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Electrical Properties Study of Three Highly Purified CdTe Ingots

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Abstract

Three high resistivity CdTe ingots have been prepared with highly purified materials. The three starting Te components were purified through three different purification processes: horizontal zone refining, vacuum distillation and by a combination of both processes. The three crystals growths were achieved by the THM method. The purity studies were achieved by the determination of the concentration of 21 impurities, using the Atomic Absorption (AASGF) method. The resistivity ρ measurements along the length of the three CdTe ingots at room temperature showed a nearly constant ρ value within the range of $10^9 - 10^{10} \Omega \cdot \text{cm}$. This represents a motivating result, in net advance with the general behavior of classic THM materials, where it began by high ρ at the starting point, and then it decreased by few decades. Values of drifting motilities μ were measured for all ingots and showed interesting high values: $\mu_e = 1100 \text{ cm}^2/\text{Vs}$ for electrons and $\mu_h = 90 \text{ cm}^2/\text{Vs}$ for holes. The position in the band gap and eventually the nature of the corresponding electrical defects levels, involved in the trapping process was studied by using the PICTS method. The uniformity of ρ , the high mobility μ and the low concentration values of impurities in all our CdTe ingots confirm the high electronic grade quality of these CdTe materials, which is better than 6N purity.

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1. Introduction

Doped cadmium telluride (CdTe) is still the subject of a promising semiconductor material for important applications such as room-temperature X- and gamma-radiation detectors, photonics, radiation sensors and infrared imaging [1]. It is well known that the essential requirements for CdTe crystals as high performance detector material are: (1) high electrical resistivity and (2) high carrier mobility. High-resistivity crystals can be reproducibly obtained without intentional doping by carefully controlling the

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stoichiometry of the feed charge, by encapsulated (B_2O_3) Bridgeman technique [2]. The electrical resistivity can be adjusted by manipulating the concentrations of intrinsic point defects (such as vacancy and interstitial) and extrinsic point defects (such as n- or p-type dopant) through the studies of defect chemistry [3]. The carrier mobility is generally believed to be affected by the structural defects, such as crystalline strain, grain boundary, second phase inclusion and precipitate, as well as dislocation and twin [4]. The large atomic number of the CdTe promotes a high registration efficiency of gamma-radiation (compared, e.g., with silicon). At the same time, with the increase in the atomic number the registration efficiency for a given energy range of gamma-radiation varies over a wider range of values. However, this energy dependence can be successfully leveled out (with an accuracy of 71.5%) both by electronic signal processing and by application of absorbing filters of sophisticated designs [5].

In this paper, three high-purity semi-insulating CdTe crystals: AB1, AB2 and AB3 have been successfully grown from melts by a stoichiometric ratio of cadmium and tellurium under the same conditions of the Traveling Heater Method (THM) such that:

- AB1: Starting tellurium (Te1) was purified by horizontal zone refining.
- AB2: Starting tellurium (Te2) was purified by vacuum distillation.
- AB3: Starting tellurium (Te3) purified by combining both processes.

We will report on the measurement of resistivity and drifting mobility of the three samples of CdTe. The nature of the defects involved in the transitions was studied by analyzing the position of the energy levels by PICTS.

2. Material growth

Cd sources of high purity (6N cominco) were used with the three different samples (AB1, AB2, and AB3) of purified tellurium at the required proportions. CdTe batches of 300g was synthesized in graphitized, evacuated quartz ampoules at 1073 K. CdTe was melted under 700 mbar of hydrogen. This was achieved by applying the appropriate temperature profile. From these ingots suitable seeds and feed rods were cut. Three CdTe ingots were grown by THM in Te-rich CdTe liquid solution with one zone heating. The growth rates of 6mm/day lead to a monocrystal of 60mm length and 20mm of diameter. All stoichiometric CdTe single crystals were grown using the same apparatus. The CdTe crystals were annealed at 600°C under argon pressure, after cutting the tellurium zone, in a closed quartz ampoule with an argon gas atmosphere. The average concentrations of 21 impurities were measured in each ingot (see table 1).

High resistivity material is obtained by introducing chlorine (in the form of $CdCl_2$ with concentration of 10^{17} - 10^{18} atoms cm^{-3} in the tellurium solvent zone. The resistivity of CdTe crystals was studied by Van der Pauw measurements at room temperature. Samples of CdTe were taken from several points. Measurements of mobility μ are also achieved: an alpha-particle Time of Flight (TOF) method was used to measure electron and hole drift mobility at room temperature. In this study TOF measurements were carried out on single crystal bulk CdTe material, with devices fabricated using planar ohmic contacts in a "sandwich" configuration.

In the thick CdTe samples used for this study typical electron and hole drift times are 1–5 μs , compared to the mean electron and hole lifetimes in this material of 1 μs . Measurement of the amplitude of the charge pulse gives the total charge Q induced at the device contact, and hence the electron and hole mobility-lifetime products $\mu_e \tau_e$ and $\tau_h \mu_h$. Commonly used as a figure of merit for radiation detectors, $\mu \tau$ is directly related to the mean carrier drift length λ , such that:

$$\lambda = \mu \tau E$$

where E is the applied field strength.

For single carrier charge transport, the Charge Collection Efficiency (CCE) is described by the simplified Hecht equation. The carrier drift time t_{dr} was directly measured. For carriers drifting across a thickness d, the drifting mobility μ is given by:

$$\mu = d^2 \times V^{-1} \times t_{dr}^{-1}$$

where V is the applied voltage across the material thickness.

Photo-induced current transient deep level spectroscopy (PICTS) Schottky diodes have been made on samples by evaporating gold under ultrahigh vacuum on freshly chemically-polished surfaces. The PICTS measurements were performed using a double box-car and an electrical pulse of 1 ms duration, allowing a complete filling of traps by electrons. The activation energies were obtained from the conventional “emission rate versus temperature” Arrhenius plot. The excitation wavelengths used in PICTS measurements were $\lambda=860\text{nm}$

Table 1: Concentration of 21 impurities in ppmw-at the middle part for the three CdTe ingots after THM.

Element	AB1	AB2	AB3
	Distilled Te	Zone refined Te	Distilled+ Zone refined Te
Ag	≤0.01	≤0.02	≤0.01
Al	≤0.03	≤0.01	≤0.01
As	≤0.07	≤0.01	≤0.05
B	≤0.1	≤0.1	≤0.08
Ca	≤0.15	≤0.02	≤0.01
Cr	≤0.03	≤0.04	≤0.01
Cu	≤0.02	≤0.02	≤0.05
Fe	≤0.03	≤0.1	≤0.06
In	≤0.1	≤0.1	≤0.01
Mg	≤0.1	≤0.05	≤0.01
Mn	≤0.06	≤0.07	≤0.06
Na	≤0.1	≤0.2	≤0.01
Ni	≤0.05	≤0.05	≤0.01
Pb	≤0.02	≤0.02	≤0.04
Pd	≤0.01	≤0.1	≤0.03
Se	≤0.1	0.5	0.07
Si	≤0.1	0.2	≤0.01
Sn	0.1	0.08	0.05
Ti	≤0.1	0.2	0.01
V	0.1	0.1	0.03
Zn	≤0.03	0.06	≤0.03

3. Results and discussion

3.1. Resistivity and mobility measurements

Electrical measurements appeared more efficient to characterize CdTe ingots. In order to produce large volume radiation detectors with the highest energy resolution, it is critical to combine high material resistivity ($>10^9\Omega\text{cm}$) with high electron and hole mobility-lifetime products ($\mu\tau$). Efficient purification was characterized by measuring the resistivity versus the distance x for each CdTe ingot at room

temperature (see Fig 1). The values of the resistivity were within the range 10^9 – 10^{10} Ω .cm. The resistivity of CdTe is thought to be controlled (i) by compensation of Cd vacancies (acceptors) by impurities and/or their complexes, (ii) by the lesser extent by tellurium inclusions that affect the mobility of carriers. The constant values of the resistivity vs. position were in net contradiction with the general trend of classical materials [6]. This was due to the saturation of tellurium zone during the growing process. In addition AB3 showed a constant resistivity versus the distance x . This was due to the efficient purification by the two methods and by THM with tellurium solvent. However, resistivity strongly decreased when the doping concentration like Bi increased, confirming the purity of CdTe ingots [7]. The room temperature mobility values of the three CdTe samples taken from the middle part of each ingot are:

AB1: $\mu_e = 840 \text{ cm}^2/\text{Vs}$ and $\mu_h = 55 \text{ cm}^2/\text{Vs}$.

AB2: $\mu_e = 1000 \text{ cm}^2/\text{Vs}$ and $\mu_h = 70 \text{ cm}^2/\text{Vs}$.

AB3: $\mu_e = 1100 \text{ cm}^2/\text{Vs}$ and $\mu_h = 90 \text{ cm}^2/\text{Vs}$.

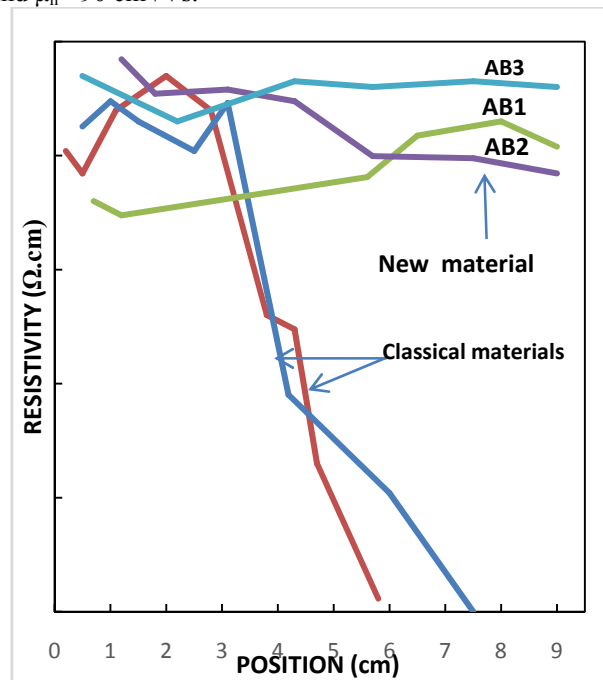


Figure 1: Resistivity versus distance for the different materials

The measured mobility values are similar to those reported by [8-9]. However there has been considerable speculation about the role of tellurium inclusions and other extended defects in degrading the signal amplitude response during the measurements of μ in CdTe. AB3 shows specific and high values of μ_e and μ_h which was due to the high purity and the good crystallinity of the bulk.

3.2. PICTS

Photoconductivity of the three CdTe crystals were increased, in regard of the usual CdTe crystal grown by Te and Cd (Comino), an improvement of two order of magnitude was reached in AB 3. The high values of the product $\mu\tau$ confirm the efficient quality of the material. In figures 2, 3, 4 of PICTS spectra, levels ≤ 0.14 appeared to be high in AB1 and AB3 samples and the increasing from the beginning to the ingot end was clearly observed. The (0.15 – 0.20) eV bands were directly correlated with resistivity and

doping, while the 0.30 eV was reversely attributed to the resistivity, then the ratio R ($R = 0.15/0.30$) was measured as a better indication of the resistivity. Values of R for the three samples showed good behavior, in concordance with the resistivity curves. We must note that 0.30 eV was usually attributed to the direct effect of transition metals like Cu, Ag.

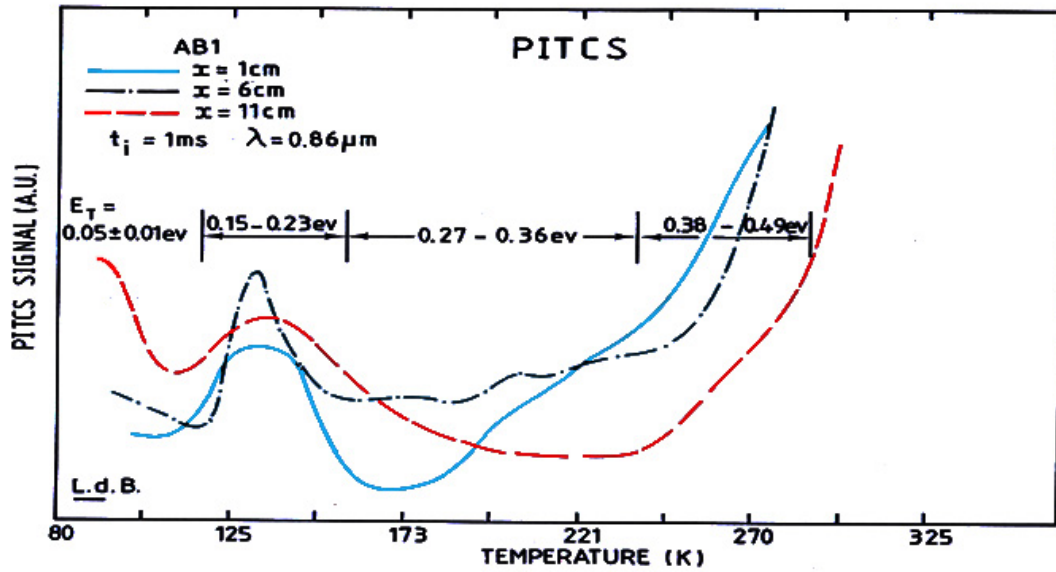


Figure 2: PICTS spectra for Samples from AB 1 at different temperatures

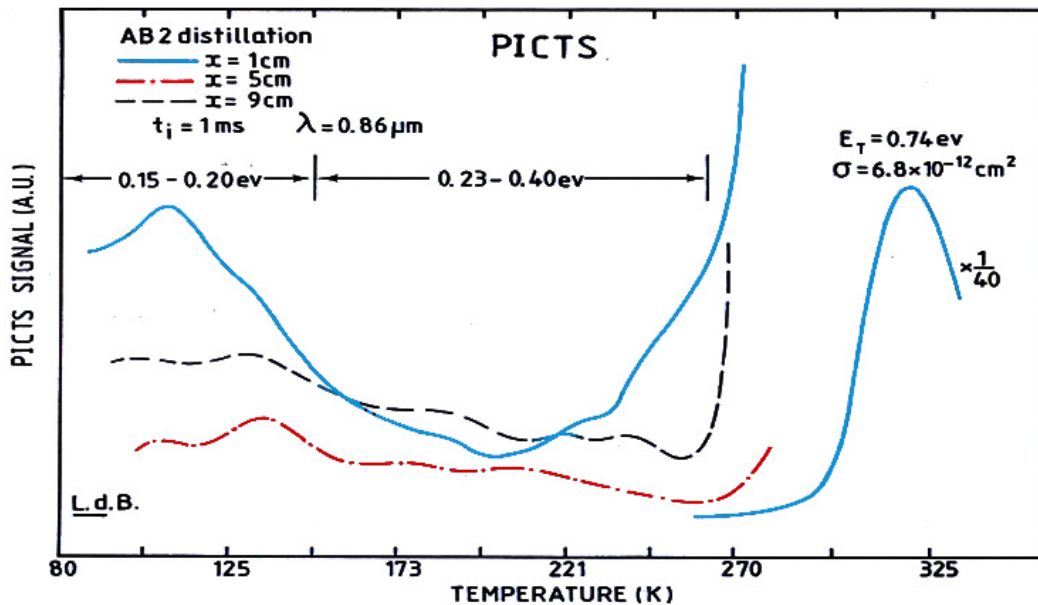


Figure 3: PICTS spectra for Samples from AB 2 at different temperatures

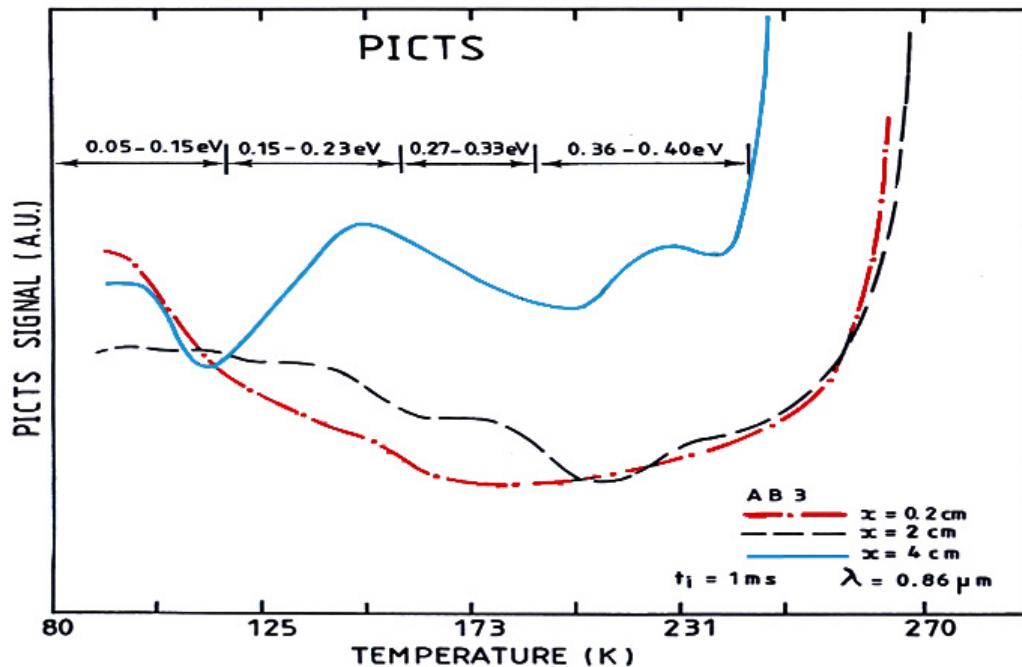


Figure 4: PICTS spectra for Samples from AB 3 at different temperatures

4. Conclusion

In this paper, we have showed that the combination of two purification methods: sublimation and zone refining was the best way to obtain a CdTe with electronic grade. The low concentration of impurities, the high values of both resistivity and mobility, the perfect quality of PICTS, lead us to conclude that the purity of CdTe samples is $\geq 6N$, a high purity level of CdTe samples ready for electronic and nuclear applications with good efficiency.

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