I–V relations in nano thin semi-conductors with mobile acceptors or donors

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Abstract

A device of the form Metal1|MIEC|Metal2 is discussed, MIEC being a mixed ionic electronic conductor which is assumed to include one mobile ionic defect (acceptors) and one electronic defect (holes). The two electrodes are assumed to be inert and blocking for material exchange. The defect distribution and I–V relations are solved numerically assuming steady-state and local equilibrium. The effects of acceptor ionization, contact potentials and space charge are taken into consideration. Different thicknesses, from nano to macro, are considered as well as different contact potentials. The results are compared with the local neutrality (analytic) limit. It is found that the device when based on thin MIEC and certain a-symmetric contact potentials shows rectification somewhat similar to a classic Schottky diode, implying that aging process may not be a real problem.

A second model is considered in which the ionic motion is replaced by electron hopping between acceptors. The model is solved numerically for the defect distributions and I–V relations. This and the previous models are compared for different thicknesses and contact potentials. The two models may present one of four families of I–V curves (though each model may exhibit them under different conditions). Thus the hopping process cannot be distinguished from the one with ionic motion by just examining the I–V relations and further information is required for identifying the model.

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1. Introduction

Mixed-ionic-electronic-conductors (MIECs) are materials that in addition to their electronic conductance have non negligible ionic conductance. In solid-state devices doping and aging processes involve migration of ions (the defects) in a semi-conducting (electronic) phase — thus they are MIECs. The aging process is expected to be enhanced in reduced scale solid-state devices for which the standard voltage used, on the order of 1 V, generates high driving forces. In addition, small movement of the defects may no longer be regarded negligible as compared to the device dimensions.

A discussion of the different I–V relations in a simple solid-state device based on an MIEC is presented [1]. The sample devices considered here are of the type Metal1|MIEC|Metal2. Where Metal1 and Metal2 are two chemically inert electrodes. The evaluation takes into consideration the effects of space charge regions and contact potentials at the electrodes. For simplicity, the discussion is limited to an MIEC that conducts a single type of electronic defects (holes) and a single type of ionic defects (acceptors), both with charge number z=1. The ionization of the acceptors is also considered. Steady state is assumed in all the calculations. Geometry is assumed to be one dimensional. For comparison we also discuss a model where hopping of electrons between acceptors replaces the acceptor ionic motion.

2. I–V relations assuming local neutrality

Riess [2] solved analytically a model of an MIEC similar to the one described above, assuming local neutrality (L.N.) and full dissociation. The model is based on holes as the electronic defects and acceptors as the mobile ionic defects. Under L.N.,

\[ p(x) = N_{\text{ion}}(x) \]  

(1)
where \( p(x) \) and \( N_{\text{ion}}(x) \) are the hole and charged acceptor concentration profiles. The defects are related by the reaction,

\[
h^* + A^i \rightarrow A^x
\]

which depicts a hole \((h^*)\) interacting with a charged acceptor \((A^i)\) to generate a neutral acceptor \((A^x)\) (we use the Kröger–Vink notation). Under local equilibrium,

\[
K p N_{\text{ion}} = N^x
\]

where \( N^x \) is the concentration of neutral acceptors and \( K \) is the ionization reaction constant. Under full dissociation conditions (i.e. the ionization reaction constant \( K \rightarrow 0 \)), all the acceptors are ionized. Their number is conserved due to the use of inert electrodes,

\[
\int_0^L N_{\text{ion}}(x) \, dx = N_{av} L
\]

where \( L \) is the thickness of the sample and \( N_{av} \) is the average defect concentration. In this case the \( I-V \) relations predicted are [3],

\[
j_h = \frac{4v_h N_{av}}{\beta L} \tanh \left( \frac{1}{4} \beta q V \right)
\]

and

\[
j_i = 0
\]

where \( j_h \) is the hole current density, \( V \) is the applied voltage, \( v_h \) is the hole mobility, \( \beta = k_B T \), \( T \) is the temperature, \( k_B \) is Boltzmann constant and \( q \) is the elementary charge.

The L.N. approximation holds as long as the voltage is limited to [4],

\[
|V| < \frac{4}{3} \ln \left[ \frac{L}{\lambda_D \sqrt{2}} \right].
\]

where \( \lambda_D \) is the Debye length. It should be noticed that according to Eq. (7) L.N. cannot prevail for thin samples of \( L < \lambda_D \sqrt{2} \). A further limitation on \( V \) is that decomposition does not occur. This limit is usually less stringent than Eq. (7).

Fig. 1 presents the \( I_h-V \) relations of Eq. (5). The limiting current arises due to depletion of the acceptors near the negative electrode which leads to depletion of the holes there as well (due to L.N.). The amplitude (see Eq. (5)) depends on the thickness of the sample, but the shape of the curve is independent of the thickness.

3. Thin vs. thick samples

\( \lambda_D \), the Debye length, acts as a characteristic length of the space-charge region. Thick and thin samples are defined with respect to a fixed \( \lambda_D \) calculated for equilibrium. For thick samples \((L \gg \lambda_D)\), the space-charge region is confined to small fraction of the sample and the majority of the sample maintains L.N. (Fig. 2a). For thin samples \((L < \lambda_D)\), on the other hand, the space charge region is large to the extent that the whole MIEC is charged (Fig. 2b) (with compensating charge on the electrodes). One would expect that thick samples are dominated by the properties of the local-neutral bulk (as long as the applied voltage is not too high), whereas thin samples are governed by the properties of the boundaries.

4. Boundary conditions

Two important conditions are the boundary values at \( x = 0 \) and \( x = L \), \( p_0 \) and \( p_L \). In this work \( p_0 \) and \( p_L \) are taken as
independent parameters. This is not only allowed formally but is justified experimentally as in devices of the type considered these values are pinned at the MIEC boundaries. This pinning and the relation of \( p_0 \) and \( p_L \) to the work functions and contact potential of the materials involved is now considered.

Under equilibrium \( p_0 \) and \( p_L \) either change with the work function of the contacting metal electrode or they are fixed by surface states in the MIEC. In a 3D solid these values may also be affected by charge transfer between surfaces of different work functions. This cannot arise in a hypothetical, one dimensional sample as being considered here.

In the first case (negligible surface states density) \( p_0 \) and \( p_L \) are fixed by the equilibrium condition (See Fig. 3),

\[
\tilde{\mu}_M|_{x=0,L} = \tilde{\mu}_{\text{MIEC}}|_{x=0,L}
\]

where \( \tilde{\mu} \) is the electrochemical potential of the holes, \( \tilde{\mu} = \mu + q\phi \)

\( \mu \) the chemical potential and \( \phi \) the electrical (Galvani) potential. The equality in Eq. (8) refers to the interface which has a width of the order of 0.1 nm. It is assumed to hold also under current as the electrons can easily cross this distance between two degenerate states. Over this distance one can also assume that \( \phi \) hardly change (\( \Delta \phi=0 \)). In the present case it changes over a characteristic distance \( \lambda_D \). Inserting then Eq. (9) into Eq. (8) yields,

\[
\mu_M|_{x=0,L} = \mu_{\text{MIEC}}|_{x=0,L}
\]

The chemical potential of the holes in the metal is fixed due to their high concentration. Their chemical potential in the MIEC can be written in the Bolzmann approximation (for dilute concentration),

\[
\mu_{\text{MIEC}} = \mu_{\text{MIEC}}^\oplus + \beta^{-1}\ln\{p(x)/p^\oplus\}
\]

where \( \mu_{\text{MIEC}}^\oplus \) is the standard potential at the standard concentration \( p^\oplus \). We choose \( p^\oplus \) as the concentration in the bulk of a thick sample, far from the boundaries, under equilibrium.

Combining Eqs. (10) and (11) yields at the two boundaries,

\[
p(x)/p^\oplus |_{x=0,L} = \exp\{\beta(\mu_M - \mu_{\text{MIEC}}^\oplus)\}|_{x=0,L}.
\]

As long as the surface states can be neglected, the boundary values \( p_0, p_L \) in a one dimensional MIEC can be related to the contact potential, i.e. the difference between the work functions of the metal and the MIEC. When separated from the metal the bands in the MIEC are a-priori flat under the present assumptions Fig. 3a. Then the work function is equal to the chemical potential up to a constant. Thus at the metal-MIEC interface,

\[
\Delta \phi_{\text{Work}} = \Delta \mu = \mu_M - \mu_{\text{MIEC}}^\oplus
\]

A-priori (before contact) \( p_0=p_L=p^\oplus \) as the bands are flat. After contact between a metal and the MIEC is established and equilibrium has been reached, \( p_0, p_L \) may change. Inserting Eq. (13) into Eq. (12) yields,

\[
\begin{cases}
\frac{p_0}{p^\oplus} = \exp(\beta \Delta \phi_{\text{Work}}|_{x=0}) \\
\frac{p_L}{p^\oplus} = \exp(\beta \Delta \phi_{\text{Work}}|_{x=L})
\end{cases}
\]

This means that \( p_0 \) and \( p_L \) are pinned. It is emphasized that Eq. (14) holds only if the contribution of surface states can be neglected.

When brought into contact with the metal, the work function of the MIEC is forced to change and become equal to that of the metal. (This is achieved by band bending due to a non uniform electric potential \( \phi \) generated by charge transfer between the metal and the MIEC, Fig. 3b). Under this condition, assuming equilibrium,

\[
\Delta \phi_{\text{Work,contact}} = 0
\]

after contact has been established. Localized electronic states at the surface of the MIEC, if of a high concentration, can also pin the

Fig. 3. Schematic illustration of the band structure, the chemical potentials and the Fermi-level before and after a metal MIEC-contact is established, assuming negligible concentration of surface states. Solid black arrow — the electron chemical potential in the metal, dotted arrow — electron chemical potential in the MIEC near the contact, solid gray arrow the work function difference (\( \Delta \phi_{\text{Work}} \)) before contact. a — Before contact. b — After contact.
boundary values $p_0$, $p_L$. The surface states arise from the discontinuity of the otherwise periodic solid (introducing one state per atom of the surface) and because of defects in the native material as well as defects introduced by interaction with oxygen from air and with the contacting metal. [5,6] The presence of surface states may result in bending of the electron energy bands due to charge transfer (within the MIEC) between these states and the conduction bands and the generation of a non uniform internal electric potential $\phi$. In this case the boundary values $p_0$, $p_L$ are different from the bulk standard value, $p^\oplus$. The fact that $p_0$, $p_L$, and
thus also $\Delta \mu$, are fixed, while Eq. (8) also holds, indicates that $\Delta \phi$ at an interface is not negligible in this case. On the contrary, $\phi$ exhibits a significant jump at the interface between the metal and the MIEC surface (as would occur at a contact between two metals).

In the present work it is assumed that no surface states exist at the boundaries, thus, there is no band bending prior to the contact with the metal. In light of Eq. (14), $p_0$ and $p_L$ are constants given by the contact potential and the standard concentration $p_0^{\beta_0}$. If the metal electrode has the same work function as the MIEC prior to contact, this results in zero contact potential and no band bending after contact is established. Otherwise depletion or accumulation of holes occurs in the MIEC if the work function of the metal is lower or higher, respectively.

5. Equations for the MIEC model

The model considered is based on the following equations, The hole current density,

$$j_h = \frac{\sigma_h}{q} \frac{\partial \tilde{p}_h}{\partial x}. \quad (16)$$

The mobile ions current density,

$$j_i = \frac{\sigma_i}{q} \frac{\partial \tilde{p}_i}{\partial x}. \quad (17)$$

In the model assumed here the electrodes are blocking this current,

$$j_i = 0 \quad (18)$$

Poisson equation,

$$\frac{\partial E}{\partial x} = \frac{q}{\varepsilon} (p - N). \quad (19)$$

The unknowns are the functions $p(x)$, $N(x)$ and $E(x)$, $j_h$ is a free parameter. There are three differential equations (Eqs. (16), (17) and (19)), and thus must be accompanied by three appropriate conditions. Two conditions are the boundary values (Eq. (14)),

$$\begin{cases} p(x = 0) = p_0 \\ p(x = L) = p_L \end{cases} \quad (20)$$

The third condition is a normalization one, since the electrodes are assumed to be blocking, the total number of acceptor is conserved.

$$\int_0^L (N_{ion} + N_a) dx = LN_{av} \quad (21)$$

Eq. (21) is an extension of Eq. (4) for the case of finite ionization reaction constant ($K$).

After a solution is found (i.e. the hole, acceptor concentration and the electric field — for a given current), the voltage drop may be calculated, using Eq. (16),

$$V = \frac{A \tilde{p}_h}{q} = \int_0^L \frac{j_h}{\sigma_h} dx. \quad (22)$$

which yields the $j_h$-$V$ relations.

6. Equations for the hopping model

In the second model considered the ionic migration is replaced by electron hopping between the acceptors. The acceptor concentration is assumed to be uniform ($N_{av}$). The difference between the MIEC model and the hopping model is two fold. First, the electrodes no longer block the second current ($j_{hop}$), as the current carriers are now electrons and not ions. Eqs. (17) and (18) are replaced by,

$$j_{hop} = -\frac{\sigma_{hop}}{q} \frac{\partial \tilde{p}_{hop}}{\partial x} \quad (23)$$

Second, the electrochemical potential for the hopping electros is given by,

$$\tilde{\mu}_{hop} = \mu_{hop}^0 + \beta^{-1} \ln \frac{c}{N_{av} - c} + q\phi. \quad (24)$$

The hopping electron need not be in equilibrium with the holes in the valance band as the reaction rate for Eq. (2) is finite [7]. However, here we assume that this rate is infinitely high and local equilibrium persists (Eq. (3)).

7. Results for the MIEC model

The set of equations presented above for the MIEC model is solved numerically for the concentration distribution ($p(x)$ and $N(x)$), the electric field ($E(x)$) and the voltage drop ($V$) for different applied currents ($j$) using MatLab. The effects of sample thickness ($L$), contact potential ($p_0$ and $p_L$) and ionization reaction constant ($K$) on the defects distribution and $I$-$V$ relations are investigated.

7.1. Behavior under voltage

Fig. 4 presents the results for the MIEC model. The parameters used are $L=15\lambda_D$, zero contact potentials ($p_0=p_L=N_{av}$) and $K \rightarrow 0$. Under these conditions, for $V=j=0$, $p(x)=N_{av}$ is uniform and $E(x)=0$. I.e. in this case there is no band bending and L.N. is maintained over the whole sample (see Fig. 4a). For finite, but low voltage ($\beta qV<3$), the sample follows the L.N. solution, only small space charge regions appear near the boundaries (Fig. 4b), but they have a negligible effect on the $I$-$V$ relations (Fig. 4c). As the voltage increase so does the deviation from L.N. (Fig. 4d and e). Under high voltage the $I$-$V$ relations (Fig. 4f) are significantly different from those predicted by the L.N. model (Eq. (5)). L.N. predicts a limiting current, and diverging resistance whereas the present model shows a decrease in the resistance under high voltage (Fig. 4f, $\beta qV>50$). The ion acceptor distribution (Fig. 4d) shows a pileup of acceptors near the positive electrode and depletion near the negative electrode. The hole distribution cannot follow the ionic distribution to maintain L.N. because of the boundary conditions, thus space charge is generated — first near the boundaries (Fig. 4b) and eventually throughout the whole sample (Fig. 4d and e). Another effect that may appear under higher voltages is the charging of the sample. Since the MIEC
may exchange electrons with the electrodes, the overall charge of the MIEC, $R_{L0}/C_0 \frac{N_{\text{ion}}(x)}{dx}$, may not vanish and may change with voltage. The total charge, in the MIEC and electrodes, must vanish at all voltages due to charge conservation.

7.2. Effects of thickness

Fig. 5 presents the results for samples with different thickness, all other parameters being the same. Thickness values considered are, $L = 1, 15 \text{ and } 100 \lambda_D$. The other parameters are as before, zero contact potential ($p_0 = p_L = N_{\text{av}}$) and $K \rightarrow 0$. Fig. 5 also presents the analytic solution for the L.N. approximation (Eq. (5)). The $I-V$ relations change from linear ones (for thin samples) to $\tanh$ like relations (for thick samples). As the sample is made thicker the $I-V$ relations approach the L.N. solution. This is expected as the thicker the sample the less important are the boundary effects (which are limited to a region on the order of $\lambda_D$). The reason is that the voltage drop occurs mainly on the high resistant bulk and only a small fraction of it appears on the boundary regions. In the other limit, as the sample becomes thinner, the $I-V$ relations become linear. In this case bulk effects become negligible and the boundary concentration dictates the electronic behavior. For the case with fixed, symmetric boundary conditions, the $I-V$ relations are linear (ohmic like).

For low voltage ($\beta qV < 3$) all curves coincide with the L.N. solution, suggesting that in this voltage range the L.N. is valid, in agreement with Eq. (7).

7.3. Effects of contact potentials

Fig. 6 presents the $I-V$ relations for a sample with a depletion region at $x = L$ ($p_L = 4.5 \times 10^{-2} N_{\text{av}}$) and with zero contact potential $x = 0$ ($p_0 = N_{\text{av}}$). The band bending is schematically presented in Fig. 6a. Two thickness values are considered, $L = 0.01 \lambda_D$ and $50 \lambda_D$. In both cases the $I-V$ relations are highly a-symmetric. In addition they are asymptotically linear for the thin sample and roughly so for thick one. Exponential relations only appear near the origin. The insert shows the $R-V$ (resistance–voltage) relations. The change in the resistance between forward and backward currents is controlled by the boundary conditions. For both cases ($L = 0.01 \lambda_D$ and $50 \lambda_D$) the ratio is roughly equal to $p_0/p_L$. The thin sample shows much lower resistance than the thick one, as the resistance is inversely proportional to the thickness. In the thick sample, unlike the thin one, the asymptotic resistance is only roughly constant.

![Fig. 5. $I-V$ relations for different thickness, high dissociation $K \rightarrow 0$ and two zero contact potentials ($p_0 = p_L = N_{\text{av}}$).](image)

![Fig. 6. A-symmetric electrodes, one leading to depletion ($p_0 = N_{\text{av}}, p_L = e^{-10 N_{\text{av}}}$) and full ionization ($K \rightarrow 0$) a — A schematic illustration of a sample with no contact potential on the left electrode and a contact potential leading to depletion on the right hand side. b — $I-V$ relations for a thin sample ($L = 0.01 \lambda_D$), c — $I-V$ relations for a thick sample ($L = 50 \lambda_D$).](image)
7.4. Effects of the ionization reaction constant \( K \)

The effect of the ionization reaction constant was investigated on three different samples. Two reaction constants were considered, \( K \rightarrow 0 \) (full dissociation) and \( K_{N_{av}}=1000 \) (high association). The three samples considered have all \( L=50 \lambda_D \), \( p_0 = N_{av} \) and different \( p_L \) values: \( p_L = 0.01N_{av} \) (depletion), \( 1N_{av} \) (weak accumulation), \( 100N_{av} \) (accumulation). Fig. 7 presents the results. For the boundary condition leading to depletion, the effect of \( K \) on the \( I–V \) relations is small and the curves are qualitatively similar, exhibiting rectification. As the contact potential is changed and \( p_L \) increases the effect of \( K \) becomes more pronounced. For high \( p_L \) values the shape of the \( I–V \) relations in the case of high dissociation (small \( K \)) have a general resemblance to a skewed \( \tanh \) shape, whereas those obtained for high association (large \( K \)) have general resemblance to a skewed \( \coth \) shape. (The use of \( \tanh \) and \( \coth \) does not imply exact mathematical dependence rather a general shape of curvatures).

7.5. MIEC model — summary

The model of an MIEC with single mobile ionic defect type (acceptors, in this case) and single electronic charge (holes) was solved for defect concentration, electric field distribution and the \( I–V \) relations. It was found that the defect distributions are affected significantly by the applied voltage \( V \), boundary values \( p_0 \) and \( p_L \), sample thickness \( L \) and the ionization reaction constant \( K \). A correlation between the migration of the mobile ions and the holes was observed; thought it was found that beyond the voltage given by Eq. (7) the sample does not yield the L.N. solution. The \( I–V \) relations calculated may vary between fundamentally different shapes, depending on \( L \), \( \Delta \phi_{Work} \) and \( K \). These shapes may be divided into four categories,

a. Linear relations are obtained only for thin samples with zero contact potentials.

b. Skewed \( \tanh \) like \( I–V \) relations are obtained for thick samples, \( K \rightarrow 0 \) with symmetric contact potentials and for a-symmetric contact potentials, which vanish or lead to accumulation.

c. Rectifying \( I–V \) relations (which are asymptotically linear) are obtained for samples with a-symmetric contact potentials, one leading to depletion. This holds for both high and low \( K \) values.

d. Skewed \( \coth \) like relations are obtained for samples with high association (high \( K \)), for conditions which do not lead to rectification.

8. Results for the hopping model

A comparison between the results of the hopping model and the MIEC model is presented. The current presented is the total one, \( j_h + j_{hop} \). The mobility ratio used is \( \nu_{hop}/\nu_h = 10^{-2} \). Usually \( j_{tot} \approx j_h \gg j_{hop} \), but not always.

8.1. Zero contact potentials (no band bending)

Two samples with thickness \( L=100\lambda_D \), \( K_{N_{av}}=1 \) and two zero contact potentials \((p_0=p_L=N_{av})\), were simulated, one using the MIEC model and one assuming the hopping model. Fig. 8 presents a comparison between the two. The MIEC in this case predicts a
skewed \textit{tanh} like \( I-V \) relations, as was discussed before, while the hopping model predicts linear \( I-V \) relations. The two lines coincide near the origin.

8.2. Two symmetric contact potentials leading to depletion

In Fig. 9 \( L=100\lambda_D \), \( KN_{av}=1 \). The contact potentials are assumed to lead to depletion on both boundaries \( (p_0=p_L=e^{-5}N_{av}) \). Unlike the previous case, the difference between the \( I-V \) relations predicted by the two models is more subtle (Fig. 9a). Interestingly, in this case the two curves do not coincide, even close to the origin. Fig. 9b and c present the defect distribution profile for the two samples. Here the differences are more pronounced. The hopping model maintains the equilibrium solution over most of the bulk (the plateau), the deviation from equilibrium (and space charge regions) are limited to small region near the boundaries — even for high voltages. The defect distribution in the MIEC model, on the other hand, deviates from the equilibrium solution, even for small voltage. Another difference is that for the MIEC model, the holes follow the mobile acceptors which pileup near the positive electrode (see e.g. Fig. 4), in the hopping model the holes distribution is shifted towards the negative electrode whereas the hopping electrons accumulate near the positive electrode.

8.3. Asymmetric contact potentials — one zero and one leading to depletion

Fig. 10 presents the \( I-V \) relations for the MIEC model and the hopping model under the conditions: zero contact potential at one electrode \( (p_0=N_{av}) \) and one electrode leading to depletion.

![Fig. 9](image1)

![Fig. 10](image2)
\( p_L = e^{-5N_{av}} \). \( L = 100 \lambda_D \) and \( KN_{av} = 1 \) for both samples. Fig. 10a present the \( I-V \) relations for a thin sample \( (L = 100 \lambda_D) \). No difference appears between the two models, and the \( I-V \) curves coincide. The two models predict asymmetric \( I-V \) relations (rectification). Fig. 10b presents the \( I-V \) relations for a thick sample \( (L = 100 \lambda_D) \). Here, the hopping model predicts, again, a-symmetric \( I-V \) relations, whereas the MIEC model predicts skewed \( \tanh \) like \( I-V \) relations, with very small a-symmetry. This results in a significant difference, for forward bias \( (V > 0) \), in the \( I-V \) relations of the two models. For backward bias \( (V < 0) \) the \( I-V \) relations are quite similar as observed before in the case of two depleting boundary conditions (Fig. 9a).

8.4. Hopping model — summary

A model including holes in the valance band and one type of immobile ionic defect (acceptors) where hopping of electrons between the acceptor sites is allowed was solved. The results are compared with the corresponding MIECs discussed above. The same three types of \( I-V \) relations, \( a-c \), appear for the hopping model as-well. Some of the results of the hopping model and the MIEC model yield identical \( I-V \) relations (for thin samples). For thick samples, in some cases the general shape is similar but the details are different (two depleting electrodes) and in other cases the results are completely different (this has been observed in the case of zero contact potential and in the case of a-symmetric boundary values \( p_0 \) and \( p_L \)).

9. Conclusions

A device of the type Metal\(_1\)|MIEC|Metal\(_2\) was considered. A model for the MIEC was presented and solved numerically, for the defect concentration profile, electric field and \( I-V \) relations. The model was analyzed under different applied voltages, electrodes (contact potentials), thicknesses and ionization reaction constants. The results were compared with the analytic limit of L.N. It was shown that the \( I-V \) relations coincide with this limit for thick samples. The L.N. approximation is invalid for very thin samples at all voltages (as \( L < \sqrt{2} \lambda_D \) — see Eq. (7)).

Different \( I-V \) relations were predicted for the different cases. Four general shapes were found: linear, skewed \( \tanh \) like, skewed \( \coth \) like and rectifying ones.

Another model was examined in which the ionic defects are immobile and the ionic current is replaced by hopping electrons between the acceptor sites. Three out of the four types of \( I-V \) relations appeared. Under the same conditions some of the cases the two models predicted identical \( I-V \) relations in some cases similar and in some completely different \( I-V \) relations.

For thin samples, and a-symmetric boundary conditions (one leading to depletion), both models predicted a-symmetric \( I-V \) relations yielding rectification. In both models, a-symmetry appeared only if the electrodes enforce it. This implies that aging by ionic motion or hopping conduction through the defect band may not be a real problem if the devices are tolerant towards finer details of the \( I-V \) curve.

No single characteristic \( I-V \) relations were found for one of the models. Therefore, in order to distinguish between ionic motion and electron hopping in the defect band one needs more information concerning \( \lambda_D, L, K \) and/or \( \Delta \phi_{\text{Work}} \). The most pronounced difference appeared in the case of \( \Delta \phi_{\text{Work}} = 0 \) in which the hopping model predicted linear \( I-V \) relations whereas the MIEC predicted skewed \( \tanh \) like \( I-V \) relations.

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