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CdZnTe BULK-CRYSTAL GROWTH AND SURFACE PROCESSING TECHNOLOGY AT METU-CGL

Yasin Ergunt[1*], Merve Pinar Kabukcuoglu[1,2], Ozden Basar Balbasi[1], Bengisu Yasar[3,4], Yunus Eren Kalay[3], Mehmet Parlak[5], Rasit Turan[1,5]

[1]Middle East Technical University (METU) Crystal Growth Laboratory (CGL), Ankara, Turkey
[2]University Freiburg, Crystallography Institute for Geo- and Environmental Sciences, Freiburg, Germany
[3]Metallurgical and Materials Engineering, METU, Ankara, Turkey
[4]Materials Science and Engineering, University of California, Berkeley, CA, US
[5]Department of Physics, METU, Ankara, Turkey

Abstract. *The study of $Cd_{1-x}Zn_xTe$ (Cadmium Zinc Telluride) bulk-crystal growth and surface processing technology at the Middle East Technical University (METU) began in 2012. The initial R&D efforts were started with the growing of CdZnTe ingots up to a size of 15 mm in diameter in a three-zone vertical Bridgman furnace located in a limited laboratory area of 15 m². Following promising development in terms of single crystal yield and the crystal growth process, a new vertical gradient freeze (VGF) multi-zone furnace setup was designed and developed to accommodate the production of 60 mm diameter CdZnTe ingots. The entire furnace setup is located in a newly founded 90 m² laboratory named the METU Crystal Growth Laboratory (METU-CGL) in 2013. The laboratory is fully dedicated to the CdZnTe material growth and surface processing technology. Currently, METU-CGL is capable of producing 60 mm diameter CdZnTe ingots with one large grain and a few small grains. CdZnTe material is continuously grown in order to serve as either a substrate material ($Cd_{0.96}Zn_{0.04}Te$) for infrared detectors or an active material ($Cd_{0.90}Zn_{0.10}Te$) for X-ray/Gamma-ray detectors. As a typical yield, 2-3 oriented wafers per radial slice are retrieved from the grown ingots. The target wafer dimensions are 20 mm x 20 mm; however, larger or smaller crystals can be obtained based on the application of interest. The crystalline quality of the produced crystals is way below 50 arcsec of FWHM (Full width at half maximum) values from the DCRC (Double crystal rocking curves) measurements and the EPD (Etch-pit density) values are typically mid-10^4/cm². Infrared (IR) transmission of the home-grown CdZnTe crystals is exceeding 60% and stays constant within 2-20 μm wavelength interval showing that the crystals have low density of inclusions and precipitates. Not only limited to CdZnTe bulk growth technology, the METU-CGL is also capable of slicing and surface processing technologies including optimized lapping, rough mechanical polishing, and performing final chemo-mechanical polishing steps with extreme care regarding surface roughness and subsurface damage. Achievable surface roughness values of produced wafers are well below 0.5 nm (R_{rms}). Various state-of-the-art characterization techniques including HRTEM (High-resolution transmission electron microscopy) and APT (Atom probe tomography) were conducted to study nanoscale defects in CdZnTe as a material property. This paper reviews many aspects of CdZnTe bulk-growth, surface finishing, and characterization technologies at METU-CGL as well as the laboratory infrastructure itself.*

Keywords: *Bulk-crystal growth, CdZnTe, polishing, surface finishing, wafer characterization, X-ray/Gamma-ray detector*

1. INTRODUCTION

There has been an increasing demand for Cadmium Telluride (CdTe) and its alloys for decades. CdTe alloys and CdZnTe single crystals are used as the active X-ray and Gamma-ray detector material in medical and nuclear imaging, nuclear safeguards, transportation security monitoring, and gauging [1]. The ternary semiconductor alloy CdZnTe has always attracted substantial attention of the industry because of its high stopping power against high energetic radiation and desirable spectral performance [2]. CdZnTe also has a high atomic number (~50), high material density (~6 g/cm3), high resistivity (~10^9 Ohms.cm), and a wide bandgap (~1.5 eV). The addition of Zn content into the CdTe alloy provides higher bandgap and resistivity leading to an operational efficiency enhancement of the detectors. The most widely preferred Zn mole fraction in $Cd_{1-x}Zn_xTe$ is the 10% Zn content (i.e. the x value is 0.10 denoted as $Cd_{0.90}Zn_{0.10}Te$) [3]. In order to grow CdZnTe crystals, various main techniques such as Bridgman [4], traveling heater method (THM) [5], and VGF are widely used. CdZnTe crystals are grown as polycrystalline ingots having only a few grains for increased material yield. CdZnTe ingots are sliced and single crystalline areas are singled out from these slices. As-cut slices are exposed to a series of surface processing steps to produce mirror-polished crystals under certain dimension limitations. Produced crystals

* ergunt@metu.edu.tr

are characterized using various techniques. X-ray diffraction (XRD), infrared (IR) transmission, etch-pit density (EPD), and surface roughness (R_{rms}) are the primary material characterization techniques or parameters for CdZnTe material technology [6].

In this paper, we report on the progress and the recent status of the CdZnTe bulk-crystal growth and surface processing technology at METU-CGL. The infrastructure present in METU-CGL was described and the technological capabilities of METU-CGL were highlighted.

2. Experimental

This section covers the details on the METU-CGL infrastructure, CdZnTe bulk-crystal growth, CdZnTe surface processing, and material characterizations under four sub-sections.

2.1. METU-CGL Infrastructure

METU-CGL covers a dedicated laboratory area of 90 m² housing a multi-zone VGF furnace, a small-scale (25 m²) indoor clean room, and a controlled area for other auxiliary processes such as quartz sealing, ingot slicing, and system maintenance. The multi-zone VGF furnace is reserved for CdZnTe bulk-crystal growth only and has a bore opening of 75 mm diameter. CGL also has single wire cutter units for CdZnTe ingot cropping and slicing. The cleanroom is composed of different contamination classes of ISO5-6-7 and houses lapping and polishing systems. A semi-automatic wet bench is also present in the cleanroom enabling cleaning operations, growth preparations and material processes. The laboratory is equipped with a scanning electron microscope (SEM) in order to investigate surface conditions and perform compositional analysis. CGL also has close access to the other critical characterization systems such as XRD, Fourier Transform Infrared (FTIR) system, white-light interferometer microscope, and transmission electron microscope (TEM).

2.2. CdZnTe Bulk-Crystal Growth

Figure 1. Custom designed multi-zone VGF furnace system and its sub-components

A multi-zone VGF furnace was designed and developed to accommodate the bulk-growths of CdZnTe crystal ingots having diameters of up to 60 mm. Designed VGF furnace system (Figure 1) is composed of a furnace body, stand, control unit, and power supply. A translation mechanism was added to the system for the CdZnTe charge loading/unloading and a crucible rotation mechanism was added in order to obtain a more homogeneous thermal distribution inside the furnace.

Prior to the crystal growth cycle, specific amounts of high purity starting charge (CdTe, ZnTe, CdZnTe) were loaded in a cleaned quartz crucible and the quartz crucible was sealed under vacuum (10^{-6} mbar). Sealed quartz crucible was then placed inside the VGF furnace and the desired thermal profile was applied on the charge in order to produce the CdZnTe ingot. The desired thermal profile was optimized after running a long series of tedious thermal profiling work in which the scenarios for the charge of homogenization, crystal growth, and cooling were present during the entire crystal-growth cycle. Once the crystal growth cycle was finished, the quartz crucible was taken out of the furnace and CdZnTe ingot was retrieved from the sealed quartz ampoule (Figure 2).

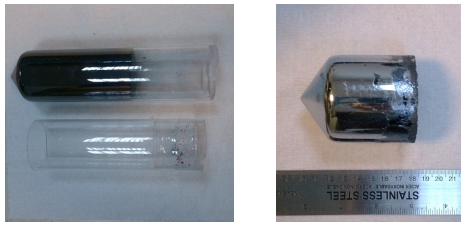

Figure 2. Quartz crucible (left); as-grown CdZnTe ingot (right)

2.3. CdZnTe Surface Processing

Following the crystal growth cycle, the conical tip and the tail sections of the CdZnTe ingot were cropped using the single wire cutter. The remaining body of the CdZnTe ingot was inspected and a series of multiple slicing process were performed in order to obtain radial slices according to target crystallographic orientation which was generally {111} (Figure 3).

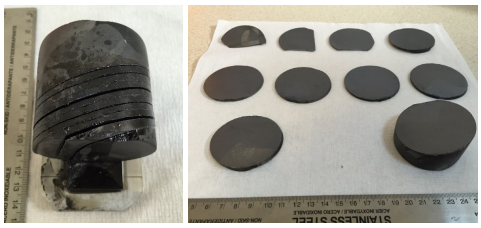

Figure 3. Sliced CdZnTe ingot body (left); as-cut radial slices (right)

Typical grain formation on the radial slices was shown in Figure 4. Single crystallinity (i.e. marked area) yield was high which provided some flexibility in the obtaining of CdZnTe crystals of desired dimensions.

Figure 4. Grain formation of 60 mm diameter radial slice

The typical required crystal dimensions were 10 mm x 10 mm, 10 mm x 15 mm, and 20 mm x 20 mm. CdZnTe crystals were singled out from the largest grain using the single wire cutter as shown in Figure 5.

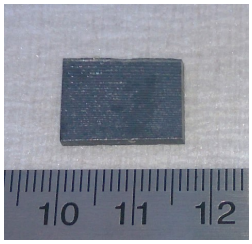

Figure 5. {111} CdZnTe crystal obtained from the radial slice, 10 mm x 15 mm

As-cut CdZnTe crystals (i.e. wafers) were lapped on both sides using a micron-scale alumina (Al_2O_3) based slurry to remove surface and sub-surface damage caused by the slicing process. Lapping was also necessary to produce flat wafers and reach intermediate thickness values down to 1-1.5 mm prior to the rough mechanical polishing process.

While removing the damage caused by the slicing, lapping brought about surface and sub-surface damage to the CdZnTe wafers and surfaces which made the wafer values far away from the target surface finishing conditions. Therefore, the rough mechanical polishing process was the intermediate polishing step that needed to be done prior to fine polishing. Rough mechanical polishing was performed on both sides of the CdZnTe wafers using a sub-micron sized Al_2O_3 polishing slurry. Double-sided polished CdZnTe wafers had mirror-polished surfaces with a moderate density of polishing lines.

As a final polishing step, mechanically polished CdZnTe wafers were polished using a silica-based polishing slurry containing a nanoscale colloidal silica solution with a pH value on the slightly basic side. This final polishing step produced smooth surfaces without major polishing lines.

2.4. Material Characterizations

In order to check and confirm the quality of home-grown CdZnTe crystals, XRD measurements, EPD analyses, FTIR measurements were conducted for each CdZnTe wafer lot. In addition to these material characterization techniques, white-light interferometer measurements were performed to confirm the quality of the surface finishing.

XRD measurements were conducted to confirm the crystallographic orientation of the CdZnTe wafers and the crystalline quality was indirectly determined by the XRD rocking curve measurements.

The dislocations on the CdZnTe wafer surface were revealed by etching mirror-polished CdZnTe wafers using HF:HNO_3:Lactic acid, (1:4:25, v) a chemical solution, which is known as the Everson etchant. The typical etching time was about 3 minutes and as an indication of the dislocations, this chemical etching produces well-defined triangular pits on the mirror-polished CdZnTe surfaces. Etch pits were visualized using SEM and/or an optical microscope. The calculation of etch pit density was done by counting etch pits on the microscope's images of the selected areas and averaging the total count followed by an extrapolation of the number of etch pits per unit area (#/cm2).

Optical characterization of CdZnTe wafers is a significant technique since there is a definite correlation between the presence of defects and optical transmission. Optical transmission measurements were performed on double-side mirror-polished CdZnTe wafers in an FTIR system over a wide-range wavelength interval of 2-20 μm. CdZnTe wafers were investigated for precipitates or inclusions by their optical transmission behaviors at shorter wavelengths. Dependence on the carrier concentration was also investigated at higher wavelengths.

In addition to the standard material characterization techniques discussed above, state-of-the-art nanoscale imaging techniques were also used. In order to investigate the Te precipitates and other defects at the nanoscale, HRTEM analyses were supported by HRTEM image simulations. The APT technique was also conducted on CdZnTe material to obtain 3D imaging and chemical composition at the atomic scale. While the details of the HRTEM analysis were previously reported [7], further details on the APT analysis are to be reported elsewhere.

3. Results and Discussion

This section covers the recent capabilities of METU-CGL regarding CdZnTe bulk-crystal growth and surface processing. Currently, CdZnTe material technology at METU-CGL is considered mature and a CdZnTe-based device technology development program for X-ray and Gamma-ray detectors has recently been initialized.

METU-CGL is currently capable of producing CdZnTe ingots 60 mm in diameter and 100 mm in length using proper quartz crucible design. Through the use of VGF technology and an improved thermal profile, single crystal yield per ingot is sufficiently high enough to obtain multiple wafers per radial slice as shown in Figure 6. Potentially, four 10 mm x 10 mm and one 30 mm x 30 mm {111} $Cd_{0.90}Zn_{0.10}Te$ wafers can be obtained from each radial slice.

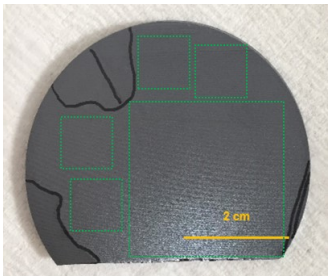

Figure 6. Single crystal yield per radial slice for {111} CdZnTe wafers

{111} $Cd_{0.90}Zn_{0.10}Te$ wafers were exposed to double-side lapping, intermediate mechanical polishing, and final chemo-mechanical/chemical polishing steps respectively in order to obtain atomically smooth surfaces as that is one of the most critical requirements affecting the CdZnTe detector performance. As shown in Figure 7, the optimized surface finishing technology provides sub-nanometer surface roughness on CdZnTe crystal surfaces.

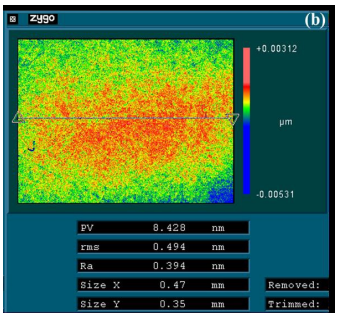

Figure 7. Single crystal yield per radial slice for {111} CdZnTe wafers

In most cases, {111} oriented $Cd_{0.90}Zn_{0.10}Te$ wafers are produced unless another specific crystallographic orientation is required. Home-grown CdZnTe wafers are of typical FWHM values well below 50 arcsec indicating a sufficient crystalline quality allowing them to be used as an active detector material in terms of efficient charge transport.

Dislocation etch-pit density of the grown {111} $Cd_{0.90}Zn_{0.10}Te$ wafers is less than $10^5/cm^2$ as revealed by dislocations (Figure 8) caused by the Everson etchant.

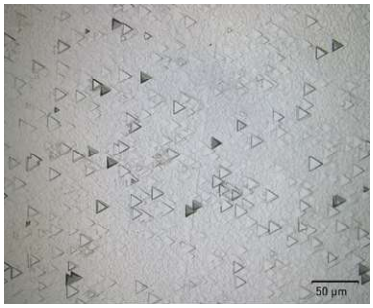

Figure 8. Dislocation etch-pits on {111} CdZnTe wafers

In a small portion of the CdZnTe wafers, micron-scale Te inclusions are rarely found (Figure 9) and these wafers are not qualified for detector processing since the Te inclusions pose deleterious effect on the charge transport.

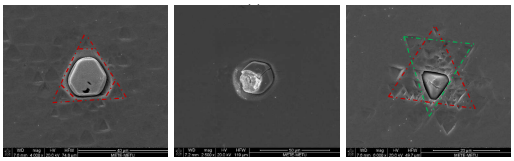

Figure 9. Micron-scale Te-inclusions in CdZnTe wafers

Infrared transmission of the CdZnTe wafers is typically higher than 60% (Figure 10) guaranteeing the absence of the micron-scale killer defects such as Te inclusions and precipitates.

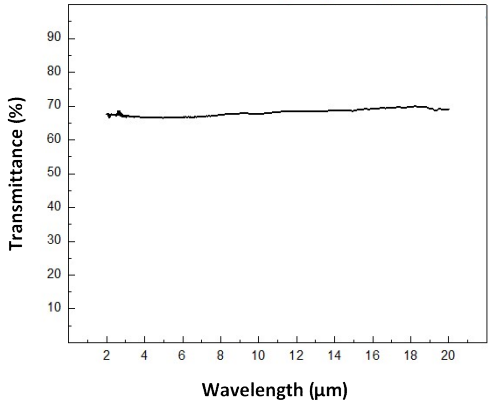

Figure 10. Infrared transmission of CdZnTe wafers

HRTEM studies show that low density of nano-scale defects is present in the grown $Cd_{0.90}Zn_{0.10}Te$ crystals as shown in Figure 11.

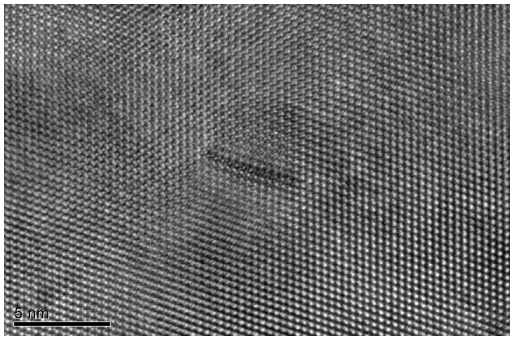

Figure 11. The HRTEM image of the nano-scale defect in grown $Cd_{0.90}Zn_{0.10}Te$ crystal

Table 1 provides a brief overview of technical capabilities of the CdZnTe production and processing technologies in order to demonstrate the technology readiness level for in-house X-ray/Gamma-ray detector development.

Table 1. Overview of technical capabilities at METU-CGL

Specification	**Value**
Ingot composition	$Cd_{0.90}Zn_{0.10}Te$
Ingot dimensions	Φ60 mm, L100 mm
Max. wafer dimensions	30 mm x 30 mm
Surface roughness (R_{rms})	< 1 nm
Crystalline quality (FWHM)	< 50 arcsec
Dislocation density (EPD)	< 10^5 cm^{-2}
IR transmission	> 60%

5. Conclusions

Overview of the CdZnTe bulk crystal-growth and surface processing technology at METU-CGL was presented. Laboratory infrastructure was briefly summarized and technical capabilities in terms of production facility and surface processing systems were declared.

Following the proven success in CdZnTe material synthesis and processing, we will extensively focus on the X-ray/Gamma-ray detector development using our home-grown CdZnTe crystals. Initial attempts of device development have recently started and are being continuously developed.

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