Morphology evolution of micron-scale secondary phases in CdZnTe crystals grown by vertical Bridgman method

Yadong Xu^{a,b}, Wanqi Jie^{a,*}, Tao Wang^a, Pengfei Yu^a, Yihui He^a, Li Fu^a, Paul Sellin^{b,1}

^a State Key Laboratory of Solidification Processing, Northwestern Polytechnical University, Xi'an 710072, China

^b Department of Physics, University of Surrey, Guildford GU2 7XH, UK

ARTICLE INFO

Article history:

Received 1 July 2010

Received in revised form 2 November 2010

Accepted 2 November 2010

Available online 11 November 2010

PACS:

81.05.Dz

78.66.Hf

81.10.Fq

61.72.-y

82.80.Gk

Keywords:

CdZnTe

Te-rich secondary phase

IR imaging

Morphology

ABSTRACT

The morphology and evolution of micron-scale Te-rich secondary phases (SP) are discussed based on IR contrast images. Well-defined, hexagonal or triangular shaped, incoherent Te-rich SP particles were generally identified in as-grown CdZnTe crystals grown with excess Te. The creation of these particles is consistent with the Te-rich droplets encapsulated within the CdZnTe matrix, which grown by accumulation of the point defects. The surrounding CdZnTe crystal dominates the morphology of Te-rich SP particles orienting themselves along crystallographic directions. Star-shaped Te-rich particles and needle-like Te-rich SP clusters were normally revealed in as-grown CdZnTe crystals, obtained under Cd-rich conditions. The former is related to the dislocation loop punching associated with SP particles, which attributed to the internal stress relief. The latter is constituted by numerous small irregular Te precipitates, which is likely produced by the aggregation of Te precipitates along specific paths through thermo-migration during the in situ annealing and cooling processes.

© 2010 Elsevier B.V. All rights reserved.

1. Introduction

II–VI compound semiconductor CdZnTe (CZT) has attracted much attention in the fields of far-infrared and room temperature radiation detectors [1,2], solar cells [3,4], photorefractive devices [5], etc. due to its excellent photoelectric properties. Recently, there has been a significant effort in developing CZT single crystal and detector fabricating for various hard X-ray and soft γ -ray imaging applications, especially in the flourishing field of space astronomy [6]. However, the material's inhomogeneity in bulk grown detector-grade CZT crystals, especially due to the structure imperfections, still creates a 'bottle-neck' in state of the art wafer assessment and screening, which has consequently reduced the availability and increased the cost of CZT materials. These commercial restrictions have prevented the wide-spread adoption of CZT for various general applications, such as medical imaging, industrial monitoring and national security [7,8].

It has been widely reported that the presence of Te-rich SP particles in as-grown CZT crystals tends to deteriorate the struc-

tural uniformity using both electrical and optical methods. Indeed, the correlation of Te-rich SP particles and their corresponding crystalline structure observed in CdTe/CZT crystals, together with the influence of Te-rich SP particles on the optical and electrical behaviors of CdTe/CZT crystals, have also been discussed according to the statistical measurements [9–13]. It is clear that a more detailed interpretation of the generation of Te-rich SP particles is still required to understand the inherent relationships mentioned above, and also to further improve the crystal growth techniques.

Generally, the solid-state precipitated defects are referred to as precipitates, whereas the crystallization of mother liquid droplets used to be named as the inclusions. According to the work on Te precipitation by Rudolph [14], Te inclusions in CdTe/CZT crystals are attributed to the morphological instability of the liquid–solid interface during growth, while Te precipitates are considered as a result of retro-grade solubility of tellurium during cooling to room temperature, including a nucleation process. However, there is still not a rigorous assignment of both kinds of particles. In this case, only an empirical method is used to distinguish them. The typical size of a precipitate is usually in the range of 10–50 nm, as observed by transmission electron microscopy [15,16], whilst the typical dimension of an inclusion is in the range of 1–50 μ m. In practice, given that there may be a continuum for the size distribution of SP particles within CZT, it can be difficult to precisely

* Corresponding author. Tel.: +86 29 88486065; fax: +86 29 88495414.

E-mail addresses: jwq@nwpu.edu.cn (W. Jie), p.sellin@surrey.ac.uk (P. Sellin).

¹ Tel.: +44 1483 686814; fax: +44 1483 686781.

Fig. 1. (a–c) Typical IR images for Te-rich SP particles observed in CZT samples grown under Te-rich conditions, with triangular and hexagonal shapes, respectively. (d) Schematic illustration of the evolution of Te-rich SP particles, considering a hollow space within the matrix (middle), with the evolution for the projection viewing along $\langle 111 \rangle$ direction (bottom). (e) A representative IR image viewed near the twin or subgrain boundary region.

identify the nature of particles within an intermediate size range. In this study, an emphasis is given to large-size ($>1 \mu\text{m}$) Te-rich SP particles presented in as-grown CZT crystals, observed using IR transmission microscopy. The morphology and evolution of these micron-scale SP particles have been evaluated.

2. Experimental

As-grown $\text{Cd}_{0.9}\text{Zn}_{0.1}\text{Te}$ wafers, sliced from the middle part of the ingots, were studied in this work. Details of the growth procedures have been described in our previous publications [17]. The wafers were consecutively polished with $3 \mu\text{m}$ SiC, $0.3 \mu\text{m}$ Al_2O_3 , and $0.05 \mu\text{m}$ Al_2O_3 abrasive pastes, respectively, prior to performing the IR transmission measurements. Imaging of Te-rich particles was carried out using an IR transmission microscopy system (with the optical resolution limit of $1 \mu\text{m}$), which contained a series of microscope objectives. A lens cone with a variable field-of-view was used to connect the IR CCD camera (with the spectral responsivity of $0.4\text{--}1.6 \mu\text{m}$), and a tungsten lamp was employed for illuminating the sample.

3. Results and discussion

3.1. CZT grown under Te-rich condition

Fig. 1 shows typical IR images for CZT samples grown under Te-rich conditions. The resulting high-contrast IR images were obtained due to the strong IR absorption of Te, corresponding to its relatively narrow band gap (with the value of 0.33 eV [18]). In these images the distinct dark areas are associated with the presence of Te-rich SP particles in the CZT wafer. These well-defined SP particles are distributed uniformly throughout the material, with a projected 2D shape close to hexagonal or triangular. The sizes of these features are typically $6\text{--}30 \mu\text{m}$ with the concentrations of $1\text{--}5 \times 10^5 \text{ cm}^{-3}$. These SP particles are generally considered as incoherent structure Te-rich inclusions due to their high definition

outlines. Rudolph et al. [19] observed that the SP inclusions were generated by Te droplets trapped at the non-planar liquid–solid interface due to the morphological instability during the growth.

In order to interpret the formation mechanism for these liquid-state precipitated SP particles, a more-detailed understanding of three dimensional SP morphologies is required. Taking into account the isotropy of melt, the trapped Te-rich droplet will tend to stabilize into a spherical shape due to surface tension. However, it subsequently faced by the surrounding CZT crystal since the distortion energy anisotropy and elastic inhomogeneity. Simultaneously, a high concentration of Cd and Zn atoms are usually encapsulated within the Te droplets. In this way, the Te droplets gradually grow up by accumulating the point defects associated with Te interstitials (Te_i), Cd vacancies (V_{Cd}) and Te antisites (Te_{Cd}). The increased droplet internal pressure is balanced by the interfacial tension and distortion force produced by the deformation of CZT lattice. As temperature decreasing after in situ annealing, the solidification begins at the periphery of the droplet and continues until the lowest equilibrium temperature of the system, maybe the eutectic temperature, is reached. Thus, Te-rich droplet gradually becomes a polyhedral which actually has to be described by the deformation of CZT lattice and the anisotropic growth.

We suggest one evolution model in Fig. 1(d). In this model, we consider the formation of a hollow near-tetrahedral polyhedron from the point of view of the CZT matrix, which is constructed by the close-packed low index planes of CZT crystal, so as to lower the interface free energy between crystal and Te droplet. Considering the geometric configuration, these polyhedrons are preferentially orientated, which build up with the main surfaces of CZT $\{111\}$ planes, the corner surfaces of CZT $\{110\}$ and the edge surfaces of CZT $\{100\}$, respectively, as represented in Fig. 1(d) (middle).

Fig. 2. (a) Typical IR image of star-shaped Te-rich SP particle obtained from Cd-rich grown CZT samples. (b) Magnified region around a star-shaped SP, with reversed processing of the brightness. (c) Schematic drawing of the orientation and location of dislocation loop planes associated with the SP core.

The projection of this kind of polyhedron looks like a well-defined hexagon when viewed along the $\langle 111 \rangle$ direction. In view of the $\{111\}$ planes provide the minimum free energy interfaces between the CZT and the liquid Te inclusions [20], it is possible that there is a higher formation potential for $\{111\}$ than for other plane families. Thus, the $\{110\}$ and $\{100\}$ planes gradually submerged during the extended in situ annealing and cooling processes. Finally, a tetrahedral configuration is formed with all the surfaces of $\{111\}$ planes. The dihedral angle for each set of two conjoined plates is 70.5° , which is in good agreement with the value for the regular tetrahedral. Consequently, this structure provides a triangle projection when viewed in 2D, which is evolved from a hexagon viewed along the $\langle 111 \rangle$ direction. Fig. 1(e) is a representative IR image showing different patterns of SP particles enriched at the twin or sub-grain boundary.

Therefore, the shapes of the final droplets are determined by the distortion of the surrounding CZT crystals and anisotropic growth of included CZT matrix during the extended in situ annealing and cooling process. The final eutectic structure fills the polyhedral space which is related with CZT matrix and Te. Since the thermal expansion coefficient of Te is considerably higher than that of CZT, a strong stress results from contraction on cooling down to room temperature, which damages the lattice around the inclusion. Thus, the inclusions are always accompanied with cracks and holes [20–22].

3.2. CZT grown with excess Cd

In the case of CZT crystals grown under Cd-rich conditions, six armed star-shaped SP particles and needle-like precipitate clusters are normally identified, as shown in Figs. 2(a) and 3(a), respectively. The star-shaped SP particles, with typical diameters between 10 and $50\text{ }\mu\text{m}$, constitute six high-contrasted arms surrounding a central dark spot. To analyze the morphology of the star-shaped SP particles, a magnified area of Fig. 2(a) is illustrated in Fig. 2(b), which has been enhanced by reversal of the brightness. The image

shows the contrasted arms radiating from the central feature at 60° intervals. The polyhedral core with the size less than $5\text{ }\mu\text{m}$ is usually faceted into a hexagonal feature in 2D, with the direction of each arm pointing to the corresponding vertex of the hexagon.

Several other researchers have observed similar star-shaped defects in CZT crystals grown not only under Te-rich melt condition [19], but also under excess Cd condition [23]. So one always confused by the component of this kind of SP particles from IR images. Ndap [24] gave an optional classification in terms of the visible features. The points of Cd stars are rounded, whereas they appear sharp for Te stars. Therefore, the SP particles in Fig. 2(a) are belonged to Te-rich particles. These star-shaped SP particles randomly located in CZT slices have non-distinct outlines when observed by IR microscopy, which could be linked to the large stress field between the particles and the CZT matrix.

For CZT grown under Cd-rich conditions, Te-rich SP droplets were also generated, since the congruent point and highest melting point are at the Te-rich side. Meanwhile, the high Cd partial pressure during CZT crystal growth will result in a non-stoichiometric melt. Additionally, considerable concentrations of Cd interstitials (Cd_i) and Te vacancies (V_{Te}) tend to be present within the lattice at high temperature. The Te-rich droplets tended to shrink by capturing Cd_i and releasing Te atoms into the CZT matrix, during the isothermal in situ annealing and cooling processes. This is consistent with the model of dislocation loop punching, which can be ascribed to the release of stress at a strain concentrator into the CZT matrix. The loop propagation directions were $\langle 110 \rangle$ and loop planes were $\{110\}$, respectively, in that the non-polarity $\{110\}$ planes exhibit the lowest surface energy [25]. The projections of these loop planes on the $\{111\}$ surfaces are inclined to each other at 60° , thus giving the characteristic star-shaped features described here. The contrast arms point to the six vertexes of the central hexagon, mostly as a result of the stress concentrated in the local area. A schematic illustration is revealed in Fig. 2(c). In addition, the loop planes also act as channels for the diffusion of Cd, Te atoms and impurities. Previous studies [26] also indicated that CZT crys-

Fig. 3. (a) Typical IR image with needle-like Te-rich SP clusters. (b) A typical enlarged SP cluster. (c) Schematic sketch of the location and formation of Te-rich SP clusters presented in CZT crystals, viewed perpendicular to a $\{1\ 1\ 1\}$ facet.

tals with star-shaped SP particles are often in low resistivity, owing to the impurities accumulated in the captured droplets diffuse into the material, which agree with our hypothesis.

With respect of the needle-like Te-rich SP clusters, a typical enlarged image is shown in Fig. 3(b). This structure is usually 50–200 μm in length and 5–20 μm in width when viewed perpendicular to a $\{1\ 1\ 1\}$ facet. These clusters were formed by the aggregation of numerous small irregular Te precipitates. The morphology of the needle-like Te clusters could be disk shaped in 3D. From Fig. 3(a), there are only three directions for the clusters, and the intersecting clusters make an angle of 60°, when viewed perpendicular to a $\{1\ 1\ 1\}$ facet. The preferentially orientated distribution of Te clusters indicated that the small Te precipitates accumulate along specific paths by thermo-migration during the in situ annealing and cooling processes after growth. CZT $\{1\ 1\ 0\}$ planes exhibit the lowest surface energy, which potentially supply the driving force for the migration of small irregular Te precipitates. In other hand, these directions are identical to the locations of dislocations and stacking faults within $\{1\ 1\ 1\}$ planes [27]. Therefore, the formation of these clusters possibly attributed to the deposition of excessive Te along dislocations and stacking faults during in situ annealing and cooling. One proposed model is illustrated in Fig. 3(c), where the projections of these Te-rich SP clusters on the $\{1\ 1\ 1\}$ surface are inclined to each other at 120°.

4. Conclusions

IR contrast imaging of as-grown CZT crystals has been evaluated, through which the morphologies and generation of various Te-rich SP particles are discussed. For CZT crystals grown with excess Te, hexagonal and triangular shaped incoherent Te-rich SP particles

with the typical sizes in the range of 6–30 μm were observed. These particles were produced from Te-rich droplets, encapsulated within the CZT matrix. The further growth of these structures is resulted by accumulation of point defects and faceting by the surrounding CZT crystals during isothermal in situ annealing and cooling process.

Star-shaped Te-rich particles and needle-like Te-rich SP clusters were normally identified in CZT crystals which grown by introducing excess Cd. The former features are related to the dislocation loop punching associated with Te-rich SP bodies, which are attributed to the stress relief through volumetric changes. The latter features are considered to be the result of the accumulation of numerous irregularly small-size Te precipitates, which likely formed by the aggregation of Te precipitates along specific paths through thermo-migration, during the extended in situ annealing and cooling process.

Acknowledgements

This work has been financially supported by the National Natural Science Foundation of China under Grants Nos. 50872111 and 50902114. It is also a part of the Program for New Century Excellent Talents supported by China Ministry of Education, NCET-07-0689. We are grateful to Dr. Christopher Mills from University of Surrey, Drs. Yuanyuan Du and Peisen Li from NPU for fruitful discussions.

References

- [1] J.M. Tsay, M. Pflughoeft, L.A. Bentolila, S. Weiss, J. Am. Chem. Soc. 126 (2004) 1926–1927.
- [2] P.J. Sellin, G. Prekas, J. Franc, R. Grill, Appl. Phys. Lett. 96 (2010) 133509.
- [3] K.M. Garadkar, S.J. Pawar, P.P. Hankare, A.A. Patil, J. Alloys Compd. 491 (2010) 77–80.

- [4] Q. Zhang, J. Ding, Y. Shen, D. Chen, Q. Zhou, Q. Chen, Z. He, J. Qiu, J. Alloys Compd. 508 (2010) L13–L15.
- [5] S. Schwartz, M. Segev, S. Berger, E. Zolotoyabko, U. El-Hanany, Phys. Rev. B 79 (2009) 193202.
- [6] J. Hong, B. Allen, J. Grindlay, N. Chammas, S. Barthelemy, R. Baker, N. Gehrels, J. Collins, W.R. Cook, R. McLean, F. Harrison, Nucl. Instrum. Meth. A 605 (2009) 364–373.
- [7] A.E. Bolotnikov, S. Babalola, G.S. Camarda, Y. Cui, S.U. Egarievwe, R. Hawrami, A. Hossain, G. Yang, R.B. James, IEEE Trans. Nucl. Sci. 57 (2010) 910–919.
- [8] T.E. Schlesinger, J.E. Toney, H. Yoon, E.Y. Lee, B.A. Brunett, L. Franks, R.B. James, Mater. Sci. Eng. Rep. 32 (2001) 103–189.
- [9] G.A. Kulkarni, V.G. Sathe, K.S.R.K. Rao, D.V.S. Muthu, R.K. Sharma, J. Appl. Phys. 105 (2009) 063512.
- [10] L. Luan, W. Jie, J. Zhang, H. Liu, J. Alloys Compd. 477 (2009) 399–402.
- [11] N.A. Shah, J. Alloys Compd. 506 (2010) 661–665.
- [12] E.S. Elshazly, G. Tepper, Appl. Phys. Lett. 93 (2008) 042112.
- [13] A. Hossain, A.E. Bolotnikov, G.S. Camarda, Y. Cui, G. Yang, K.-H. Kim, R. Gul, L. Xu, R.B. James, J. Cryst. Growth 312 (2010) 1795–1799.
- [14] P. Rudolph, Prog. Crystal Growth Charact. 29 (1994) 275–381.
- [15] G. Li, S. Shih, S. Mu, Y. Xu, W. Jie, J. Mater. Res. 25 (2010) 1298–1303.
- [16] T. Wang, W. Jie, D. Zeng, Mater. Sci. Eng. A 472 (2008) 227–230.
- [17] G. Li, X. Zhang, H. Hua, W. Jie, J. Electron. Mater. 34 (2005) 1215–1224.
- [18] H.N. Jayathirtha, D.O. Henderson, A. Burger, M.P. Volz, Appl. Phys. Lett. 62 (1993) 573–575.
- [19] P. Rudolph, A. Engel, I. Schentke, A. Grochowski, J. Cryst. Growth 147 (1995) 297–304.
- [20] M.C. Duff, D.B. Hunter, A. Burger, M. Groza, V. Buliga, J.P. Bradley, G. Graham, Z.R. Dai, N. Teslich, D.R. Black, A. Lanzirotti, J. Mater. Res. 24 (2009) 1361–1367.
- [21] C.H. Henager Jr., D.J. Edwards, A.L. Schemer-Kohn, M. Bliss, J.E. Jaffe, J. Cryst. Growth 311 (2009) 2641–2647.
- [22] M.C. Duff, K.G. Lynn, K. Jones, R. Soundararajan, J.P. Bradley, H. Ishii, J. Aguiar, P. Wozniakiewicz, Proc. SPIE 7805 (2010) 780503.
- [23] H.G. Brion, C. Mewes, I. Hahn, U. Schaufele, J. Cryst. Growth 134 (1993) 281–286.
- [24] J.O. Nday, CdTe and Related Compounds; Physics, Defects, Hetero- and Nano-structures, Crystal Growth, Surfaces and Applications, Elsevier, Netherlands, 2010, pp. 228–257 (Chapter VB).
- [25] M.A. Berding, S. Krishnamurthy, A. Sher, A.B. Chen, J. Appl. Phys. 67 (1990) 6175–6178.
- [26] Y. Xu, W. Jie, X. Bai, T. Wang, L. Fu, G. Zha, Proc. SPIE ISPD 7385 (2009), 73850T1–73850T8.
- [27] R. Korenstein, R.J. Olson, D. Lee, P.K. Liao, C.A. Castro, J. Electron. Mater. 24 (1995) 511–514.