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Impurity gettering effect of Te inclusions in CdZnTe single crystals

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ABSTRACT

The local impurity distribution in Te inclusions of CdZnTe (CZT) crystal was investigated by the time-of-flight secondary ion mass spectrometry (Tof-SIMS) technique. Direct evidence of impurity gettering in Te inclusions has been observed for the first time. The impurity gettering in Te inclusions originated from the diffusion mechanism during crystal growth and segregation mechanism during crystal cooling. This phenomenon is meaningful, because it reveals how Te inclusions affect CZT properties and provides a possible approach to reduce the impurities in CZT by the way of removing Te inclusions.

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1. Introduction

CdZnTe (CZT) has gained a lot of attention recently because it has promising potential for nuclear radiation detection applications. The unique physical properties, such as high-average atomic number, large enough band-gap, high resistivity, and good electron transport properties allow CZT to work at room temperature with good detection efficiency and high energy resolution [1–3]. It is well known that the presence of various impurities introduces different defect levels, which distinctly affect the electrical properties of CZT [1,2]. However, due to the low content of impurities, normally at the level of parts per billion by weight (ppbw), it is difficult to trace the impurities in CZT. Glow discharge mass spectrometry (GDMS) and inductively coupled plasma mass spectrometry (ICP-MS) have been employed to investigate the impurities of CZT crystals; nevertheless, these techniques can only provide the average bulk information for CZT materials [3,4]. Clarifying the impurity micro-distribution in CZT has been a long-standing challenging problem, which has yet to be effectively solved. Fortunately, the development of time-of-flight secondary ion mass spectrometry (Tof-SIMS) provides the possibility to address this problem, because Tof-SIMS technique possesses sensitivity as high as ppm/fmol and a lateral resolution as high as 300 nm. Previous research has demonstrated that Te inclusions, as inherent structural defects, are prevalent in as-grown CZT crystals and significantly limit the performance of CZT detectors [5]. In this letter we used Tof-SIMS technique to investigate the local impurity distribution in Te inclusions of CZT crystals. The direct evidence of impurity gettering in Te inclusions has been observed for the first time, and the impurity gettering effect of Te inclusions for several impurities has been reported.

2. Experimental procedure

CZT single crystals were grown by the modified Bridgman method. The Zn mole fraction of CZT is ~0.1. A Nikon OPTIPHOT2-POL microscope coupling infrared (IR) light microscopy and visible light microscopy was used to locate and identify Te inclusions near the surface of CZT wafers. A Tof SIMS-5 system, produced by IONTOF Inc., was employed for impurity analysis. Before the Tof-SIMS measurement, the CZT sample surfaces were sputtered with O_2^+ ion beam for 10 min to remove any remaining contaminants on the surface of the CZT. A highly collimated synchrotron X-ray radiation from Brookhaven's National Synchrotron Light Source (NSLS) was shot on Te inclusions and the

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surrounding CZT matrix and the corresponding energy spectra were collected.

3. Results and discussion

Several typical Te inclusions were chosen for impurity analysis. The impurity distribution is similar among all the Te inclusions. A representative hexagon Te inclusion, shown in Fig. 1, is used to illuminate the distribution behavior of different impurities. The Tof-SIMS system has two operating modes including a high-mass resolution mode and a high-lateral resolution mode. The first mode has a greater capability to distinguish different impurities, while the second one can describe the distribution of different impurities with a better lateral resolution. Fig. 2 gives the high-mass resolution Tof-SIMS images of impurities in the hexagon Te inclusion, which has been made by selecting only the Tof-SIMS signal associated with individual elements. Different brightness of these images indicates the change of impurity concentration. First, one can see that there is an obvious lack of Zn and Cd and an enrichment of Te in the inclusion site (see Figs. 1 and 2). This

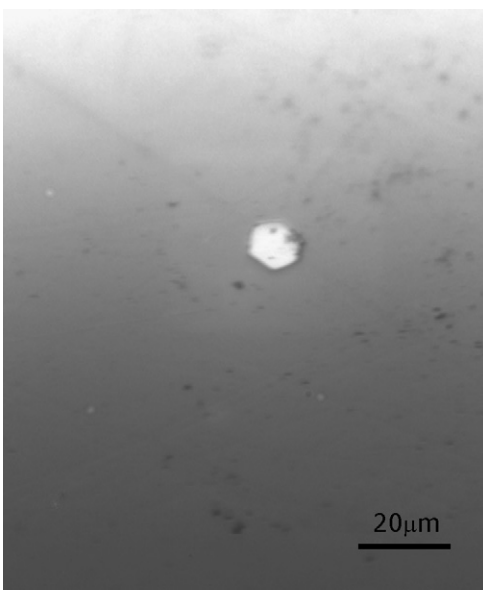

Fig. 1. A representative hexagon Te inclusion region for Tof-SIMS impurity analysis.

confirms that the main component of the so called 'Te inclusion', is indeed Te. More importantly we observed higher impurity levels of Na, Ag, In and Bi accumulated in the Te inclusion. It looks that the Te inclusions cannot effectively getter some impurities, such as Al and Cu. Tof-SIMS scans in high-lateral resolution mode, shown in Fig. 3, were employed to give more details. The contours of accumulation regions of Na, Ag, In and Bi coincide exactly with the shape of the Te inclusion.

The impurities gettering phenomenon in Te inclusions is intriguing, and the question arises as to why the impurities are gettered selectively. Impurity segregation during the CZT crystal cooling could be one important mechanism for impurity gettering. During the growth of CZT, Cd evaporates out of the melt due to its high partial pressure and, therefore, results in CZT melt composition off the ideal stoichiometry. Correspondingly Cd vacancies (V_{Cd}) and excess Te are produced during this process. The latter exists as Te-rich droplets in the CZT melts [6]. When the CZT melt begins to solidify, there usually exist some morphologically unstable sites before the crystallization front such as re-entrant angles of grain boundary and twin crossing the interface, which prefer to trap the Te-rich droplets from the diffusion boundary layer in front of the growing interface due to the release of the excess free energy of the system. Since the melting point of Te ($\sim$450 °C) is far below the growing temperature of CZT ($\sim$1120 °C), and the growth of CZT takes weeks, these trapped liquid Te-rich droplets will be embedded in the CZT matrix. During the subsequent CZT cooling, the liquid Te-rich droplet experiences a quasi-symmetrical crystallization from the droplet edge to droplet center. Table 1 gives the segregation coefficient (k) of different impurities in CZT [7–10]. It is easy to see the k value of Na, In, Ag and Bi are very low, which means the segregation of these impurities is very serious and will result in exclusion of these four impurities into the Te-rich droplet embedded in the surrounding solid CZT matrix. While the k value of Cu is relatively larger, its absolute value is lower than unity. That implies the segregation of Cu is not obvious. As for Al, the k value is much larger than unity. It results in that Al are almost totally depleted into the CZT matrix.

Even among those impurities gettering in Te inclusions, there is also a difference of gettering extent. The brightness of Tof-SIMS image is proportional to the concentration of impurity. From the brightness difference of Tof-SIMS images of impurities, one can deduce the change of impurity concentration. We define the relative concentration of some certain impurity, I_R, as

$$I_R = \frac{I_1 - I_2}{I_2}, \quad (1)$$

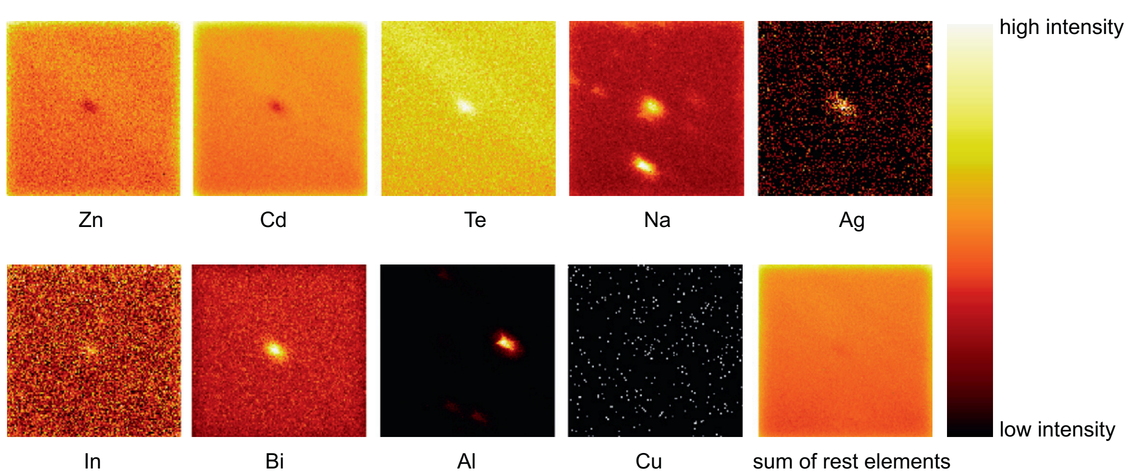

Fig. 2. High-mass resolution Tof-SIMS images of impurities around the hexagon Te inclusion region. The size of the Tof-SIMS images is $150 \times 150\,\mu m^2$.