SPACE CHARGE LIMITED CURRENTS IN HIGH RESISTIVITY CdTe CRYSTALS

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DC-measurements of SCLC of high resistivity Cl-compensated p-type crystals of CdTe have been performed in the temperature range of 230—300 K. The evaluation of voltage-current characteristics by means of a simple model with discrete trap levels led to activation energies of approx. 0·65 and 0·4 eV above the valence band and trap concentrations of the order 10^{11} to 10^{12} cm^{-3}.

1. INTRODUCTION

Cadmium telluride attracts increasing interest due to its application in γ- and X-ray detectors. Its energy resolving power, still inferior to Ge- and Si-detectors, is being impaired by difficult control of crystal perfection. The latest developments of travelling heater techniques and compensation of native defects by halogen doping [1] seem to be the most promising ways of improvement. Identification of localized levels in this material is the aim of intense investigation by different methods. The present paper shall demonstrate the feasibility of space charge limited currents (SCLC) for the study of deep trap levels with low concentrations which are not easily detected by other methods.

Only few measurements of SCLC on CdTe-single crystals have been reported hitherto. Eberle [2] found a quasi-continuous distribution of hole traps between E_V + (0·2 to 0·4) eV on pure and antimony doped crystals of p-type grown by directional freezing. Canali et al. [3] published pulsed and DC measurements of SCLC resulting in an electron trap level 0·65 eV below the conduction band.

2. A SIMPLE MODEL OF SCLC

a) Shallow traps

The well known model of SCLC in a trap free insulator proposed by Mott and Gurney can be extended to the case of crystal with shallow traps by introducing the effective mobility $\mu^* = \mu\Theta$. Here Θ denotes a reducing factor given by the ratio of free to free plus trapped carrier concentrations and μ the true mobility as measured by means of Hall effect.

With a voltage U across a sample of thickness L, permittivity ε, the injection current density $j = J/A$ is given by (1) (see e.g. [4])

$$j = \frac{9}{8}\Theta\mu\varepsilon\frac{U^2}{L^3}. \tag{1}$$

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The trap free (TF) case corresponds to (1) with $\Theta = 1$. The definition of Θ is:

$$\Theta = \frac{p}{p + p_t}\,. \tag{2}$$

We shall refer to p-type crystals. The energy of holes will be taken as positive from the top of the valence band downwards, so that the levels in the energy gap will have negative energies. This notation will preserve the same signs and relations as in the n-type crystal with injection of electrons.

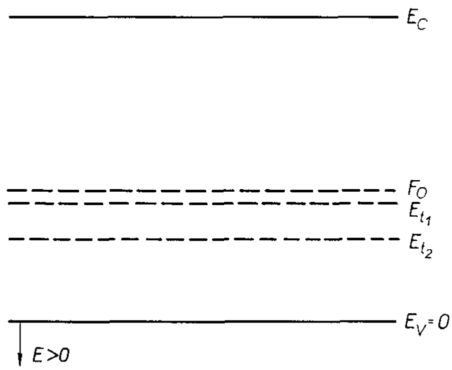

Fig. 1. Energy band scheme of a semiinsulator with two shallow hole trap levels.

Supposing quasi-equilibrium between traps and valence band during injection, we can define the quasi-Fermi level F of holes by

$$p = P_V \exp\left(\frac{F}{kT}\right) \tag{3}$$

where p is the concentration of free holes, P_V the effective density of states in the V-band. In thermal equilibrium F becomes F_0 (Fig. 1).

If trapping occurs on a discrete level E_t with trap concentration P_t and spin weight factor g,

$$\Theta = \left[1 + \frac{P_t}{P_V} \cdot \frac{1}{\exp\left(\frac{F}{kT}\right) + \frac{1}{g}\exp\left(\frac{E_t}{kT}\right)}\right]^{-1}. \tag{4}$$

In a special case, when $F < E_t - kT$ ("shallow trap") Θ is approx. proportional to $\exp(E_t/kT)$.

The population of traps increases with the voltage. At a threshold voltage, trap filled limit, U_{TFL}, the traps are completely filled up, the current rises abruptly and theoretically should reach the value of SCLC of the trap free material according to (1) with $\Theta = 1$. The break in the characteristic occurs approx. at

$$U_{TFL} = \frac{eL^2 P_t}{2\varepsilon}\,. \tag{5}$$

Rarely the TF-law is attained by DC-measurements. A trivial reason might be overheating of the sample. Alternatively, prior to reaching the TF-state, another group of traps may become dominant, preventing thus the carriers injected at $U > U_{\mathrm{TFL}}$ to move freely. This can occur, if the second trap is shallower than the first one, $E_{t_2} > E_{t_1}$ and has a higher concentration, $P_{t_2} > P_{t_1}$.

Let us now suppose, that we have two such discrete traps. The first one becomes filled up at U_1, with corresponding current j_1. At a voltage $U = U_1 + \Delta U$ the increment Δj above the current j_1 can be expressed approximately by $j - j_1 \equiv \Delta j_1 = (e\mu_p/L)(\Delta pU + p(U_1)\,\Delta U)$.

Because the first term increases rapidly at $U > U_1$, the second term becomes negligible and we have

$$\Delta j_1 \simeq \frac{e\mu_p}{L}\,\Delta pU\,.$$

To estimate Δp we can refer to the condenser model [4], according to which

$$\Delta p \simeq \frac{\varepsilon}{eL^2}(U - U_1)\,.$$

With this, we obtain

$$\Delta j_1 = \frac{e\mu_p\varepsilon U^2}{L^3}\left(1 - \frac{U_1}{U}\right). \tag{6}$$

Neglecting a factor of the order of unity, the first factor on the righthand side of (6) is the SCLC in the TF-state. The Eq. (6) describes thus the transition to the TF-state in the presence of one trap level only. If there is the second shallow trap level, we can assume that the current Δj_1 is reduced by a factor Θ_2 defined by (4) with the appropriate parameters E_{t_2}, P_{t_2}, g_2 and F given by the instantaneous concentration of holes, p.

$$\Delta j_2 = \frac{e\Theta_2\mu_p\varepsilon U^2}{L^3}\left(1 - \frac{U_1}{U}\right). \tag{7}$$

Measuring Δj_2 at different temperatures, we can evaluate E_{t_2} if $E_{t_2} > F + kT$ and subsequently from the magnitude of Θ_2, the concentration P_{t2}.

This procedure can yield only rough estimates of trap parameters not only on the reason of oversimplification, but also due to inaccurate determination of U_1 and the influence of gradual filling of the second species of traps. The latter effect causes a steeper increase of Δj_2 at higher voltages than predicted by (7).

This state of affairs exists only when the concentration P_{t_2} is not much larger than P_{t_1}. If this is not true, the second trap can interfere at voltages below U_1 with different weight depending on temperature. It is worthwhile to mention that the combined action of two shallow traps leads to an overall factor Θ, such that

$$\Theta^{-1} = \Theta_1^{-1} + \Theta_2^{-1}\,.$$

Evidently, the trap with lower Θ_i dominates. Commonly, the deeper trap dominates at lower temperatures and as Θ_1 rises more steeply than Θ_2, the second trap may become dominant before the first trap becomes filled up. If P_{t_1} and P_{t_2} are comparable, the deeper trap E_{t_1} may dominate up to U_1 in the whole temperature range.

b) Deep traps

In the case of a single "deep trap", the equilibrium Fermi level F_0 lies in our diagram below the trap level, $F_0 > E_t + kT$, the majority of traps are filled in equilibrium. The number of free places $n_{t,0}$ is approximately

$$n_{t,0} \simeq \frac{P_t}{g} \exp\left(\frac{E_t - F_0}{kT}\right).$$

The characteristic lacks the quadratic part, the ohmic branch is succeeded by a rapid rise of current at a voltage U_{TFL}, when the rest of the traps becomes filled. It holds in analogy with (5)

$$n_{t,0} = \frac{2\varepsilon U_{TFL}}{eL^2}.$$

Here again, the second shallower trap may reduce the current in the region near U_{TFL} and above.

The terms "deep" and "shallow" traps do not have an absolute meaning. A "shallow" trap $(E_t > F_0 + kT)$ may become "deep" simply adding more shallow acceptors by doping. The electrons from the traps move into the acceptors, the traps become almost filled with holes; Fermi level F_0 falls down and the trap level becomes "deep" by definition $(E_t < F_0 - kT)$.

3. EXPERIMENTAL

The samples were cut from p-type crystals of CdTe grown by a modified travelling heater method [1]. The high resistivity was obtained by doping with chlorine. They were sliced or cleaved, lapped and mechanically polished. The sandwich electrodes were deposited by chemical precipitation of platinum. The lower electrode covered the whole face of the platelet, the upper one was a circle of smaller diameter to reduce the leakage currents.

Current-voltage characteristics were measured by a standard DC technique. The temperature in the cryostat could be stabilized electronically in the range between 80 and 300 K with an accuracy of approx. 0·3 K. Before each series of measurements the short circuited sample was heated for 30 min. at a temperature of 350 K and slowly cooled down to the measuring temperature. The characteristics had to be measured point by point at intervals up to 30 min in order to reach the steady state, especially at low temperatures.

4. RESULTS

Typical I – V characteristics of samples with the highest resistivity (approx. $10^9\ \Omega$ cm) are shown in Fig. 2. The curves display a short linear branch followed by a rapid rise, which is especially pronounced at lower temperatures. Then the curve becomes less steep and shows a voltage dependence with power 3 to 4, which is slightly temperature dependent.

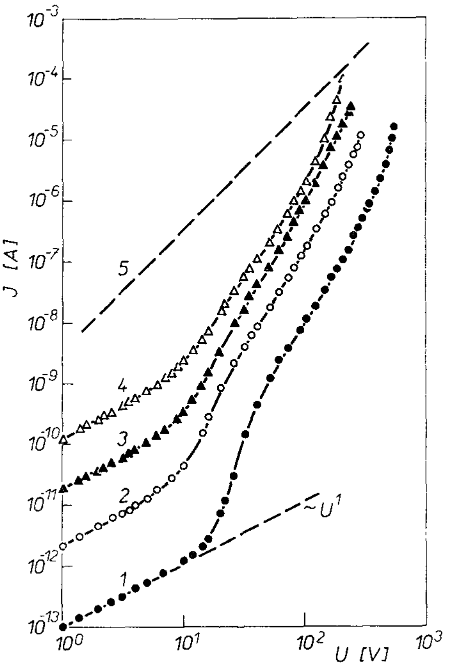

Fig. 2. V-A characteristics of the sample 29/3 with $L = 0{\cdot}852$ mm, $A = 2{\cdot}4\ \text{mm}^2$. Curve 1 at 233 K, 2 at 253 K, 3 at 273 K, 4 at 293 K. Curve 5 is the idealized TF case.

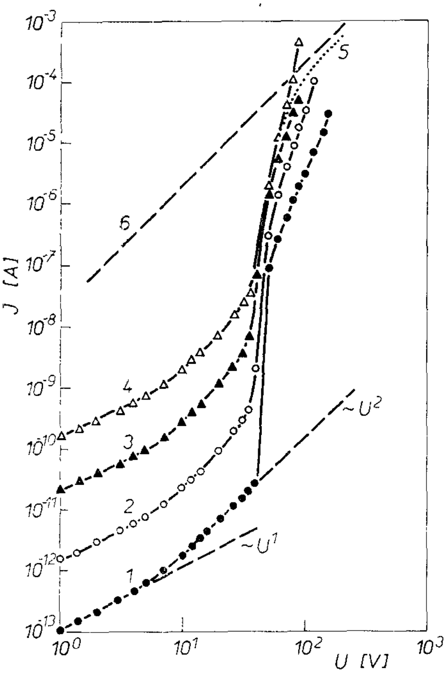

Fig. 3. V-A characteristics of the sample 29/2 with $L = 0{\cdot}577$ mm, $A = 4{\cdot}2\ \text{mm}^2$. Curve 1 at 233 K, 2 at 253 K, 3 at 273 K, 4 at 293 K. Curve 5 is theoretical according to (6), curve 6 is the idealized TF state.

The temperature dependence of the voltage U_x which is the end of the linear part is weak. From this it can be concluded that ohmic part and trap filling region have the same activation energy. That means that the trap involved must lie close to the equilibrium Fermi level F_0, which was estimated to be $-0{\cdot}69$ eV. It is observed that this level is dominant at low temperatures. At higher temperatures the filling of a shallower trap becomes significant.

Figure 3 shows an other type of I – V characteristics, which occured less frequently with similar samples. The main feature is the presence of a quadratic part which can be ascribed to a shallow trap at E_{t_1}. After a steep rise corresponding to the filling of this trap, the curve bends off still far below the expected quadratic TF curve. We suppose that this deviation is caused by the presence of another trap level $E_{t_2} > E_{t_1}$. The filling of the shallower trap supposedly should lead to the TF-state.

To evaluate the I−V characteristics of the type of Fig. 3 we deduce at first from the conductivity in the linear region the equilibrium Fermi level assuming $\mu_p = 80\ \mathrm{cm^2\,s^{-1}\,V^{-1}}$, $\varepsilon = 10^{-12}\ \mathrm{F\,cm^{-1}}$ and $P_V = 2{\cdot}5 \times 10^{19}\ \mathrm{cm^{-3}}$. In the first approximation we take the product $P_V\mu_p$ as temperature independent in the range between 230 and 300 K. With this, $F_0 = -0{\cdot}71$ eV.

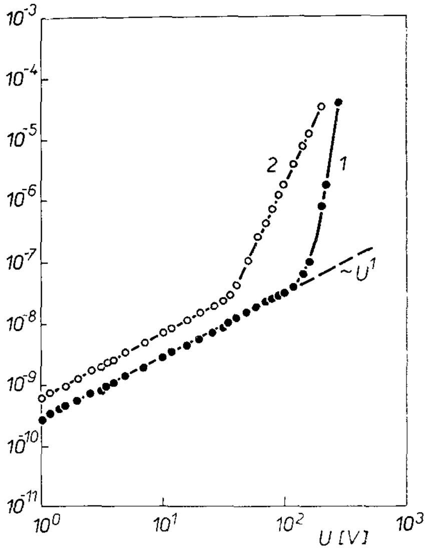

Fig. 4. V-A characteristics of the sample 35/2 with $L_1 = 0{\cdot}855$ (curve 1) and $L_2 = 0{\cdot}386$ mm (curve 2) at 273 K. $A = 6{\cdot}2\ \mathrm{mm}^2$.

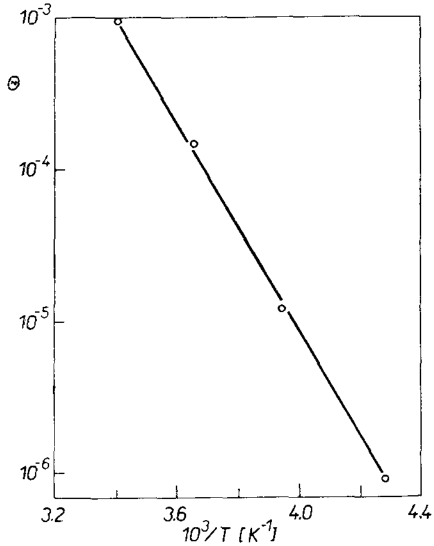

Fig. 5. The log Θ_1 vs. $1/T$ — plot for sample 29/2.

The activation energy of the first trap is evaluated from the slope of the curve log Θ_1 vers. $1/T$ as $|E_{t_1}| = 0{\cdot}64$ eV (Fig. 5). The concentration P_{t_1} can be obtained from the magnitude of Θ_1 and from $U_{\mathrm{TFL}\ 1}$ respectively. Both ways led to the identical value of $P_{t_1} = 1{\cdot}9 \times 10^{11}\ \mathrm{cm^{-3}}$. This agreement supports the simple model with discrete trap levels. Comparing the measured current with the expression (6) we obtain Θ_2 at −40 °C (Fig. 3). From the difference $U_{\mathrm{TFL}\ 2} - U_{\mathrm{TFL}\ 1}$ we estimate roughly $P_{t_2} \simeq 10^{11}\ \mathrm{cm^{-3}}$ and combining with Θ_2 we obtain $|E_{t_2}| = 0{\cdot}45$ eV. From the temperature dependence of Θ_2 we get $|E_{t_2}| = 0{\cdot}41$ eV in sufficiently good agreement. Due to uncertainty in determination of $U_{\mathrm{TFL}\ 2}$ and Θ_2 these values must be regarded as rough estimates.

In samples with lower resistivity ($\varrho \simeq 10^7\ \Omega\,\mathrm{cm}$) at room temperature the linear part of the I−V characteristic extends up to approx. 100 V (with $L = 0{\cdot}8$ mm) and merges into a steep rise (Fig. 4). Supposing that this behaviour is due to a discrete deep trap, we tested the quadratic dependence of U_{TFL} on thickness and obtained $U_{TFL} = 160$ V for $L = 855$ μm and $U'_{TFL} = 40$ V for $L' = 386$ μm, giving

$$\frac{L^2}{L'^2} = 4{\cdot}9 \quad \text{and} \quad \frac{U_{TFL}}{U'_{TFL}} = 4{\cdot}0\,.$$

Regarding the uncertainity in electrode geometry, this agreement is satisfactory.

In the high resistivity samples the thickness tests failed. With some samples the shape of the I – V curves changed with different thicknesses from the type of Fig. 3 to the type of Fig. 4. Probably, F_0 lies in these samples very close to E_{t_1}, so that even a small local variation of F_0 can greatly influence the shape of the curves. The presence of such inhomogeneities can be, too, the cause of the observed fact that in some samples the shape of characteristics depends on the polarity of electrodes.

In some samples the measured curve at high currents extends at higher temperature beyond the ideal trap free SCLC curve. The reasons for this can be different: heating by Joule heat, uncertainty in the parameters used for the calculation and in the geometry of the electrodes, injection of electrons from the cathode or field enhanced reexcitation of holes from traps (Frenkel-Poole effect).

5. DISCUSSION

The nature of traps was tested in the same way as described by CANALI et al. [3]. Several samples were provided with sandwich electrodes of unequal areas. The current was always greater, when the larger electrode was positive and this assymetry increased with increasing injection level. This indicates that the injected carriers are holes and, consequently, the observed activation energies of approx. 0·4 eV and 0·65 eV denote the distances of hole trap levels from the valence band.

The origin of the observed traps cannot be deduced from our measurements. The level at 0·4 eV above the valence band falls into an energy interval 0·3 ./. 0·5 eV, where a great number of localized levels were determined by different methods such as conductivity, photoluminescence, photoconductivity, thermally stimulated currents, SCLC etc. Previously, these levels were often ascribed to impurities such as Cu, Ag, Au, Sb, P. At present it is generally assumed that simple impurity defects form hydrogen-like shallow acceptors or donors, whereas native defects and their complexes with impurities in different charge states are responsible for deeper levels. BRYANT and WEBSTER [5] report an acceptor level at 0·46 eV ascribed to interstitial Te or Te-vacancy from luminescence measurements. HÖSCHL et al. [1] found three acceptor levels from Hall-efect measurements at 0·15 eV, 0·5 eV and 0·9 eV ascribed to V'_{Cd}, $(V_{Cd}Cl_{Te})'$ and V''_{Cd} respectively. VUL et al. [6] found from electroabsorption an acceptor level at 0·4 eV attributed to a single ionized vacancy V'_{Cd}.

In our material we assume the complexes of chlorine with native defects to be dominant. Taking the basic energy of a single vacancy V'_{Cd} as a well established level at

0·15 eV above the valence band, the shift of energy due to association with substitutional chlorine can be estimated [7]. For the first two levels of a complex $(V_{Cd}Cl_{Te})'$ in the nearest and next-to-nearest neighbour configurations, the energies from the top of the valence band are approx. 0·6 and 0·4 eV respectively. Whether these levels are identical with our observed traps must be confirmed by more measurements and calculations. Recently Mousa [8] performed careful measurements on the same material as described in the present paper separating the surface and bulk conductivity and found an acceptor level at 0·57 eV, which might be identical with our trap near 0·6 eV. A more detailed analysis of the VA characteristics and extension of measurements to lower temperatures are in progress.

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