Determination of the parameters of semiconducting CdF$_2$:In with Schottky barriers from radio-frequency measurements

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Physical properties of semiconducting CdF$_2$ crystals doped with In are determined from measurements of the radio-frequency response of a sample with Schottky barriers at frequencies $10^{-6}$ Hz. The $dc$ conductivity, the activation energy of the amphoteric impurity, and the total concentration of the active In ions in CdF$_2$ are found through an equivalent-circuit analysis of the frequency dependencies of the sample complex impedance at temperatures from 20 K to 300 K. Kinetic coefficients determining the thermally induced transitions between the deep and the shallow states of the In impurity and the barrier height between these states are obtained from the time-dependent radio-frequency response after illumination of the material. The results on the low-frequency conductivity in CdF$_2$:In are compared with submillimeter ($10^{11}-10^{12}$ Hz) measurements and with room-temperature infrared measurements of undoped CdF$_2$. The low-frequency impedance measurements of semiconductor samples with Schottky barriers are shown to be a good tool for investigation of the physical properties of semiconductors.

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INTRODUCTION

CdF$_2$ belongs to a large family of fluorides crystallizing in the cubic fluorite structure $O5h$ ($Fm\overline{3}m$), with parameters typical for this family: it is an ionic dielectric with a wide band gap and only one dipole-active lattice mode centered near $6\cdot10^{12}$ Hz [1]. The latter provides an almost frequency and temperature independent lower frequency (static) dielectric constant $\varepsilon \approx 8$ [2, 3].

If CdF$_2$ crystals doped with In are heated up in a reducing atmosphere of hydrogen or alkali metal vapors in a so-called additive coloration process, when a part of the interstitial F$^{-}$ ions leaves the crystal, and afterwards are cooled down to a quite low temperature, half of the In ions reveal a completely ionized state, $\text{In}^{1+}$, without any valence electron, and the other half exhibits an $\text{In}^{1+}$ state, with two valence electrons [4, 5]. Thus the nonlocal neutrality of the crystals is satisfied, and almost full self-compensation of the donor impurities is realized. Since, due to the Coulomb interaction, a localization of two electrons at one orbital is energetically not profitable, a compensating local lattice distortion appears around the $\text{In}^{1+}$ ions, the ions being moved along a 4th order axis into a neighboring cell of eight F$^{-}$ ions not occupied by a Cd ion [3]. Consequently, a transition of the In ion from $\text{In}^{3+}$ state into the $\text{In}^{1+}$ state requires a local lattice distortion. In other words, there is a significant potential barrier between the $\text{In}^{1+}$ and $\text{In}^{3+}$ states. Thus, $\text{In}^{1+}$ impurities in CdF$_2$ form a deep level, which is similar to the $DX$-centers in typical semiconductors [6, 7]. A fraction of electrons is captured by $\text{In}^{3+}$ ions, forming a hydrogen state ($\text{In}^{3+} + e_{\text{hydr}}$), a shallow donor level, being the basic reason that the CdF$_2$:In reveals semiconducting properties. The relative concentrations of the shallow $\text{In}^{3+} + e_{\text{hydr}}$ and the deep $\text{In}^{1+}$ centers depend on the temperature. Fig. 1 shows an energy level diagram for the deep, $E_{\text{deep}}$, and the shallow, $E_{\text{sh}}$, states of the bistable In centers in CdF$_2$ as function of the configuration coordinate $Q$ (position of the In impurity relative to the surrounding ions). For a transition from one state to another the electron has to overcome an additional capture barrier, $E_{\text{cap}}$, and consequently the upper state is metastable. The energy of the states measured from the bottom of the conducting band are $E_{\text{deep}} = 0.25$ eV [5] and $E_{\text{sh}} = 0.1$ eV [6]. The electrons of the $DX$-centers can be transferred to the shallow state either by light irradiation or by temperature. The changing of the $DX$-center state leads to a change of polarizability and, consequently, to a local change of the refractive index. This fact allows to use the metastable shallow states to write reversible phase holograms. The efficient writing of such holograms in the semiconducting CdF$_2$ doped with In or Ga has been demonstrated in [7] and [8]. The interest in these materials is caused mainly by their holographic application.

Traditionally, investigations of the semiconducting...
transport properties of doped CdF$_2$ were carried out using ohmic contacts. The technique to produce such contacts is quite complicated and often is a kind of art. In this paper we report on the radio-frequency investigations of CdF$_2$: In which were carried out without a use of ohmic contacts. We have determined characteristic features of CdF$_2$: In, as the temperature dependencies of the $dc$ conductivity and of the ion concentration on the donor level, the activation energy of impurities, $E_a$, the total concentration of the active In ions, $N$, the barrier height, $E_{cap}$, and the values of the kinetic coefficients which determine the speed of the thermally induced transfers between the deep and the shallow states of the In ions in the CdF$_2$ matrix. All these parameters have been defined from low frequency ($10^{-6}$ Hz) measurements of the complex impedance of thin plane-parallel CdF$_2$: In samples with metallic electrodes which were either sputtered on their surfaces or just brought into contact with the surfaces. This method is the basis of our previous study [1].

SAMPLES AND EXPERIMENT

In most of the experiments we used a homogeneous transparent plane-parallel sample of CdF$_2$ with an InF$_3$ concentration in the raw material of 0.02 mole %. This concentration of the In impurities gives the sample a red-brownish color. The absorption coefficient $\alpha$ for light with a wavelength of $\lambda = 488$ nm has been measured to be of the order of 50 cm$^{-1}$ at room temperature. Control experiments have been also performed for a pure CdF$_2$ sample without In doping. Both surfaces of the sample have been covered by gold electrodes made by plasma sputtering. The area of each electrode was 20 mm$^2$ and the electrode thickness was about 10 nm. The light transmittance through this electrode for $\lambda = 488$ nm has been estimated as high as 50 %.

The lead wires from the electrodes were soldered to terminals of the cryostat. The terminals were connected with an LCR meter HP4284A. The analyzer HP4284A covers a frequency range from 20 to $10^6$ Hz, an amplitude $ac$ voltage $V_s$ from 0 to 20 V and a bias voltage from -40 to 40 V. Usually $V_s = 0.1$ V and zero bias have been used. Results of the complex impedance of a sample with electrodes, $Z$, were obtained as an equivalent capacitance $C_p$ and an equivalent conductance $G_p$ (i.e. the complex conductance is $1/Z = G_p + i\omega C_p$, where $\omega$ is the angular frequency). Additional experiments have been carried out for frequencies extending to 320 MHz.

In these experiments an HP4191A impedance analyzer with working range of 1 MHz - 1 GHz has been utilized. For the measurements the sample was placed at the end of a coaxial line, and a calibration procedure with three standard loads was required to eliminate the contributions of the line itself [2].

RESULTS AND DISCUSSION

Schottky barriers and a non-homogenous layered Maxwell-Wagner capacitor model

Typical results of our measurements of the frequency dependencies of $C_p$, and $G_p/\nu$ for the sample with gold electrodes are plotted in Fig. 2 ($\nu = \omega/2\pi$). These measurements were performed with the sample cooled in darkness. They clearly show the signature of a relaxation process for frequencies 20 Hz to 1 MHz, the relaxation frequency $\nu_p$ strongly depending on the temperature. When
the temperature changes from 110 K to 200 K, \( \nu_p \) rises by a factor of 10000.

Since in a cubic electronic semiconductor like CdF₂:In it is very difficult to imagine a low frequency microscopic mechanism for this relaxation, we propose, that a macroscopic Maxwell-Wagner relaxation process accounts for this behavior. (This statement has been strongly supported by the experiments described below, where isolating layers between sample and electrodes have been used.) The Maxwell-Wagner relaxation is a quite common feature for a non-homogenous layered capacitor \[ \text{[13]} \]. The layered structure results from the formation of Schottky barriers in the regions of semiconducting CdF₂:In close to the metal electrodes \[ \text{[14]} \]. If the electron work function \( \varphi_m \) in a metal is higher than in an electronic semiconductor, \( \varphi_s \), the electron concentration in the contact region of the semiconductor is suppressed, and a depletion layer appears. Its thickness is equal to

\[ d_c = \sqrt{2\varepsilon\varepsilon_0 V_c/e n_d}, \]  

where \( e \) is the electron charge, \( V_c = (\varphi_m - \varphi_s)/e \) is the contact potential difference, \( n_d \) is the donor concentration (total ionization of donors is supposed), and \( \varepsilon \) and \( \varepsilon_0 \) are the dielectric constants of the semiconductor and of the vacuum.

Thus, the sample with two electrodes may be considered as a structure of three condensers in series: two of them are formed by the depletion layers with small conductivity, and the third (the middle) one represents the bulk material with the real sample conductivity. If the material of both electrodes are the same and both sample surfaces had the same treatment, then two depletion-layer capacitors with capacity \( C' \) may be presented in the equivalent circuit scheme as one capacitor with capacitance \( C_1 = C'/2 \). The rest of the sample may be considered as a capacity \( C_2 \) with a parallel active conductivity \( G \). Overall we arrive at the equivalent circuit indicated in Fig. 2. Neglecting the conductivity of the depletion layers, the impedance of this scheme is:

\[ Z = \frac{1}{i\omega C_1} + \frac{1}{G + i\omega C_2}, \]

and the complex conductance is \( 1/Z = G_p + i\omega C_p \), where

\[ G_p = \frac{C_1^2 \omega^2 G}{\omega^2 (C_1 + C_2)^2 + G^2}, \]

\[ C_p = \frac{C_1 \left[ G^2 + \omega^2 (C_1 C_2 + C_2^2) \right]}{\omega^2 (C_1 + C_2)^2 + G^2}. \]

An analysis of (3) and (4) shows that at \( \omega \to 0 \)

\[ C_p \to C_{p0} = C_1, \]

\[ G_p \to G_{p0} = 0; \]

and at \( \omega \to \infty \)

\[ C_p \to C_{p\infty} = C_1 C_2 / (C_1 + C_2), \]

\[ G_p \to G_{p\infty} = GC_1^2 / (C_1 + C_2)^2. \]

If \( C_1 \gg C_2 \) (that usually holds for the Schottky barriers), then:

\[ C_{p\infty} = C_2, \]

\[ G_{p\infty} = G. \]

Thus, the high frequency limit represents the bulk material parameters, while the low frequency one depends strongly on the contact phenomena. In addition, \( C_p(\omega_p) = (C_{p\infty} + C_{p0})/2 \), where the relaxation frequency is:

\[ \omega_p = 2\pi\nu_p = G/(C_1 + C_2). \]

FIG. 2: Frequency dependencies of \( C_p \) (upper panel) and \( G_p/\nu \) (bottom panel) for a sample with gold-sputtered electrodes at various temperatures. The points are experimental data, the solid lines are least square fits by formulas \[ \text{(3)} \] and \[ \text{(4)} \] deduced from the equivalent circuit indicated in the lower panel.
The experimental values of $\varepsilon$ and $\sigma$ of the bulk material obtained from the radio-frequency measurements with three different kinds of linings at the electrodes: 1) Teflon linings, 2) mica linings, and 3) without any linings (marked as "Schottky barrier"). The values are presented for three temperatures. The experimental accuracy for $\varepsilon$ is: 30 % for the Teflon linings, 20 % for the mica linings, and 10 % for the measurements without linings. The experimental accuracy for $\sigma$ is: 30 % for the Teflon linings, 10 % for the mica linings, and 4 % for the measurements without linings.

| $T(K)$ | Teflon | Mica | Schottky barrier |
|--------|--------|------|------------------|
|        | 109    | 124  | 148             |
| $\varepsilon$ | 8.7    | 9.4  | 10.9            |
| $\sigma(\Omega^{-1}cm^{-1})$ | $1 \cdot 10^{-8}$ | $1 \cdot 10^{-7}$ | $1 \cdot 10^{-6}$ |
|        | 109    | 124  | 148             |
| $\varepsilon$ | 10.2   | 10.3 | 11.0            |
| $\sigma(\Omega^{-1}cm^{-1})$ | $1.4 \cdot 10^{-8}$ | $1.3 \cdot 10^{-7}$ | $2.2 \cdot 10^{-6}$ |
|        | 110.5  | 125.3| 149.4           |
| $\varepsilon$ | 7.3    | 7.7  | 8.3             |
| $\sigma(\Omega^{-1}cm^{-1})$ | $1.3 \cdot 10^{-8}$ | $1.2 \cdot 10^{-7}$ | $2.2 \cdot 10^{-6}$ |

The frequency dependencies of $C_p$, and $G_p/\nu$ calculated from formulas [3] and [4] are shown in Figs. 2 and 3 as solid lines. The parameters $C_1$, $C_2$ and $G$ have been fitted with the least square method. As can be seen from Fig. 2, all the characteristic features of the experimental curves are well described by the formulas of the Maxwell-Wagner model [2]. For the higher temperatures, at low frequencies deviations of experimental data and fits show up in $G_p/\nu$. They can be ascribed to a small, but non-zero conductivity of the depletion layers, which for very low frequencies would lead to a $1/\nu$ divergence. We note, that $C_{p0}$ and $C_{pc0}$ are almost temperature independent. Consequently, the strong temperature dependence of the relaxation frequency $\nu_a = G/2\pi(C_1 + C_2)$ is due to the temperature dependence of $G$. Using the temperature dependencies of the fitting parameters $C_2(T)$ and $G(T)$, we have calculated the real part of the dielectric permittivity $\varepsilon'(T) = C_2(T)\epsilon_0/(\epsilon_0 S)$ and the conductivity $\sigma(T) = G(T)d/S$ of the bulk material ($S$ is the electrode area, and $d$ is the sample thickness).

Since the frequency dependencies of $C_p(\omega)$ and $G_p(\omega)$ (Eqns. 3 and 4) have the same shape as the frequency dependencies of $\varepsilon'$ and $\sigma = \varepsilon''_0\omega\sigma$ for homogeneous dielectrics with Debye relaxation (here $\varepsilon'$ and $\varepsilon''$ are real and imaginary parts of the dielectric permittivity), we have conducted two control experiments for the CdF$_2$: In sample with electrodes isolated from the sample by 55 $\mu$m thick Teflon ($\varepsilon_{Teflon} = 2$) and 35 $\mu$m thick mica ($\varepsilon_{mica} = 8$) layers. In these experiments no Schottky barriers are formed, and one can directly calculate the electrode capacitances $C' = 2C_1 \approx 2C_{p0}$ of the Maxwell-Wagner layered system. We have found, that the value of $C_1$ for Teflon is two orders of magnitude smaller and for mica it is one order of magnitude smaller than $C_{p0}$ in the experiments with sputtered gold electrodes (2.5 pF and 20 pF, respectively), while $C_2$ remains at 3 - 4 pF. Accordingly, for a fixed temperature the values of $C_{p0}$ decrease and the characteristic relaxation frequencies increase by 2 (1) orders of magnitude for Teflon (mica) linings. Such a behavior is expected in the case of a Maxwell-Wagner relaxation (see Eqn. 13), since the bulk conductance $G$ does not depend on the type of the contacts. At the same time, in the case of the Debye relaxation, the characteristic frequency of which does not depend on the electrode capacitances, one would obtain other, more complex, frequency dependencies of $C_p$ and $G_p$ due to a superposition of the Maxwell-Wagner relaxation and the Debye relaxation.

The evaluated values of $\varepsilon'$ and $\sigma$ of the bulk material are presented in Table I for three temperatures together with the values determined from the measurements with Schottky barriers. Table 1 documents, that the values of the dielectric constant and of the conductivity determined through the Maxwell-Wagner equivalent circuit analysis coincide with each other within experimental accuracy for all temperatures. This again proves the validity of the Maxwell-Wagner relaxation as a model for the treatment of our results.

According to the weak temperature dependence of $C_{pc0}$, the capacity $C_2$ does not depend significantly on temperature: at temperatures between 70 K and 300 K $C_2 \approx 3$ pF, and consequently $\varepsilon \equiv 8$ (at lowest T = 25 K, $\varepsilon \equiv 7$). The same values of $\varepsilon$ have been determined for an undoped sample. Contactless measurements made in the submillimeter frequency range give the same values for doped and pure CdF$_2$ as well [4].

### Temperature and frequency dependencies of the conductivity

The temperature dependence of the conductivity obtained by fitting the experimental results $C_p(\omega)$, $G_p(\omega)$ with the Maxwell-Wagner model is shown in Fig. 4. For temperatures 100 K $\div$ 250 K the temperature dependence of the conductivity can be well described by a thermally activated behavior:

$$\sigma(T) \propto \exp(-E_a/k_BT),$$

with an activation energy $E_a = 0.197 \pm 0.008$ eV. This value, being actually "an weighted-mean activation energy" of the deep, $E_{deep}$, and the shallow, $E_{sh}$, states of the In ions, takes into account both the electron transfers from the deep and the shallow levels into the conduction band, and the process of transferring electrons between the deep and the shallow metastable donor levels. As can be seen from Fig. 4, at low temperatures the slope of the $ln\sigma(1/T)$ curve decreases, corresponding to the decrease
in the electron replenishment of shallow levels from the deep ones. The value of $E_a$, consequently, should approach the activation energy of the shallow state at quite low temperatures. This behavior has been indeed observed in Ref. [15] at temperatures 40 K to 80 K.

Since the electron mobility $\mu$ in CdF$_2$ depends only weakly on temperature (at the temperatures 70 \div 300 K, $\mu \approx 15 \text{ cm}^2\text{V}^{-1}\text{s}^{-1}$ [3]), we can calculate the electron concentration $n_e$ in the conduction band. For example, for $T = 150$ K one finds $n_e = \sigma / e\mu = 1 \cdot 10^{12}$ cm$^{-3}$. For this value of the electron concentration the total effective concentration of the In ions with the activation energy of $E_a = 0.197$ eV, should be $N = n_e \exp(E_a/k_B T) = 4 \cdot 10^{18}$ cm$^{-3}$, that coincides with $N = (3.5 \pm 0.7) \cdot 10^{18}$ cm$^{-3}$ obtained from our absorption coefficient data $\alpha \approx 50$ cm$^{-1}$ at room temperature for $\lambda = 488$ nm.

Fig. 4 compares our results on the low-frequency conductivity in CdF$_2$:In with the measurements in the submillimeter range carried out on a different In-doped sample at 10 K and 300 K [2] and with room-temperature infrared measurements in undoped CdF$_2$ [4]. The radio-frequency experimental data shown in Fig. 4 extended up to 1 GHz, were obtained on the same sample as the results of Fig. 2, but with contacts made from silver paint. The dielectric-loss results up to 1 MHz (not shown) are similar to those shown in Fig. 2. In the conductivity representation of Fig. 4, the loss peaks are transformed into a steep increase of $\sigma(\omega)$, followed by the approach of a nearly frequency-independent plateau value. The initial increase of $\sigma(\omega)$ can be ascribed to the successive shorting of the high resistance of the depletion layer by its capacitance. One should be aware that in the contact-dominated region $\sigma(\omega)$ shown in Fig. 4, which was calculated from the conductance $G(\omega)$ using the geometry of the sample, does not reflect the true conductivity of the sample material. Only when the plateau region is reached, the intrinsic bulk response is measured. At the lower temperatures, following this plateau, $\sigma(\omega)$ starts to increase again with increasing frequency. Such a behavior is often observed in amorphous and doped semiconductors and usually ascribed to hopping conductivity of localized charge carriers [17]. It can be parameterized by the so-called "Universal Dielectric Response" (UDR): $\sigma = \sigma_{dc} + \sigma_0 \omega^s$, $s < 1$ [18]. The dashed lines in Fig. 4 have been calculated using the equivalent circuit of Fig. 2, with an additional UDR element (including its contribution to $\sigma''$ via the Kramers-Kronig relation [19]) connected in parallel to $G$ and $C_2$ [20]. In this way the general behavior of the experimental spectra can be satisfactorily reproduced. Values of $s$ between 0.8 and 0.88 were obtained, which lies in a reasonable range for hopping conduction [17]. The deviations showing up at low frequencies, again indicate that there is a non-zero conductivity of the depletion layers. For 300 K, the low-frequency curve matches well with the submillimeter data and possibly the increase of $\sigma(\omega)$ observed in the submillimeter region can also be taken into account by the UDR. Up to now UDR behavior only rarely has been observed up to such high frequencies (e.g., [20]). However, as mentioned above, the measurements in the submillimeter range were performed on a different sample, which may have a slightly different In content and therefore Fig. 4 can only provide a qualitative comparison of the low- and high-frequency response. It may be
noted that in CdF₂:In there is no indication for the characteristic frequency dependence connected with Drude behavior: when the frequency becomes comparable to the scattering rate of the charge carriers, a characteristic frequency-dependent decrease of the conductivity should show up. The absence of this feature possibly is due to the fact that the high-frequency conductivity seems to be governed by hopping of localized charge carriers, while Drude-like transport of “free” electrons, excited into the conduction band, dominates at low frequencies and dc only.

The submillimeter-range data for 10 K, where the low-frequency conductivity in the doped sample can be expected to be extremely low, agree well with the infrared data for CdF₂ without impurities (solid line). The latter, showing a peak at around 10¹³ Hz represents a dipolar lattice mode.

Light excitation and measurements of the shallow state kinetics

In order to determine the kinetic coefficients which affect the rate of the thermally induced transfers between the deep and shallow states, we have carried out experiments with illumination of the sample by light with a wavelength λ = 488 nm. This wavelength hits into the wide photoionization absorption band in CdF₂:In centered around 400 nm. The sample was cooled to the required temperatures in darkness and illuminated afterwards. We found, that the characteristic relaxation frequency νₚ is proportional to the intensity of the light, I_laser, at all the temperatures (50 K ÷ 150 K) at which under illumination νₚ hits into the instrumental frequency window of the HP4284 analyzer. This behavior can be ascribed to the conductivity being proportional to the light intensity (at least for that used in our experiments I_laser < 6 mW/cm²), since at C₁ ∝ const and C₂ ∝ const the conductance of the sample is G = 2πνₚ(C₁ + C₂) ∝ I_laser (cf. Eqn. [1]). As an example, Fig. 5 shows the sample conductance versus the laser power for T = 110 K. The linear dependencies G(I_laser) show the absence of any saturation effects for the illumination power used in our experiments. After switching off the illumination, the frequency νₚ and the conductance G relax with time. The rate of this relaxation is not constant. During first minutes G rapidly drops by 1 or 2 orders of magnitude, but then decreases rather gradually with a characteristic time being from half an hour to several hours (Fig. 6) depending on temperature. This process is connected with the capture of a part of the non-equilibrium carriers by the In³⁺ ions into the metastable donor state In³⁺ + e_hydr, and line is the best fit by Eqn. [1] (only those G(t) data points have been used here, for which the calculated N_sh is much less than the total concentration of active impurity N = 4 · 10¹⁵ cm⁻³).

Fig. 5: The CdF₂:In sample conductance G versus the laser power at T = 110 K (G is obtained from the fitting of Cₚ(ν) and Gₚ(ν) curves).

Fig. 6: Time dependencies of the conductance G (upper panel) and of the shallow donor concentration N_sh (bottom panel) of CdF₂:In after its irradiation with 488 nm laser light at T = 78 K. Upper panel: points are the experimental data, line is guided for eye. Bottom panel: points are calculated from Eqns. [2] using nₑ(t) = G(t)dψ/duₑ, and line is the best fit by Eqn. [1] (only those G(t) data points have been used here, for which the calculated N_sh is much less than the total concentration of active impurity N = 4 · 10¹⁵ cm⁻³).
where the In ions into the hydrogen-like state with an energy $E_{sh}$. The reverse process of the thermal decay of the shallow centers with capture of the released electrons by other shallow centers occurs in accordance with the bimolecular reaction:

$$2(In^{3+} + e_{hydr}) + kT_B \rightarrow In^{1+} + In^{3+}.$$ (14)

The thermal decay of the shallow states after the light illumination is described by the kinetic equation [3]:

$$\frac{dN_{sh}}{dt} = -cN_{sh}^2 + b(N - N_{sh})^2/4,$$ (15)

where $N_{sh}$ is the concentration of the shallow centers, $c$ and $b$ are the kinetic coefficients of the decay and the creation of the shallow center, correspondingly. It is assumed here, that the concentration $N_{sh}$ of the completely ionized $In^{3+}$ is equal to $N$ and, consequently, $N_{sh} \approx N/2$ and the free electron concentration is negligible. The solution of the Eqn. 15 yields the following time dependence for $N_{sh}$:

$$N_{sh}(t) = \frac{n_1 \exp \left[ \frac{N\sqrt{c/b}(t + t_0)}{N\sqrt{c/b}(t + t_0)} \right] - n_2}{\exp \left[ \frac{N\sqrt{c/b}(t + t_0)}{N\sqrt{c/b}(t + t_0)} \right] - 1},$$ (16)

where $n_1 = N/(1 + 2\sqrt{c/b})$, $n_2 = N/(1 - 2\sqrt{c/b})$, $t_0$ is a constant of integration.

In order to compare our results for $G(t)$ with Eqn. 16 we have calculated the electron concentration $n_e(t) = G(t)\cdot d/(Se\mu)$, and then obtained $N_{sh}(n_e)$ using the procedure described below.

Since in the CdF$_2$:In crystals, after the additive coloration process, the $In^{3+}$ ions play a role of donors, and the $In^{1+}$ ions, capturing an additional electron, play a role of acceptors, and since the effective concentration of donors $n_d$ in a compensated donor semiconductor is equal to the difference between the concentrations of donors and acceptors [4], we obtain $n_d$ equal to the concentration of the shallow hydrogen-like centers $N_{sh}$, formed via capture of electrons to a hydrogen-like orbit by a little part of the In$_{3+}$ ions. We assumed thermal equilibrium between the conduction electrons and the shallow states. We also assume that all the conduction electrons are formed through ionization of the shallow states and that the direct electron transitions between the deep levels and the conduction band are negligible. The conduction electron concentration in a semiconductor with donor and acceptor impurities with concentrations of $N_d$ and $N_a$, correspondingly, is [21]:

$$N_c = \frac{N_d - N_a}{2N_a} \exp(-E_d/k_B T),$$ (17)

where $E_d$ is the energy of the donor level, $N_c = 2(2\pi m^*k_B T)^{3/2}/\hbar^3$ is the density of states in the conduction band and $m^*$ the effective electron mass. Eqn. 3 is valid for low enough temperatures, when $E_d/k_B T \gg 1.$

In our case $N_d \equiv N^{3+}$, $N_a \equiv N^{1+}$ and $N_d - N_a = N_{sh}$, $N_{sh} \approx N/2$, $E_d \equiv E_{sh} = 0.1$ eV and the condition of Eqn. 3 is always satisfied. Consequently, the electron concentration is given by:

$$n_e = \frac{N_{sh}}{N} \exp(-E_{sh}/k_B T),$$ (19)

and

$$N_{sh}(t) = (n_e(t)/N_e) \exp(E_{sh}/k_B T).$$ (20)

Substituting to Eqn. 20 the data for $N$ and $n_e(T)$, defined in our experiments ($N = 4 \cdot 10^{18}$ cm$^{-3}$, $n_e(T) = \sigma(T)/e\mu$, and the values of $m^* = 0.45m_e$ [4] and $E_{sh} = 0.1$ eV), we obtain $N_{sh}/n_e = 1.15 \cdot 10^7$ at $T = 78$ K and $N_{sh}/n_e = 9.07 \cdot 10^4$ at $T = 110$ K. In accordance with assumed thermal equilibrium between the conduction electrons and the shallow states we use these ratios for calculating $N_{sh}(t)$ through the experimentally found time-dependent electron density $n_e(t) = G(t)d/(Se\mu)$. The strong identity of the time dependencies of the infrared absorption ($\propto N_{sh}(t)$) and of the conductivity ($\propto n_e(t)$) after an optical excitation has been experimentally shown in [3]. Since Eqn. 3 implies that $N_{sh} \ll N$, we used only those experimental $G(t)$ data points, for which the calculated $N_{sh}$ is much less than $4 \cdot 10^{18}$ cm$^{-3}$.

The results for $N_{sh}(t)$ and the calculated fit curve Eqn. 16 are shown in Fig. 3 (bottom part) for $T = 78$ with the best fit parameters ($N = 10^{18}$ cm$^{-3}$, $t_0 = 335$ s, $c = 7.6 \cdot 10^{-22}$ cm$^2$s$^{-1}$, and $b = 3.4 \cdot 10^{-24}$ cm$^2$s$^{-1}$). For the thermal decay curve at $T = 110$ K the best fit parameters are $N = 4 \cdot 10^{18}$ cm$^{-3}$, $t_0 = 2875$ s, $c = 1.17 \cdot 10^{-19}$ cm$^2$s$^{-1}$, and $b = 3.7 \cdot 10^{-25}$ cm$^2$s$^{-1}$. Using these values of $c$ and $b$, we compare the shallow center decay and creation processes for $T = 78$ K and $T = 110$ K. At $t = 1000$ s and $T = 78$ K, the first term of Eqn. 17 is two orders of magnitude larger than the second one, i.e. the thermal decay of the shallow states is dominating. At $T = 110$ K and $t = 1000$ s these terms are nearly equal, i.e. the thermal decay begins to be compensated by the thermal activation. It is interesting, that $c(110$ K) is two orders of magnitude larger than $c(78$ K), while $b(110$ K) is one order of magnitude smaller than $b(78$ K).

Assuming that the temperature dependence of the kinetic coefficient $c$ can be described by activated behavior, $c(T) = A \cdot \exp(-E_{ac}/k_B T)$, from $c(78$ K) and $c(110$ K) we found $E_{ac} = 0.12$ eV. This value coincides with $E_{ac}$ obtained in [3] by the kinetic measurements of the shallow state infrared absorption. The kinetic coefficient $c$ may be presented as $c(T) = const \cdot p_1 \cdot p_2$, where
$p_1 = \nu_1 \cdot \exp(-E_{sh}/k_B T)$ is the rate of the electron releasing out the first shallow center to the conduction band, and $p_2 = \nu_2 \cdot \exp(-E_{cap}/k_B T)$ is the rate of the thermally activated electron hopping over the barrier $E_{cap}$ and simultaneous capture of a conduction electron by the second shallow center \[1\]. Here $\nu_1$ and $\nu_2$ are the attempt frequencies: $\nu_1$ is the impurity vibration frequency and $\nu_2$ is the "configuration phonon mode" frequency of the impurity. The electron-impurity collision frequency $\nu_{coll}$ in our case is much higher than $\nu$: since the electron mobility at $T \leq 150$ K is determined mainly by the ionized impurity scattering \[1\], the first can be calculated as $\nu_{coll} \approx \epsilon/m^* \mu = 2.6 \times 10^{12}$ Hz, while for the last the upper estimate would be the Debye frequency $\nu_{Debye} \approx 6 \times 10^{12}$ Hz. Thus, at least several dozens of electron-impurity collisions occur during one cycle of the impurity "configuration phonon mode" and at the moment of the local lattice distortion near the In impurity there is always a conduction electron ready to be captured. Thus, for the activation energy of the kinetic coefficient $c$ one has

$$E_{ac} = E_{sh} + E_{cap},$$

and the capture barrier is equal to

$$E_{cap} = E_{ac} - E_{sh} = 0.12 \text{ eV} - 0.1 \text{ eV} = 0.02 \text{ eV}.$$  

For a higher temperature ($T = 150$ K) the shallow state decay curve is not fitted exactly by Eqn. \[16\]. The change of the decay kinetics type on increasing temperature may be explained by formation of a shallow states impurity band in CdF$_2$:In. The levels of the hydrogen-like states In$^{3+} + e_{hydr}$ may form such a band due to Coulomb interaction with statistically distributed F$^{-}$, In$^{3+}$ and In$^{1+}$ ions \[13\]. For increasing temperature, the higher levels of this band become populated, leading to an effective decrease of $E_{cap}$. At $T = 150$ K the levels up to $k_B T = 0.013 \text{ eV} \approx E_{cap}$ are populated and the barrier is eliminated.

The knowledge of the key parameters $E_{cap} = 0.02 \text{ eV}$, $E_{sh} = 0.1 \text{ eV}$ \[1\], $E_{deep} = 0.25 \text{ eV}$ \[1\], $E_{opt} = 1.9 \text{ eV}$ \[2\] (the optical ionization energy of the deep state) and $Q_0 - Q_1 = 1.84 \text{ Å}$ \[8\] (the difference of configuration coordinates of the deep and the shallow states) allows to define concretely the energy diagram (presented schematically in Fig. \[1\]), assuming $Q_1 = 0$ and a quadratic $Q$-dependence of the levels:

$$E_{cond}(Q) = a_1 Q^2,$$
$$E_{sh}(Q) = a_1 Q^2 - E_{sh},$$
$$E_{deep}(Q) = a_0 (Q - Q_0)^2 - E_{deep}.\tag{21}$$

Here the energies are measured in eV and the coordinates are in Angstroms. Then for $a_1$ and $a_0$ one has:

$$a_1 = \frac{E_{opt} - E_{deep}}{Q_0},$$
$$a_0 = \frac{E_{deep} E_{sh} + E_{cap}}{(Q_{cap} - Q_0)^2},$$
$$Q_{cap} = \sqrt{\frac{E_{cap}}{a_1}},\tag{22}$$

consequently, $a_1 = 0.487 \text{ eV/Å}^2$, $a_0 = 0.063 \text{ eV/Å}^2$, $Q_{cap} = 0.20 \text{ Å}$. The corresponding diagram is given in Fig. \[1\], which shows that the walls of the potential well of the shallow states are much steeper then those of the deep state. Therefore, according to the values of $a_1$ and $a_0$, the "return force" $F = -dE/dQ$ is 8 times larger for the shallow state. Besides, the barrier position $Q_{cap}$ is very close to the potential well minimum of the shallow state. It is interesting to note, that a similar calculation made for CdF$_2$ doped with Ga ($E_{sh} = 0.116 \text{ eV}$ \[22\], $E_{opt} = 3 \text{ eV}$, $E_{cap} = 1.12 \text{ eV}$ \[23\], $E_{deep} = 0.7 \text{ eV}$ and $Q_0 - Q_1 = 1.82 \text{ Å}$ \[9\]) gives the opposite picture of the potential curves (Fig. \[3\]). Now $a_1 = 0.694 \text{ eV/Å}^2$, $a_0 = 5.63 \text{ eV/Å}^2$, $Q_{cap} = 1.27 \text{ Å}$, i.e. the "return force" for the shallow state is 8 times weaker than one for the deep state, and the barrier position $Q_{cap}$ is far away from the shallow state potential well minimum. In addition, while the "return forces" for the shallow states of In and Ga in CdF$_2$ are close to each other, the "return force" for the deep state of Ga is 90 times larger then one for In. Now we can calculate the impurity "configuration phonon mode" frequencies of the deep, $\nu_{deep} = \frac{1}{2\pi} \sqrt{2a_0/M}$, and of the shallow, $\nu_{sh} = \frac{1}{2\pi} \sqrt{2a_1/M}$, states. Here $M$ is the
reduced mass of the impurity ion and of the surrounding ions, involved in the "configuration phonon modes". As the first approximation we have taken the values of the impurity ions masses for $M$ and obtained for the In impurity $\nu_{\text{deep}} = 5.18 \cdot 10^{11}$ Hz, $\nu_{\text{sh}} = 1.44 \cdot 10^{12}$ Hz and for the Ga impurity $\nu_{\text{deep}} = 6.28 \cdot 10^{12}$ Hz, $\nu_{\text{sh}} = 2.2 \cdot 10^{12}$ Hz.

We should note, that the data obtained for the values of kinetic coefficients are at some extent qualitative, because the assumption that the direct transitions between the deep levels and the conduction band is negligible is not strongly fulfilled in CdF$_2$:In at temperatures between 78 and 150 K. Nevertheless, the used ratios $N_{\text{sh}}/n_c$ calculated by the simple approximate Eqn. (20) for $T = 78$ K and $T = 110$ K coincided within a few tenth of a percent with the ratios obtained with the formulae of exact statistical calculation derived in [11]. Similar measurements and data analysis for the CdF$_2$:Ga crystals would give accurate results, since in this crystal $E_{\text{deep}} = 0.7$ eV [4], and the assumption mentioned above is fulfilled.

Unfortunately, the CdF$_2$:Ga samples reveal often some amount of the In impurities as well [24], influencing the experimental results, since there are actually two activation energies and two capture barriers in these samples.

CONCLUSIONS

In this paper we report on the low frequency conductivity measurements of semiconducting CdF$_2$:In crystals with metal-coating electrodes, producing Schottky barriers at the sample surface. The results allow to determine a whole lot of the material characteristics: the temperature dependence of the $dc$ conductivity, the activation energy of the impurity $E_a$, the total concentration of the active In ions $N$, the shallow donor concentration $N_{\text{sh}}$, the height of the capture barrier $E_{\text{cap}}$, and the values of the kinetic coefficients determining the rate of the thermally induced transitions between the deep and shallow states of In in the CdF$_2$ matrix. These measurements do not require ohmic contacts, preparation of which is necessary for standard $dc$ measurements and often is quite complicated and not always realizable task.

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