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Dark Conductivity in Semi-Insulating Crystals of CdTe:Sn

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Abstract—**We prepared semi-insulating CdTe for radiation detectors by isothermal annealing of single crystals grown by Bridgeman technique in a sealed quartz container filled with Sn vapor. The resistivity of CdTe:Sn samples thus obtained was of order of 10^{10} Ohm·cm at room temperature with electrons lifetime of 2×10^{-8} s, which is appropriate for the applications desired. Analysis of electric transport characteristics depending on temperature, sample thickness and voltage applied revealed the presence of traps with concentration of about (4-5)$\times10^{12}$ cm^{-3} with the corresponding energy level at 0.8 – 0.9 eV counted from the bottom of conduction band. The conductivity was determined by electron injection from electrodes in space charge limited current mode.**

Index Terms—Isothermal annealing, semi-insulating CdTe, space charge limited currents, traps saturation

I. INTRODUCTION

Cadmium telluride recently became a very popular semiconductor, first of all, due to its wide utilization in photovoltaic solar energy converters. This is a consequence of its direct band gap [1, 2] of 1.5 eV at room temperature, which is close to the optimal value for solar cells. However, this material has many other important applications, including radiation detectors. The use of CdTe for detection of ionizing radiation requires crystals with high specific resistivity ρ and low defects concentration. The defects are not desirable as they downgrade transport properties of the material and trap the carriers [3, 4]. To obtain the crystals with lowest concentration of non-controllable impurity defects, it is obligatory to grow the material from extra pure Cd and Te precursors. However, the specific resistivity of the samples obtained using such an approach is usually lower than 10^6 Ohm·cm at 300 K, which is insufficient to provide low values of dark currents and the optimal signal-to-noise ratio. The resistivity ρ can be increased by compensating material with the proper impurities (Cl, Cu, In, Ge, Sn, etc.) that are added during crystal preparation process [3, 5]. These impurities form local levels in the band gap, the parameters of which usually can be accessed from the temperature-dependant measurements of dark conductivity σ.

For highly-compensated wide-band compounds, especially when several types of electrically active centers are present, the interpretation of $\sigma(T)$ plots becomes complicated due to multiple interactions between the impurity levels [6]. In such case it will be inappropriate to define the thermal activation energy E_a directly from $\sigma(T)$ measurements, because the obtained values may not correspond to really existing levels in the band gap. To check the relevancy of analysis, it is imperative to use additional methods, one of which focuses on measurements of space charge limited conduction (SCLC) [7, 8]. Analysis of current-voltage curves (CVC) under SCLC provides information on local centers defining dark conductivity of high-resistive

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semiconductors. The present paper illustrates an example of such approach used for study of semi-insulating CdTe doped with Sn impurity from the vapor phase.

II. SAMPLE PREPARATION AND EXPERIMENTAL METHODOLOGY

The substrates with dimensions 4×4×1 mm^3 ($L\times L\times t$) were cut from the bulk crystal grown by Bridgeman method from the melt of stoichiometric composition. Under room temperatures the substrates featured conductivity $\sigma_n \approx 10^{-2}$ Ohm^{-1}·cm^{-1}, defined by intrinsic defect centers. The doping of the samples with Sn was carried out by isothermal annealing at 800 - 900 ^{o}C in a sealed quartz container under the pressure of 10^{-4} Torr. The substrate and Sn impurity were put in the opposite ends of annealing container. The conditions of annealing were chosen so that Sn impurity will diffuse over the thickness of the substrate. The fact of complete diffusion is proved by measurements of specific resistivity ρ_n, which is independent on substrate thickness t. To perform such measurements, we manufactured a batch of samples that were reduced in thickness by etching in bromine-methanol solution. Upon reaching the required value of t, the samples were carefully and thoroughly rinsed in pure methanol. To perform the measurements of resistivity, the ohmic contacts were deposited on the opposite large faces of the sample by sputtering indium, so that external voltage is applied along the sample thickness. This technology allows achievement depreciably low current loss that is confirmed by linearity of the measured resistivity curve (obtained by normalizing resistivity values over contact area). The reduction of current loss is important for high-resistive semiconductors such as CdTe:Sn, the specific resistivity of which is about 10^{10} Ohm·cm at 300 K [9]. Referring to the energy band structure of the material obtained, it was shown in [10] that the thermal treatment used (vapor pressure, temperature and time of treatment) does not affect it, so the band gap at 300 K is 1.5 eV, same as in CdTe undoped crystals.

The CVC were obtained in DC mode, with current variation in the ranges 10^{-12}-10^{-2} A. To measure small currents we used a special current/voltage convertor developed by the authors (VPM & VMS). The measurements were performed in temperature ranges 290-350K for several samples of different thickness. All the samples were formed on the base of substrates cut from the same CdTe:Sn wafer, which enabled us to focus namely on $I(t)$ dependence by keeping all other material parameters constant (*e.g.* type and concentration of deep level impurity, degree of compensation, mobility of the carriers and so on).

III. RESULTS AND DISCUSSION

We report that all experimental CVC obeyed the generalized expression

$$I \sim U^n, \qquad (1)$$

which is characteristic for the currents formed by injection of the carriers into an isolating material with two kinds of traps [8]. By plotting $I(U)$ dependence in a double logarithmic scale, one can distinguish three sections characterized with different slopes and values of the exponent n (Fig. 1). The first section corresponds to low bias and obeys the Ohms law ($I \sim U$) with n=1. Upon reaching the voltage U_x, the character of the curve changes to quadratic dependence ($I \sim U^2$), which corresponds to a case when the current is limited to space charge area under the presence of traps [11]. The third section displays fast increase of the current ($I \sim U^4$) and is observable under high bias exceeding the threshold value of U_{ST}, which corresponds to saturation of the traps.

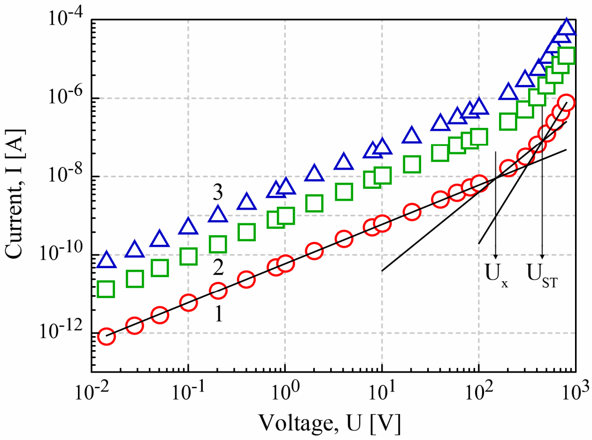

Fig. 1. Current-voltage curves for the In-CdTe:Sn-In structure with substrate thickness 350 μm, measured under different temperatures:1) 293K, 2) 323K, 3) 350K.

As one can see from Fig. 1, the threshold voltage U_x at which the CVC change from linear to quadratic remains the same, which suggests that CdTe:Sn samples are weakly compensated [12]. The voltage U_x can be calculated using parameters of the material:

$$U_x = \frac{e n_0 t^2}{\varepsilon \Theta}, \tag{2}$$

introducing the capture factor of a trap characterized with energy level E_t:

$$\Theta = \frac{N_c}{g N_t} \exp\left(-{E_t}/{kT}\right). \tag{3}$$

The concentration of traps is given by N_t, g corresponds to the degeneration factor, ε is material's dielectric constant, and N_c is effective density of states in the conduction band [8]. All the samples featured electronic conductivity [9], so that the latter expression is useful for finding concentration of electrons in weakly-compensated semiconductor [5, 6]:

$$n_0 = N_c \frac{N_d - N_a}{N_t} \exp\left(-{E_t}/{kT}\right), \tag{4}$$

using the donor and acceptor concentrations N_d and N_a. By substituting (3) and (4) into Eq. (2) one can show that threshold bias U_x is indeed independent on the temperature T, but it varies with the sample thickness t. The experimental data shown in Fig. 2 corroborate this, revealing that dependence $U_x(t)$, plotted in the coordinates (U_x, t^2) is essentially linear.

The voltage defining saturation of the traps depends of sample thickness [11, 12]:

$$U_{\mathrm{ST}} = \frac{1}{2} g N_t \frac{t^2}{\varepsilon}. \tag{5}$$

As one can see from Fig. 2, the experimental data show the same dependence. The formula (5) provides an easy way to calculate trap concentration N_t when the other parameters entering the equation are known. Using the experimental values, we obtained the concentration of traps for the material studied as $N_t \approx (4\text{-}5) \times 10^{12}\,\mathrm{cm}^{-3}$.

The energy depth of the trap level can be found from the expression relating resistivity ρ_n, carrier concentration n_0 and mobility μ_n:

$$\rho_n = (e \mu_n n_0)^{-1}. \tag{6}$$

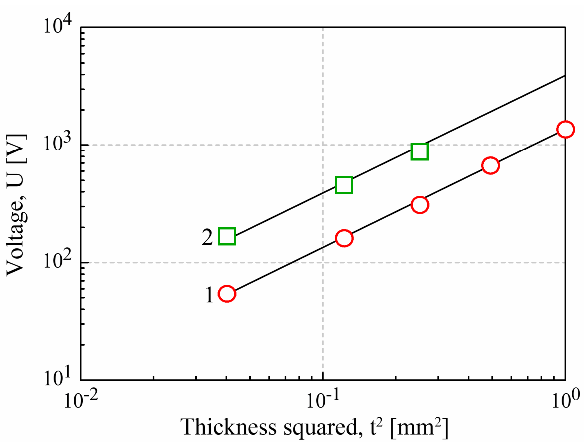

Fig. 2. Dependence of threshold voltage U_x (curve 1) and U_{ST} (curve 2) on sample thickness t of In-CdTe:Sn-In structure.

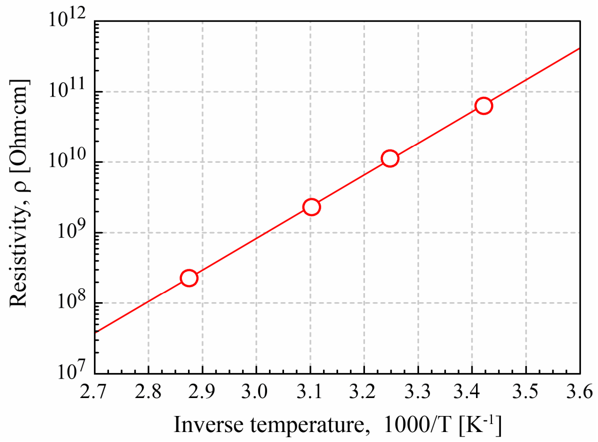

Fig. 3. Temperature dependence of resistivity ρ_n measured for the linear branch of CVC under the bias of 1 V.

As one can see from Fig. 3, the temperature dependence of specific resistivity in coordinates ($\ln\rho_n$, $10^3/T$) is linear, suggesting the plot in normal coordinates will be exponential. Such dependence in Eq. (6) can be provided only by $n_o(T)$, because mobility $\mu_n(T)$ remains constant in the temperature range studied [9]. Returning to (4) and accounting for a weak dependence $N_c \sim T^{3/2}$, one will find that activation energy E_t defining the slope of $\rho_n(T)$ essentially depends on $n_o(T)$.

The calculations based on our experimental data yield E_t to be approximately 0.8 eV in agreement with results published in [9], which is close to the depth of tin donor level $E_{Sn} = E_c - 0.8$ eV in cadmium telluride [13, 14].

It could be assumed that Sn atoms diffuse through CdTe as neutral species. Having ionic radius of 1.4 Å larger than that of Cd, they provoke formation of Cd vacancies acting as shallow acceptors in CdTe (see [15]), being thus responsible for material compensation. Some of Sn ions substitute Cd ions (Sn^{2+} ion has radius of 1.1 Å, practically the same as Cd^{2+}) creating deep donor states with their donor character reported in ref. [13]. Comparing the results presented in Fig. 3 with the expression (4), we find the ratio of $(N_d - N_a)/N_t$ is approximately equal to 10^4 that means that $N_d - N_a$ will have an order of 10^{16} cm^{-3}. In other words, all initial shallow donors in non-compensated material with concentration of about 10^{15} cm^{-3}, have lost their charge due to large amount of acceptors generated. Under these circumstances, the conductivity of the material is determined by deep Sn donors. Only a small fraction thereof – around 10^{-4} – is positively charged and acting as traps for electrons denoted here as N_t.

If the assumption about the acceptor nature of this deep level is made, one will be expecting to find the sample with far larger degree of compensation, leading to variation of threshold voltage U_x with temperature. Such behavior is not observed in the experiment, so that it can be safely concluded that the deep level in question has donor nature in agreement with [13]; this is also confirmed by estimation of capture cross section below.

Upon saturation of these traps, the CVC changes its character to $I \sim U^4$ after exceeding the bias U_{ST}. When the traps are not saturated, the compensation degree will vary depending on the quantity of trapped carriers, resulting in different activation energy for the three sections of CVC mentioned above. Such behavior is clearly seen from our experimental data (Fig. 4) as slight decrease of CVC slope with higher power *n*.

The transition between the CVC sections corresponding to ohmic into square-power dependence occurs when carriers lifetime τ_n matches their expected travel time $\tau_L = t^2/\mu_n U_x$. The threshold voltage defining such equality is

$$U_x = \frac{t^2}{\mu_n \tau_n}. \quad (7)$$

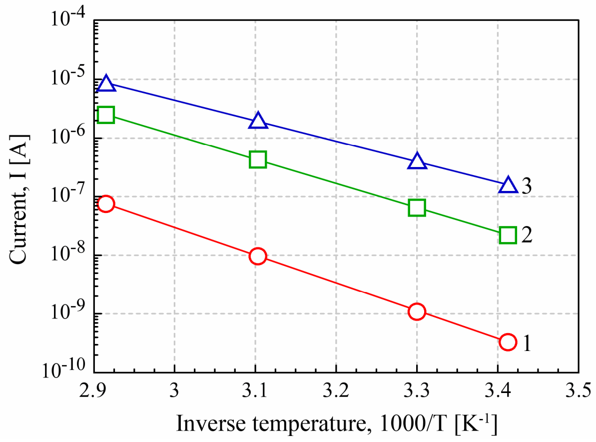

Fig. 4. Temperature dependence of dark current under variations of applied bias *U*: 1) 5 V (*n*=1), 2) 200 V (*n*=2), and 3) 500 V (*n*=4).

The Eq. (7) provides a way to find τ_n from the measured threshold U_x, sample thickness *t* and carrier mobility μ_n, yielding the value $\tau_n = 2\times10^{-8}$ s. On the other hand, carriers' lifetime is connected with effective trap cross-section S_n and thermal velocity of the carriers v_{nt} in the following way:

$$\tau_n^{-1} = S_n \cdot v_{nt} \cdot N_t\,. \quad (8)$$

Using this formula, we estimate cross-section S_n to be 10^{-12} cm^2. Such a large value is characteristic of electron's capture by an attractive center (ionized donor, as it was stated above).

All analysis up to this point was performed neglecting strong field effects. However, if the applied bias produces the field *F* sufficiently high, it may influence mobility and velocity of the carriers, varying effective trap cross-section S_n as well. In the system studied, for the case of small *t* and large *U* the field *F* may exceed the value of 10^5 V/cm, requiring consideration of high field effects. Under these circumstances, the equation governing CVC will be [16, 17]:

$$I = Kt^{-(\alpha_n+3/2)}U^{[\alpha_n+1/2]}\,. \quad (9)$$

The latter formula was obtained assuming that high field modifies effective trap cross-section $S_n \sim F^{-\alpha_n}$, yet carrier mobility remains independent on both *T* and *F* (considering μ_n independent on the applied field, the

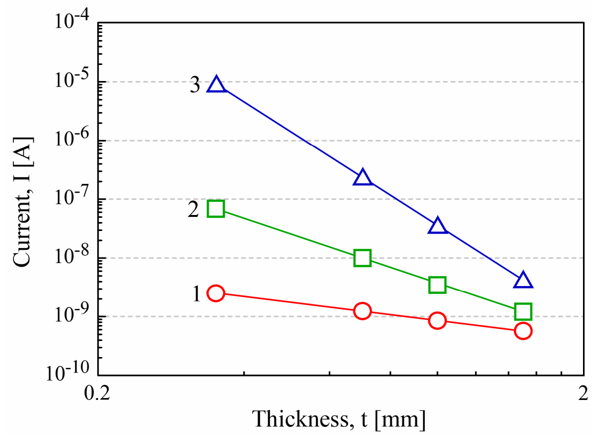

Fig. 5. Dependence of dark current I on the sample thickness t for a constant bias fixed at the different sections of CVC: 1) U=40 V, 2) U=150 V and 3) U=1500 V.

quantity U_x is expected to be proportional to t^2 [18], which matches our experimental evidence (Fig. 2)). As one can see from (9), for the constant U and T the scaling coefficient for the current is $t^{-(\alpha_n+3/2)}$; plotting this curve in double logarithmic scale, one will find that the slope of ln I(ln t) will scale as (α_n+3/2). Exactly this behavior is seen in our experiments for constant temperature and varied bias; the measurements were performed for CVC sections characterized with the powers n=1, 2 and 4 (Fig. 5).

All curves shown in Fig. 5 are linear, featuring the slopes of 1.1, 3 and 5.4, which yields the values of α_n as -0.4, 1.5 and 3.9, respectively. Substituting the obtained values into Eq. (9), we calculated the powers for U^n dependence as 0.1, 2.0, and 4.4 that reasonably agree with the experimental values of n, except for the low-field region; most probably, the assumed field-dependence of capture cross-section is not manifested yet at these low field values.

At the same time, strong electric field is not expected to modify considerably the energy position of deep impurity level. This suggestion is proved by Fig. 4 illustrating the dependence of ln I as a function 10^3/T measured under fixed bias at different segments of the CVC. The slopes of resulting curves vary from 0.76 to 0.9 eV, which generally fits the energy position of deep tin level E_{Sn}. The dispersion observed is due to variation of trap's occupation, as stated above.

IV. CONCLUSIONS

We report that dark current in In-CdTe:Sn-In structures is controlled by electron injection into semi-insulating semiconductor with deep traps. The current-voltage characteristics observed are in a good agreement with theory of space charge limited currents in weakly-compensated material, with account of the strong electric field influence on the effective trap's cross-section.

REFERENCES

[1] Mathew X. Band gap of CdTe thin films – The dependence on temperature. *J. Mater. Sci. Lett.* 21 (2001) 529-0531.

[2] Mathew X., Sebastian P.J. Optical properties of electrodeposited CdTe thin films. *Solar Energy Mater. and Solar Cells.* **5**9 (1999) 85-98.

[3] Lutz G. *Semiconductor radiation detectors: device physics*. Berlin: Springer-Verlag, 2007.

[4] Spieder H. *Semiconductor detector systems.* Oxford University Press, 2005.

[5] Bhattacharya P. *Semiconductor optoelectronic devices.* 2nd ed. Prentice-Hall, Inc., USA, 1997.

[6] Balkanski M., Wallis R.F. *Semiconductor physics and applications.* Oxford University Press, 2000.

[7] Roberts G.G. Smidlin F.W. Study of localized levels in semi-insulators by combined measurements of thermally activated ohmic and space-charge-limited conduction. *Phys. Rev.* 180 (1969) 785-794.

[8] Grinberg A.A., Luryi S., Pinto M.R., Schryer N.L. *Space Charge Limited Current in a film.* IEEE Trans. Electron. Dev. 36 (1989) 1162-1170

[9] Makhnii V.P. Semi-insulating layers of cadmium telluride. *Technical Physics* 50 (2005) 1513-1514

[10] Makhnii V.P., Kosolovskiy V.V., Slyotov M.M., Skrypnik M.V., Slyotov A.M. The nature of edge luminescence of CdTe:Mg diffusion layers. *Semiconductors* 44 (2010) 1167-1169.

[11] Lampert M.A., Mark P. *Current Injection in solids.* Academic Press Inc, 1970.

[12] Tutov E. A., Tuma F. A. and Kukuev V. I. Mechanisms of current transferring in Al/ZnO/Si structure, *Condens. Environ. Interphas. Bound.*, 8 (2006) 334-340.

[13] Brunthaler G., Jantsch W., Kaufman U., Schneider

J. Electron-spin-resonance analysis of the deep donors lead, tin, and germanium in CdTe. *Phys. Rev. B.* 31 (1985) 1219-1243.

[14] Franc J., Fiederle M., Babentsov V., Faluler A., Benz K.W., James R. Defect structure of Sn-doped CdTe. *J. Electron. Mater*. 32 (2003) 773-777.

[15] Berding M.A. Native defects in CdTe. *Phys. Rev. B.* 60 (1999) 8943-8950.

[16] Milnes A.G. *Deep impurities in semiconductors*. Wiley, 1973.

[17] Milnes A.G., Miner C.J. *Semi-insulating III-V materials.* Science, Toronto, 1990.

[18] Ashley K.L., Milnes, A.G. Double injection in deep lying impurity semiconductors. *Journal of Applied Physics* 35 (1964) 369.

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