Solution growth of cadmium telluride[†]

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Abstract. Cadmium telluride crystal has been grown by solution method from Te-rich ($\text{Cd}_{0.3}\text{Te}_{0.7}$) melt. Ingots having 9 mm diameter and length up to 30 mm were grown by cooling the melt slowly (1°C/h) under a vertical temperature gradient of about 30°C/cm . As-grown ingots were characterized for optical transmission and resistivity. The middle portion of the ingots exhibited better optical transmission properties. Resistivity (p -type) was found increasing, towards the last-to-grow end, from 10^3 to $10^6 \Omega\text{-cm}$. Surface barrier type of detectors, made from low resistivity ($\approx 10^4 \Omega\text{-cm}$) materials, were found suitable for detection of X - and low energy gamma radiations. In case of high resistivity ($\approx 10^6 \Omega\text{-cm}$) detectors, the performance was seen to be affected by polarization.

Keywords. Cadmium telluride; solution growth; gamma ray.

1. Introduction

Cadmium telluride (CdTe), a high Z (48, 52) and wide band gap (1.5 eV) semiconductor, is a suitable material for detection of γ -rays in nuclear applications such as medicine, reactor instrumentations and safety (Cuzin 1987; Entine *et al* 1989). Crystal growth by solution method at temperature lower than its melting point (1090°C) has been found to yield CdTe with lower dislocation density, a reduced precipitate density due to reduced deviation from stoichiometry and lesser contamination from container during growth (Wald and Entine 1978). Purification during growth due to the process of solvent (Te) extraction has also been reported (Zanio 1974). The purity and perfection so obtained is expected to yield crystal of higher values of resistivity, carrier mobility and excess carrier lifetime required for achieving better detector performance (Zanio 1978; Siffert 1983).

We have grown CdTe crystals by solution method (Zanio 1974) from tellurium-rich ($\text{Cd}_{0.3}\text{Te}_{0.7}$) melt. The extra amount (40% atomic) of Te in the melt acts as a solvent. As-grown ingots were characterized for some of the relevant optical and electrical properties. Surface barrier type of devices were fabricated from the grown crystals and tested for detection of γ -rays of various energies.

2. Crystal growth

The solution growth was based on unidirectional precipitation of CdTe from Te-rich melt by slow cooling in a vertical temperature gradient furnace. The starting melt composition was fixed at $\text{Cd}_{0.3}\text{Te}_{0.7}$. About 20 g of 99.99% purity Cd (Cominco, Canada) and Te (Leico, USA) in the required proportion was vacuum (10^{-4} torr) sealed in cleaned silica ampoule after repeated flushing with iolar argon gas. The charged ampoule was then positioned in a crystal growth furnace (Sahoo and Srikantiah 1991) such that an axial temperature gradient of about 30°C/cm is imposed on the melt (figure 1). The power to the furnace was fed through a temperature controller cum

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Figure 1. Axial temperature profile of the furnace used for growth of CdTe crystal by solution method.

programmer (Eurotherm 818P, UK). The temperature of the ampoule tip was raised at a rate of 120°C/h to 980°C (30°C above the liquidus temperature) and then brought down slowly at a rate of 1°C/h to 300°C for growing the crystal. The crystal was expected to grow as the melt at bottom gets supersaturated with CdTe due to fall of its temperature below the liquidus value. After the growth was over, the ingot was cooled down to the room temperature at a faster rate of 20°C/h . Temperature was controlled within $\pm 0.1^{\circ}\text{C}$ throughout the growth process by auto tuning of the PID control parameters. It took nearly a month to grow a 25 mm long ingot.

CdTe ingots having lengths up to 30 mm and diameter of 9 mm were grown under the same conditions. They did not stick to the ampoule and were free from any visible crack or void. Ingots were taken out of the ampoule without any damage by etching the silica wall in hydrofluoric acid. As expected from the composition–temperature phase diagram (Zanio 1978), the extra Te was seen to have got displaced to the top (figure 2). The CdTe/Te interface region was not sharp but consisted of both CdTe and Te phases. This could be due to poor growth conditions at temperature close to the melting point of Te (450°C). Slices cut across the ingots, when lapped, showed that the ingots were not entirely single crystal but contained grains of sizes up to 5–6 mm.

3. Characterization

The ingots were characterized for optical and electrical properties at room temperature to evaluate the quality of the crystals and also to see the suitability of the growth technique to produce detector grade CdTe.

Figure 2. CdTe ingots grown by solution method.

3.1 Optical properties

The grown ingots were qualitatively analysed for CdTe phase purity by carrying out optical transmission measurements on about 1 mm thick samples with 5 mm diameter sampling area over the wavelength ranges of 0.8 to 1.1 and 2.5 to 40 μm . Mechanically polished samples were given a chemical polish in Br (3%)-methanol solution to improve transmission. The typical transmission curves obtained for samples taken from different positions of the ingots are given in figures 3 and 4. Sharp absorption edge was found at wavelength 850 nm that closely matched the bandgap (1.5 eV) of CdTe. Samples from the middle portion of the ingots showed IR (2.5–25 μm) transmission percentages close to the theoretical values of about 66% (Gentile 1988). The reduction in IR transparency of the tip region, grown at temperature close to 950°C, and the top region, grown at temperature close to 450°C, is attributed to higher concentration of Te precipitates and/or inclusions (Wald and Entine 1978). It may be noted that the growth temperature in the case of another Te solvent technique, the travelling heater method, is chosen between 700 and 900°C to grow good quality crystals (Siffert 1983).

3.2 Electrical properties

The basic electrical properties like resistivity, carrier concentration and excess carrier lifetime are required to be known for the design and fabrication of any possible device.

Figure 3. Optical transmission spectra of samples from different positions of a solution grown CdTe ingot (from tip side): (1) 10 mm (1.2 mm thick) and (2) 26 mm (0.9 mm thick).

Figure 4. Infrared transmission spectra of samples from different positions of a solution grown ingot (from tip side): (1) 15 mm (1.5 mm thick) and (2) 8 mm (1.2 mm thick).

The as-grown CdTe ingots were thoroughly characterized for resistivity at room temperature. Their carrier type was found from the polarity dependence of current-voltage ($I-V$) characteristics of metal/CdTe rectifying contacts. Carrier concentration was estimated from the resistivity we measured and the reported figure of carrier mobility. Direct measurement of carrier concentration by dc Hall method could not be carried out due to the instability of contacts. The diode capacitance-voltage ($C-V$) technique (Hilibrand and Gold 1960) could not be followed, because the rectifying

metal/CdTe contacts, we prepared, were not of Schottky type. Measurement of excess carrier lifetime by photoconductive decay method was not possible due to trapping (Bray and Many 1959). When samples with low resistive contacts were exposed to short (a few μs) infrared pulses, the photoconductive decay curves were found nonexponential in nature and have long (a few ms) tail indicating the occurrence of trapping and detrapping of carriers.

3.2a Resistivity: First of all we looked for an ohmic contact to our samples. As the Te-rich melt grown crystals were expected to be *p*-type (Zanio 1978), electroless plating of gold from aqueous gold chloride solution was tried (Mancini *et al* 1982). The plating was said to provide a p^+ layer by depleting Cd below the gold layer and thus helped in making low resistive contact (Aven and Swank 1969). About 1 mm thick samples were chemically polished, except at the edge, in Br(3%)-methanol solution and then provided with two asymmetric circular type of contacts to see their behaviour from I - V characteristics (Henisch 1984). The measurements were carried out with Keithley 617 electrometer. The presence of contact induced surface barrier was confirmed by 5.48 MeV ^{241}Am - α counting (in unbiased condition). In case of Au contacts on samples from lower portion of the ingots, the nonohmic behaviour was evident from the polarity dependence of I - V characteristics (figure 5a). Nearly ohmic contact could only be made on samples from the top portion.

Behaviour of a few other contacts (evaporated Al, Au, Ag paste) made on samples after different surface treatments (lapping, mechanical polishing and/or chemical polishing) was studied. The Au plated on bromine polished surface and Ag paste applied on lapped surface of any sample were the least and the most rectifying of all the contacts respectively. The Ag contact got reverse biased on application of positive voltage, whereas Au contact required negative voltage to behave in the same way (see figure 5).

Resistivity was measured on 1 mm thick samples provided with two circular type of symmetrical contacts. First of all a figure on higher side of the actual resistivity was found out from the slope of I - V characteristic of the sample with low resistive Au

Figure 5. I - V characteristics of a $10^4 \Omega\text{-cm}$ resistivity 1 mm thick sample with two asymmetric contacts (C1: 2.5 mm dia.; C2: 4 mm dia.) of electroless plated gold (a) and silver paste (b).

contacts. In case of samples with nearly ohmic Au contacts, a better figure for the resistivity ($\gtrsim 10^4 \Omega\text{-cm}$) was obtained from a.c. conductance measured with Keithley 590 1 MHz $C-V$ (capacitance-voltage) analyser.

In case of samples for which an ohmic contact was not available, the resistivity figure ($< 10^5 \Omega\text{-cm}$) was determined from the series resistance of a sample provided with rectifying Ag paste contacts. The series resistance (at zero bias), R_s , was measured with Keithley $C-V$ analyser. The contribution of the Ag contacts to the series resistance was ensured to be negligible from the proportionality of R_s with sample thickness. For low resistivity ($\leq 10^4 \Omega\text{-cm}$) CdTe, the 1 MHz bulk dissipation factor, $D_B (= 1/\omega\epsilon_0\epsilon\rho)$, is greater than 15. Thus, the value of bulk resistance,

$$R_B (= [(1 + D_B^2)/D_B^2] \times R_s),$$

was taken to be same as that of the series resistance. The contact induced depletion widths ($< 20 \mu\text{m}$) were neglected for 1 mm thick low resistivity samples (Siffert 1978), to find the bulk resistivity, ρ_B , from the expression given as:

$$\rho_B = R_s [A/(L - 2W)] \approx R_s A/L, \quad (\text{for } W \ll L),$$

where A is the contact area, L the sample thickness and W the contact induced depletion width.

Resistivity was found increasing along the ingots from $10^3 \Omega\text{-cm}$ at the tip to $10^6 \Omega\text{-cm}$ at the top. The major portion, at the middle, which exhibited better optical transmission properties, showed resistivity of the order of $10^4 \Omega\text{-cm}$. The samples taken from the top portion, which were less transparent to IR, exhibited higher resistivity. The resistivity of CdTe is thought to be controlled by compensation of Cd vacancies (acceptors) by impurities and/or their complexes (Siffert 1983; Samimi *et al* 1989) and also to a lesser extent by Te inclusions which affect the mobility of carriers.

3.2b Carrier concentration: The p -type behaviour of the as-grown CdTe was evident from the polarity dependence of $I-V$ characteristics of samples with asymmetric Ag contacts (figure 5b). The behaviour of the low resistive Au contacts, as shown in figure 5a may be explained by taking the contact structure as that of $\text{Au}/p^+/p\text{-CdTe}$ (Aven and Swank 1969; Mancini 1982). The low resistive Au contacts were not suitable to determine carrier concentration by dc Hall method. Capacitance measurements (Hilibrand and Gold 1960) were carried out on 1 mm thick as-grown samples with 2 mm diameter surface barrier type of metal (Au, Al) contact (deposited on mechanically polished surface by thermal evaporation) on one side and the least resistive 2 mm diameter Au back contact (plated on Br polished surface) on the other. Measurements were carried out with Keithley 1 MHz $C-V$ analyser. As the 1 mm thick samples were expected to have large values of series resistance, capacitance was obtained in series model. The $1/C^2$ vs reverse bias voltage curves did not show the characteristics expected of a Schottky diode (figure 6). The effect of bias voltage on capacitance was found decreasing with increase in material resistivity. For $10^6 \Omega\text{-cm}$ materials the dependence of capacitance on voltage was not appreciable. The presence of deep level states either at the surface or in the bulk, which affects the capacitance behaviour of metal/CdTe diodes (Rabin *et al* 1978), was evident from the large values (a few seconds) of diode recovery time. For high resistivity ($> 10^5 \Omega\text{-cm}$) materials, the bulk region is also expected to interfere in obtaining the high frequency (1 MHz) diode capacitance.

Figure 6. Plot of $1/C^2$ vs reverse bias for Au/p-CdTe diodes for two different bulk resistivities.

Hole concentration in the as-grown ingots, as estimated from the measured resistivity and hole mobility of $80 \text{ cm}^2/V\cdot\text{sec}$ (Siffert 1983), varied between 10^{11} to $10^{14}/\text{cm}^3$. We find that the carrier concentration determined from the slope of $1/C^2$ - V curve matches the estimated figure better at higher bias voltage.

4. Detector performance

Surface barrier type of low energy γ -ray detectors was fabricated using 0.5 mm thick and about 5 mm diameter low resistivity ($\approx 10^4 \Omega\text{-cm}$) samples. The radiation sensitive 1.5 to 2.5 mm diameter front contact (C1) was prepared by either applying Ag paste or depositing Al by thermal evaporation on lapped surface. The low resistive 3 mm diameter back contact (C2) was prepared by electroless plating of Au on Br polished surface. Devices were encapsulated either in metal housing with microdot connector for front side exposure of radiation or directly inside BNC connector for back exposure (figure 7). Figure 8 shows the typical I - V characteristics of the devices. Performance testing was carried out at room temperature in reverse biased as well as photovoltaic mode of operation. Pulse height spectra for γ -rays were taken by applying positive (reverse) bias to the C1 contact with a load resistance of $110 \text{ M}\Omega$ and then followed by charge sensitive preamplifier (Gyanic 9421), shaping amplifier (ORT 571) and multi-channel analyser (EC4010).

The typical spectrum for ^{241}Am 59.5 KeV γ -rays, obtained with optimum bias and shaping time, is shown in figure 9. Detectors having sensitive area of 2 mm^2 showed full width at half maximum (FWHM) energy resolution of 8 to 15 KeV. For ^{57}Co 122 KeV

Figure 7. Device encapsulation: (a) Detector geometry, (b) direct mounting inside BNC connector and (c) mounting inside metal housing with microdot connector.

Figure 8. I - V characteristics of a p -type CdTe surface barrier detector (Bulk resistivity $\approx 10^4 \Omega\text{-cm}$).

γ -rays, the resolution was not that good (figure 10). In photovoltaic mode, the output (shortcircuit photocurrent) of the devices was found linearly increasing with 60 KeV- γ exposure rate up to 1R/h (figure 11). Detectors having sensitive area up to 12 mm^2 could produce photocurrent density of about 20 pA/mm^2 for an exposure rate of 1R/h.

Figure 9. ^{241}Am γ -ray pulse-height spectrum obtained with a p -type CdTe surface barrier detector (Bulk resistivity $\approx 10^4 \Omega\text{-cm}$, sensitive area diameter = 1.5 mm, thickness = 0.5 mm, bias = 180 V, pulse shaping time = 1 μs).

Figure 10. ^{57}Co γ -ray pulse-height spectrum obtained with the same detector as mentioned in figure 9.

Detectors were also made from 1 to 1.5 mm thick high resistivity ($\approx 10^6 \Omega\text{-cm}$) materials for detection of γ -rays of higher energy (Siffert 1978). The method of making the contacts was kept the same as that of low resistivity detector. The pulse height spectrum for ^{137}Cs 662 KeV γ -rays is produced in figure 12. As expected, the detectors showed more efficiency in counting 662 KeV γ -ray. However, their count rate was found dropping slowly over a period of hours. This kind of behaviour is attributed to polarization (under bias) causing reduction in thickness of the detector sensitive volume (Siffert 1978).

Figure 11. Photocurrent output of a photovoltaic CdTe detector for front side exposure of ^{241}Am γ -rays (Detector bulk resistivity $\approx 10^4 \Omega\text{-cm}$, sensitive area diameter = 1.5 mm, thickness = 0.3 mm).

Figure 12. ^{137}Cs γ -ray response (logarithmic) of a high resistivity ($10^6 \Omega\text{-cm}$) CdTe detector (Detector sensitive area diameter = 1.5 mm, thickness = 0.9 mm, bias = 550 V, pulse shaping time = 2 μs).

5. Conclusions

CdTe ingots containing crystallites of size up to 5 mm were grown from Te-rich ($\text{Cd}_{0.3}\text{Te}_{0.7}$) melt by slow cooling under a vertical temperature gradient. They exhibited reproducible optical transmission and electrical properties. The resistivity was found increasing along the 30 mm long ingots from $10^3 \Omega\text{-cm}$ at the tip to $10^6 \Omega\text{-cm}$ at

the top. Thus the yield for a material of particular resistivity was quite low. However, the major portion of the ingots, at the middle, showed resistivity of the order of $10^4 \Omega\text{-cm}$.

In the absence of a suitable ohmic contact on low resistivity ($\lesssim 10^4 \Omega\text{-cm}$) *p*-type CdTe, the resistivity was obtained from the series resistance of sample with rectifying contacts.

The as-grown low resistivity ($\approx 10^4 \Omega\text{-cm}$) materials were suitable for making surface barrier type of detectors for use as energy discriminators as well as dosimeters for X- and low energy ($\leq 150 \text{ KeV}$) gamma radiations. Performance of high resistivity ($\approx 10^6 \Omega\text{-cm}$) detectors was found to be affected by polarization.

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