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High compositional homogeneity of CdTe$_x$Se$_{1-x}$ crystals grown by the Bridgman method

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Abstract

We obtained high-quality CdTe$_x$Se$_{1-x}$ (CdTeSe) crystals from ingots grown by the vertical Bridgman technique. The compositional uniformity of the ingots were evaluated by X-ray fluorescence at BNL’s NSLS X27A beam line. The compositional homogeneity was highly uniform throughout the ingot, and the effective segregation coefficient of Se was ~ 1.0. This high uniformity offers potential opportunity to enhance the yield of the materials for both infrared substrate and radiation-detector applications, so greatly lowering the cost of production and also offering us the prospect to grow large-diameter ingots for use as large-area substrates and for producing higher efficiency gamma-ray detectors. The concentration of secondary phases was found to be much lower, by eight- to ten-fold compared to that of conventional Cd$_x$Zn$_{1-x}$Te (CdZnTe or CZT).
For the past two decades, Cd$_x$Zn$_{1-x}$Te (CdZnTe) has proven an excellent choice as a room-temperature radiation-detector material due to its favorable physical- and optoelectronic-properties\textsuperscript{1,2}. In addition, the material with a 4% Zn content has long been known to be an excellent substrate material for infrared (IR) detectors and night-vision instruments due to its lattice matching with HgCdTe (MCT)\textsuperscript{3-6}. Both applications demand material of high quality, but due to the poor thermo-physical properties of molten and solid CdZnTe near the growth temperature, the production of a high yield of large-volume acceptable crystals still remains a challenge. One of the main limitations in enhancing the yield is the high segregation coefficient (~1.35)\textsuperscript{7} of Zn in the CdTe matrix. This non-unity segregation coefficient not only results in a compositional gradient along the ingot’s length but also along the ingot’s diameter. A convex-shaped growth interface is the most suitable for growing large grain/single crystalline ingots, and the composition follows the shape of the interface for non-unity segregation coefficients. Thus, for convex-shaped growth, the radial gradient of composition in CdZnTe is variable. Recently, Zhang et al.\textsuperscript{7} demonstrated compositional non-uniformity in CdZnTe ingots growth by the electro-dynamic gradient freeze technique for a 10% nominal concentration of Zn. The Zn concentration was demonstrated to vary from 15% near the first-to-freeze portion to 5% near the last-to-freeze portion. Radial compositional non-uniformity was also observed in the samples. Thus, only a small portion of the ingot satisfies the lattice-matching condition for epi-layer growth of MCT. Moreover, non-uniformity in the CdZnTe alloy composition is the primary cause for the very high cost of acceptable material, particularly for large-area substrates. Compositional variations due to segregation not only reduce the yield of uniform large-area substrates, they also are the main bottleneck for growth of large-volume uniform detector-grade
CdZnTe crystals. The availability of large-area CdZnTe at an acceptable cost for substrate material is the main hurdle preventing the large-area epitaxial growth of MCT for IR applications. The compositional gradient also adversely affects the performance of gamma-ray detectors. The presence of a high concentration of Te inclusions/precipitates of the order of 5-7x10^5 cm^-3 in CdZnTe ingots, along with the high concentration of sub-grain boundary networks, also have deleterious effects on the device performance. These defects also severely hamper the substrate’s quality. Although it is well known that the Te inclusions/precipitates can be eliminated by thermal annealing, they leave behind a high concentration of residual defects and lattice distortions in the vicinity of the Te sites, which severely degrade the uniformity of the charge collection for X- and gamma-ray detectors and the quality of the MCT epitaxial layer for IR uses.

CdTexSe_{1-x} (CTS) offers several distinct advantages over presently available CZT for both detector and substrate material applications. Its main advantage is the near unity (0.98) segregation coefficient of Se in the CdTe matrix that can substantially enhance the yield of acceptable crystals for radiation detectors and substrate applications. Thus, CTS has tremendous potential for drastically lowering the costs of devices. Unlike CZT, the CTS crystals are known to be free from sub-grain boundary networks due to the effectiveness of Se in assuring solid solution hardening, as compared to Zn, in the CdTe matrix. Moreover, the etch-pit density in CTS crystals is one order of magnitude less than that in the commonly used CZT crystals, and the reduced concentration of dislocations is one of the biggest advantages of CTS as a substrate material. In the early stage of CZT development as a gamma-ray detector, Fiederle et al. reported growth of high resistivity (10^{10} ohm-cm) CTS crystals and demonstrated CTS’s better efficiency in charge collection compared to CZT.
Thus, improved growth of CTS potentially offers an excellent outcome in important technology areas. In the present study, we grew CdTe$_{x}$Se$_{1-x}$ crystals with 10% nominal concentration of selenium (x=0.9) using the vertical Bridgman technique. They were grown in conically tipped graphite-coated ampoules with a 22-mm inner diameter. The starting material used was 6N purity CdTe from 5N Plus, Inc., and 6N purity CdSe from Azelis Electronics. The synthesized material was further purified by sublimation before being used for the growth runs. The crystals were grown at a speed of ~3 cm/day; and after completion of the growth, the ingots were cooled to room temperature at a rate to 8°C/hr, and then removed from the ampoule.

Wafers were cut from the as-grown ingot using a diamond-impregnated wire saw. Two wafers were cut perpendicular to the ingot’s axis from the top of the ingot (last-to-freeze part), and the rest of the ingot was cut along its length (Figure 1); the resulting wafer was ~8.7-cm long. In order to polish it with parallel faces, the wafer was cut into two halves (Fig. 1) to fit into the polishing chuck. To obtain the Se composition as a function of position, we performed Energy Dispersive X-ray (EDAX) along the ingot length, as well as along the radial direction. The average value of (1-x), i.e. the concentration of Se along the entire length, was found to be 0.1027± 0.0043. Considering the accuracy of EDAX to be ± 1 atomic %, the composition is fairly constant along the length of the ingot and agrees well with the initial composition of 10 atomic % of Se. Similar compositional uniformity in the radial direction was obtained by the EDAX measurements. The band-gap for CTS with 10% Se composition was measured and found to be about 1.42 eV, which agrees well with the reported value of 1.41 eV by Kim et al. High-resolution qualitative elemental mapping for Cd, Se, and Te was carried out by X-ray fluorescence at the X27A beam line of Brookhaven’s National Synchrotron Light Source (NSLS). A probe beam with a diameter of 20 µm and step size of 50 µm was used for scanning
the entire wafer. The measurements were taken on the finished polished wafers followed by etching them in 1% bromine methanol solution for two minutes. Figures 2a and 3a show the high-resolution X-ray fluorescence map of the SeKα line of the lower- and the upper-part of the entire wafer cut along the length of the as-grown CTS ingot. The very high compositional uniformity throughout the entire wafer is evident from figures 2 and 3. We note that, due to very high compositional uniformity, the growth interface is not observable in the present case, while, for CZT, the growth interface is visible due to the non-uniform segregation coefficient of Zn in CdTe. Figs. 2b and 3b, respectively, depict the line profile of Se along the white lines shown in Figs. 2a and 3a; the high compositional uniformity is evident. For convenience, a horizontal line has been added to the line profiles. As is evident from the line profiles for both the lower- and the upper-part of the ingot, the counts are almost the same from the start to the end of each wafer, depicting high axial compositional uniformity, reflecting the segregation coefficient of Se of ≈ 1. The minor fluctuation on the counts on the line profile as shown in Figures 2b and 3b might be due to surface roughness of the samples. In a previous report, the segregation coefficient of Se was reported as 0.98; and the Se concentration was reported to increase gradually with the solidification fraction for CTS grown by the Bridgman technique. Similar measurements were collected from a wafer, cut perpendicular to the ingot’s axis as shown in Fig. 1 from the top of the ingot. Figure 4a shows the high-resolution X-ray fluorescence map for the Se Kα line for the whole wafer, and depicts very high compositional uniformity across the entire wafer. As shown in this illustration, the large difference in counts for a region ~2 mm in the vertical scale is due to the beam dumping during the measurement, and the different count rates in the two regions reflect the different intensity of the beam’s flux before and after beam dumping. A similar beam dumping effect is also seen in Figs. 2a and 3a for the strip indicated by
the arrows. Fig. 4b shows the line profile for the Se K$_\alpha$ along the grey line in Fig. 4a. Very high compositional uniformity also is evident across the radius. The absolute count differed in the two parts of the wafer along the length and also for the cross-sectional wafer, possibly caused by the different sample-to-detector distance due to the different thickness of the wafers.

In fact, the fluorescence map reveals a very high compositional uniformity over the entire ingot, promising very high yield of uniform alloy content for both substrate- and detector-applications. This high compositional uniformity offers tremendous potential for drastically lowering their production costs. Very high compositional/lattice constant homogeneity of the substrate material is a stringent requirement for better epitaxial growth; further, radiation detectors demand such homogeneity, especially for large-volume thick ones. It is known that compositional inhomogeneity along the detector’s thickness degrades the charge-transport properties, resulting in degradation of the detector’s performance.$^8$

The size distribution and concentration of Te inclusions/precipitates (secondary phases) is also a key factor, and they have deleterious effects for IR substrate and radiation-detector applications. The presence of secondary phases on the substrate’s surface causes localized distortion of the lattice parameter that adversely affects the epitaxial layer. Figure 5 shows the typical size distribution and concentration of Te inclusions/precipitates from two different positions for a CTS ingot with 10 % nominal concentration of Se. For most positions, the distribution and concentrations are similar. The size distribution for the secondary phases is similar to that in the conventional Bridgman-grown CZT. For the CTS samples investigated in this study, the average concentrations of Te inclusions/precipitates are in the range of 3-8x10$^4$ cm$^{-3}$. For commercial CZT samples the typical concentration was reported$^9$ to be 5-7x10$^5$ cm$^{-3}$. Thus in CTS, the concentration of Te inclusions/precipitates is about 8-10 times lower than in
conventional CZT. We believe that Se is possibly responsible in reducing the bulging of the retrograde solidus line near stoichiometry and effective in reducing the concentration of secondary phases by an order of magnitude compared to conventional CZT. According to the theoretical prediction of the device’s performance versus concentration of Te inclusions/precipitates of different sizes\textsuperscript{16}, the size distribution and concentration of the Te inclusions/precipitates in our CdTe\textsubscript{0.9}Se\textsubscript{0.1} ingot fall below the threshold level where the device’s performance will be degraded.

From the standpoint of compositional homogeneity and concentration of secondary phases, CTS is far superior to conventional CZT, and, in this study, the segregation coefficient was almost unity. This high compositional homogeneity throughout the ingot greatly enhances the yield of large-area substrate material and large-volume detector material. The high uniformity of CTS ingots are expected to allow at least a three-fold reduction in production costs compared to CZT for both applications. Furthermore, the near-unity segregation coefficient of Se also offers the opportunity to scale up to larger diameter ingots while maintaining high uniformity.

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Figure 1. CTS wafers cut along the length and across the growth direction.
Figure 2. X-ray fluorescence elemental map of SeKα line across the whole wafer cut along the length (8.7 cm) of the ingot: a) lower part of the ingot, b) the line profile of Se Kα, and c) the lower part along the length as measured along the white line in a).
Figure 3. X-ray fluorescence elemental map of SeK$_\alpha$ line across the whole wafer cut along the length (8.7 cm) of the ingot. a) Upper part of the ingot, and b) the line profile of Se K$_\alpha$ of the lower part along the diagonal as measured along the white line in a).

Figure 4. a) X-ray fluorescence elemental map of SeK$_\alpha$ line across the whole wafer cut perpendicular to the length of the ingot, and b) the line profile of Se as measured along the grey line across the diameter indicated in Fig. 3a.
Figure 5. Typical size distribution of Te inclusions/precipitates in a Bridgman-grown CdTe$_{0.9}$Se$_{0.1}$ ingot. Figs. 5a and 5b are the typical distribution at two different positions of the ingot. The investigated volume for each measurement is 1.1x1.5x8 mm$^3$. 