

phys. stat. sol. (a) **100**, 251 (1987)

Subject classification: 71.55; S8.13

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## About the Origin of the 0.15 to 0.20 eV Defect Level in Cadmium Telluride

By

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The exact origin of the defect levels present in cadmium telluride in the 0.15 to 0.20 eV energy band is under discussion since the beginning of the microscopic characterization of this II–VI semiconductor. Physical defects, residual chemical impurities, and complexes have been successively considered. In this paper, the results are presented of investigations on a large number of crystals grown by THM which are characterized both, by thermally stimulated current (TSC) and photoinduced current transient spectroscopy (PICTS). These materials are grown either undoped, chlorine and copper doped, and some are irradiated by a strong  $\gamma$ -ray source. The concentration of chemical residuals is determined in each case by atomic absorption measurements. It appears that the defects origin is more complicated than generally considered, as will be discussed.

Die genaue Ursache der Defektniveaus in Kadmitellurid im Energiebereich von 0,15 bis 0,20 eV wird seit Beginn der mikroskopischen Charakterisierung dieses II–VI-Halbleiters diskutiert. Physikalische Defekte, chemische Restverunreinigungen und Komplexe wurden dabei in Betracht gezogen. Es werden die Ergebnisse von Untersuchungen an einer großen Zahl von THM-gezogenen Kristallen mitgeteilt, die sowohl mittels thermisch stimulierter Ströme (TSC) als auch mittels Spektroskopie transienter Photoströme (PICTS) charakterisiert werden. Diese Materialien sind entweder undotiert oder mit Chlor und Kupfer dotiert, und einige werden durch eine starke  $\gamma$ -Strahlenquelle angeregt. Die Konzentration der chemischen Restverunreinigungen wird für jeden Fall mittels Atomabsorptionsmessungen bestimmt. Es scheint, daß der Ursprung der Defekte, wie diskutiert wird, komplizierter ist, als allgemein angenommen wird.

### 1. Introduction

Cadmium telluride is a wide-band-gap II–VI compound semiconductor involving an inevitably large concentration of defects produced during crystal growth and material processing. As many as 30 defects have been reported using different techniques [1, 2]. Since several years ago we have undertaken a high scope study of these defects. An important part of our effort was the development of high resolution defect characterization techniques capable of revealing the fine details of the CdTe defect structure. Up to 20 deep levels were identified and it was shown that these defect levels are persistent in all materials, the difference between varying materials being in the density of different defects [3, 5]. These defect levels form several bands or clusterings of individual levels in the band gap, with each band consisting of up to seven discrete levels.

However, in a great majority of crystals, a high density band around 0.15 eV is predominant. This high density cluster traditionally considered as a single level at 0.15 eV has been the subject of discussion for about three decades.

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We have carried out a comprehensive study of this band using several high resolution techniques.

## 2. Microscopic Characterization Techniques

### 2.1 TSC studies

In this technique, the traps are filled by illuminating the sample at low temperature with interband light ( $\lambda = 0.63 \mu\text{m}$  using a helium-neon laser or  $0.2 \mu\text{m}$  using a UV filter). Then the discharge current is measured in the dark and recorded as a function of temperature. An efficient exploitation of the TSC technique required the filtering of the overlapped peaks, the reduction of the dark current, and rigorous analytical developments. The improved TSC procedure involves a precise calculation of the defect levels [5, 6] and further uses a microcomputer-based deconvolution procedure of the experimental spectra recorded in a cryostat over a temperature range from 4.2 to 450 K. The effect of the dark current has been minimized by a special technique [3].

Fig. 1 shows the thermally stimulated current spectrum of the 0.15 eV band for several THM-grown high-resistivity materials. Curve a shows the entire band using liquid helium cooling. The band is quite wide and extends from about 30 to 120 K. Curves a', b, and c show the 0.15 eV band of the same sample and two other high-resistivity samples using supercooled nitrogen (64 K). On the continuous spectra at least four peaks can be distinguished at 67, 78, 84, and 104 K covering an energy range of 0.1 to 0.2 eV.

### 2.2 PICTS studies

The photo-induced current transient deep level spectroscopy involves carrier generation by light pulses and sampling of the transient current response. The sampling method resembles that of the DLTS techniques [7] and uses a dual gated pulse to determine the emission rate of traps. The presence of each trap is indicated by a peak as a function of temperature. The heights of these peaks are proportional to the respective trap concentrations and the positions of the peaks are determined by the integrated gate setting and the thermal emission properties of the respective traps. To separate the peaks effectively we changed several parameters such as the pulse width the sampling times ( $t_1$  and  $t_2$ ) and the light intensity to enhance the filling and emission of one level compared to the other levels.

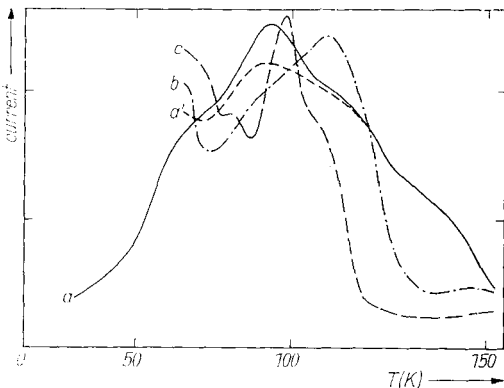


Fig. 1. TSC spectra of the 0.15 eV band in high-resistivity CdTe. (a) The entire band as characterized by liquid helium cooling, (a') same samples as in (a), characterized by supercooled nitrogen, (b) and (c) different samples from the same ingot using supercooled nitrogen

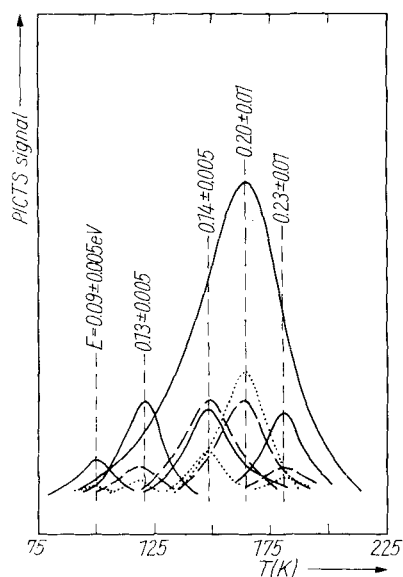


Fig. 2. PICTS spectra of the 0.15 eV band for three sample with different resistivities along an ingot: —  $\rho = 10^8$ ,  $\cdots \cdots 5 \times 10^6$ ,  $--- 1.2 \times 10^5 \Omega \text{ cm}$

A pulsed laser beam emitting at 860 nm with pulse frequencies in the order of 3 Hz and pulse duration of about 20 ms was used with a sampling time ratio in the order of  $t_2/t_1 = 4$ . The thermal emission rates are determined as a function of temperature providing the energy level, capture cross section, and concentration of traps [8].

Fig. 2 shows a PICTS spectrum of the filtered 0.15 eV band of a chlorine compensated material. As shown in the figure up to five levels in the 0.09 to 0.23 eV range are distinguished. The figure shows the corresponding trap concentrations for three samples taken from different positions along an ingot with three different resistivities.

### 3. The 0.15 eV Band Characteristics

#### 3.1 Properties

This defect has been reported by us [3, 4] as being a compensating defect, present in high-resistivity, high-resolution nuclear detectors with a concentration depending almost linearly on the resistivity [9, 10]. In THM-grown CdTe this defect is present mainly in Cl or In compensated crystals and has a low density in uncompensated or

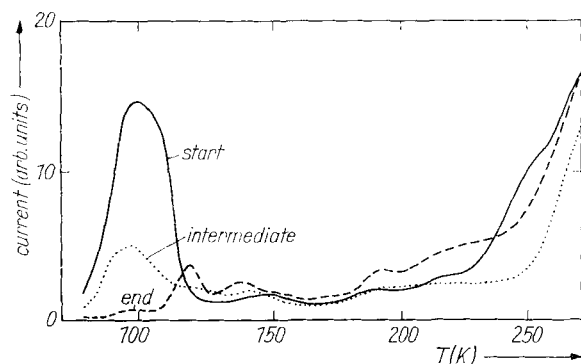


Fig. 3. The tendency toward lower-resistivity materials along the ingot corresponding to a proportional decrease in the 0.15 eV and a proportional increase in the 0.30 eV band densities

insufficiently compensated materials. We have already reported two categories of high- and low-resistivity materials basically giving rise to two families of spectra [4]. However, even in high-resistivity ingots the resistivity decreases as the end of the crystal is approached. This decrease in the resistivity corresponds to a gradual decay in the 0.15 eV band concentration and a parallel increase in the 0.30 eV band density as shown in Fig. 3.

#### 4. Main Characteristics of the 0.15 eV Band

This level, first seen by De Nobel [11] was attributed to a singly charged cadmium vacancy  $V_{Cd}^-$ . This level was observed in non-intentionally doped indium-compensated as well as chlorine-compensated crystals. Chapnin [12] after a series of Hall effect measurements performed on thermally treated samples suggested that this level is due to an acceptor complex incorporating a native defect and a chemical impurity. Agrinskaya [13] as well as Furgolle [14] suppose that the complex is  $(V_{Cd}^-X^+)$ , where X is a donor from column III or VII. A similar interpretation was given by Prenner and Weil [15] to explain the observed fluorescence in this material, when doped. Their theoretical approach results in an energy level shift by 20 meV when X goes from column III to VII elements. Such a shift has been observed by several authors in CdTe: Furgolle [14], Ottaviani [16], Stuck [17]. Recently, Pautrat and Molva [18, 19] by extensive photoluminescence experiments performed at low temperature on both CdTe and ZnTe attributed the existence of the 0.15 eV level to copper as a residual chemical acceptor. However, James et al. [20, 21] state that the 1.5896 eV bound exciton spectral line intensity, related to the 0.15 eV level, is not a good indication of the copper concentration in CdTe. Given the abundance of the seemingly unrelated and often controversial findings, it appears that the 0.15 eV defect has not yet been fully investigated.

##### 4.1 Properties of this level on as-grown material

First of all, it is important to notice that the 0.15 eV level observed by all the above authors, appears in both our TSC and PICTS spectra as having in fact a series of well-defined peaks over a more extended energy range typically from 0.10 to 0.20 eV, that we call an energy band.

The 0.15 eV band is present in all crystals investigated, but its intensity is highest for the semi-insulating chlorine-compensated crystals.

In THM-grown, chlorine-compensated crystals the resistivity decreases progressively along the ingot and in parallel the intensity of the 0.15 eV band follows almost linearly this evolution. However, no such evolution in the concentration of the material impurities is found along the ingot, as shown by atomic absorption spectroscopy measurements.

##### 4.2 Evolution of the 0.15 eV band after strong $\gamma$ -ray irradiation

A  $^{60}Co$   $\gamma$ -ray source emitting at 1.17 and 1.33 MeV with a radiation flux of 200 Gy/h was used to follow the evolution of the defects with radiation damage (300 K irradiation). The overall evolution of the defects is shown in Fig. 4 and 5. The most important feature is an almost exponential decrease in the density of the 0.15 to 0.20 eV band. A similar decay is observed in the density of midgap levels having a comparable concentration. We note that the midgap defects, in turn, constitute a band of several high-density defects in the 0.8 eV range (Fig. 6). The fact that the 0.15 eV band and the midgap defect band have comparable concentrations and follow a similar

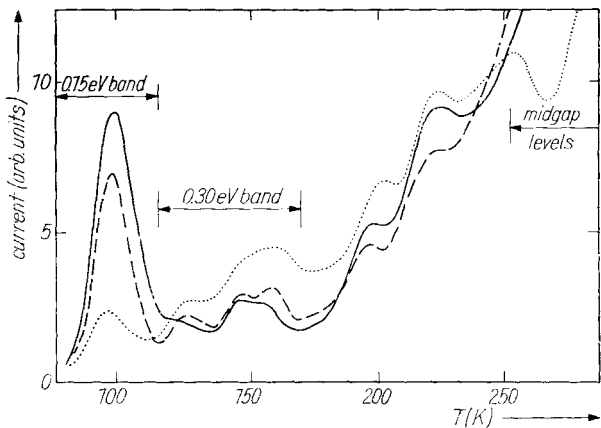


Fig. 4. The evolution of the defects with strong  $\gamma$ -ray irradiation damage (300 K) — before irradiation, --- after 6 h of  $\gamma$ -irradiation, ..... after 120 h of  $\gamma$ -irradiation

evolution with  $\gamma$ -bombardment suggests a common origin for 0.15 eV and midgap levels.

Another effect observed on Fig. 4 and 5 is an increase in the concentration of the 0.30 eV band. These levels have been found to disturb material properties with a degrading effect on the resistivity and nuclear detection properties and represent

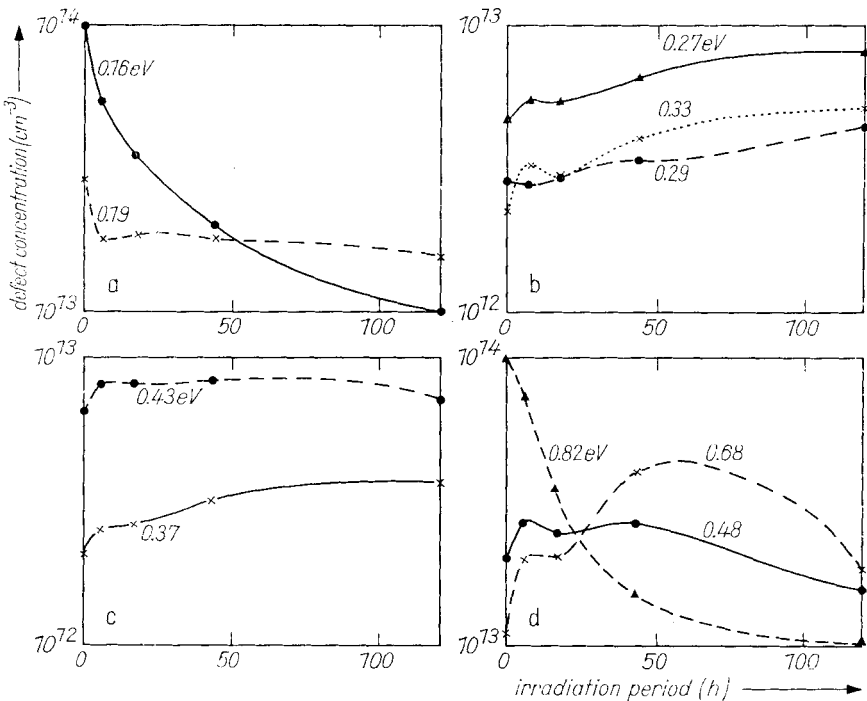


Fig. 5. The evolution of different defect densities as a function of irradiation exposure period in high-resistivity CdTe materials

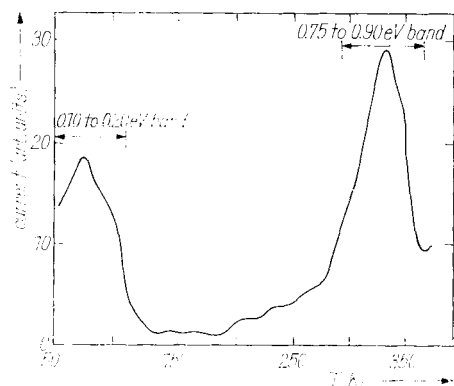


Fig. 6. Density contrast between the 0.15 eV band and midgap level densities

the dominant peaks on the low-temperature side of low-resistivity material spectra. They also appear to be related to the 0.15 eV band as their increase corresponds to the decrease of the 0.15 eV band density [4].

#### 4.3 Carrier trapping behaviour of the 0.15 eV band

An important observation on the carrier trapping mechanism of the 0.15 eV band levels is that their carrier trapping dynamics is highly dependent on the filling state of the midgap levels. In fact the 0.15 eV states can be filled much faster and to a higher degree when the midgap states are empty and much slower and only partially when midgap states are full. This is an additional support in favour of a common centre for the 0.15 eV and midgap states. In fact, if the same centre produces both energy states, the selective filling of one of the states by holes would charge the centre positively and thus decrease trapping of additional holes by the other energy state. Selective filling is performed by charging the midgap states at ambient temperature prior to cooling.

#### 4.4 The effect of light-ion implantation

In our hydrogen passivation studies [22], using ion implantation in the keV and MeV ranges, drastic changes in the concentration of most defect levels and notably that of the 0.15 eV band were observed. In high-resistivity crystals a strong decrease in the concentration of the 0.15 eV band occurred (Fig. 7). However, in order to filter out the effect related to the irradiation by implantation a helium bombardment study

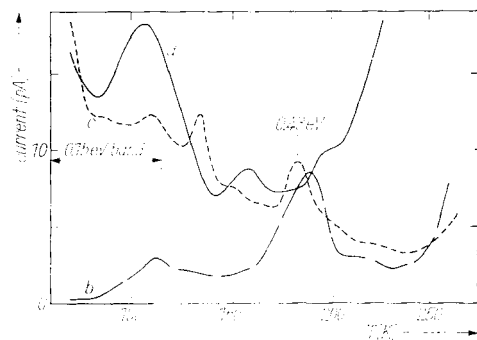


Fig. 7. The evolution of the TSC spectra of a high-resistivity sample with hydrogen implantation and subsequent annealing: (a) before implantation, (b) after implantation (3 MeV protons), (c) after annealing the implanted sample (3h, 150°C)

using the same energy range was performed. Several of the changes including that of the 0.15 eV band were reproduced indicating that a similar effect as in strong  $\gamma$ -irradiation takes place.

## 5. Discussion

Our experiments lead to the following results:

- A single copper acceptor cannot be directly responsible for the 0.15 eV band, since concentrations of this band in excess of  $10^{16} \text{ cm}^{-3}$  are identified for less than  $10^{14} \text{ cm}^{-3}$  residual copper atoms, when investigated by atomic absorption measurements.

- There is no reason that the intensity of the 0.15 eV band would decrease so rapidly with  $\gamma$ -ray irradiation if copper, as an acceptor, would be the origin of the band.

- It is a known fact that in most cadmium-based semiconductors (CdTe, CdS, CdSe, etc. . . .) cadmium vacancies are predominant defects in the material. These vacancies can be present both with singly or doubly charged states and, in general, produce defect states near midgap.

- Chlorine has a strong affinity for many chemicals, as well as vacancies interacting not only electronically, but also chemically by inducing self-purification and association with residual impurities.

- Chlorine acts also as a donor in CdTe, therefore, this halogen can compensate acceptors, like the pairing occurring in silicon or germanium. Acceptors may be of both a physical or a chemical nature.

- We observe a common defect underlying both the 0.15 eV and the midgap states.

- The 0.15 eV band has high densities in well-compensated crystals. Thus, both chlorine and cadmium vacancies are candidates as at least a part of the constituting elements of this defect.

- Our high resistivity chlorine compensated materials show a decrease in the density of the 0.15 eV band upon high-energy particle bombardment. This is more in favour of a complex centre disintegrating under irradiation.

Considering all these experimental facts, it appears that the nature of the 0.15 eV band is not a simple acceptor, but that various contributions occur. Our speculations consider that  $V_{\text{Cd}}$ , Cl, and probably one or more impurities participate in its formation.

The strong affinity of chlorine with cadmium vacancies, the high density of the cadmium vacancies, and the dominating nature of the 0.15 eV band suggest that at least in chlorine-compensated materials two main constituents of this defect are chlorine and cadmium vacancies. However, the structure of the defect might vary from a single  $[\text{Cl}^+\text{V}_{\text{Cd}}^-]$  bonding to a more complex  $[\text{Cl}_n^+\text{V}_{\text{Cd}}^-\text{X}_q^\pm]^{-k}$  where X is an impurity and where  $n$ ,  $p$ ,  $q$ , and  $k$  are the multiplicity of elements and the charge state. Other complexes including interstitial tellurium, interstitial cadmium, and more than one impurity may also be possible alternatives. The existence of the different levels in the band may be due to small variations in the number of the constituting elements that lead to slightly different patterns and give rise to several levels with varying densities. However, in materials compensated by other elements such as indium the same structure would hold where only chlorine is replaced by the compensating element.

## 6. Conclusion

Despite the great amount of work devoted to the determination of the 0.15 eV level the origin of this defect is not yet well understood. Our investigations show that in

fact an energy band between 0.10 and 0.20 eV is present, that the 0.15 eV level cannot be copper as a simple acceptor even if copper can contribute to its formation and that several parameters including at least a physical defect and a compensating element participate in its structure.

### Acknowledgements

The authors are grateful to Mrs. C. Ritt and Miss M. F. Masson for valuable technical assistance and Miss M. Cobut for typing and preparing the manuscript.

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*(Received September 24, 1986; in revised form December 23, 1986)*