{S_i}, \mu^n, \mu^p\}, \tag{12}$$

were obtained for extrinsic semiconductors in different cases, by analyzing the entropy inequality and expanding the free energy in Taylor series with respect to a particular natural state.

In [8] the entropy inequality (10) was analyzed by Liu's theorem [28], and constitutive relations were obtained, for extrinsic defective semiconductors, using isotropic polynomial representations of proper constitutive functions satisfying the objectivity and material frame indifference principles (see Smith's theorem [29]). Disregarding the effects due to internal defects, from [8] we obtain the following relevant results:
the couple c_i in (4) is vanishing, so that the stress tensor T_{ij} is symmetric,
the free energy function $\psi = e - \theta S - \frac{1}{\rho}\mathcal{E}_i P_i$ has the following domain

$$C_1 = \{\varepsilon_{ij}, \mathcal{E}_i, n, p, \theta, j_i^n, j_i^p, q_i\}, \qquad \psi = \psi(C_1) \tag{13}$$

the entropy flux has the form

$$J_{S_k} = \frac{1}{\theta}(q_k - \mu^n j_k^n - \mu^p j_k^p), \tag{14}$$

the residual dissipation inequality reads

$$\theta\frac{\partial J_{S_k}}{\partial n} n_{,k} + \theta\frac{\partial J_{S_k}}{\partial p} p_{,k} + \theta\frac{\partial J_{S_k}}{\partial \theta}\theta_{,k} + (j_k^n + j_k^p)\mathcal{E}_k -$$

$$-\Pi_i^n J_i^n - \Pi_i^p J_i^p - \Pi_i^Q Q_i - \mu^n g^n - \mu^p g^p \geq 0, \tag{15}$$

with

$$\rho\frac{\partial \psi}{\partial j_i^n} = \Pi_i^n, \qquad \frac{\partial \psi}{\partial j_i^p} = \Pi_i^p, \qquad \rho\frac{\partial \psi}{\partial q_i} = \Pi_i^Q, \tag{16}$$

affinities.
The constitutive functions T_{ij}, P_i, S, μ^n and μ^p have the following domain

$$C_2 = \{\varepsilon_{ij}, \mathcal{E}_i, n, p, \theta\},$$

$$T_{ij} = T_{ij}(C_2), \quad P_i = P_i(C_2), \quad S = S(C_2), \quad \mu^n = \mu^n(C_2), \quad \mu^p = \mu^p(C_2), \tag{17}$$

the electron, hole and heat flux sources depend on the set C (see equ. (1))

$$J_k^n = J_k^n(C), \qquad J_k^p = J_k^p(C), \qquad Q_k = Q_k(C). \tag{18}$$

In [8] the constitutive functions were written only for n type defective semiconductors but here, using Smith's theorem, we have obtained these constitutive relations for n and p types perfect semiconductors as new results. In particular, we have

$$T_{ij} = \alpha_\tau^1\delta_{ij} + \alpha_\tau^2\varepsilon_{ij} + \alpha_\tau^3\varepsilon_{ik}\varepsilon_{kj} + \alpha_\tau^4\mathcal{E}_i\mathcal{E}_j +$$
$$\alpha_\tau^5(\varepsilon_{jk}\mathcal{E}_i\mathcal{E}_k + \varepsilon_{ik}\mathcal{E}_j\mathcal{E}_k) + \alpha_\tau^6(\varepsilon_{jk}\varepsilon_{ks}\mathcal{E}_i\mathcal{E}_s + \varepsilon_{ik}\varepsilon_{ks}\mathcal{E}_s\mathcal{E}_j), \tag{19}$$

$$P_i = (\alpha_P^1\delta_{ik} + \alpha_P^2\varepsilon_{ik} + \alpha_P^3\varepsilon_{ij}\varepsilon_{jk})\mathcal{E}_k, \tag{20}$$

$$S = \alpha_s^1 n + \alpha_s^2 p + \alpha_s^3\theta + \alpha_s^4\mathcal{E}_k\mathcal{E}_k +$$
$$+(\alpha_s^5\delta_{ij} + \alpha_s^6\varepsilon_{ij} + \alpha_s^7\varepsilon_{jk}\varepsilon_{ki} + \alpha_s^8\mathcal{E}_i\mathcal{E}_j + \alpha_s^9\varepsilon_{jk}\mathcal{E}_i\mathcal{E}_k)\varepsilon_{ij} \tag{21}$$

$$\mu^n = \alpha_n^1 n + \alpha_n^2 p + \alpha_n^3\theta + \alpha_n^4\mathcal{E}_k\mathcal{E}_k +$$
$$+(\alpha_n^5\delta_{ij} + \alpha_n^6\varepsilon_{ij} + \alpha_n^7\varepsilon_{jk}\varepsilon_{ki} + \alpha_n^8\mathcal{E}_i\mathcal{E}_j + \alpha_n^9\varepsilon_{jk}\mathcal{E}_i\mathcal{E}_k)\varepsilon_{ij}, \tag{22}$$

$$\mu^p = \alpha_p^1 n + \alpha_p^2 p + \alpha_p^3\theta + \alpha_p^4\mathcal{E}_k\mathcal{E}_k +$$
$$+(\alpha_p^5\delta_{ij} + \alpha_p^6\varepsilon_{ij} + \alpha_p^7\varepsilon_{jk}\varepsilon_{ki} + \alpha_p^8\mathcal{E}_i\mathcal{E}_j + \alpha_p^9\varepsilon_{jk}\mathcal{E}_i\mathcal{E}_k)\varepsilon_{ij}, \tag{23}$$

where $\alpha_\tau^\alpha, \alpha_P^\beta, \alpha_s^\gamma, \alpha_n^\delta, \alpha_p^\delta$ can be functions of the following invariants

$$n, p, \theta, \mathcal{E}_i\mathcal{E}_i, \varepsilon_{kk}, \varepsilon_{ij}\varepsilon_{ij}, \varepsilon_{ij}\varepsilon_{jk}\varepsilon_{ki}, \varepsilon_{ij}\mathcal{E}_i\mathcal{E}_j, \varepsilon_{ij}\varepsilon_{jk}\mathcal{E}_i\mathcal{E}_k. \tag{24}$$

The rate equations for electron, hole and heat fluxes read

$$\overset{*}{j}{}_k^n = \alpha_n^1\mathcal{E}_k + \alpha_n^2 n_{,k} + \alpha_n^3 p_{,k} + \alpha_n^4\theta_{,k} + \alpha_n^5 j_k^n + \alpha_n^6 j_k^p + \alpha_n^7 q_k, \tag{25}$$

$$\overset{*}{j}{}_k^p = \alpha_p^1\mathcal{E}_k + \alpha_p^2 n_{,k} + \alpha_p^3 p_{,k} + \alpha_p^4\theta_{,k} + \alpha_p^5 j_k^n + \alpha_p^6 j_k^p + \alpha_p^7 q_k, \tag{26}$$

$$\overset{*}{q}_k = \alpha_q^1\mathcal{E}_k + \alpha_q^2 n_{,k} + \alpha_q^3 p_{,k} + \alpha_q^4\theta_{,k} + \alpha_q^5 j_k^n + \alpha_q^6 j_k^p + \alpha_q^7 q_k, \tag{27}$$

where $\alpha_n^\eta, \alpha_p^\eta, \alpha_q^\eta$ can depend on invariants built on the set C. Equations (25) and (26) are the generalized Fick-Ohm's laws concerning relaxation features of the electron and hole fields and equation (27) is the generalized Vernotte-Cattaneo relation concerning relaxation features of the heat flux.

The laws (19)-(27) are very general because they include all the possible linear and higher order simple and cross effects which occur in the media under consideration.

Inserting constitutive equations into the balance equations (3)-(5) and (7), taking into account of (2), (8) and (9), we obtain the so-called "balances on the state space", that form

a system of partial differential equations, whose order depends on the special choice of constitutive equations. That system governs the evolution of the "wanted fields" [30].

To obtain field equations which allow to consider and solve analytically and/or numerically particular problems, the theory can be linearized, obtaining a mathematical model to describe the physical reality in many situations (see [6]-[8] and [31] for comparing experimental data).

3. A geometric model for extrinsic semiconductors

Now, taking into account the model and the results presented in the previous section, we construct a geometric model for semiconductors with impurities following [12]-[14] and [15]-[18]. We introduce the transformation induced by the process and we derive the dynamical system for a *simple material element* of extrinsic semiconductors. Finally, we obtain the expressions for the entropy function and the entropy 1-form. Thus, we consider a material element and we define the state space at time t as the set B_t of all state variables which "fit" the configuration of the element at time t. B_t is assumed to have the structure of a finite dimensional manifold. The "total state space" is the disjoint union

$$\mathcal{B} = \bigcup_t \{t\} \times B_t$$

with a given natural structure of fibre bundle over $\mathbb{R}$ where time flows (see [12]-[14]). If the instantaneous state space B_t does not vary in time, then $\mathcal{B}$ has the topology of the Cartesian product: $\mathcal{B} \simeq \mathbb{R} \times B$.

Moreover, we consider an abstract space of processes (see [12]-[14] and [15]-[18]), i.e. a set Π of functions

$$P_t^i : [0,t] \to \mathcal{G}, \tag{28}$$

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. Then a continuous function is defined [12]-[14]

$$\begin{aligned} \chi : \mathbb{R} \times \Pi &\to C^0(B,B) \\ (t, P_t^i) &\to \rho_t^i, \end{aligned} \tag{29}$$

with $\rho_t^i : b \in D_t^i \subseteq B \to \rho_t^i(b) = b_t \in R_t^i \subseteq B$ (where D_t^i and R_t^i are called "domain" and "range" of the i-th process of duration t, P_t^i , respectively), so that for any instant of time t and for any process $P_t^i \in \Pi$ a continuous mapping, ρ_t^i , called transformation induced by the process, is generated, which gives point by point a correspondence between the initial state b and the final state $\rho_t^i(b) = b_t$. Now, we can define the following function of time:

$$\lambda_b^i(\tau) = \begin{cases} b & if\ \tau = 0 \qquad with\ \ b \in D_t^i \\ \rho_t^i(b) & if\ \tau \in]0,t] \end{cases} \tag{30}$$

such that the transformation for the medium is given by $\delta : \mathbb{R} \longrightarrow \mathbb{R} \times B$

$$\delta : \tau \in \mathbb{R} \longrightarrow \delta(\tau) = (\tau, \lambda_b^i(\tau)) \in \mathbb{R} \times B. \tag{31}$$

With these positions the transformation is interpreted as a curve δ in the union of all state spaces such that it intersects the instantaneous state space just once.

In this geometric model we assume that the state variables are

$$(F_{ij}, D_i, B_i, n, p, e, j_i^n, j_i^p, q_i, n_{,i}, p_{,i}, \theta_{,i})\,.$$

The full state space is then

$$B = Lin(\mathfrak{V}) \oplus \mathfrak{V} \oplus \mathfrak{V} \oplus \mathbb{R} \oplus \mathbb{R} \oplus \mathbb{R} \oplus \mathfrak{V} \oplus \mathfrak{V} \oplus \mathfrak{V} \oplus \mathfrak{V} \oplus \mathfrak{V} \oplus \mathfrak{V},$$

where $\mathfrak{V} \simeq \mathbb{R}^3$.

The process P_t^i defined by (28) is described by the following functions

$$P_t^i(\tau) = [\mathbf{L}(\tau), \boldsymbol{\mathcal{H}}(\tau), \boldsymbol{\Xi}(\tau), G^n(\tau), G^p(\tau), h(\tau), \boldsymbol{\mathcal{J}}^n(\tau), \boldsymbol{\mathcal{J}}^p(\tau),$$
$$\boldsymbol{\mathcal{Q}}(\tau), \boldsymbol{\mathcal{N}}(\tau), \boldsymbol{\mathfrak{P}}(\tau), \boldsymbol{\Theta}(\tau)] \in \mathcal{G},$$

where

$$\mathcal{H}_i = \epsilon_{ijk} H_{k,j} - (j_i^n + j_i^p) - \rho \mathcal{Z} v_i \qquad \Xi_i = -\epsilon_{ijk} E_{k,j}, \qquad G^n = g^n - j_{i,i}^n,$$

$$G^p = g^p - j_{i,i}^p, \qquad h = (j_i^n + j_i^p)\mathcal{E}_i - \frac{\dot{\rho}}{\rho}\mathcal{E}_i P_i + \mathcal{E}_i \dot{P}_i - q_{,i}$$

$$\mathcal{J}_i^n = J_i^n + \Omega_{ik} j_k^n, \qquad \mathcal{J}_i^p = J_i^p + \Omega_{ik} j_k^p, \qquad \mathcal{Q}_i = Q_i + \Omega_{ik} q_k,$$

and $\mathcal{G}$ is given by

$$\mathcal{G} = Lin(\mathfrak{V}) \oplus \mathfrak{V} \oplus \mathfrak{V} \oplus \mathbb{R} \oplus \mathbb{R} \oplus \mathbb{R} \oplus \mathfrak{V} \oplus \mathfrak{V} \oplus \mathfrak{V} \oplus \mathfrak{V} \oplus \mathfrak{V} \oplus \mathfrak{V}.$$

Moreover, the constitutive functions θ, $\mathbf{T}$, $\mathbf{P}$, $\mathbf{J}^n$, $\mathbf{J}^p$, $\mathbf{Q}$, g^n and g^p are defined in the following way

$$\theta : \mathbb{R} \times B \longrightarrow \mathbb{R}^{++}, \qquad \mathbf{T} : \mathbb{R} \times B \longrightarrow Sym(\mathfrak{V}), \qquad \mathbf{P} : \mathbb{R} \times B \longrightarrow \mathfrak{V},$$

$$\mathbf{J^n} : \mathbb{R} \times B \longrightarrow \mathfrak{V}, \qquad \mathbf{J^p} : \mathbb{R} \times B \longrightarrow \mathfrak{V}, \qquad \mathbf{Q} : \mathbb{R} \times B \longrightarrow \mathfrak{V}.$$

$$g^n : \mathbb{R} \times B \longrightarrow \mathbb{R}, \qquad g^p : \mathbb{R} \times B \longrightarrow \mathbb{R},$$

(see equ.s (19), (20) and (25)-(27)).

We assume that for each pair (P_t^i, b), the following dynamical system holds (see [12]-[14] and [15]-[18])

$$\left\{\begin{array}{rcl} \dot{\mathbf{F}} &=& \mathbf{L}(\tau)\mathbf{F}(\tau) \\ \dot{\mathbf{D}} &=& \boldsymbol{\mathcal{H}}(\tau) \\ \dot{\mathbf{B}} &=& \boldsymbol{\Xi}(\tau) \\ \rho\dot{n} &=& G^n(\tau) \\ \rho\dot{p} &=& G^p(\tau) \\ \rho\dot{e} &=& \mathbf{T}(\delta)\cdot\mathbf{L}(\tau) + h(\tau) \\ \dot{\mathbf{j}}^n &=& \boldsymbol{\mathcal{J}}^n(\delta) \\ \dot{\mathbf{j}}^p &=& \boldsymbol{\mathcal{J}}^n(\delta) \\ \dot{\mathbf{q}} &=& \boldsymbol{\mathcal{Q}}(\delta) \\ \dot{\nabla} n &=& \boldsymbol{\mathcal{N}}(\tau) \\ \dot{\nabla} p &=& \boldsymbol{\mathfrak{P}}(\tau) \\ \dot{\nabla}\theta &=& \boldsymbol{\Theta}(\tau). \end{array}\right. \tag{32}$$

The set $(B, \Pi, \theta, \mathbf{T}, \mathbf{P}, \mathbf{J^n}, \mathbf{J^p}, \mathbf{Q}, g^n, g^p)$ defines the simple material element of extrinsic semiconductors (see [18]).

By using the system of differential equations (32), following standard procedures (see [12]-[14] and [15]-[18]) 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 b and $\rho_t^i(b) = b_t$, respectively, in the following way:

$$s(\rho_t^i, b, t) = -\int_0^t \frac{1}{\rho} \nabla \cdot \mathbf{J}_S d\tau, \tag{33}$$

where $\mathbf{J}_S$ is defined according to equation (11). Using the internal energy balance and equ. (6), we obtain the following expression for $\nabla \cdot \mathbf{q}$:

$$\nabla \cdot \mathbf{q} = -\rho \dot{e} + \mathbf{T} \cdot (\dot{\mathbf{F}} \mathbf{F}^{-1}) + (\mathbf{j}^n + \mathbf{j}^p) \cdot \boldsymbol{\mathcal{E}} - \frac{\dot{\rho}}{\rho} \boldsymbol{\mathcal{E}} \cdot \mathbf{P} + \boldsymbol{\mathcal{E}} \cdot \dot{\mathbf{P}}. \tag{34}$$

Then, we get

$$s = \int_0^t -\frac{1}{\rho\theta} \nabla \cdot \mathbf{q} d\tau + \int_0^t \frac{1}{\rho\theta^2} \mathbf{q} \cdot \nabla\theta d\tau - \int_0^t \frac{1}{\rho} \nabla \cdot \mathbf{k} d\tau \tag{35}$$

so that the final expression for $s(\rho_t^i, b, t)$ reads (see [12]-[14])

$$s(\rho_t^i, b, t) = \int_\delta \Omega, \tag{36}$$

with

$$\begin{aligned} \Omega = -\frac{1}{\rho\theta} (\mathbf{T}\mathbf{F}^{-T}) \cdot d\mathbf{F} - \frac{1}{\rho\theta} (\mathbf{E} + \mathbf{v} \wedge \mathbf{B}) \cdot d\mathbf{D} + \frac{1}{\theta} de + \\ + \left[\frac{1}{\rho\theta^2} \mathbf{q} \cdot \nabla\theta - \frac{1}{\rho\theta} (\mathbf{j}^n + \mathbf{j}^p) \cdot (\mathbf{E} + \mathbf{v} \wedge \mathbf{B}) + \frac{1}{\rho^2\theta} \dot{\rho} (\mathbf{E} + \mathbf{v} \wedge \mathbf{B}) \cdot \mathbf{P} + \right. \\ \left. + \frac{\varepsilon_0}{\rho\theta} (\mathbf{E} + \mathbf{v} \wedge \mathbf{B}) \cdot \dot{\mathbf{E}} - \frac{1}{\rho} \nabla \cdot \mathbf{k} \right] d\tau. \end{aligned} \tag{37}$$

In equ. (37) we have used the relation $\mathbf{T} \cdot (\dot{\mathbf{F}} \mathbf{F}^{-1}) = (\mathbf{T}\mathbf{F}^{-T}) \cdot \dot{\mathbf{F}}$, with $\mathbf{F}^{-T} = (\mathbf{F}^{-1})^T$ (T denoting matrix transposition). Thus, the entropy function is now calculated as an integral along a path into the space $\mathbb{R} \times B$ of all thermodynamic variables together with the independent time variable and Ω is a 1-form in $\mathbb{R} \times B$ called the entropy 1-form. In components the entropy 1-form Ω becomes:

$$\Omega = \omega_\mu d\mathfrak{q}^\mu + \omega_0 dt = \omega_A d\mathfrak{q}^A, \quad (A = 1, 2, ..., 13) \tag{38}$$

where

$$\mathfrak{q} \equiv \left(\mathfrak{q}^A\right) = (\mathbf{F}, \mathbf{D}, \mathbf{B}, n, p, e, \mathbf{j}^n, \mathbf{j}^p, \mathbf{q}, \nabla n, \nabla p, \nabla\theta, t)$$

and

$$\begin{aligned} \boldsymbol{\omega} \equiv (\omega_A) = \left(\left(-\frac{1}{\rho\theta} \mathbf{T}\mathbf{F}^{-T} \right), \left[\frac{1}{\rho\theta} (\mathbf{E} + \mathbf{v} \wedge \mathbf{B}) \right], 0, 0, 0, \left(\frac{1}{\theta} \right), 0, 0, 0, 0, 0, 0, 0, \right. \\ \left[\frac{1}{\rho\theta^2} \mathbf{q} \cdot \nabla\theta - \frac{1}{\rho\theta} (\mathbf{j}^n + \mathbf{j}^p) \cdot (\mathbf{E} + \mathbf{v} \wedge \mathbf{B}) + \frac{1}{\rho^2\theta} \dot{\rho} (\mathbf{E} + \mathbf{v} \wedge \mathbf{B}) \cdot \mathbf{P} \right. \\ \left. \left. + \frac{\varepsilon_0}{\rho\theta} (\mathbf{E} + \mathbf{v} \wedge \mathbf{B}) \cdot \dot{\mathbf{E}} - \frac{1}{\rho} \nabla \cdot \mathbf{k} \right] \right). \end{aligned}$$

Thus, by external differentiation, a 2-form is obtained:

$$d\Omega = \frac{1}{2} A_{\mu\lambda} d\mathfrak{q}^{\mu} \wedge d\mathfrak{q}^{\lambda} + E_{\lambda} dt \wedge d\mathfrak{q}^{\lambda}, \tag{39}$$

with $A_{\mu\lambda} = \partial_{\mu}\omega_{\lambda} - \partial_{\lambda}\omega_{\mu}$ and $E_{\lambda} = \partial_{0}\omega_{\lambda} - \partial_{\lambda}\omega_{0}$.

Applying the closure conditions for the entropy 1-form, the necessary conditions for the existence of the entropy function during the processes under consideration are:

$$\begin{aligned}
&\partial_e \left(-\tfrac{1}{\rho\theta}\mathbf{T}\mathbf{F}^{-T}\right) = \partial_{\mathbf{F}} \left(\tfrac{1}{\theta}\right), \\
&\partial_{\mathbf{D}} \left(-\tfrac{1}{\rho\theta}\mathbf{T}\mathbf{F}^{-T}\right) = \partial_{\mathbf{F}} \left[-\tfrac{1}{\rho\theta}(\mathbf{E} + \mathbf{v} \wedge \mathbf{B})\right], \\
&\partial_{\mathbf{D}} \left(\tfrac{1}{\theta}\right) = \partial_e \left[-\tfrac{1}{\rho\theta}(\mathbf{E} + \mathbf{v} \wedge \mathbf{B})\right], \\
&\tfrac{\partial \omega_A}{\partial \mathfrak{q}^B} = 0 \qquad (A = 1, 2, 6, 13;\ B = 3, 4, 5, 6, 7, ..., 12), \\
&\partial_{\mathbf{t}} \left(-\tfrac{1}{\rho\theta}\mathbf{T}\mathbf{F}^{-T}\right) = \partial_{\mathbf{F}} \Big[\tfrac{1}{\rho\theta^2}\mathbf{q} \cdot \nabla\theta - \tfrac{1}{\rho\theta}(\mathbf{j}^n + \mathbf{j}^p) \cdot (\mathbf{E} + \mathbf{v} \wedge \mathbf{B}) + \\
&\qquad \tfrac{1}{\rho^2\theta}\dot{\rho}(\mathbf{E} + \mathbf{v} \wedge \mathbf{B}) \cdot \mathbf{P} + \tfrac{1}{\rho\theta}\epsilon_0(\mathbf{E} + \mathbf{v} \wedge \mathbf{B}) \cdot \dot{\mathbf{E}} - \tfrac{1}{\rho}\nabla \cdot \mathbf{k}\Big], \\
&\partial_{\mathbf{t}} \left(\tfrac{1}{\theta}\right) = \partial_e \Big[\tfrac{1}{\rho\theta^2}\mathbf{q} \cdot \nabla\theta - \tfrac{1}{\rho\theta}(\mathbf{j}^n + \mathbf{j}^p) \cdot (\mathbf{E} + \mathbf{v} \wedge \mathbf{B}) + \\
&\qquad \tfrac{1}{\rho^2\theta}\dot{\rho}(\mathbf{E} + \mathbf{v} \wedge \mathbf{B}) \cdot \mathbf{P} + \tfrac{1}{\rho\theta}\epsilon_0(\mathbf{E} + \mathbf{v} \wedge \mathbf{B}) \cdot \dot{\mathbf{E}} - \tfrac{1}{\rho}\nabla \cdot \mathbf{k}\Big], \\
&\partial_{\mathbf{t}} \left[-\tfrac{1}{\rho\theta}(\mathbf{E} + \mathbf{v} \wedge \mathbf{B})\right] = \partial_{\mathbf{D}} \Big[\tfrac{1}{\rho\theta^2}\mathbf{q} \cdot \nabla\theta - \tfrac{1}{\rho\theta}(\mathbf{j}^n + \mathbf{j}^p) \cdot (\mathbf{E} + \mathbf{v} \wedge \mathbf{B}) + \\
&\qquad \tfrac{1}{\rho^2\theta}\dot{\rho}(\mathbf{E} + \mathbf{v} \wedge \mathbf{B}) \cdot \mathbf{P} + \tfrac{1}{\rho\theta}\epsilon_0(\mathbf{E} + \mathbf{v} \wedge \mathbf{B}) \cdot \dot{\mathbf{E}} - \tfrac{1}{\rho}\nabla \cdot \mathbf{k}\Big].
\end{aligned} \tag{40}$$

Moreover, if the entropy 1-form is closed and its coefficients are regular, this form is exact and the existence of an upper-potential S satisfying relation

$$S(b_t) - S(b) \geq s \tag{41}$$

is ensured, for all $P_t^i \in \Pi$, with $b_t = \rho_t^i(b)$ (see [17] and [18]).

Starting from the entropy 1-form it's possible to introduce an extended thermodynamical phase space in a suitable way [23]. Furthermore, from the conditions obtained for the existence of the entropy function, the state laws can be investigated following [24].

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