



CdTe and CdZnTe crystals for room temperature gamma-ray detectors

J. Franc*, P. Höschl, E. Belas, R. Grill, P. Hlíděk, P. Moravec, J. Bok

Institute of Physics, Charles University, Ke Karlovu 5, CZ-121 16 Prague 2, Czech Republic

Abstract

CdTe(Cl) detectors from CdTe single crystals, grown by the Bridgman method from Te-rich melt, were fabricated. The quality of the detectors was tested with ^{57}Co and ^{241}Am sources. In the ^{57}Co spectrum low noise is demonstrated by the presence of a 14 keV peak and good resolution ≈ 7 keV (FWHM) evident from the separation of 122 and 136 keV peaks. A review is given of the state-of-the-art properties of (CdZn)Te single crystals prepared for substrates in the Institute of Physics of Charles University. The quality of samples is tested by measurements of the diffusion length of minority carriers, from which the mobility–lifetime product is evaluated. © 1999 Elsevier Science B.V. All rights reserved.

1. Introduction

Semiconductor X-ray and gamma detectors based on Ge and Si began to be used intensively in the 1960s. In comparison to other types of detectors they have high resolution with FWHM ≈ 1 keV. Gradually, however, some disadvantages in certain applications appeared (especially in medical science). These include low efficiency for detection of radiation with energy higher than 20 keV, in the case of Si detectors, difficulty in obtaining a relatively high volume (up to 100 cm³) in the case of Ge and the necessity of cooling down during operation in the case of both materials. Therefore, intensive search was made for new materials having a high detection efficiency, lower volume and a comparable resolution when operating at room temperature. Require-

ments for material suitable for construction of spectrometric gamma-ray detectors with a resolution ~ 1 keV and operational temperature 300 K are given in Table 1 [1]. CdTe, HgI₂, GaAs and, especially recently, CdZnTe appeared as suitable materials.

2. Comparison between CdTe and CdZnTe detectors

Among the semiconductor materials, CdTe and Cd_{1-x}Zn_xTe (CZT) offer some of the best sets of properties [2]:

- (1) High atomic number (~ 50) and high density (~ 6 g/cm³), which imply high quantum efficiency for photon energies below 180 keV even for a thickness smaller than 4 mm.
- (2) Area of single-element detectors or pitch sizes of segmented electrode monolithic detectors

*Corresponding author.

E-mail address: franc@karlov.mff.cuni.cz (J. Franc)

Table 1

Parameter	Demand
Atomic number	$Z > 40$
Detector thickness	$L > 2$ mm
Energy gap	$E_g \sim 1.0$ eV
Trapping centres	$N_T < 5 \times 10^{12} \text{ cm}^{-3}$
Carrier mobility	$\mu > 100 \text{ cm}^2/\text{V s}$
Donors, acceptors	$ N_D - N_A \leq 5 \times 10^{11} \text{ cm}^{-3}$
Contacts	Non-injecting

can be small, allowing for good spatial resolution in imaging systems.

- (3) CdTe and CZT detectors have energy resolutions much superior to scintillator detectors. They are therefore preferred in energy dispersive systems where selected photon energy groups are needed or in applications where scattered photon rejection is important.
- (4) The higher resistivity of CZT detectors, implying lower leakage currents compared to CdTe detectors, allows their use in low-photon-energy dispersive systems. It also enables the use of relatively large detector volumes.
- (5) Direct conversion of the energy deposited by the photon interaction produces larger induced currents than those obtained with scintillator detectors. This is beneficial in systems operating both in pulse mode or in current (charge integration) mode.
- (6) The low leakage current, in particular that of CZT, allows their use with power-miniaturized hybrid or integrated low-power electronic systems.

Because of these advantages, CdTe and CdZnTe have great potential for medical and nuclear imaging applications. The main drawback of CdTe and CdZnTe is low efficiency for collection of holes. The total charge collection is related to the mobility–lifetime product of electrons and holes which is strongly influenced by electrically active defects. These defects act as trapping or recombination centres that decrease the effective charge collection, leading to a degradation of CZT detector performance. This ensues from Hecht's relation [3] for

Table 2

Characteristics	CdTe(Cl)	$\text{Cd}_{(1-x)}\text{Zn}_{(x)}\text{Te } x = 0.1$
Band gap (eV)	1.47	1.65
Mobility ($\text{cm}^2/\text{V s}$)	e: 1000–1100 h: 80	e: 1000–1100 h: 50
Mobility–lifetime product $\mu\tau$ (cm^2/V)	e: 10^{-4} – 2×10^{-3} h: 10^{-5} – 10^{-4}	e: 8×10^{-4} – 9×10^{-3} h: 3×10^{-6} – 6×10^{-5}
Resistivity ($\Omega \text{ cm}$)	10^9 – 3×10^9	5×10^{10} – 10^{11}
Typical operating electrical fields (V/cm)	300–500	900–1500

the charge collection efficiency dependence on the photon conversion depth.

The most frequently used source materials so far are:

- (a) CdTe single crystals prepared from Te solution and Cl doped (CdTe(Cl)),
- (b) CdZnTe single crystals produced by the High Pressure Bridgman Method.

A comparison is given of the properties of CdTe(Cl) and CdZnTe containing 10% of Zn in Table 2 [2].

3. CdTe(Cl)

We prepared CdTe(Cl) single crystals by a Bridgman method from Te solution. Cl with a concentration $\approx 10^{18} \text{ cm}^{-3}$ was used as a dopant [4]. The samples had resistivity $\rho \approx 2 \times 10^8 \Omega \text{ cm}$ and mobility $\mu \approx 40 \text{ cm}^2/\text{V s}$ at room temperature. Detectors were fabricated with dimensions $5 \times 5 \times 1 \text{ mm}^3$ and Au contacts prepared chemically from AuCl_3 solution. The quality of the detectors was tested with ^{57}Co and ^{241}Am sources. In the ^{57}Co spectrum (Fig. 1), low noise is demonstrated by the visibility of the 14 keV peak and good resolution $\approx 7 \text{ keV}$ (FWHM) evident from the separation of the 122 and 136 keV peaks. In the ^{241}Am spectrum (Fig. 2) both L_α 14 keV and L_β 18 keV peaks are well resolved.

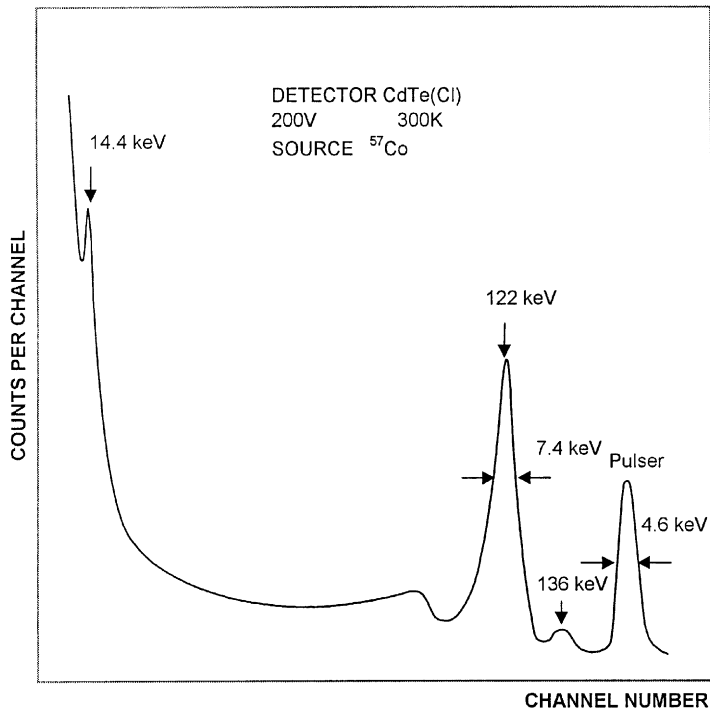


Fig. 1. ^{57}Co gamma-ray spectrum of our CdTe(CI) at room temperature.

4. CdZnTe

The CdZnTe detectors are not yet prepared in our institute, but their fabrication will be started within a year. So far we concentrated on developing technologies for HgCdTe epitaxial growth of high purity, large diameter (up to 10 cm) single crystal-line substrates (for long wavelength infrared focal plane arrays) and on methods of crystal characterization.

4.1. Crystal growth

$\text{Cd}_{1-x}\text{Zn}_x\text{Te}$ ($x = 0.04\text{--}0.1$) single crystals with a diameter up to 100 mm and height at most 35 mm were prepared in a vertical arrangement by gradual cooling of the melt (the Vertical Gradient Freeze method). Source material of high purity (CdZn)Te polycrystals, synthesized from 6N source materials, was placed in unseeded ampoules in a commercial single zone furnace. The temperature gradient was

$\Delta T \approx 1\text{--}2^\circ\text{C}/\text{cm}$ and an overpressure of Cd ≈ 1 atm was maintained in the quartz ampoule during the growth. The crystals grew in $\langle 111 \rangle$ or $\langle 100 \rangle$ orientations, the $\langle 111 \rangle$ orientation being superior. In the case of normal crystallization, the surface of our single crystals does not deviate from the (111) plane by more than 3° . The $\langle 111 \rangle$ crystals are twin-free and from SEM and microprobe analysis no precipitates with diameter greater than $1\text{ }\mu\text{m}$ were observed. The average density of dislocation etch pits revealed by the Nakagawa etchant [5] is around $5 \times 10^4\text{ cm}^{-2}$. The samples have almost constant transmittance in the spectral range $4000\text{--}500\text{ cm}^{-1}$ ($2.5\text{--}20\text{ }\mu\text{m}$), with a value determined by reflectivity losses only (transmissivity $> 60\%$).

4.2. Crystal structure

A very good microstructure was observed using an X-ray diffraction rocking curve method, especially

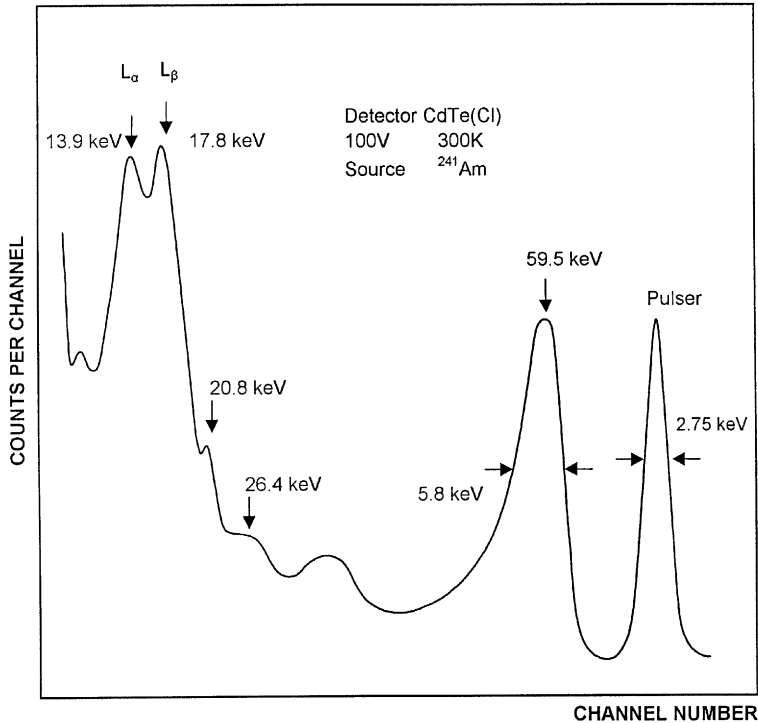


Fig. 2. ^{241}Am gamma-ray spectrum of our CdTe(Cl) at room temperature.

in the central part of crystals with orientation $\langle 111 \rangle$. Some single crystals showed low values of the full-width at half-maximum (FWHM) (in the range of 10–20 arcs) even at the edge of 90 mm diameter wafers. We found the minimum FWHM to be about 8 arcs (the theoretical value is 5.6 arcs).

4.3. Electrical properties

The as-grown single crystals are both p-type and n-type, depending on the Cd overpressure during the growth and on cooling conditions. The mobility of p-type samples at 300 K varies typically between 25 and 80 $\text{cm}^2/\text{V s}$. The n-type samples have an electron mobility of 500–1000 $\text{cm}^2/\text{V s}$.

The diffusion length of minority carriers, L , and the corresponding $\mu\tau$ product ($\mu\tau = L^2 e/kT$) were determined by electron beam induced current (EBIC) measurements using a JEOL JSM-50 SEM with computer-controlled beam scanning and digital data acquisition. The determination of the

diffusion length L was accomplished from EBIC measurements in the SEM on a planar Schottky structure produced by evaporation of Au on a part of the sample surface through a metallic mask [6].

The measured values of L , together with other galvanomagnetic data measured at 300 K, are given in Table 3. It should be noted that these values are longer in comparison with those published for pure CdTe (typically around 1 μm). Fig. 3 shows the temperature dependence (90–300 K) of the mobility–lifetime product for electrons in three p-type samples listed in Table 3. A steep increase of L and of the corresponding mobility–lifetime product ($\mu\tau$) is observed with decreasing temperature in some samples, while other samples show a much slower increase. Comparison of photoluminescence spectra measured at 6 K shows that in our samples with low diffusion length at 90 K (No. 4 in Fig. 3), donor–acceptor pair (DAP) recombination prevails. On the contrary, in high diffusion length samples (Nos. 1 and 2 in Fig. 3), conduction band to

Table 3
Electrical parameters of (CdZn)Te samples at 300 K

Sample	Conduct. type	Resistivity (Ω cm)	Conc. (cm^{-3})	Mobility of majority ($\text{cm}^2/\text{V s}$) carriers	Diffusion length of minority carriers (μm)	$\mu\tau$ (cm^2/V) (minority carriers)
1	P	1.4×10^5	4.4×10^{13}	25	15	8.7×10^{-5}
2	P	2.3	3.5×10^{16}	77	6.6	1.7×10^{-5}
3	P	75	1.5×10^{15}	70	5.8	1.3×10^{-5}
4	P	911	1.2×10^{14}	57	6.6	1.7×10^{-5}

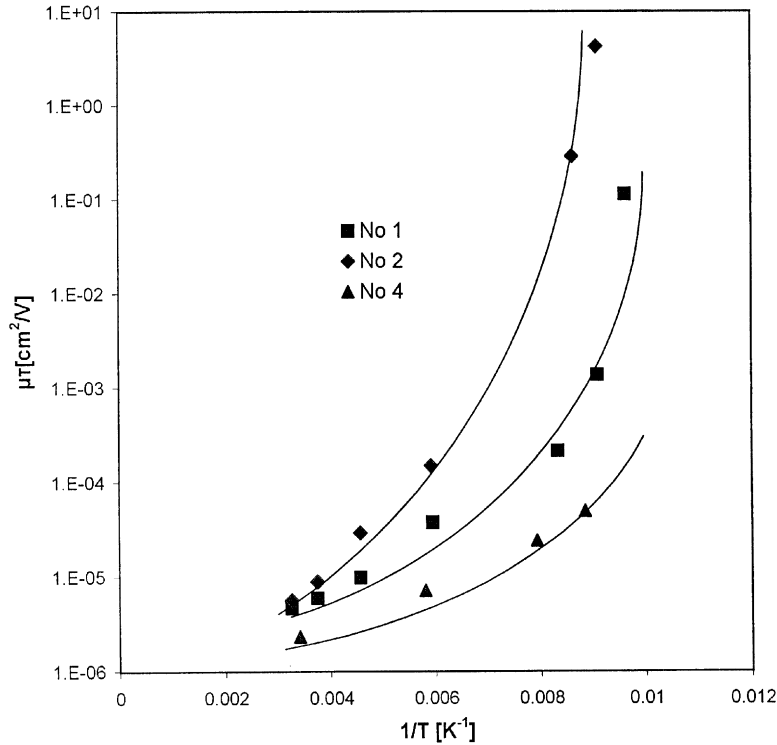


Fig. 3. Mobility–lifetime product of electrons in p-(CdZn)Te samples from 90 to 300 K.

acceptor recombination (e, A^0) dominates this part of the spectra, even at low temperature. In both types of sample the luminescence was low in the deeper acceptor region ($200 \text{ meV} < (h\omega/2\pi) - E_g < 120 \text{ meV}$) where, for example, recombination at A-centres, V_{Cd} -donor, appears.

We suppose that more convenient arrangement of point defects into complexes with low binding energy causes slower recombination through deep levels. This is manifested by long diffusion length (at 90 K).

The goal of our activity in the future is to reach, by proper annealing or doping, detector grade quality in our (CdZn)Te single crystals currently prepared by Vertical Gradient Freezing method as substrates for epitaxial technologies.

5. Conclusion

Spectra of CdTe(Cl) detectors prepared by the Bridgman method from a Te-rich melt are presented.

The quality of the detectors was tested with ^{57}Co and ^{241}Am sources. A good resolution is observed in both cases. A review is given of state-of-the-art properties of (CdZn)Te single crystals prepared for substrates in the Institute of Physics of Charles University.

Acknowledgements

This work was supported in part by a grant from the Ministry of Schools, Youth and Sport of the Czech Republic under contract No. VS 97113, grant agency of the Czech Republic under contract No. 202/96/1188 and 202/97/SP072 and the grant

agency of the Charles University under Nos. 176/1996 and 42/1997.

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