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New approaches in order to enlarge the grain size of bulk CdZnTe (CZT) crystals

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For the few decades, II-VI compound semiconductors are gaining attention because of its numerous applications in the field of detector technology, photovoltaic, nuclear medicine, astronomy etc. In the recent past, materials scientists focused their attention for the growth of CdTe/CdZnTe single crystals because it doesn't require any specialized cooling and detects higher energy photos as in comparison with the existing Ge, Si and HgI_2 detectors. In the present study, we are going to discuss five main approaches in order to get good quality CZT crystal and we have successfully grown the CZT crystal by adopting these approaches. They are: i) oscillatory Bridgman technique previous to the growth process, ii) modifying the thermal environments in a Bridgman geometry using a Pt tube as a cold finger in order to reduce the growth velocity iii) growth from the vapour phase using Bridgman geometry with a pyrolitic boron nitride (PBN) crucible to locate the feed material, and with a special temperature profile, iv) microgravity experiments in the FOTON M3 mission using magnetic field prior to the growth process and v) growth by a boron oxide encapsulation. The detailed discussions are given in the following sections.

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1. Introduction

In the recent years, solid state detectors are gaining attention due to its excellent behaviour and smart characteristics. These types of solid state detectors which converts the incident photons into electrical pulses and they are made from a variety of materials including: Germanium –Ge-, Silicon –Si-, Cadmium Telluride –CdTe-, Mercuric Iodide –HgI_2-, and Cadmium Zinc Telluride –CZT- [1-3]. In this list, Ge detectors have shown best resolution, but it requires liquid nitrogen cooling which makes them impractical for portable applications, where as Si and HgI_2 is inefficient to detect higher energy photos and poor stability at room temperature [4]. For these reasons, detectors made from CdTe compounds are routinely used for nowadays. In fact, CZT is one of the most important material which is used in a wide variety of applications such as X and γ-ray detectors, medical imaging and security fields. It is also used in space applications and is ideally suited for small-sized satellites.

Detectors made from CZT crystals are very compact and requires minimum power and compatible with modern electronics. Nevertheless, the best CZT detector for a given application depends several factors, which includes an optimization in the physical and chemical properties such as: i) high resistivity properties, where an intrinsic donor probably involving Te- antisite seems to be necessary, ii) high mobility lifetime for electrons and holes which is a mandatory requirement, with an optimization of the compensation mechanism due to a reduction of the deep intrinsic acceptor Cd-vacancy; and iii) excellent sample quality, which includes large areas single crystals with a minimum content of Te inclusions [5-11]. Whereas the first two factors are very well known and practically solved, but the grain size and the Te inclusions problems are yet to be solved and require intensive research.

For these reasons, in the present paper we are going to focus our attention in the above said aspect, and which we have been carried out the experimental study for the past few months in our consortium group, with the main objective of enlarging the grain size, which is the mandatory requirement for device fabrications.

2. Results and discussion

2.1. Oscillatory Bridgman (OBR) method with superheating conditions

The first approach for obtaining large size CZT single crystal is by adopting the Oscillatory Bridgman –OBR-technique, following the ideas of a recent paper published by Edgardo et al [12] for CdTe bulk crystals. In the present

study, the same technique was implemented for the title compound growth by considering its physico-chemical properties.

After carrying out the preliminary cleaning process of the quartz ampoule, the starting single element materials of Cd, Zn, Te (6N purity) were introduced into the graphitized ampoule. After a period of 12 hours at dynamic high vacuum, the ampoule was closed with a quartz rod situated on the top of the ampoule and the proximity of the charge, leaving a fixed empty space which represents approximately the same volume compared with the melted charge.

The molten process has been carried out in four steps: the pre heating process starts from RT to 500 ºC at a rate of 50 ºC/h and remains at this temperature for 12hrs, followed by a second heating process at a rate of 50º/C in order to reach 900 ºC and remains same for another 12hrs; then it will attain 1000 ºC at a ramp of 50 ºC/h and remains for 12hrs, and finally reaching the maximum temperature of 1185 ºC in 4h. This maximum temperature is used when the composition of $Cd_{1-x}Zn_xTe$ (x= 15%) is prepared, considering a superheating of 20 ºC. The subsequent step is the oscillation of the furnace at this maximum temperature and that has been carried out by oscillating the furnace from the vertical position between +15º and -15º for about 30 minutes. This operation has been performed around 60 times. Both the experimental approaches viz. oscillation and superheating were executed with the objective of obtaining a good mixture and breaking down of the Te inclusions respectively, as an important step for the production of large grain size in CZT bulk crystals.

Fig.1. Wafer of the ingot grown by OBR with superheating conditions.

The next stage is the growth process which is accomplished by the displacement of the ampoule at a rate of 0.4mm/h and followed by cooling. In the present study, the growth has been achieved at different cooling rates such as: from maximum temperature to 900 ºC at a rate of 5 ºC/h, followed by 10 ºC/h till 750 ºC, and finally a rate of 25 ºC/h till it reaches to RT. The bulk crystals obtained after the experimental process which is described earlier have considerable grain size, with a double average value compared with the diameter of the ampoule. Whereas, this situation doesn't occur when the absence of both the experimental approaches in a conventional Bridgman process. Figure 1 shows the ingot wafer grown by OBR technique with superheating conditions, where the grain size has an average value of about 10 cm^2 for a given 27 cm diameter of the ampoule. Finally we conclude that the proposed experimental approaches of superheating and oscillation of the furnace at high temperature in a Bridgman process improve considerably the possibility of getting larger grain size CZT single crystals.

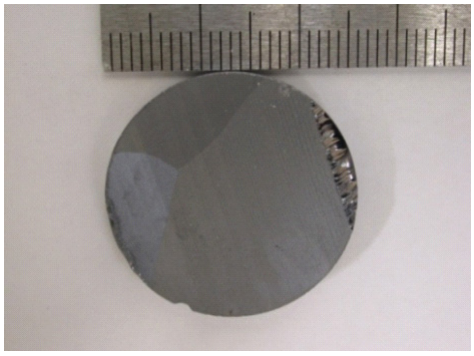
2.2. Modifying the thermal environments in a Bridgman process using a platinum (Pt) tube as a cold finger

The Bridgman method is the most commonly used growth method for obtaining larger size CZT crystals. Nevertheless there are some common problems due to its growth geometry, being most of them consequence of the thermal environments given by a fixed geometry, and the wetting of the melt with the quartz ampoule. These two problems will be discussed in the following comments using two approaches: by modification of the thermal environments by using a Pt tube, and the use of a Pyrolitic Boron Nitride (PBN) crucible. The thermal environments during the process of crystal growth are extremely important by considering the influence of its solid liquid interface. Moreover, in the case of CZT crystals, where the thermal conductivity of the liquid is double when compared with the solid (0.02 and 0.01 W/cm ºK respectively), and the heat exchange during the process of crystal growth must be carefully considered.

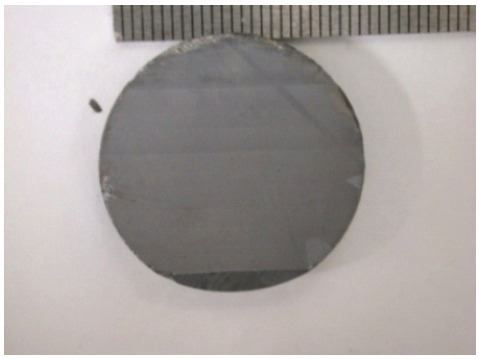
In fact, the conventional Bridgman growth method shows the general temperature profile which comes from the fixed geometry of a commercial furnace, although this can be modified by the incorporation of extra furnaces in a fixed or movable positions. The another approach is the use of Pt cold finger tube in order to create a suitable thermal gradient in the Bridgman furnace, following an idea proposed by Derby et al [13], whereas they have used graphite and mullite as a crucible support. Considering the last conclusion of the commented paper [13], where an anisotropic cold finger could be an appropriate solution for improving the thermal environment and getting a slightly convex solid liquid interface. In the present study, we have carried out the experiments by using the Pt tube in order to increase the axial heat flow and simultaneously decrease the radial heat flow, by taking into account of its thermal conductivity (0.716W/cm ºK).

The Pt tube was introduced at the bottom of the quartz ready ampoule containing the charge and prepared in the way described in section 2.1. The Pt tube has the same diameter of the quartz ampoule with a value of 27 mm, and a length of 20 cm having the thickness of 1mm. The top portion of the Pt tube is in touch with the bulb portion of the CZT quartz ampoule in order to modify the heat transfer from the crystallized material to the cold part of the Pt tube. One must understand that the temperature difference between the hot and the cold part of the Pt tube is around 300 ºC, by considering our experimental conditions. A series of fixed thermocouples which were located spirally along the whole external part of the quartz ampoule at a distance of 10 mm with each other, while the other series of thermocouples were placed below the

quartz ampoule, in order to have a complete picture of the thermal environments during the growth process.

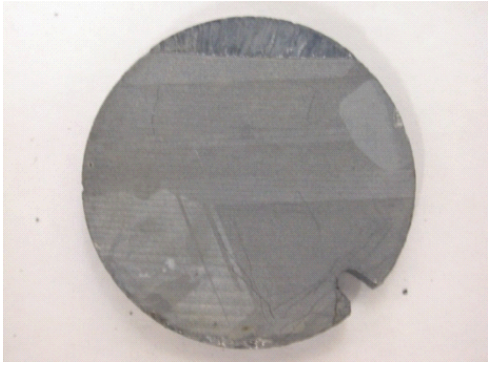


Radial section of ingot growth with Pt



Radial section of ingot growth with Pt

Radial section of ingot growth whitout Pt



Radial section of ingot growth whitout Pt

Fig. 2. Comparison between different wafers of the ingot grown by Bridgman method with and without Pt tube

One must comprehend that the heating, growth and cooling processes is similar to the one presented in section 2.1, although the geometry of the Bridgman furnace used for this approach is different. The experimental results obtained from this approach shows two important conclusions, if one compare both the experiments carried out with and without platinum tube:

i) There is a dramatic change in the temperature profile and modifying the total thermal environment of the system when a Pt tube is used as a cold finger. At the same time, when the absence of Pt tube the temperature gradients has a value of 1 ºC/cm, 1.5ºC/cm and 3 ºC/cm at a given position of the solid/liquid interface. Whereas the temperature gradient values at the same positions when a Pt tube is used are as follows: 4.5 ºC/cm, 5 ºC/cm and 5.5 ºC/cm.

ii) On the other hand, the value of the growth rate is drastically changed and it is 6 mm/h when the presence of the Pt tube whereas it is 3.9 mm/h when the Pt tube is absent. It is worth to mention here that in both the measurements the growth rate is measured with the thermocouples which indicate the evolution of the melting point with the time for a given CZT composition.

Fig. 2 shows the wafer grown in two different experimental conditions (with and without platinum tube) and clearly indicates the crystal obtained in this approach is clearly enlarged. From the above said discussion it is clearly observed that the small number of grains which appear when a Pt tube is used as a cold finger, as a clear consequence of this experimental approach.

2.3. Growth from the vapour phase by Bridgman method using PBN crucible

In this approach, Bridgman equipment is used with three independent commercial heating elements having a total length of 48 cm, coupled with each other in such a way to achieve the temperature profile shown in Fig. 3. The objective of this temperature profile is to obtain three temperature regions which are: i) a first plateau of nearly constant temperature, in order to obtain a given superheating of the melt, ii) a second region where the objective of the temperature profile is to create a fast drop in the temperature gradient in order to make the fast evaporation of the source material from the melt when the ampoule is moving down, and iii) whereas in the third region, annealing is to be performed in the resulted specimen. The entire growth experiment is controlled by a set of thermocouples located strategically along the external wall of the quartz tube.

The 230 mm lengthy quartz tube consists of a PBN crucible having the dimensions of 150 mm long, having the internal diameter of 24 mm, with a 1 mm wall thickness. The PBN crucible is located 60 mm from the bottom of the quartz tube and properly fixed by leaving a gap of 1mm between the PBN crucible wall and the internal wall of the quartz tube. The starting single elements of Cd, Zn and Te (6N purity) are loaded into the PBN crucible, leaving an empty volume space in the

quartz tube when the material is melted with a ratio 1:1 among the material melted and the empty volume.

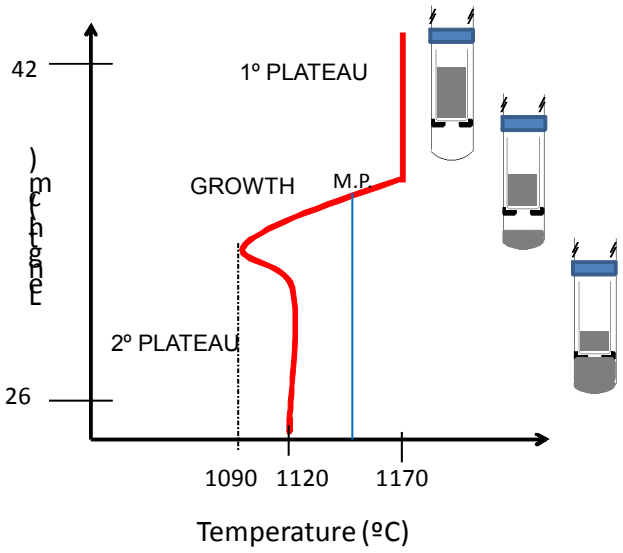


Fig. 3. Temperature profile of the vapour phase growth using Bridgman geometry with a PBN crucible

The molten process has been started in such a way that the first plateau follows the temperature procedure used in the approach 2.1, and leaving the second and third temperature regions at a temperature closer and lower than the melting point. When the temperature of the heaters placed in the furnace is adjusted in order to get the same profile trend which is given in Figure 3, and finally the growth process begins by moving down the quartz tube at a rate of 0.4 mm/h. Then the ampoule containing the charge will be slowly translated into the second plateau. The temperature setting for the growth and cooling process is one and the same which is described in section 2.1. Fig. 3 shows the schematic representation of the temperature profile and the position of the quartz tube which is used for the experimental study.

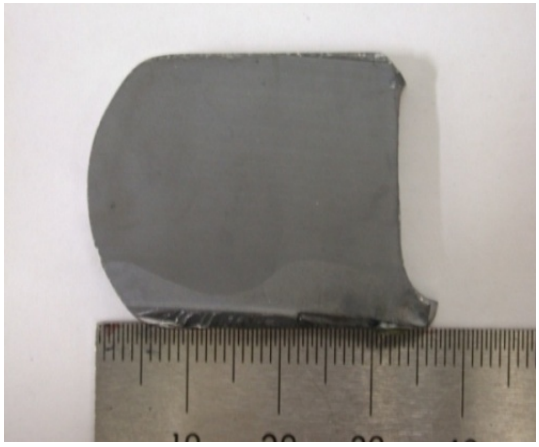


Fig. 4. Grown CZT specimen cut in an axial direction

The temperature profile is designed in such a way to allow the crystallization of $Cd_{1-x}Zn_xTe$ material on a vapour phase from melt by using the Bridgman configuration. The superheating of 20 ºC is imposed in the first plateau region, whereas the growth takes place in the second temperature region from vapour phase, and an in-situ annealing is carried out in the third temperature region in order to improve the quality of the crystals.

The results of this approach are spectacular in such a way that the entire crystal is a single crystal along the axial direction, although some small grains remain on the wall of the crucible. Figure 4 shows the crystal which is cut along the axial direction. On other hand, other advantage of this approach is that the twins which appear on the crystal follows a parallel line to the axial direction, in a contrary what it happens on the crystals grown from the melt on a Bridgman geometry, which they form an angle of around 30-40º with the axial growth direction.

2.4. Effect of the microgravity on the growth of CdZnTe using magnetic field prior to the growth process

The use of magnetic fields during crystal growth has been studied and improved during the last 20 years. Their main advantage is to provide an additional steering of the melt and thus to enhance the chemical homogeneity of the grown crystals. In the case for the growth of (Cd,Zn)Te, a Rotating Magnetic Field (RMF) can reduce the number of tellurium clusters in the melt during the step of the melt homogenization. The standard procedure to reduce this structural defect is to apply a superheating of 20 K above the melting point before starting the crystal growth. Rudolph [14] demonstrated a significant improvement in the crystallinity by this method. The same effect can be achieved using a RMF before starting the seeding process. The forced convection generated by the RMF transports these tellurium clusters into the hot zone of the melt in order to destroy them. This approach was proposed by Duffar et al. Under microgravity conditions, the influence of the magnetic field is stronger due to the drastic drop of the earth gravitational acceleration. The effect of reduction of the tellurium clusters should be more efficient.

In September 2007, two Bridgman experiments were carried out onboard FOTON M3 mission in the Polizon facility. Two (Cd,Zn)Te crystals were grown with 10 % zinc content and indium doping. The basic idea of these experiments was to study the phenomenon of dewetted growth in a conventional Bridgman configuration. Furthermore, a RMF was applied at the beginning of the experiment FMF-5-M during 1 hour in order to mix the melt and reduce the tellurium clusters. The RMF intensity was 4.5 mT with 100 Hz frequency. The RMF was switched off during the crystal growth. The pulling rate was 1.5 mm/h during 12 hours.

The grown specimen was characterized and it shows that the rotating magnetic field improved the structural quality of the crystal. The size of the single crystal is larger for the crystal of which melt was mixed during one

hour with the RMF than without it. Figure 5 shows the crystal grown under microgravity with and without RMF. There is a large grain starting in the seeding area going through the complete crystal. Resistivity was measured by Contactless Resistivity Mapping (COREMA) and it yields a homogeneous distribution of resistivity along the complete crystal. The average resistivity is 2 x 10^9 ohm·cm. Further detailed characterizations will be performed, and especially on the analysis of the tellurium inclusions density with the help of the infrared microscopy

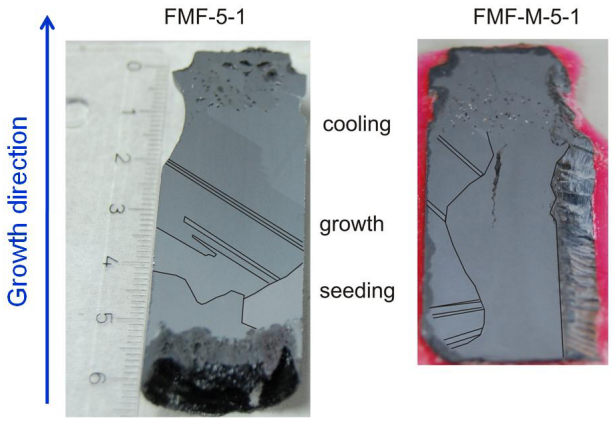


Fig. 5. (Cd,Zn)Te crystals grown under microgravity FMF-5-1 without and FMF-M-5-1 with RMF.

2.5. Growth of CZT by boron oxide encapsulation

One of the problems connected with the growth of CdZnTe crystal is the crucible-crystal interaction. Particularly detrimental results to be the use of quartz crucibles that cause the formation of twins and dislocations. Due to this reason, many researchers make use of graphite crucibles or graphite-coated quartz crucibles.

Recently, a different melt growth approach has been presented [15-16]. The polycrystalline material is charged inside a quartz crucible and a boron oxide pellet is placed above it. Then, the crucible is introduced in a vertical Bridgman furnace that can operate at a pressure up to 10 bars. During heating, boron oxide melts and covers the charge. Thus, in order to prevent charge evaporation, it is enough to pressurize the furnace chamber with inert gas at about 5-6 bars. This means that no soldering operations are required for the crystal growth, and it is easy to scale up the process. Moreover, due to the fact that no free volume is present above the charge during growth, the stoichiometry of the charge is not altered by the not-congruent sublimation of the compound at the melting point.

It has been experimentally demonstrated that, after melting, boron oxide fully encapsulates the CdZnTe charge, as previously reported in the case of GaAs crystals [17]. As a consequence, the crystal, during the growth, is completely surrounded by a liquid boron oxide layer that prevents the crystal-crucible interaction. With this technique 1-inch and 2-inches CZT crystal have been grown with large single grains (Figure 6).

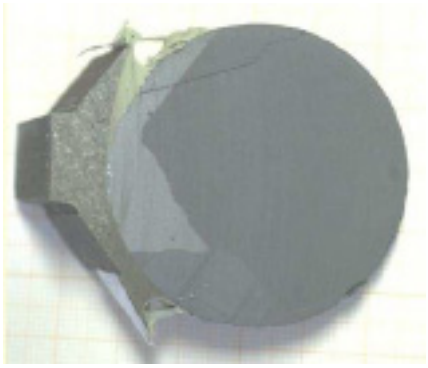


Fig. 6. Two-inches CZT wafer obtained by the boron oxide encapsulated vertical Bridgman technique. The main part of the wafer is constituted by a large single grain.

The etch pit density (EPD) was determined on (111) oriented surfaces by means of Nakagawa etching [18]. In the case of 1-inch crystals, the EPD is always lower than $8x10^{-3}$ cm^{-2}. In the case of 2-inches crystals the EPD is in the range $1\text{-}2x10^{-4}$ cm^{-2}. These values are about one order of magnitude lower than the ones typically reported for CZT crystals. We suggest that the low EPD values are due to the fact that during growth and also during the crystal cooling (down to about 500°C), the crystal is surrounded by the liquid boron oxide layer that prevents the stress of the crucible.

3. Conclusions

We have successfully grown the larger grain size CZT single crystals by adopting the new novel approaches. The crystal growth has been carried out by using OBR technique and the quartz crucible was placed above the Pt cold finger tube in order to create the suitable thermal environments. The temperature profile has been studied with and without Pt tube and found that the presence of Pt cold finger tube promotes the better thermal environments for CZT growth. The temperature profile of the conventional Bridgman furnace has been modified by the incorporation of additional furnaces and the profile is designed in such a way to allow the crystallization of $Cd_{1-x}Zn_xTe$ for the growth of CZT crystal by vapour phase. The effect of microgravity for the growth of CZT single crystals under rotating magnetic field has been studied and found that it enhances the chemical homogeneity of the grown crystals. The average resistivity of the grown specimen was found to be 2 x 10^9 ohm cm. The presence of boron oxide encapsulation is preventing the CZT charge evaporation during melting and is completely surrounded

by a liquid boron oxide layer that prevents the crystal-crucible interaction.

Acknowledgements

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