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Schottky diodes as a possible supplementary method for ionic transport investigations in semiconducting ionic solids — application to \( n \)-CdF\(_2\)

R. J. Iwanowski (*), A. Lemańska-Bajorek and J. M. Langer

Institute of Physics, Polish Academy of Sciences, Warsaw, Poland

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Résumé. — On présente des mesures de transport comprenant les caractéristiques \( I(V) \) et \( C(V) \) de diodes Au/n-CdF\(_2\) : (Y, Mn) obtenues à température ambiante. On étudie les variations dans le temps des profils de concentration en donneurs \( N_{\text{eff}}^d(W(V)) \) pour des diodes polarisées par une tension inverse constante \((V_-)\) et pour \( V_- = 0 \); dans le cas de n-CdF\(_2\) : Y, les résultats sont interprétés au moyen de la structure du défaut ponctuel concerné. Ils montrent que le transport ionique dans la couche appauvrie d’une jonction métal-semiconducteur peut être étudié par cette méthode si la hauteur de la barrière est grande et si l’énergie d’activation du défaut est relativement faible.

Abstract. — Transport measurements, including \( I-V \) and \( C-V \) characteristics, of the Au/n-CdF\(_2\) : (Y, Mn) diodes have been performed at room temperature. Time changes of the net donor concentration profiles, \( N_{\text{eff}}^d(W(V)) \), for the diodes biased with constant reverse voltage \((V_-)\) as well as for \( V_- = 0 \) are studied and interpreted using a model of the native point defect structure for the case of n-CdF\(_2\) : Y. The results obtained show the possibility of observation of ionic transport in the depletion layer of MS junction for which the conditions of large barrier height and relatively small activation energy of the defect motion are fulfilled.

1. Introduction. — The ionic transport in nominally pure and doped fluorite-structured compounds has been the subject of numerous investigations (see e.g. [1-3]). Within this group of highly ionic materials CdF\(_2\) is of special interest because it can exist in either insulating or semiconducting states [4]. Undoped cadmium fluoride is an insulator (with a bandgap of about 8 eV) whereas CdF\(_2\) doped with certain trivalent impurities and annealed in Cd [4] or H\(_2\) [5] atmosphere becomes an \( n \)-type semiconductor. In the latter case the electrical conductivity of the crystal is dominated by electrons released in the conversion process [6-8]. Ionic transport in CdF\(_2\) has usually been studied in highly resistive pure and/or doped crystals by the d.c. or a.c. conductivity measurements in the range of moderate and high temperatures [9-12, 3].

Existence of CdF\(_2\) in semiconducting state and the fact that with particular metals it can form ordinary metal-semiconductor rectifying junction [13-16] opened quite unique possibility for observation of the ionic transport in \( n \)-CdF\(_2\) within the volume of a depletion layer produced by the Schottky barrier. Relatively low activation energy for the migration of fluorine vacancies and interstitials in CdF\(_2\), determined earlier by Kessler and Caffyn [10], appeared to be a strongly favorable factor in this case.

The aim of this work was to determine whether high electric field of MS junction could induce ionic motion in a depletion layer and then determine how the point defects in the crystal influence the electrical properties of the diodes studied. For this purpose Schottky diodes made on semiconducting \( n \)-CdF\(_2\) : (Y, Mn) crystals with Au electrodes have been investigated. The choice of electrode metal was made because of the high value of the barrier height \((\phi_B \approx 1.4 \text{ eV})\) at the Au/n-CdF\(_2\) contact [13-16].

2. Native point defects in CdF\(_2\) : Y. — The major disorder in CdF\(_2\) (as well as in the other fluorite structures) is of Frenkel type in the anion sublattice \((F, V_p)\) [1], whereas the cadmium sublattice is immobile [4]. In CdF\(_2\) doped with YF\(_3\), the yttrium ions occupy cation sites and the resulting defect situation
can be approximately described by the following quasichemical reaction:

\[ \text{YF}_3 \rightleftharpoons \text{Y}_\text{Cd} + \text{F}_1^+ + 2 \text{F}_2^- \]  

(1)

The charge introduced by a trivalent cation impurity is completely or partially compensated by an excess of fluorine interstitials, depending on the applied heat treatment process [4, 5]. It had been shown from ionic conductivity measurements in doped CdF₂ crystals [9, 10] that the so-called association effects between the added impurity and its corresponding defect may be observed in the low temperature region, \( T \gtrsim 300 \text{ K} \) (extrinsic ionic conductivity). In our case the neutral complexes (pairs) can be formed between yttrium ions and fluorine interstitials

\[ \text{Y}_\text{Cd} + \text{F}_1^+ \rightleftharpoons (\text{Y}_\text{CdF}_1)^x \]  

(2)

Hence, the net donor concentration in the depletion layer of an MS junction is given by

\[ N_{D}^{\text{ef}} = N_Y - N_1 + N_2 - N. \]  

(3)

\( N_Y \) is the concentration of Y ions, \( N_1 = [\text{F}] \) and \( N_2 = [\text{V}^*_\text{F}] \). \( N \) denotes the concentration of neutral complexes (2). In this model we can also introduce the effective concentration of centres which compensate a positive charge of Y dopant (Eq. (1)), \( N_e = N_1 - N_2 + N \).

For simplification purpose the symbols corresponding to the fluorine interstitials and vacancies will be denoted further in the text by subscripts 1 and 2, respectively.

\( N_1 \) and \( N_2 \) are related by the mass action law:

\[ N_1 N_2 = N_0^2 \]  

(4)

where \( N_0 \) is an equilibrium constant.

Within the above model of point defects in CdF₂ : Y the relation \( N_1 > N_2 \) is usually expected. Ionized fluorine vacancies and interstitials are both mobile and dominate in the ionic transport in CdF₂ : Y, their relative contributions being dependent on the Y-doping level [9, 10]. It has been shown for CdF₂ that at moderate temperatures (including 300 K) the mobility of \( V^*_\text{F} \) is much larger than that of \( F^\text{1+} \), \( \mu_1 \ll \mu_2 \). The same situation occurs in most of the fluorite structured crystals [1, 2].

3. Experiment. — Partially converted CdF₂ : (Y, Mn) crystals with different doping level of Y were used. The crystals were made in Research and Production Centre of Semiconductor Materials, Warsaw. Slices of about 0.5 mm thick had In ohmic contacts made on the back wall. The Au electrodes in the form of discs (\( \sim 1.1 \text{ mm diameter} \)) were evaporated on the front wall under UHV conditions. All the diodes were prepared in the same conditions.

\( C-V, N(W(V)) \) and \( I-V \) characteristics at 300 K were measured with use of an automatic C-N-I bridge. The standard capacitance bridge measurements were performed at the frequency \( f = 3 \text{ kHz} \). The experimental \( C-V \) curves have been differentiated by an operation unit of the bridge in order to obtain the net donor concentration plots, \( N_{D}^{\text{ef}}(W(V)) \), following the well known dependences (see e.g. [17]):

\[ N_{D}^{\text{ef}}(W(V)) = \frac{C^3}{\varepsilon_0 e S^2} \left( \frac{dC}{dV} \right)^{-1} \]  

(5)

\[ W(V) = \frac{\varepsilon_0 S}{C} \]  

(6)

where \( W \) is depletion layer width, \( \varepsilon_0 \) is semiconductor permittivity and \( S \) denotes junction area. It is worth to emphasize that relation (6) is valid for an arbitrary distribution of the uncompensated donors in the depletion layer. The \( I-V \) characteristics were recorded in the range \( 10^{-9} - 10^{-3} \text{ A} \) of the forward current.

Time changes of the net donor concentration profiles, \( N_{D}^{\text{ef}}(x) \), for the diodes biased with constant reverse voltage (\( V_- \)) as well as for \( V_- = 0 \) were studied. The applied voltage was fixed close to \( V_{\text{max}}(V_- \leq V_{\text{max}}) \) which was the boundary voltage for capacitance measurements. For \( V > V_{\text{max}} \), the diode capacitance decreased rapidly due to an abrupt increase of reverse current (\( I_\text{b} \)). Under this condition the reverse current flowing through the junction biased with \( V_- \) was always below \( 10^{-9} \text{ A} \). It enabled us to neglect the effects resulting from an impact ionization of the defects by electrons in a depletion layer.

Table I presents doping and concentration parameters of the applied Au/CdF₂ : (Y, Mn) junctions. The diodes studied have been divided into 3 groups (case A, B, C) depending on the concentration of Y-dopant and the concentration of the compensating centres, which within the assumed model of point defect structure (§ 2) equals \( N_1 - N_2 + N \). Here, \( N_{D}^{\text{ef}} \) corresponds to the effective net donor concentration in the depletion layer, obtained from \( C-V \) measurements performed after evaporation of Au electrodes.

### Table I. — Doping and compensation parameters of the investigated Au/CdF₂ junctions.

<table>
<thead>
<tr>
<th>Case</th>
<th>( N_Y ) [cm(^{-3})]</th>
<th>( N_{D}^{\text{ef}} ) [cm(^{-3})]</th>
<th>( N_e ) [cm(^{-3})]</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>( 6.37 \times 10^{19} )</td>
<td>( \sim 8 \times 10^{17} )</td>
<td>( \sim 6.29 \times 10^{19} )</td>
</tr>
<tr>
<td>B</td>
<td>( 1.27 \times 10^{19} )</td>
<td>( 3 \times 10^{17} )</td>
<td>( 1.24 \times 10^{19} )</td>
</tr>
<tr>
<td>C</td>
<td>( 1.27 \times 10^{19} )</td>
<td>( 2.1 \times 10^{18} )</td>
<td>( 1.06 \times 10^{19} )</td>
</tr>
</tbody>
</table>

4. Results and discussion. — The \( N_{D}^{\text{ef}}(x) \) profiles measured when the diodes (case A, B, C) had been biased with constant \( V_- \) voltage within several hours are shown in figures 1-3, where \( x \) denotes distance from the MS interface. Concentration plots denoted by O were measured before experiment. Figures 4-6 present how the donor concentration...
Fig. 1. — Time changes of the net donor concentration profile for the diode A biased with $V_- = 10$ V. Curve $0 - N_D^p(x)$ before experiment; curves 1-4 — $N_D^p(x)$ after 20, 40, 60 and 100 min. of $V_-$ polarization, respectively.

Fig. 2. — Time changes of the $N_D^p(x)$ profile for the diode B biased with $V_- = 15$ V. $0 - N_D^p(x)$ before experiment; curves 1-3 — after 1, 2.5 and 3.5 h of $V_-$ polarization, respectively.

Fig. 3. — Time changes of the $N_D^p(x)$ profile for the diode C biased with $V_- = 5$ V. $0 - N_D^p(x)$ before experiment; 1-3 — after 20, 60 and 100 min. of $V_-$ polarization, respectively.

Fig. 4. — Changes of $N_D^p(x)$ in time for the diode A after switching off $V_-$ bias. 5-7 — $N_D^p(x)$ after 7, 18 and 31 days, respectively. Curves 0 and 4 — taken from figure 1.

Fig. 5. — Changes of $N_D^p(x)$ in time for the diode B after switching off $V_-$ bias. 4-6 — $N_D^p(x)$ after 6, 17 and 30 days, respectively. 0 and 3 — taken from figure 2.

Fig. 6. — Changes of $N_D^p(x)$ in time for the diode C after switching off $V_-$ bias. 4, 5 — $N_D^p(x)$ after 6 and 17 days, respectively. Curves 0, 3 — taken from figure 3.

Profiles of the diodes A, B and C, respectively, change in time after switching off $V_-$. Additionally, table II reports the data obtained from the analysis of the thermionic part of $I-V$ characteristics measured for the above three cases.

Taking into account that the junctions were fabricated in the same conditions, then the results obtained suggest that the net donor concentration in the depletion layer is determined mainly by the bulk properties of the crystal, i.e. the concentration of Y-dopant and the concentration of compensating centres.

It can be seen from figures 1-3 that the concentration...
Table II. — Results of analysis of thermionic parts of the $I$-$V$ characteristics.

<table>
<thead>
<tr>
<th>Case</th>
<th>$n_0$</th>
<th>$J_0$ $\left[ \frac{A}{cm^2} \right]$</th>
<th>$\phi$ [eV]</th>
</tr>
</thead>
<tbody>
<tr>
<td>A 2</td>
<td>1.01</td>
<td>$3.24 \times 10^{-18}$</td>
<td>1.30</td>
</tr>
<tr>
<td>A 3</td>
<td>1.02</td>
<td>$4.08 \times 10^{-18}$</td>
<td>1.29</td>
</tr>
<tr>
<td>B 2</td>
<td>1.01</td>
<td>$1.68 \times 10^{-16}$</td>
<td>1.20</td>
</tr>
<tr>
<td>B 3</td>
<td>1.01</td>
<td>$2.06 \times 10^{-16}$</td>
<td>1.19</td>
</tr>
<tr>
<td>C 2</td>
<td>1.08</td>
<td>$9.96 \times 10^{-15}$</td>
<td>1.10</td>
</tr>
<tr>
<td>C 3</td>
<td>1.59</td>
<td>$4.80 \times 10^{-11}$</td>
<td>0.88</td>
</tr>
<tr>
<td>C 3</td>
<td>1.06</td>
<td>$9.01 \times 10^{-15}$</td>
<td>1.10</td>
</tr>
</tbody>
</table>

Indices 1-3 mean, respectively: before experiment, after biasing with $V_- > 0$, after a month of storage at 300 K.

plots of the diodes biased with fixed $V_-$ voltage change in different ways. In the case B the donor concentration changes very weakly during the polarization time. The only similarity in the observed $N^0_D(x)$ characteristics consists in the hollow which appears near the edge of the depletion layer (corresponding to the $V_- = \text{const.} \geq V_{\text{max}}$) and which becomes deeper with polarization time. Figures 1-3 treated separately do not enable us to state what type of ionic carriers (ionized defects) influence the above changes of the donor concentration. It could be only supposed that they are mainly due to the fluorine interstitials (§ 2).

Investigation of the changes of the $N_D^0(x)$ profiles measured several days and weeks after switching off $V_-$ voltage (Figs. 4-6) provide useful information on the diffusion processes in the layer adjacent to the depletion layer of the unpolarized junction.

In the case A high $Y$ concentration leads to the domination of ionized fluorine interstitials in the ionic transport. Even for $V_- = 0$ electromigration in the depletion layer should occur, because the resulting diffusion of $F_1^-$ from this layer to the crystal volume is observed (Fig. 4). The slope of the concentration profile increases and shifts to the right.

Analogous changes of the $N_D^0(x)$ profile with the storage time can be seen for the B-type diode (Fig. 5). Here these changes are rather weak comparing with the case A, because of the lower concentration of $N_c$ and $N_y$ (Table I).

In the case C, where $N_c$ is lower than for B, no influence of the diffusion of $F_1^-$ from the depletion layer has been observed (Fig. 6). It can be seen in figure 6 that diffusion tends to level the starting $N_D^0(x)$ dependence (curve 3) and after about two weeks the profile described by curve 5 is obtained — it was checked that this profile had not been changed in time later.

The above results (Figs. 4-6) clearly confirm that diminishing the compensation level, $N_c$, results in the decrease of the contribution to the ionic conductivity given by $F_1^-$. Reduction of $N_y$ and $N_z$ gives the increase of $N_2$ due to relation (4). Following [9] $N_0(300 \text{ K}) \approx 2.5 \times 10^{13} \text{ cm}^{-3}$. Therefore, if association effect does not occur ($N = 0$), the estimated contribution of $V_F^-$ is of order of $10^{11} \text{ cm}^{-3}$. It should be reminded that the mobility of $V_F^-$ is orders of magnitude higher than that of $F_1^-$ [9, 10]. But even then, qualitative difference between the cases A and C in time changes of the $N_D^0(x)$ profiles (Figs. 4 and 6) could be understood only under assumption that part of fluorine interstitials form immobile neutral complexes with $Y$ ions (see § 2) thus reducing the effective concentration of $F_1^-$ which give contribution to ionic transport. Hence, it is reasonable to suppose that $N_3$ is significantly higher than the roughly estimated value of $10^{11} \text{ cm}^{-3}$ and in the case C the influence of second type of ionic carriers, i.e. $V_F^-$, should not be neglected.

The results gathered in table II seem to confirm this suggestion. It can be seen that within this experiment the $I$-$V$ characteristics of the A- and C-type diodes show qualitatively different changes. Reduction of the barrier height in the diode C due to $V_-$ biasing seems to be probably due to the formation of a thin surface layer with $N_D^0$ significantly higher than in the depletion layer [18]. This could be formed by the highly mobile positively charged fluorine vacancies supported by the high electric field of MS junction. Formation of this layer induces the increase of the contribution of resonant barrier tunnelling to the thermionic current [19] and hence, a drastic growth of the saturation current $J_0$ (see C1, C2 — Table II).

It is also worth to pay attention to the values of the barrier height obtained from the analysis of the $I$-$V$ characteristics of the diodes studied, measured before the polarization experiment (A1, B1, C1 — Table II). These values are separated in table III. For each case the Schottky lowering of the barrier, $\Delta \phi_0$, was cal-

Table III. — Barrier height obtained from experiment and Schottky lowering of the barrier for the studied Au/$n$-CdF$_2$ junction.

<table>
<thead>
<tr>
<th>Case</th>
<th>$\phi$ [eV]</th>
<th>$\Delta \phi_0$ [eV]</th>
<th>$\phi_B = \phi + \Delta \phi_0$ [eV]</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>1.29</td>
<td>0.11</td>
<td>1.40</td>
</tr>
<tr>
<td>B</td>
<td>1.20</td>
<td>0.09</td>
<td>1.29</td>
</tr>
<tr>
<td>C</td>
<td>1.10</td>
<td>0.16</td>
<td>1.26</td>
</tr>
</tbody>
</table>
culated in the «flat» profile approximation. Hence, after including $\Delta \phi_0$ we obtain the value of the barrier height $\phi_B = \phi + \Delta \phi_0$ (at the MS contact).

It can be seen from Table III that in the case A the value $\phi_B$ corresponds well with the barrier height at the Au/n-CdF$_2$ contact [13-16]. However, the values corresponding to the cases B and C are significantly lowered. The barrier height lowering $\Delta \phi_B$ for C-type diode reaches 0.14 eV. This reduction of $\phi_B$ can also be ascribed to the previously mentioned effect arising from the formation of a thin highly doped layer (produced by mobile positively charged defects) at the MS interface [18].

$\Delta \phi_B$ can be estimated using a simplified formula [18] derived for the following «step» distribution of uncompensated donors in the depletion layer

$$N_D(x) = \begin{cases} \frac{N_{\text{D1}} + N_{\text{D0}}}{2}, & 0 \leq x \leq x_1 \\ N_{\text{D0}}, & x_1 < x \leq W \end{cases}$$

(7)

and assuming that $N_{\text{D1}} \gg N_{\text{D0}}$

$$\Delta \phi_B = \left( \frac{e^2}{4 \pi \varepsilon \varepsilon_0} \right)^{1/2} \left( N_{\text{D1}} x_1 \right)^{1/2}.$$  

(8)

Here $\varepsilon'$ denotes the dynamic permittivity of the semiconductor. Lack of the dielectric interfacial layer has also been assumed. In this case we can substitute $\varepsilon' = \varepsilon_0 [13, 17]$. Simple calculations show us that in the case C, where we have approximately $N_{\text{D0}} \approx 2.5 \times 10^{18}$ cm$^{-3}$, a thin layer of $x_1 = 10$ Å and $N_{\text{D1}} = 5 \times 10^{19}$ cm$^{-3}$ can give the barrier lowering $\Delta \phi_B = 0.14$ eV.

The changes of the $N^*_{\text{Df}}(x)$ profiles in time for the diodes considered here, stored at room temperature (under $V_- = 0$ bias), had been also investigated. In the case C the concentration profiles did not depend on time. Figure 7 presents the changes of the $N^*_{\text{Df}}(x)$ dependence with storage time for the A-type diode, where, as it has been stated before, fluorine interstitials dominate in the ionic transport (1). It was checked by redrawing the profiles 1-7 (from Fig. 7) in linear scale that the slope of $N^*_{\text{Df}}$ vs. $x$ (especially in the region adjacent to the depletion layer of unpolarized junction) remained constant for them, within the accuracy of this measurement. This enabled us to estimate the diffusion coefficient of fluorine interstitials at 300 K, $D_{\text{f}}(300 \text{ K}) = 1.8 \times 10^{-18}$ cm$^2$/s as well as the mobility of $\mu_{\text{f}}(300 \text{ K}) = 7.3 \times 10^{-15}$ cm$^2$/Vs.

Since the mobility of fluorine vacancies reported in [9] is $\mu_2(300 \text{ K}) = 6.3 \times 10^{-3}$ cm$^2$/Vs, the resulting mobility ratio is $\mu_2/\mu_{\text{f}} \approx 9 \times 10^{13}$ - it corresponds well with the estimate made in [9]. Taking into account the approximate value of the concentration $N_1$ we obtain the value of electrical conductivity, $\sigma = 7.4 \times 10^{-16} \Omega^{-1}$ cm$^{-1}$, given by fluorine interstitials, which agrees well with the ionic conductivity data of CdF$_2 : Y$ [9].

In the case B the changes of the $N^*_{\text{Df}}(x)$ profiles with storage time were analogous to those of case A, however they were not so quick and significant.

5. Conclusions. - Transport measurements of the Au/n-CdF$_2 : (Y, \text{Mn})$ diodes, performed at room temperature, have shown the possibility of observation of ionic transport in the depletion layer of MS junction for which the conditions of large barrier height and relatively small activation energy of the defect motion are fulfilled. The results obtained prove the usefulness of the Schottky diodes as a supplementary method for ionic transport investigations in semiconducting ionic solids in the temperature range $T \geq 300$ K.

References


