Advances in the High-pressure Crystal Growth Technology of Semi-insulating CdZnTe for Radiation Detector Applications

Csaba Szeles, Scott E. Cameron, Jean-Olivier Ndap, Michael D. Reed
eV PRODUCTS a division of II-VI, Inc., Saxonburg, PA 16056

ABSTRACT

The properties of large diameter (140 mm) semi-insulating Cd$_{1-x}$Zn$_x$Te (x = 0.1) ingots grown by the vertical High-Pressure Electro-Dynamic Gradient (HP EDG) technique are discussed. The HP EDG crystal growth technology recently developed and introduced at eV PRODUCTS significantly improves the downstream CdZnTe detector fabrication yield compared to earlier versions of the HP crystal growth technology. These yield improvements stem from the improved structural and charge transport properties of the HP EDG CdZnTe ingots. Improvements were achieved in three areas: a) reduced thermal stress in the ingots, b) improved single crystal yield, and c) improved electron transport properties. The new state-of-the-art HP EDG crystal growth systems offer exceptional flexibility, thermal and mechanical stability and allow the growth of high purity CdZnTe materials. The flexibility of the multi-zone heater system allows the dynamic control of heat flow to optimize the growth-interface shape during crystallization. This flexibility combined with an advanced control system, improved system diagnostics and realistic thermal modeling provides an excellent platform for further process development. Results on the initial HP EDG CdZnTe ingots grown with low temperature gradient show the complete elimination of ingot cracking. The increased single crystal yield combined with the improved electron transport properties allows the fabrication of large-volume electron-only devices at higher yield. The CdZnTe ingots regularly contain sections with electron mobility-lifetime product $\mu\tau_e \geq 5.0 \times 10^{-3}$ cm$^2$/V and occasionally yield material with $\mu\tau_e \geq 8.0 \times 10^{-3}$ cm$^2$/V.

Keywords: semi-insulating Cadmium Zinc Telluride (CdZnTe), nuclear radiation detectors, electro-dynamic gradient technique, x-ray and $\gamma$-ray spectroscopy

1. INTRODUCTION

The physical properties of semi-insulating (SI) Cadmium Zinc Telluride (CdZnTe) such as high atomic number, high density, wide band gap, low chemical reactivity and long term stability make it an excellent material candidate for high efficiency, high-resolution room-temperature nuclear radiation detectors. Intense research on electrical compensation and defect formation in Cd$_{1-x}$Zn$_x$Te, 0 $\leq$ x $\leq$ 1 in the last 10-15 years led to the development of crystal growth processes that allow the growth of fully compensated SI CdZnTe crystals with low defect density and very good charge transport properties. Few industrial companies around the world significantly contributed to this research and pioneered the commercialization of both CdTe and CdZnTe crystals. Today, SI CdZnTe crystals are available commercially and the CdZnTe based room-temperature radiation detectors and detector arrays are steadily gaining acceptance in many medical, industrial, security, safeguards and scientific X-ray and $\gamma$-ray imaging and spectroscopic applications.\(^\text{1,2,3}\)

While CdZnTe crystals are readily available for simpler counting and monitoring applications, large field-of-view imaging and high-sensitivity, high-resolution spectroscopic applications continuously demand larger and larger and more and more uniform CdZnTe single crystals. The growth of SI CdZnTe crystals, with spatially uniform charge transport properties that are required by these applications, poses a considerable challenge due to the inherent complexity of the crystallization and defect formation processes in these II-VI compounds.\(^\text{4,5}\)

Commercially available SI CdZnTe with charge transport properties satisfactory for detector applications has been mostly grown by the high-pressure Bridgman (HPB)\(^\text{6,7,8}\) or conventional horizontal Bridgman\(^\text{9}\) techniques while, commercial SI CdTe is typically grown by the traveling-heater method.\(^\text{10}\) Recently, the growth with conventional vertical Bridgman approach has been also successfully introduced.\(^\text{12,11}\) Most of the CdZnTe ingots are grown from melt containing 10% Zn. Due to Zn segregation, the Zn concentration varies along the growth direction of the ingot between 5 % and 13 %. The electrical resistivity of the crystals is in the (1.0 – 4.0)×10$^{10}$ $\Omega$cm range. Such a high resistivity is achieved with some form of active electrical compensation technique. Typically good electron transport is reported with electron mobility-lifetime product in the $\mu\tau_e = (0.5 - 6.0) \times 10^{-3}$ cm$^2$/V range, while hole transport is typically found to be poor $\mu\tau_h = (0.2 - 5.0) \times 10^{-5}$ cm$^2$/V (all measured at room temperature).
eV PRODUCTS has been practicing the high-pressure Bridgman (HPB) growth of CdZnTe since 1992. Between 1992 and 1998, the process development team introduced two new improved HPB crystal growth systems and scaled up the growth from 3.5" (90 mm) diameter 4 kg ingots to 5.5" (140 mm) diameter 10 kg ingots. Between 1998 and 2000, the high-pressure gradient freeze (HPGF) technique was developed and introduced to production. The HPGF technique eliminates the motion of the crucible relative to the heater and reduces some of the heat transport problems associated with HPB growth. The HPGF technique improved the single crystal yield and virtually eliminated the formation of pipes in the CdZnTe ingots. The HPGF grown CdZnTe ingots, however, still suffered from cracking due to the excessive thermal stress during crystallization and cool-down of the ingots. In 2000, eV PRODUCTS initiated the development of a multi-zone High-Pressure Electro-Dynamic gradient (HP EDG) crystal growth system and process to reduce thermal stress in the CdZnTe ingots and eliminate ingot cracking and improve the downstream detector device fabrication yield. In the EDG technique, the crucible and the heater are stationary and the gradient is translated through the molten CdZnTe electronically. The EDG technique avoids many of the inherent problems of the Bridgman and gradient freeze techniques that lead to poor control of heat transport during crystallization. The goal of the project was to develop an advanced high-pressure crystal growth system with flexibility and stability that will allow the growth of CdZnTe ingots a) without cracking, b) higher single crystal yield, and c) improved charge transport properties reproducibly.

In this paper, we discuss the development of the vertical High-Pressure Electro-Dynamic Gradient (HP EDG) crystal growth system and the properties of the large diameter (140 mm) semi-insulating Cd$_{1-x}$Zn$_x$Te (x = 0.1) ingots grown by the technique. The experimental results confirm the predictions of the computational fluid dynamics model for the dramatic reduction of thermal stress, and the elimination of cracking of the ingots grown in moderate temperature gradients. The CdZnTe 10 kg ingots grown by the HP EDG systems also show increased single crystal yield and improved electron transport. The increased single crystal volume is associated with more stable growth conditions throughout the crystallization of the ingot using the EDG technique. The 14 ingots grown to date with the two new HP EDG systems show electron mobility-lifetime product ($\mu\tau$) in the (2.5-7.5) x 10$^{-3}$ cm$^2$/V range and display excellent ingot-to-ingot reproducibility.

**2. HP EDG SYSTEM DEVELOPMENT**

Since the main goal of the HP EDG development project was to improve the control over heat transport in the high-pressure growth system, we chose to employ heat transport modeling and thermal stress analysis to design the new crystal growth system. The eV PRODUCTS process development team worked with Cape Simulations Inc. to develop the computational fluid dynamics (CFD) model of heat and mass transport. The 2D CFD model uses the Fluent CFD package and describes heat and mass transport in the whole high-pressure chamber including radiative, convective and conductive transport in the solid, liquid and gas phases. It predicts the shape of the crystallization interface, convection patterns in the molten CdZnTe and performs a stress analysis in the solidified CdZnTe ingot. The modeling tool has been installed at eV PRODUCTS to aid further process development and growth system engineering efforts.

The thermal modeling project was set up in four phases. In phase one the CFD model of the existing HPB/HPGF furnace (Gen-2+) was developed. In phase two the validity of the CFD model was evaluated. The transport model, geometry and material properties were adjusted to describe the measured temperature distribution in the furnace with satisfactory accuracy. Once the model was experimentally validated for the Gen-2+ HPB/HPGF furnace, the CFD model of the HP EDG furnace was developed in phase three. Finally in phase four, various growth scenarios were evaluated and the predicted thermal stress analyzed. Results from the CFD model and stress analysis are discussed below.

Once the thermal model was completed and the model predicted that the system will meet the design goals and will allow the growth of CdZnTe with much reduced thermal stress, the mechanical design of the system was completed. The design and process development team maintained the 5.5" (140 mm) ingot diameter and high-pressure chamber size. This allowed us to keep some of the mechanical components of the Gen-2+ HP systems and more importantly will allow faster future upgrades of the Gen-2+ HPB/HPGF systems to the HP EDG system. The power, control and data acquisition systems for the new HP EDG systems also included several upgrades to improve the stability and consistency of the systems. The flexibility of the multi-zone heater system allows the dynamic control of heat flow to optimize the growth-interface shape during crystallization. This flexibility combined with an advanced control system, improved system diagnostics and realistic thermal modeling provides an excellent platform for further process development.
2.1 Thermal Model

Fig. 1 shows the simulated temperature distribution and melt-flow pattern for CdZnTe growth in the HP EDG furnace. In this example about one third of the melt is solidified.

2.2 Stress Analysis

Figs. 2 and 3 compare the temperature distribution and distribution of von Mises stresses for CdZnTe ingots solidified in the Gen-2+ HPB/HPGF and HP EDG systems. The results confirm the excessive stress in ingots grown in the Gen-2+ HPB/HPGF systems and the 8 to 10 fold reduction in the thermal stress in the HP EDG system. The maximum stress predicted for the Gen-2+ HPB/HPGF system (~350 N/cm$^2$) is well above the critical resolved stress reported for CdZnTe (~43 N/cm$^2$). In the HP EDG system the maximum stress (~38 N/cm$^2$) is below the critical resolved stress. The model also predicts stress distribution similar to those predicted by others in the literature. More importantly the model correctly predicts the maximum stress points in the CdZnTe ingots and shows excellent agreement with the cracking pattern observed experimentally. This result provides further
confirmation that the model gives a correct description of the heat transport phenomena in the HP EDG system.

3. CRYSTAL GROWTH RESULTS

3.1 Structural Properties

We have performed 14 CdZnTe crystal growths in the two new HP EDG furnaces to date. Fig. 4 shows a typical ingot (360 degrees rotation). No cracking is observed in these ingots, verifying that furnaces perform according the design specifications, and the thermal stress is sufficiently low during crystallization and cool-down of the ingot.

Fig. 5 shows a typical axial slice from a CdZnTe ingot grown by the HP EDG system. The slice shows few large volume single crystals dominating a large fraction of the slice. Numerous smaller secondary grains are also observed particularly in the first-to-freeze (tip) section and along the periphery of the ingot. This indicates that considerable secondary grain nucleation takes place along the crucible wall. Some of the grains show twins. Overall the concentration of twins is lower than in ingots grown by the HPB and HPGF processes. The origin of twinning is not fully understood in CdZnTe but it is often associated with unstable growth conditions. The observed less twinning correlates well with the better heat flow control and more stable growth conditions in the HP EDG systems.

Fig. 6 shows an infrared (IR) microscopy map of an axial slice from the first ingot grown by the HP EDG furnace. IR microscopy is a convenient tool to visualize Te inclusions in CdZnTe ingots. Since the inclusions are pure Te phases they strongly absorb infrared light and appear as dark features in the IR images. The formation of Te inclusions is expected as we chose to grow the ingots from Te rich melt. It is to be noted here that the Te phases resolved by IR microscopy with diameter $\geq 1 \mu m$ are often incorrectly called Te precipitates in the literature. Although Te precipitates form in large concentration during CdZnTe crystallization from Te rich melt; their average diameter is in the $10 - 30$ nm range and cannot be resolved with IR microscopy.
Precipitates originate from the retrograde solubility of Te in CdZnTe and their nucleation and growth is controlled by atomic diffusion and precipitation process.\textsuperscript{18,19} In contrast to precipitates, the typical diameter of Te inclusions is in the $1 - 50$ $\mu$m range. The maximum solubility of Te in CdZnTe cannot supply enough excess Te to form such a large size Te agglomerates. Inclusions originate from morphological instabilities at the growth interface, as Te-rich melt droplets are captured from the boundary layer ahead of the interface.

Most of the inclusions seen in Fig. 6 have a triangular or faceted polyhedron shape, indicating that they have a well-defined crystallographic orientation relative to the surrounding CdZnTe matrix.\textsuperscript{4,20} Te inclusions have elongated plate or saucer shape within grain boundaries; but even, here they tend to line up with the neighboring grains and form sharp boundaries.\textsuperscript{21} There is significant evidence that Te inclusions and the surrounding defect field have a strong detrimental effect on electron transport in CdZnTe crystals and poor performance of the fabricated detector devices.\textsuperscript{22,23} It was also shown that the region of degraded charge transport near Te inclusions extend well beyond the volume of the inclusions themselves. This might be due to the field of dislocations and Te precipitates surrounding Te inclusions. Recently, it was indeed shown that dislocations cause severe carrier trapping and hamper charge transport in CdZnTe.\textsuperscript{24} It is therefore reasonable to expect that suppression of the formation of Te inclusions and the defect-field around them will improve carrier transport in CdZnTe crystals and the performance of radiation detector devices fabricated from these crystals.

The two main parameters controlling the formation of Te inclusions are the melt composition and the temperature gradient at the solidification interface. Due to the in-congruent nature of CdZnTe solidification from non-stoichiometric melt, the solid rejects a fraction of the excess Te in the melt that is gradually enriched in Te as solidification proceeds. In addition, due to the limited mixing of the melt near the solidification interface, a Te rich boundary layer is formed at the interface. This Te-rich boundary layer provides the supply of the excess Te that is captured at instability locations along the interface. By controlling the melt stoichiometry, the Te enrichment of the boundary layer can be reduced and the formation of Te inclusions can be suppressed. This can be achieved by passive (load composition) or active (component partial pressure) control of the melt stoichiometry. The growth of virtually Te inclusion free SI CdZnTe crystals has been demonstrated with this technique.\textsuperscript{4,25} Alternatively, imposing a larger temperature gradient during the growth can also reduce Te inclusion formation. Indeed we observe a lower Te inclusion density in CdZnTe ingots grown using much larger temperature gradients in our older HPB systems.
Fig. 6.  IR microscopy map of an axial slice from an early CdZnTe ingot grown by the HP EDG technique. In the full area map Te inclusion rich areas appear as dark sections. These are typically grain boundaries decorated with Te inclusions. The inset shows a high Te inclusion density area close to the heel (last-to-freeze) section. Individual inclusions up to 50 µm in diameter are clearly resolved in this image.

Fig. 7.  IR microscopy map of an axial slice from a CdZnTe ingot grown by the HP EDG technique with larger temperature gradient. In the full area map Te inclusion rich areas appear as dark sections. These are typically grain boundaries decorated with Te inclusions. The inset shows an area close to the heel (last-to-freeze) section of the ingot containing randomly dispersed Te inclusions. Individual inclusions up to 50 µm in diameter are visible in this image. The diagonal crack occurred during cutting the slice.
Since Cd loss from the crucible cannot be completely eliminated in the current version of our HP EDG system, we opted to explore the use of somewhat larger temperature gradients to suppress Te inclusion formation. Fig. 7 shows IR microscopy map of an axial slice from a CdZnTe ingot grown with a nominally larger temperature gradient. Note that only the nominal temperature gradient imposed by the heater can be measured. The actual temperature gradient controlling crystallization is expected to be lower than the imposed gradient, and varies along the growth interface with distance from the ingot axis. Fig. 7 shows an overall reduction in the density of Te inclusions. The larger magnification inset shows a single crystal area with a more dispersed distribution of Te inclusions.

Preliminary results show that the lower Te inclusion density improved the charge transport uniformity of the CdZnTe crystals from this ingot, and the fabricated detector devices display improved energy resolution.

3.2 Charge Transport Properties

To study the charge transport properties of the CdZnTe crystals grown by the HP EDG process 10×10×2 mm³ samples were fabricated from radial slices cut close to the first-to-freeze (tip, ~ 0.1 solidified fraction) and last-to-freeze (heel, ~ 0.95 solidified fraction) section of the ingot. The samples were etched in dilute Br - methanol solution to remove the surface damage introduced during cutting. Platinum electrodes were deposited by sputtering onto the 10×10 mm² area surfaces of the crystals to form detector structures. The bulk electrical resistivity of the material is determined from the low-voltage region of current-voltage (I-V) measurements. The measured resistivity of the ingots is in the (2-3)×10¹⁰ Ωcm range and shows very little variation between the tip and heel section of the ingots. The measured resistivity variation from tip to heel is less than the one expected from the band gap variation due to the Zn distribution (~ 12% tip and ~ 6% heel). This suggests that impurity segregation compensates for the band gap variation. The high measured resistivity indicates that the material is fully compensated throughout the ingot volume (at least within the 0.1–0.95 solidified fraction region studied).

The mobility lifetime product (μτ) of the charge carriers was determined from the bias dependence of the charge collection efficiency. To evaluate the collection efficiency, and estimate the μτ values, the shift of the pulse height of the photopake from the 5.5 MeV alpha particles from an ²⁴¹Am source was measured as a function of the bias voltage and the resulting data fitted to the Hecht equation.²⁶ Fig. 8 shows the Hecht curves for electrons obtained on 14 samples from a

![Fig. 8. Peak-position vs. bias voltage (Hecht curve) for 14 samples from the same CdZnTe ingot grown by the HP EDG technique. The data show little variation from sample to sample indicating good charge transport uniformity in the ingot. The high average μτ_e = 5.3×10⁻³ cm²/V shows very good electron transport in the material.](image-url)
CdZnTe ingot grown by the HP EDG process. The average electron mobility-lifetime product was $\mu_\tau_e = 5.3 \times 10^{-3} \text{ cm}^2/\text{V}$ for these 14 samples. The Hecht curves and electron mobility lifetime products show very little variation from sample to sample indicating that the material is very uniform on a macroscopic scale (micro-scale variation is discussed below). The hole mobility-lifetime product of the material was estimated to be in the $\mu_\tau_h \approx (0.2-1) \times 10^{-5} \text{ cm}^2/\text{V}$ range. For such a low value it is difficult to reliably measure $\mu_\tau_h$ with the current technique. For the 14 ingots grown to date in the two HP EDG systems, we find $\mu_\tau_e$ to vary in the $(2.5-7.5) \times 10^{-3} \text{ cm}^2/\text{V}$ range and some ingot sections yield material with $\mu_\tau_e \geq 8.0 \times 10^{-3} \text{ cm}^2/\text{V}$.

The detector response of $15 \times 15 \times 7.5 \text{ mm}^3$ crystals from CdZnTe grown by the HP EDG technique is illustrated in Fig. 9. These data were taken in the Co-Planar Grid (CPG) configuration with bias voltage and differential bias optimized to get the best energy resolution for the 662 keV photopeak from $^{137}\text{Cs}$. The 3.0% and 3.5% resolution full width half maximum (FWHM) is worse than expected from the electron mobility-lifetime product and biasing conditions. One possible explanation for the poor energy resolution is the microscopic scale spatial non-uniformity of the charge transport in the volume of the detectors.²²,²³ With the effort to suppress Te inclusion formation in the ingots, we hope to reduce this microscopic scale charge transport non-uniformity and improve the energy resolution of these devices.

4. CONCLUSIONS

In this paper, we discussed the development of the vertical High-Pressure Electro-Dynamic Gradient (HP EDG) crystal growth system and the properties of the large diameter (140 mm) semi-insulating Cd$_{1-x}$Zn$_x$Te ($x = 0.1$) ingots grown by the technique. The HP EDG crystal growth technology significantly improves the CdZnTe detector fabrication yield compared to earlier versions of the HP crystal growth technology, due to the a) reduced thermal stress in the ingots, b) improved single crystal yield, and c) improved electron transport properties. The new state-of-the-art HP EDG crystal growth systems offer exceptional flexibility, thermal and mechanical stability and allow the growth of high purity CdZnTe materials. The flexibility of the multi-zone heater system allows the dynamic control of heat flow to optimize the growth-interface shape during crystallization. This flexibility combined with advanced control system, improved system diagnostics, and realistic thermal modeling provides excellent platform for further process development. Results on the initial HP EDG CdZnTe ingots grown with low temperature gradient show complete elimination of ingot cracking. The increased single crystal yield combined with the improved electron transport properties allows the fabrication of large-volume electron-only devices at higher yield. For the 14 CdZnTe ingots grown to date in the two HP EDG systems we find $\mu_\tau_e$ to vary in the $(2.5-7.5) \times 10^{-3} \text{ cm}^2/\text{V}$ range and some ingot sections yield material with $\mu_\tau_e \geq 8.0 \times 10^{-3} \text{ cm}^2/\text{V}$.
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