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CARRIER TRANSPORT AND TRAPPING PROCESS IN HIGH-RESISTIVITY CdTe GROWN BY A MODIFIED THM

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Résumé. — On a étudié les propriétés de piégeage et de dépiégeage des porteurs dans le tellure de cadmium par la méthode du temps de vol. Les cristaux semi-isolants de type p étaient préparés par une méthode THM en solvant avec adjonction d'un réservoir de cadmium. On a observé, pour les électrons un centre de piégeage situé à 0,05 eV au-dessous de la bande de conduction et pour les trous, un niveau localisé à 0,14 eV environ au-dessus de la bande de valence. Ce résultat a été obtenu en supposant la présence d'un seul niveau respectivement pour les électrons et les trous. L'influence de la pression de cadmium sur les propriétés de piégeage des matériaux sera discutée. Les meilleurs valeurs du temps de piégeage que nous ayons obtenues sont de 360 ns pour les électrons et 1,0 μ s pour les trous pour une suppression de cadmium de 5×10^{-3} atm environ.

Abstract. — Carrier trapping and detrapping processes in high-resistivity p-type crystals grown by a travelling heater method which is modified to provide a Cd reservoir (modified THM) have been investigated using a time-of-flight method. It is found that the trapping centers are located at about 0.05 eV below the conduction band for electrons and at about 0.14 eV above the valence band for holes, respectively. The carrier transport properties have been simply analyzed by assuming the presence of only one type trap level for electrons and holes, respectively. The influence of the Cd overpressure on carrier trapping and detrapping is discussed. The best values of the observed trapping time are 360 ns for electrons and 1.0 μ s for holes in the crystals grown under Cd over-pressures of about 5×10^{-3} atm.

1. Introduction. — Recent results of studies on carrier transport in high-purity CdTe crystals have indicated that the presence of certain trapping centers is a major factor limiting the performance of radiation detectors. Mayer *et al.* [1] by the time of flight method using α -particle irradiation have shown that a deep electron trap lies at about 0.6 eV below the conduction band in semi-insulating crystals grown by the Bridgman method. Ottaviani *et al.* [2] and Martin *et al.* [3] have investigated the trapping and detrapping processes both for electrons and holes in crystals grown by the regular THM method ; employing the time-of-flight method with pulsed electron bombardment. Recently, Martin *et al.* [4] have identified the existence of shallow and deep trapping levels for both electrons and holes using thermally stimulated current measurements.

This paper discusses trapping and detrapping effects in high-resistivity CdTe single crystals [5, 6] grown by a travelling heater method using a controlled Cd overpressure. Injection of carriers in the time-of-flight method is achieved by a short pulse of a N₂ laser. It appears that the crystals grown by this modified THM yield better properties in comparison with undoped or Cl-doped ones prepared by the usual THM [7]. In the crystals grown under a low Cd over-pressure ($< 10^{-3}$ atm) in the modified THM, detrapping effects at room temperature for electrons are not observed. In the case of holes, the detrapping effects are due to the thermal release of carriers trapped on a level

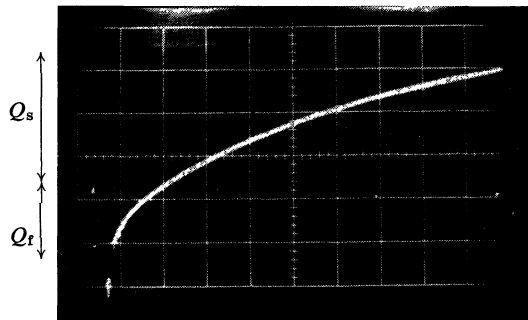
lying at 0.14 eV above the valence band. This level is identical with the acceptor at $E_v + 0.15$ eV which has been observed by measurements of the Hall effect [8, 9] and photoluminescence [10]. It is found that the detrapping processes for holes become dominant when increasing the Cd over-pressure ; this appears to be related to the enhancement of the emission intensity of the 1.42 eV band.

2. Experimental procedures. — Undoped and Cl-doped CdTe single crystals were grown from Te-solution by the standard THM. Also, the undoped p-type crystals used in this study were prepared by THM from Te-solution under a controlled Cd overpressure (this we shall call *modified THM*). Crystals obtained under a relatively low Cd over-pressure without intentional chemical impurities show p-type conduction with resistivities higher than 10^6 Ω -cm. Samples cut from an ingot were shaped into a thin plate of $10 \times 10 \times 1$ -2 mm³ and then Au was evaporated as electrode onto both surfaces after either chemical etching with Br-methanol solution or after only polishing.

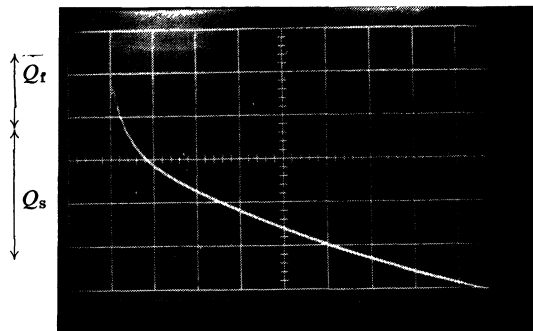
Time-of-flight measurements were performed by using a short light pulse with 3 ns duration from a N₂ laser. The sample was mounted on a BeO plate attached to a Cu cold finger in a cryostat. The light pulse was focussed through a quartz lens. The charge induced by the carrier drift in the sample was observed on an oscilloscope. The ambient temperature of samples was

varied from 330 to 120 K. In order to investigate the detrapping mechanism both for electrons and holes, white light from a W-lamp or monochromatic light from a GaAs light emitting diode was employed.

3. Results. — Figure 1 shows the transient charge waveform for holes and electrons at room temperature under an electric field of 1.3 kV/cm in undoped crystals



a) hole : Hori. 1 μ /div. Vert. 20 mV/div.



b) électron : Hori. 20 n/div. Vert. 50 mV/div.

FIG. 1. — Transient charge waveform for holes and electrons at room temperature under an electric field of 1.3 kV/cm in usual THM crystals. Q_f due to fast component, Q_s due to slow component.

grown by standard THM. This clearly shows two components with fast (Q_f) and slow (Q_s) rise times. The fast rise part depends on temperature only weakly both for holes and electrons, as will be shown later, however, the slow part both for holes and electrons is strongly dependent on the temperature of the samples. We believe that the slow component is due to the thermal release of carriers (electrons or holes), captured at the trapping center, into the conduction or the valence band, respectively. Therefore, with decreasing temperature the detrapping time (τ_D) defined by following relation [11] becomes longer.

$$\frac{1}{\tau_D} = S \exp\left(-\frac{E_T}{kT}\right) \quad (1)$$

where S is a frequency factor and E_T is the activation energy of the trapping center. Under certain conditions ($\tau_D \gg \tau^+ \gg T_R$) we can make a simple estimate of the trapping time (τ_D) for holes and electrons from the

observed transient charge waveform using the following formula,

$$Q_s = Q_0 \left[1 - \exp\left(-\frac{t}{\tau_D}\right) \right] \quad (2)$$

where Q_0 indicates the saturation charge at $t \rightarrow \infty$.

Figures 2 and 3 show the temperature dependence of detrapping time for holes and electrons in the crystals grown by standard THM at an electric field of 1.8 kV/cm, respectively. We obtain an activation energy (E_T) of about 0.14 eV for holes and about 0.05 eV for electrons from the slope of the semi-log plot, respectively. At room temperature the detrapping time of holes and electrons showed strong scatter from sample to sample. We observed that the event of detrapping for holes and electrons is very sensitive to illumination by infrared light. In particular, the

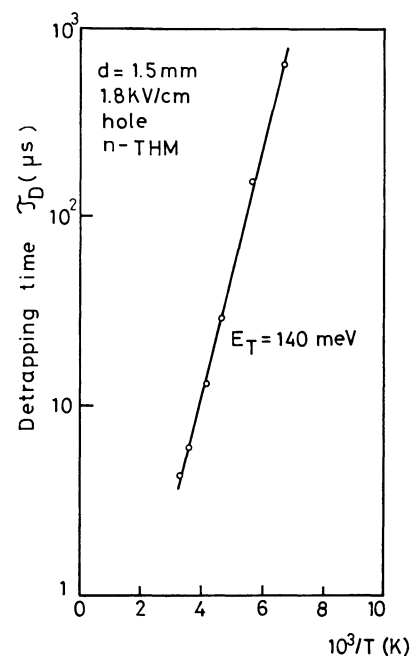


FIG. 2. — Temperature dependence of detrapping time of holes in usual THM crystals.

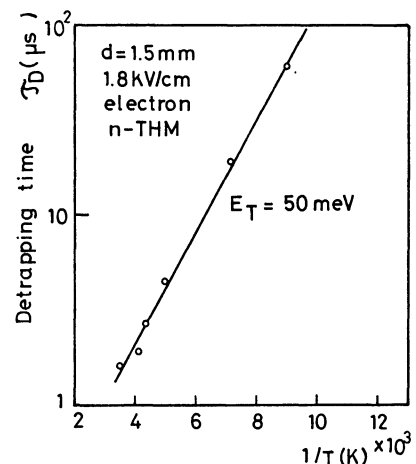


FIG. 3. — Temperature dependence of detrapping time of electrons in usual THM crystals.

detrapping effects for holes vanished under the illumination of weak light emitted from a GaAs LED.

Figure 4 shows the room-temperature resistivity and the emission intensity of the 1.42 eV band at 4.2 K as a function of Cd over-pressure in undoped p-type crystals grown by the modified THM. A detailed explanation about the growth and the character of the crystals is given elsewhere [6]. At lower Cd over-pressures (below about 7×10^{-3} atm), we have high-resistivity samples (over $10^6 \Omega\text{-cm}$) without intentional doping with chemical impurities.

Figure 5A, B and C show the transient charge waveform for electrons and holes in the crystals prepared at the position of a, b and c described in figure 4, respectively. With increasing Cd over-pressure the detrapping effect for electrons at low electric fields is clearly affected as shown in fig. 5C.

The fast component both for electrons and holes which is shown in figure 5A and B presents the initial response [12] for

$$t \leq T_R$$

where T_R is transit time of carriers between electrodes. The transit time obeys the following relation

$$T_R = \frac{d^2}{\mu_d V} \tag{3}$$

where μ_d is the drift mobility of carriers, V the applied field and d the thickness of the sample.

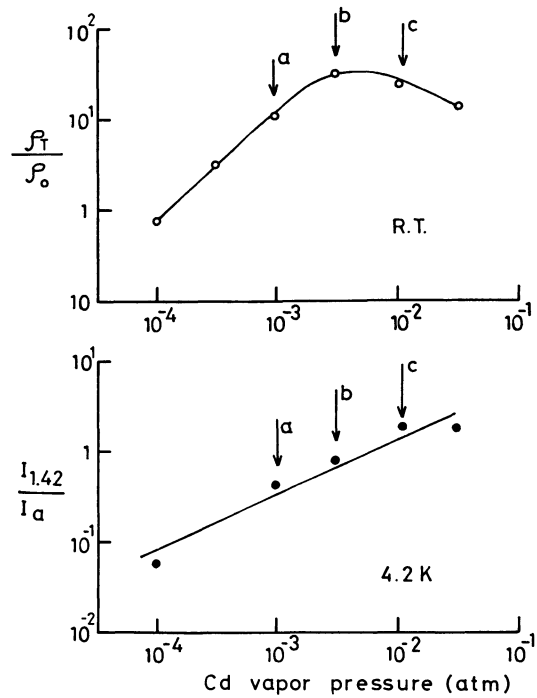


FIG. 4. — Room temperature resistivity and the emission intensity of the 1.42 eV emission band at 4.2 K as a function of Cd over-pressure in crystals grown from a modified THM. ρ_0 , room temperature resistivity of the original crystals grown from usual THM. ρ_T , room temperature resistivity of the modified THM crystal. $I_{1.42}$, emission intensity of the 1.42 eV band at 4.2 K. I_α , emission intensity of excitons [5] bound to neutral acceptor at 4.2 K.

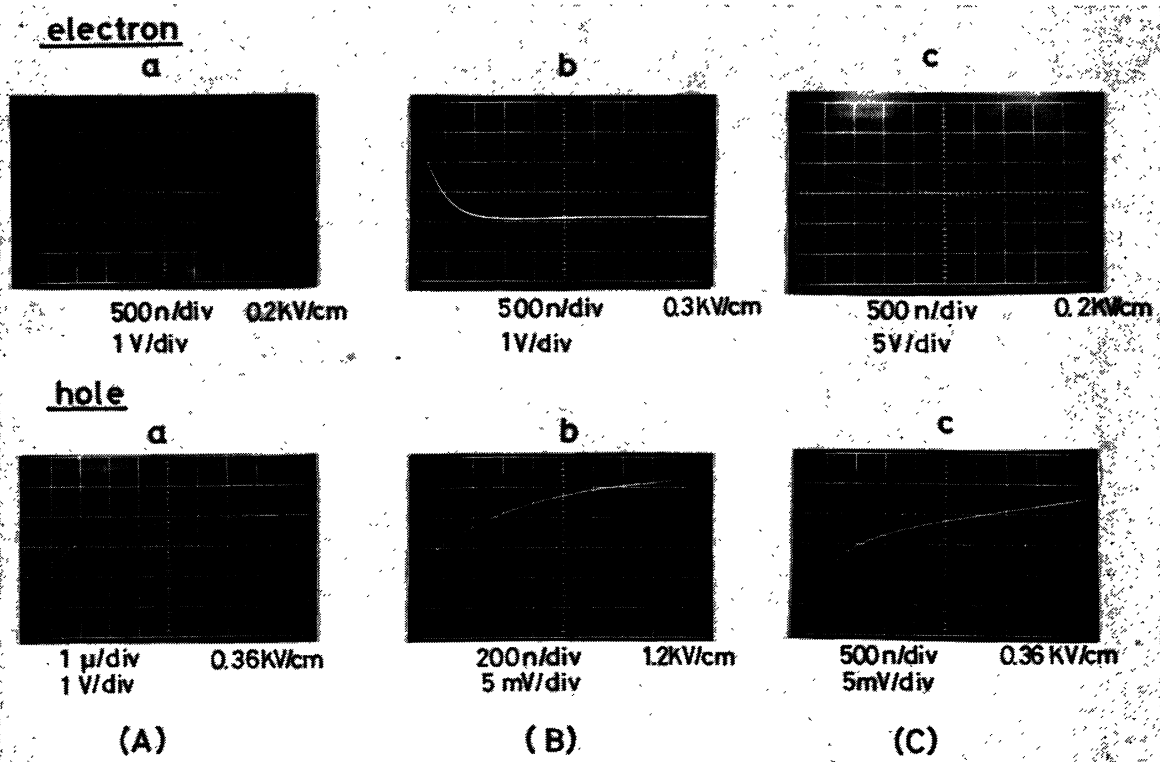


FIG. 5A, B and C. — Transient charge waveform for electrons and holes at room temperature in crystals grown from a modified THM. A), crystals at the position of a shown in figure 4, B), crystals at the position of b shown in figure 4, C), crystals at the position of c shown in figure 4.

The fast component gives the mean time that the electron (or hole) is free before trapping and we shall call it the carrier trapping time (τ^+) [13]. The value of τ^+ can be determined directly from the following equation [12, 13] (if $\tau^+ \ll \tau_D$)

$$Q(t) = \frac{eN_0 \tau^+ \mu_d V}{d^2} \left[1 - \exp\left(-\frac{t}{\tau^+}\right) \right] \quad (4)$$

where N_0 are the initial carriers generated by the pulsed laser light, μ_d drift mobility of carriers, V applied voltage and d the thickness of the sample. We can estimate the value of τ^+ from an analysis of the relation between $\log [{}^6Q(t = \infty) - Q(t)]$ versus time (t) for the case of figure 5A and B. For example, in

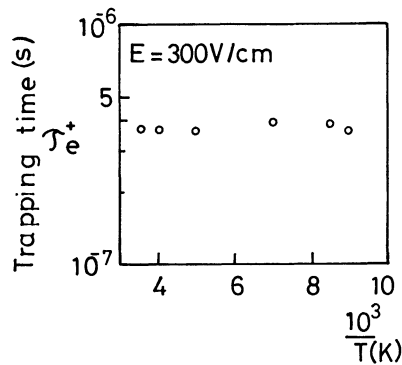


FIG. 6. — Temperature dependence of trapping time of electrons in crystals of B) in figure 5.

figure 5B we obtain the value of 360 ns for electrons and 1.0 μ s for holes at room temperature, respectively.

Figure 6 shows the temperature dependence of the trapping time for electrons in the crystals grown from position of b as shown in figure 4. The electron-trapping time is essentially temperature independent.

4. Discussion. — Transient measurements using the time-of-flight method permit the determination of the carrier-drift mobility (μ_d), trapping and detrapping times (τ^+ , τ_D), and ($\mu\tau^+$) products both for electrons and holes which are important factors in the performance of CdTe detectors.

If detailed balance considerations are applicable in our case, the ratio between τ^+ and τ_D is given by the classical relation as follows [12, 13],

$$\frac{\tau^+}{\tau_D} = \frac{N_{v,c}}{N_T} \exp\left(\frac{E_T}{kT}\right) \quad (5)$$

where $N_{v,c}$ describes the effective density of the valence band or conduction band, N_T trap density, E_T trap depth and k is the Boltzmann factor. We can apply this then to the estimation of trap density by assuming one type of trap level in a weak electric field under the presence of trapping and detrapping effects.

4.1 COMPARISON BETWEEN « STANDARD » THM AND « MODIFIED » THM CRYSTALS. — To date the performance of CdTe detectors has been dominated by

TABLE I

Characteristic of various p-type THM crystals and comparison between our results and previous ones obtained by Martin et al. and Bell et al. at room temperature

	Crystal	Resistivity (Ω -cm)	Trapping level (eV)		μ_H μ_{dc} μ_{dh}			τ_e^+ τ_h^+		$(\mu\tau)$		trap density	
			electron	hole	(cm ² /V.s)	(ns)	electron	hole	electron ($E_c-0.05$ eV)	hole ($E_v+0.14$ eV)			
Our	undoped THM	6×10^4	$E_c-0.05$	$E_v+0.14$	90	610	81	100	250	6.1×10^{-5}	2×10^{-5}	1×10^{17}	6.4×10^{17}
	Cl-doped THM	10^8	0.06	0.14	62	740	44	160	500	1.4×10^{-4}	2.2×10^{-5}	4.5×10^{16}	6.4×10^{16}
	undoped modified THM	7×10^7	0.05	0.14	84	650	80	120	350	7.8×10^{-5}	2.8×10^{-5}	10^{17}	5.1×10^{16}
	undoped modified THM	8×10^6	not-detected	0.14	94	1 100	100	360	1 000	4×10^{-4}	9.6×10^{-5}		4.8×10^{15}
Martin et al. [3, 4]	Cl-doped THM	(*)	0.06	0.14	(*)	800-1 000	45-90	150	1 200	(*)	(*)	(*)	(*)
Bell et al. [7]	Cl, Br-doped THM	10^6	0.02 0.05	0.14 0.35	80	1 130	80	< 40	(*)	10^{-3}	2.5×10^{-5}	1×10^{15}	2.5×10^{16}

(*) It is not clear because the value is not given in the literature.

trapping and detrapping effects. In CdTe detectors, it has been known that the timing properties are controlled by the shallow levels [4, 7] ($E_c - 0.02$ eV for electrons and $E_v + 0.14$ eV for holes) and the resolution is determined by deeper levels [7] ($E_c - 0.05$ eV for electrons and $E_v \sim + 0.4$ eV for holes). We have observed that trapping centers occur at 0.05 eV below the conduction band for electrons and at 0.14 eV above the valence band for holes in undoped and Cl-doped crystals grown by standard THM. However, the shallow level at $E_c - 0.02$ eV for electrons and the deeper level at $E_v \sim + 0.4$ eV for holes have not been observed in our case. In modified THM crystals, with increasing Cd over-pressure the detrapping effect for electrons appeared and the trap level was estimated to be 0.05 eV below the conduction band from the temperature dependence of the detrapping times. However, we have not observed the detrapping effect for electrons at room temperature in the modified THM crystals grown under Cd over-pressure of about 4×10^{-3} atm. It may be thought that this trapping center is related to the level found by the measurements of Hall effect [14] and photoluminescence [8]. However, the origin of the trapping center has not been clear so far. On the other hand, the trapping level at 0.14 eV above the valence band for holes has been observed in all crystals investigated here. But these detrapping effects for holes vanished at room temperature under light of 8 880 Å emitted by a GaAs LED. The detrapping process for holes becomes dominant with increasing Cd over-pressure, and the 1.42 eV

emission band as shown in figure 4 is also enhanced. The detailed transport properties of holes trapped to this level have been first investigated by Ottaviani *et al.* in high-resistivity crystals grown from Bridgman [15] and THM [7]. They obtained a value of about 5×10^{16} cm⁻³ for the density of the trap center at $E_v + 0.14$ eV. In our case, the density of the trap at room temperature was estimated to be about 5×10^{15} - 1×10^{17} cm⁻³ in the modified THM crystals.

5. Conclusion. — Carrier trapping and detrapping effects in high-resistivity p-type crystals grown from a modified THM have been investigated using a time-of-flight method.

We can summarize the results obtained as follows :

1) Trapping centers for electrons and holes are located at 0.05 eV below the conduction band and at 0.14 eV above the valence band, respectively.

2) The trapping effect for holes is related to the enhancement of the 1.42 eV emission band.

3) The detrapping effect for electrons at room temperature does not occur in the modified THM crystals grown under Cd vapor pressure of about 5×10^{-3} atm, and the best values of the observed trapping time are 360 ns for electrons and 1.0 μs for holes at room temperature.

4) The trap density, simply estimated by assuming the presence of one trap level each for electrons and holes, leads to a value of about 5×10^{15} cm⁻³ for hole-trapping centers in the best crystals.

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