

### Voltage-controlled structure of certain *p-n* and *p-i-n* junctions

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It is shown by solving the transport equations that an *a priori* uniform semiconductor which conducts ions as well as electrons and holes, in contact with two different chemical environments, will become a *p-n* or *p-i-n* junction exhibiting a new kind of rectifying properties. When the junction is placed in an electrical circuit the *I-V* relation will show a strong asymmetry under reversal of the applied voltage *V*. For large values of  $|V|$ , the current *I* is linear in *V* but  $dV/dI$  is different by a few orders of magnitude for the forward and reverse biases. The distributions of donors in the *n* region and of acceptors in the *p* region, are shown to depend on *V*. This suggests that the shape of the *p-n* or *p-i-n* junction can be controlled at elevated temperatures, at which the ions are mobile, by applying a suitable voltage *V*. The junction can then be frozen in by quenching the solid to room temperature, at which state the applied voltage can be removed.

#### I. INTRODUCTION

It has been observed that nonstoichiometric solids can be *n*-type or *p*-type semiconductors due to native atomic disorder. Typical examples are  $\text{Bi}_2\text{O}_{3-\delta}$  (Ref. 1) and  $\text{Ag}_{2+\delta}\text{S}$  which are *n*-type semiconductors, and  $\text{Fe}_{1-\delta}\text{O}$  which is a *p*-type semiconductor.<sup>2</sup> The concentrations of quasifree electrons and holes depend on the degree of deviation from stoichiometry. A semiconductor may change from *p* type to *n* type as  $\delta$  is varied. This was observed, e.g., for  $\text{Cu}_2\text{O}$ ,  $\text{PbS}$ ,<sup>3</sup>  $\text{Ta}_2\text{O}_3$ ,<sup>4</sup>  $\text{TiO}_2$ ,<sup>5</sup>  $\text{MnO}$ ,<sup>6</sup> stabilized  $\text{ZrO}_2$ ,<sup>7</sup> and  $\text{CaO}$ .<sup>8</sup> Some of these semiconductors are also good ionic conductors.  $\text{Ag}_{2+\delta}\text{S}$ , for example, conducts  $\text{Ag}^+$  ions and stabilized  $\text{ZrO}_2$  (*S-ZrO*<sub>2</sub>) conducts  $\text{O}^{2-}$  ions at elevated temperatures. In these semiconductors the donor- or acceptor-type defects are mobile. We shall concentrate on those solids for which the native atomic disorder is large also in the absence of deviation from stoichiometry. The discussion will be limited to low values of  $\delta$ . The change  $\delta N_i$ , in the concentration of defects,  $N_i$ , due to local changes in stoichiometry is then expected to be small ( $\delta N_i/N_i \ll 1$ ). In other words, the chemical potential of defects,  $\mu_i$ , can be considered approximately uniform also for the nonstoichiometric solid:

$$\nabla\mu_i = 0. \tag{1}$$

The concentrations of (quasifree) electrons and holes, on the other hand, depend on  $\delta$ . They are not uniform unless the deviation from stoichiometry is constant throughout the solid.

An interesting situation may arise if an *a priori* homogeneous solid is to be placed in contact with two different environments, so that it becomes an *n*-type semiconductor on one side and a *p*-type semiconductor on the other side (see Fig. 1). (It is assumed that the temperature is sufficiently high that equilibrium is attained at both boundaries and that changes in stoichiometry are facilitated through diffusion of defects, electrons, and holes.)  $\delta$  and the concentrations of electrons  $n_0, n_L$  and holes  $p_0, p_L$  at the semiconductor boundaries (at  $x=0, x=L$ ) are fixed

by the interactions with the surroundings. The distributions of defects within the semiconductor depend on the applied voltage, as the calculation below will show. Thus the form of the *p-n* or *p-i-n* junction can be controlled by the applied voltage. That this indeed occurs has been shown before experimentally,<sup>9</sup> and has been treated theoretically<sup>10</sup> for a particular value of the applied voltage, the polarization voltage, in which one electrode blocks the ionic current.

It is the purpose of this work to propose a model for these materials and to analyze it. The calculations will yield the electron, hole, and defect concentrations, and

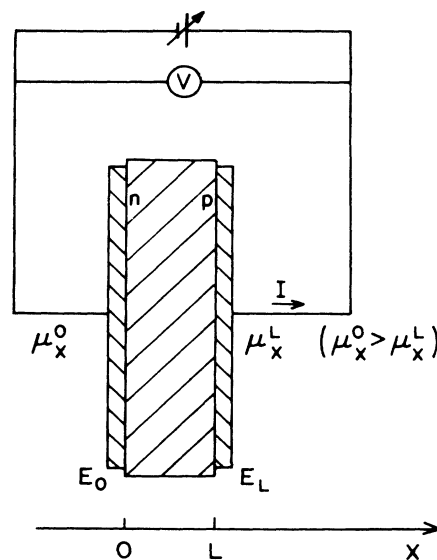


FIG. 1. Schematic presentation of a semiconductor conducting electrons, holes, and ions ( $X^+$ ), connected to an external voltage *V*.  $E_0, E_L$  are reversible electrodes.  $\mu_X^0, \mu_X^L$  are the chemical potentials of atoms *X* in the environment in contact with the semiconductor through  $E_0, E_L$ , respectively.

their currents as a function of the dc applied voltage, temperature, and the nature of the surrounding interacting with the semiconductor.

## II. THE MODEL

The mixed (ionic electronic) semiconductor will for simplicity of notation, be presented by  $XY$ . It conducts electrons, holes, and one kind of defect, say  $X^+$ . The latter represents either real ionic species, e.g., interstitial silver ions  $Ag_i^+$  in  $Ag_{2+\delta}S$ , or effective charge carriers such as copper vacancies  $V_{Cu}'$  in  $Cu_2O$ , or oxygen vacancies  $V_O^{\cdot\cdot}$  in  $S-ZrO_2$ . The disorder in the  $X$  sublattice is large so that Eq. (1) holds for  $X^+$ . The  $Y$  sublattice is assumed to be rigid. The quasifree electrons interacts with the ions to form neutral species



An  $n$ -type semiconductor is formed by excess of  $X$  species (high  $\mu_X$ ), while a  $p$ -type semiconductor is formed by a deficiency in  $X$  species (low  $\mu_X$ ). The electron-hole recombination is,



The semiconductor interacts with two different environments having the chemical potentials  $\mu_X^0$ ,  $\mu_X^L$ . The semiconductor is not at equilibrium but in a steady state in which material and charge is transported due to the difference  $\mu_X^L - \mu_X^0$  and the applied voltage  $V$ . In the steady state the Fermi level (the electrochemical potential of electrons) is not uniform. It is the ionic current density ( $j_i$ ) and the combined electronic ( $j_e$ ) and hole ( $j_h$ ) current density that are uniform throughout the semiconductor, i.e.,

$$\frac{\partial j_i}{\partial x} = 0, \quad (4a)$$

since there is no accumulation or depletion of material in the solid. Charge conservation, and using Eq. (4a), yields,

$$\frac{\partial(j_e + j_h)}{\partial x} = 0. \quad (4b)$$

Local neutrality is maintained due to the possible flow of ionic and electronic charge carriers. Yet, as will be shown, a quasi- $p-n$  or quasi- $p-i-n$  junction may exist in the locally neutral region. The latter state can be changed if it is possible to quench the semiconductor without precipitating material while freezing the defects motion, yet keeping most of the electrons and holes in the conduction and valence bands, respectively. When the applied voltage is switched off the semiconductor will now possess a nonuniform distribution of  $X^+$  defects, a  $p$  region, an  $n$  region, no currents, and a space charge. The difference to a common  $p-n$  or  $p-i-n$  junction is that (a) the defects are native ones, (b) at elevated temperatures they drift under the applied voltage  $V$ , and (c) their distribution is controlled by  $V$ ,  $T$ ,  $\mu_X^0$ , and  $\mu_X^L$  (see below).

At elevated temperatures, at which the defects are mobile, their motion can be decoupled from that of electrons and hole by applying a sufficiently-high-frequency

ac voltage in addition to a dc bias. The defects will not follow the ac signal while the electronic charges will. However, no rectification of the ac electronic current is expected since no potential barrier exists in the semiconductor.

The semiconductor is assumed to be nondegenerate. The concentrations of quasifree electrons and holes are small and Boltzmann's statistics can be applied to them:

$$\mu_e = \mu_e^\ominus + k_B T \ln(n/n^\ominus), \quad (5a)$$

$$\mu_h = \mu_h^\ominus + K_B T \ln(p/p^\ominus), \quad (5b)$$

where  $\mu$  denotes chemical potential,  $k_B$  is the Boltzmann constant,  $T$  the temperature, and  $n, p$  ( $n^\ominus, p^\ominus$ ) the concentration (standard concentrations<sup>7</sup>) of electrons and holes, respectively.  $n^\ominus, p^\ominus$  depend on  $T$  but are independent of  $n, p$ , and  $x$ .  $n, p$  are of the order of the concentrations of the defects introduced by the deviation from stoichiometry and therefore by our assumptions, much smaller than the total defect concentration  $N_i = [X^+]$ ,

$$n, p \ll [X^+]. \quad (6)$$

(The conductivity can still be mainly electronic since the electrons and holes have, usually, much higher mobilities than the ionic defects.)

The current densities of electrons  $j_e$ , holes  $j_h$ , and defects  $X^+$ ,  $j_i$ , are determined by the transport equations,

$$j_e = \frac{\sigma_e}{q} \nabla \tilde{\mu}_e = k_B T \nu_e \frac{\partial n}{\partial x} - q \nu_e n \frac{\partial \varphi}{\partial x}, \quad \sigma_e \equiv q \nu_e n \quad (7a)$$

$$j_h = -\frac{\sigma_h}{q} \nabla \tilde{\mu}_h = -k_B T \nu_h \frac{\partial p}{\partial x} - q \nu_h p \frac{\partial \varphi}{\partial x}, \quad \sigma_h \equiv q \nu_h p \quad (7b)$$

and

$$j_i = -\frac{\sigma_i}{q} \nabla \tilde{\mu}_i = -q \nu_i [X^+] \frac{\partial \varphi}{\partial x}, \quad \sigma_i = q \nu_i [X^+] \quad (7c)$$

together with the equations obtained by applying the mass action law to the reactions of Eqs. (2) and (3)

$$n = K(T) a_X \quad (8a)$$

and

$$np = c^2. \quad (8b)$$

Here  $\sigma$  denotes conductivity,  $\tilde{\mu}$  electrochemical potential,  $\nu$  mobility,  $\varphi$  is the electrical potential,  $c$  is the concentration of electrons (and holes) in the intrinsic semiconductor,  $a_X$  is the activity of atoms  $X$ , and  $\mathcal{E} = -\partial\varphi/\partial x$  is the internal electric field. The latter is independent of  $x$  as can be seen from Eqs. (1), (4a), and (7c).

## III. CALCULATION OF ELECTRONIC CHARGE CARRIERS DISTRIBUTIONS AND CURRENTS

A relation between  $\tilde{\mu}_e$  and  $\tilde{\mu}_h$  can be found from Eq. (3),

$$\nabla \tilde{\mu}_e = -\nabla \tilde{\mu}_h. \quad (9)$$

Combining Eqs. (7a), (7b), and (9) yields

$$j_{el} \equiv j_e + j_h = \frac{\sigma_e + \sigma_h}{q} \nabla \tilde{\mu}_e. \quad (10)$$

Making use of Eqs. (7a), (7b), and (8b) in Eq. (10), yields

$$j_{el} = \left[ v_e + \frac{v_h c^2}{n^2} \right] \left[ k_B T \frac{\partial n}{\partial x} + q n \mathcal{E} \right]. \quad (11)$$

Using Eq. (4b) it is possible to integrate Eq. (11)

$$-q\beta\mathcal{E}L\bar{x} = \ln \bar{n} + \frac{\bar{j}_{el}}{\mathcal{E}} \int_1^{\bar{n}} \frac{d\bar{n}}{\bar{n}^2 - \bar{n}\bar{j}_{el}/\mathcal{E} + \bar{c}^2 v_h/v_e}, \quad (12a)$$

where

$$\bar{x} = \frac{x}{L}, \quad \bar{j}_{el} = \frac{j_{el}}{qv_e n_0}, \quad \bar{n} = \frac{n}{n_0}, \quad \bar{c} = \frac{c}{n_0}, \quad \beta = \frac{1}{k_B T} \quad (12b)$$

which yields

$$-q\beta\mathcal{E}L\bar{x} = \ln \bar{n} + JI(\bar{n}), \quad (13a)$$

where

$$I(\bar{n}) = \begin{cases} \frac{1}{\sqrt{\Delta}} \ln \left| \frac{2\bar{n} - J - \sqrt{\Delta}}{2\bar{n} - J + \sqrt{\Delta}} \frac{2 - J + \sqrt{\Delta}}{2 - J - \sqrt{\Delta}} \right|, & \Delta > 0 \\ \frac{2}{J - 2\bar{n}} - \frac{2}{J - 2}, & \Delta = 0 \\ \frac{2}{\sqrt{-\Delta}} \left[ \arctan \frac{2\bar{n} - J}{\sqrt{-\Delta}} - \arctan \frac{2 - J}{\sqrt{-\Delta}} \right], & \Delta < 0 \end{cases} \quad (13b)$$

and

$$\Delta = (J^2 - 4\bar{c}^2 v_h/v_e), \quad J = \bar{j}_{el}/\mathcal{E}. \quad (13c)$$

Equation (13) is an implicit equation for  $n(x)$ . It contains two parameters  $\bar{j}_{el}$ , and  $\mathcal{E}$  which have not yet been determined. We notice first that the boundary values  $n_0$ ,  $n_L$  are related by Eq. (8a),

$$\frac{n_0}{n_L} = e^{\beta q V_{th}}, \quad -qV_{th} \equiv \mu_X^L - \mu_X^0. \quad (14)$$

$\mathcal{E}$  can be shown to be<sup>10</sup>

$$\mathcal{E} = \frac{V_{th} - V}{L}. \quad (15)$$

To determine the electronic current  $j_{el}$ , Eq. (13) is evaluated at  $x=L$  with the known boundary value  $n_L$ . This yields the  $I$ - $V$  relations,

$$\beta q V = JI(\bar{n}_L). \quad (16)$$

The calculations are carried out in the following order. Equation (16) is solved to determine  $j_{el}$  as a function of the parameters  $V$ ,  $T$ , and  $V_{th}$ . The result is inserted into

Eq. (13) to yield  $n(x)$ .  $p(x)$  is then calculated from  $n(x)$  using Eq. (8b). The current densities of electrons only,  $j_e$ , and holes only,  $j_h$ , are then obtained from Eqs. (7a), (7b), and (15). For  $V=0$  and  $V=V_{th}$  one can solve for  $n$ ,  $p$ ,  $j_e$ , and  $j_h$  explicitly as has been shown before.<sup>10</sup>

We may obtain better insight into the solution by considering a particular configuration in which  $n_0 = p_L$ ,  $n_L = p_0$ ,  $v_e = v_h \equiv v_{el}$ . In this configuration  $n(x) = p(L-x)$ . For these conditions the asymptotic value of  $j_{el}$  for large applied voltages can be evaluated explicitly. For  $V > 2V_{th}$  the  $n$ - and  $p$ -type regions are wide,  $(dn/dx)_{x=0} = 0$  and Eqs. (7a) and (10) evaluated at  $x=0$  yield [with Eq. (15)]

$$j_{el}^+ \equiv j_h |_{x=L} = j_e |_{x=0} = qn_0 v_{el} \frac{V_{th} - V}{L}, \quad V > 2V_{th}. \quad (17)$$

For  $-V > V_{th}$ , on the other hand, the  $n$ - and  $p$ -type regions are very narrow, and the electronic current  $j_{el}$  is determined by the conductivity of the wide intrinsic region. Evaluating  $j_{el}$  at  $x=L/2$  yields

$$j_{el}^- \equiv 2qc v_{el} \frac{V_{th} - V}{L}, \quad -V > V_{th}. \quad (18)$$

Comparing Eqs. (17) and (18) yields the ratio of asymptotic resistances in the forward and reversed bias,

$$\frac{\partial j_{el}^+}{\partial V} / \frac{\partial j_{el}^-}{\partial V} = \frac{n_0}{2c}. \quad (19)$$

In the semiconductor considered here  $n_0 \gg c$  and that ratio is larger than unity. For  $V > 2V_{th}$ , the width,  $\Delta x_{np}$ , of the (narrow) transition region from the  $n$ -type to the  $p$ -type semiconductor can be determined from the slope  $dn/dx$  at  $x=L/2$  by the definition

$$\frac{\partial n}{\partial x} \Big|_{x=L/2} \Delta x_{np} \equiv n_0, \quad V > 2V_{th}. \quad (20)$$

$[(\partial n/\partial x)_{x=L/2}]$  is calculated from  $j_e$  [Eq. (7a)] evaluated for  $V > 2V_{th}$  at  $x=L/2$ . There,  $j_{el}^+ = j_e + j_h = 2j_e$  and  $j_{el}^+$  is given in Eq. (17)]. This and Eq. (20) yield an expression for the width,

$$\Delta x_{np} = \frac{L}{V - V_{th}} \frac{k_B T}{q}, \quad V > 2V_{th}. \quad (21)$$

In a similar way one can determine the width of the narrow  $n$  (or  $p$ ) region  $\Delta x_n$  ( $\Delta x_p$ ) for  $-V > V_{th}$  [from  $\partial n/\partial x$  ( $\partial p/\partial x$ ) calculated at  $x=0$  ( $x=L$ ) using Eqs. (7a), (7b), and (18)],

$$\Delta x_p = \Delta x_n = \frac{1}{2} \frac{L}{V_{th} + |V|} \frac{k_B T}{q}, \quad -V > V_{th}. \quad (22)$$

The dependence of the ionic currents on  $V$  is [from Eqs. (7c) and (15)]

$$j_i = \sigma_i \frac{V_{th} - V}{L}. \quad (23)$$

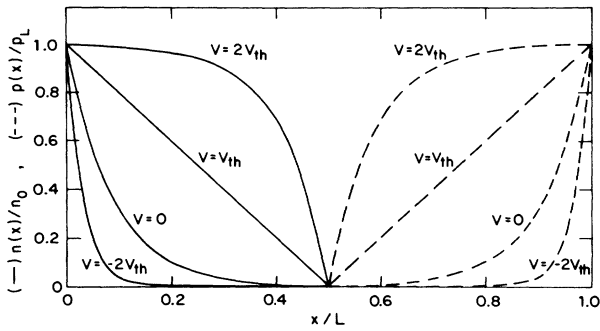


FIG. 2.  $n(x)$  and  $p(x)$  vs  $x$  for different values of  $V$  (for  $V_{th}=1$  V;  $T=1000$  K;  $n_L/n_0=10^{-5}$ ;  $p_0=n_L$ ;  $p_L=n_0$ ;  $v_e=v_h=v_{el}$ ).

#### IV. DISCUSSION

The transport equations solved in Sec. III describe the semiconductor in the steady state. We pay attention, first, to the distribution of electrons  $n(x)$  and holes  $p(x)$ . (In the  $n$  or  $p$  region these concentrations represent also the concentration of ionic defects introduced by deviation from stoichiometry because of local neutrality conditions.)  $n(x)$  [ $p(x)$ ] varies between its boundary values  $n_0, n_L$  [ $p_0, p_L$ ]. The detailed variation depends on the applied voltage. This is demonstrated in Fig. 2, which is a solution of Eq. (13) for  $T=1000$  K,  $V_{th}=1$  V,  $n_0=p_L$ ,  $n_L=p_0$ , and  $v_e=v_h=v_{el}$ . The width of the  $n$  and  $p$  regions increases with the forward bias ( $V>0$ ). This is due to a change in stoichiometry induced in each region by the increasing voltage. For  $V>0$   $X^+$  defects are driven from the right-hand side (rhs) of the sample towards the left (Fig. 1). The rhs is depleted of  $X$ . The width of the depleted region increases with  $V$ . Since a deficiency in  $X$  contributes holes [Eqs. (2) and (3)] the  $p$  region is widened. At the lhs of the sample, the region with excess  $X$  and  $e'$ , is widened by  $V$ . The transition from the  $n$  to  $p$  region becomes narrow as  $V$  increases [see Eq. (21)] and, as mentioned before, it does not contain a space charge. However if the semiconductor is quenched and the applied voltage is removed, a space charge will build up provided the semiconductor still contains quasifree electrons and holes. The semiconductor then becomes a normal  $p-n$  junction, the properties of which have been governed at the elevated temperature by  $V$ ,  $T$ ,  $\mu_X^0$ , and  $\mu_X^L$ . For  $V<-V_{th}$  the  $n$ - and  $p$ -regions are rather narrow [see Eq. (22)], and the semiconductor forms a  $p-i-n$  junction which at elevated temperatures conducts electrons, holes and

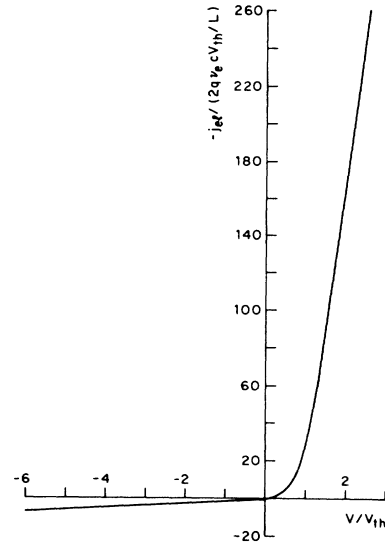


FIG. 3. Electronic current  $j_{el}$  vs  $V$  [for  $V_{th}=1$  V;  $T=1000$  K ( $n_L/n_0=10^{-5}$ );  $p_0=n_L$ ;  $p_L=n_0$ ;  $v_e=v_h=v_{el}$ ].

ionic defects and has no space charge. A linearly graded junction occurs for  $V=V_{th}$ .

Let us consider next the current voltage relations at the high-temperature steady state in which the defects are mobile. The electronic current  $j_{el}$ , calculated for  $T=1000$  K,  $V_{th}=1$  V,  $n_0=p_L$ ,  $n_L=p_0$ , and  $v_e=v_h=v_{el}$  is shown in Fig. 3. An asymmetry in the  $j_{el}-V$  relation with respect to the change  $V\rightarrow -V$  is seen. The "forward" current (for  $V>0$ ) is much larger than the reverse one (for  $V<0$ ). However, this is not the rectification encountered in a common  $p-n$  junction. Here the current  $j_{el}$  depends linearly on  $V$  for large  $|V|$ . The quasirectification is due to the changes in stoichiometry caused by the applied voltage, that were mentioned before. The rectification is not due to a potential barrier (associated with a space charge) as in a common  $p-n$  junction.  $j_{el}^+$  is large due to the high concentrations of electrons or holes that exist throughout the semiconductor for  $V>2V_{th}$  while  $j_{el}^-$  is much smaller since it is determined by the low concentration of electrons and holes in the wide intrinsic region.

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