Improvement of the productivity in the growth of CdTe single crystal by THM for the new PET system

Hiroyuki Shiraki, Minoru Funaki, Yukio Ando, Shinya Kominami, Kensuke Amemiya, and Ryoichi Ohno

Abstract– **The effect of the THM growth rate on the CdTe crystalline quality and the detector performance was intensively investigated. The maximum growth rate for the single crystal growth was found to be approximately 15mm/day which was 3 times greater than the conventional one. By optimizing other growth conditions, 90 % of every ingot volume has become a single crystal. Te inclusions in the CdTe single crystal grown at various growth rates were also investigated by IR transmission microscopy. There was no correlation between the behavior of Te inclusions and the growth rate. The detector performance was also independent of the growth rate.**

Taking advantage of the large volume CdTe single crystals, about 700,000 Schottky detectors with 4 mm x 7.5 mm x 1 mm were fabricated for the research and development of the new PET system using CdTe detectors. The average FWHM for the 662keV line from ^{137}Cs and its standard deviation were 2.24 % and 0.48 %, respectively. This uniformity was essential for the development of the new PET system.

For the further improvement of productivity, the growth technology of a 100mm diameter crystal by THM is in the development and is presented.

I. INTRODUCTION

CADMIUM Telluride (CdTe) is an excellent material candidate for high detection efficiency and good energy resolution room-temperature nuclear radiation detectors. Traveling Heater Method (THM) has been known to grow uniform CdTe single crystals. It had been thought that large single crystals suitable for commercial applications could not be grown by THM [1], [2], [3], [4], while ACRORAD was manufacturing 50 mm diameter CdTe single crystals in 1999 and creating radiation detectors which were commercially available [5]. In 2002, the THM crystal growth technology for the CdTe single crystal with 75 mm diameter has been developed. Owing to continuous improvements of crystal growth condition, we can currently grow high quality Cl doped CdTe single crystals with 75 mm in diameter and 200 mm in length by THM, in which the typical growth rate is 5 mm/day [6]. This is the largest CdTe single crystal grown by THM that has ever been reported. The bulk resistivity in the crystal is greater than $1\times 10^9\ \Omega\cdot$cm estimated from current-voltage characteristic in the Pt/CdTe/Pt ohmic type detector [7]. Furthermore, the effective resistivity becomes higher than $1\times 10^{11}\ \Omega\cdot$cm in the In/CdTe/Pt Schottky type detector under a reverse bias condition, in which the diode resistance is nearly equal to the depletion layer resistance [8], [9], [10]. As drift velocities are proportional to applied electrical field strength, the apparent high resistance is capable of applying high reverse bias voltage and reducing the charge collection time in the Schottky type detector.

However, for the medical and industrial imaging applications, the reproducibility of the single crystal with uniform detector quality is the most important issue. In this work, we investigated the effect of the THM growth rate on the CdTe crystalline quality and the detector performance in order to achieve further productivity. Furthermore, we present our growth technology of a 100 mm diameter THM-CdTe single crystal.

II. EXPERIMENTAL

A. CdTe single crystal growth by THM

All quartz ampoules used in our crystal growth process were coated with a thin graphite layer by pyrolysis of high purity methane.

The CdTe poly crystal and Te-rich Cl doped Cd-Te alloy were synthesized in each ampoule. The CdTe single crystal seed was cut from the previous grown crystal. The ampoule for THM crystal growth was charged with the seed, the solvent alloy, and the poly crystal. After the ampoule was evacuated and sealed, the ampoule was set in a THM furnace. The ampoule was rotated, and the furnace was heated up to the growth temperature. In this experiment, we varied the THM growth rate from 5 mm/day to 30 mm/day. The grown crystal diameter and length were 75 mm and 200 mm, respectively. The Cl concentration in the grown crystal was in the range from 2 weight-ppm to 3 weight-ppm.

B. Characterization of the grown crystal

On the crystalline quality, we performed visual inspections of the grown crystal and Infra-Red (IR) transmission microscopy to investigate the size and density of Te inclusions. The mobility-lifetime ($\mu\tau$) products of the carriers were also estimated by using the "$\mu\tau$-model" spectral fitting method proposed by G. Sato et al. [11]. In this model, the escape peak components that are results of photo fluorescence of 23 keV for Cd and 27 keV for Te are taken into account. Samples were 10 ohmic type detectors with dimensions of 4 mm$\times$4 mm$\times$1 mm where 1 mm was the thickness of the detector. The detector was irradiated with gamma-rays from ^{57}Co through the cathode electrode. We obtained spectra at three different bias voltages to utilize the peak shifts due to the changes in the electrical field strength.

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On the CdTe detector performance, we fabricated Schottky type detectors with dimensions of 4 mm× 7.5 mm× 1 mm where 1 mm was the thickness of the detector, and investigated yield of leakage current and energy resolution. Criteria for each item are yield of leakage current less than 10 nA and energy resolution less than 4 % for 662 keV line from ^{137}Cs at 500 V.

III. Results and Discussion

A. Effect of THM growth rate on the CdTe crystalline quality

Fig. 1 shows the outward appearance of the CdTe crystal grown with the stepwise growth rate increase method. In this growth experiment, the growth rate was increased from 5 mm/day to 30 mm/day. Plenty of micro grains were generated by the stepwise increase of the growth rate from 15 mm/day to 20 mm/day, so that the growing portion suddenly changed from a single crystal to a poly crystal. From this result, the maximum growth rate for the single crystal growth was found to be approximately 15 mm/day which was three times greater than the conventional one.

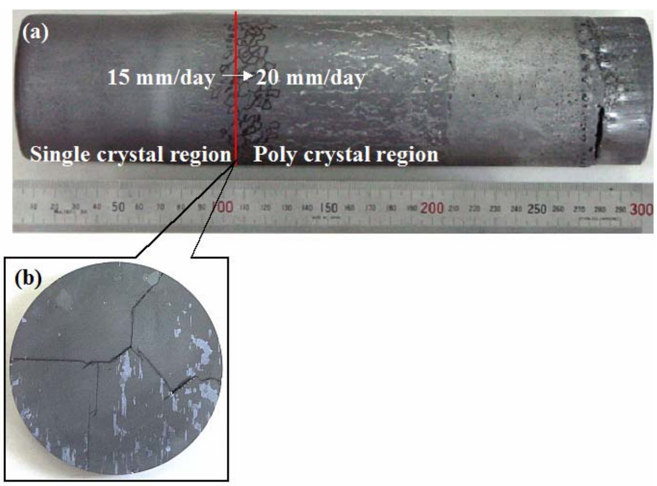

Fig. 1. CdTe crystal grown with the stepwise growth rate increase method. The growth rate was increased from 5 mm/day to 30 mm/day at an interval of 5 mm/day. (a) The outward appearance and (b) the cross sectional appearance at the stepwise growth rate increase from 15 mm/day to 20 mm/day.

To reconfirm crystalline quality below the maximum growth rate, we performed another growth experiment with growth rates less than 15 mm/day, in which the growth rate varied from 5 mm/day to 13.6 mm/day. As shown in Fig. 2 (a), the single crystal was successfully obtained. Consequently, the maximum growth rate for the 75 mm diameter single crystal growth was found to be in the range from 13.6 mm/day to 15 mm/day. From the manufacturing point of view, the growth rate used in production was determined to be 10 mm/day shown in Fig. 2 (b). Now, 90 % of every ingot volume has become a single crystal.

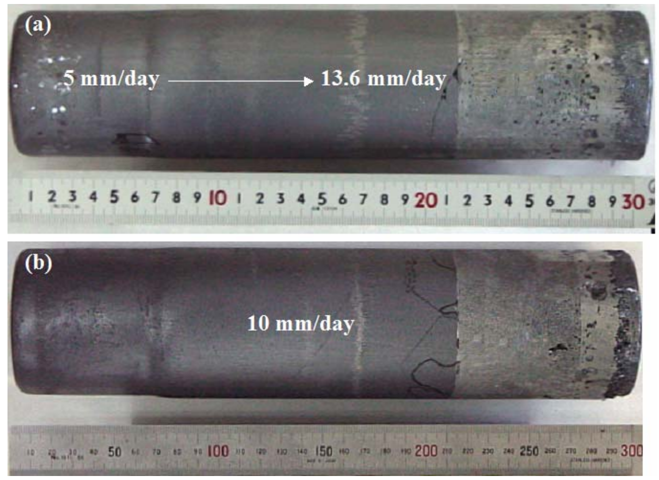

Fig. 2. CdTe single crystals grown with (a) the stepwise growth rate increase method below 15 mm/day and (b) 10 mm/day.

Furthermore, the behavior of Te inclusions in grown crystals with various growth rates was investigated by IR transmission microscopy which had been known to be one of the most effective ways of detecting Te inclusions. Typical IR images are shown in Fig. 3 and Fig. 4. Samples were, wafers polished on both sides, with 1 mm in thickness. The size of Te inclusions observed here were less than 15 μm. Te inclusions greater than 10 μm have faceted-polyhedron shape, while the shape of smaller ones less than 5 μm, appears to be spherical. There was no difference in the size and the shape of Te inclusions among CdTe crystals grown with two different growth rates. Fig. 5 shows the growth rate dependence of the density of Te inclusions. It was clearly seen that the density of Te inclusions was less than 1×10^{5} cm^{-3} and nearly constant. From these results, it was concluded that there was no correlation between the behavior of Te inclusions and the THM growth rate investigated here.

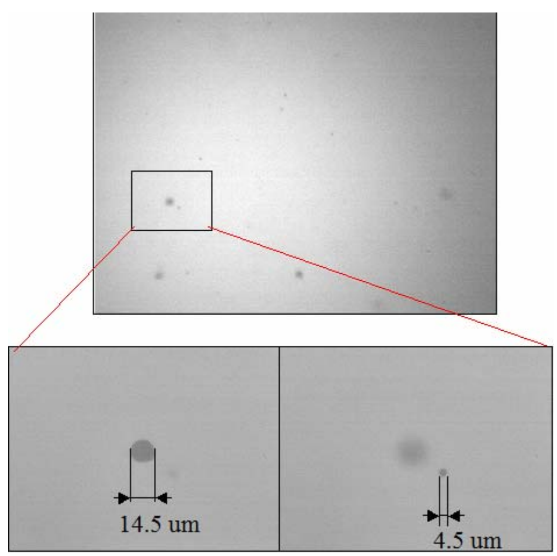

Fig. 3. IR microscope images of Te inclusions in CdTe single crystals grown at 5 mm/day. Dimensions of upper and lower images are 0.822 mm× 0.617 mm and 0.165 mm× 0.124 mm, respectively.

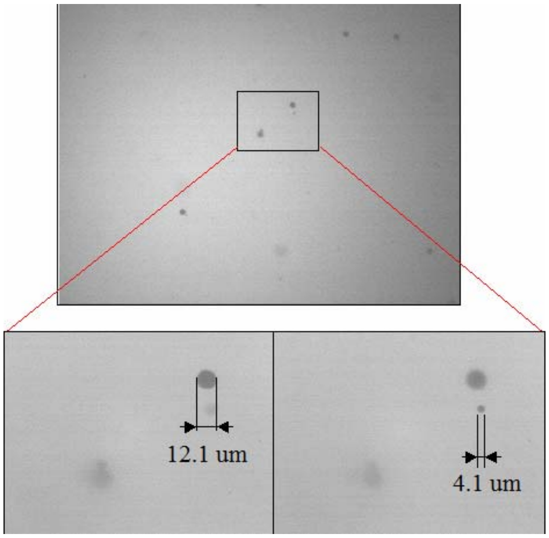

Fig. 4. IR microscope images of Te inclusions in CdTe single crystals grown at 10 mm/day. Dimensions of upper and lower images are 0.822 mm× 0.617 mm and 0.165 mm× 0.124 mm, respectively.

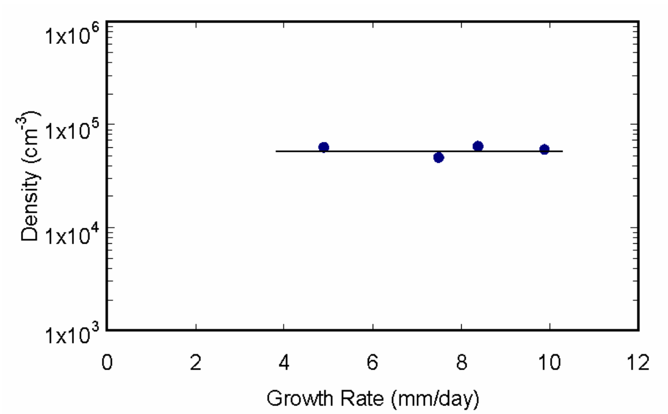

Fig. 5. Growth rate dependence of the density of Te inclusions in CdTe single crystals grown with various growth rates from 5 mm/day to 10 mm/day. The density of Te inclusions was nearly constant.

The $\mu\tau$ products of the carriers in grown crystals play an important role in the charge collection efficiency of CdTe nuclear radiation detectors. To study effects of the THM growth rate on the charge-transport properties, we performed estimations of $\mu\tau$ products in CdTe single crystals grown with two different growth rates (5mm/day and 10 mm/day) by using the " $\mu\tau$ -model" spectral fitting method. Fig. 6 shows the typical electrical field strength dependence of the energy spectra for the 122 keV line from ^{57}Co. Cross marks and solid lines represent measured spectra and calculated spectra based on the " $\mu\tau$ -model" in which the so-called escape peak components are taken into account, respectively. In this spectral fitting, we properly selected the energy window to minimize Compton scattering influences on the main peak, because the Compton scattering component from the surrounding materials produced an excess tail structure in the lower energy region. The calculated spectra were found to reproduce well the experimental electrical field dependence of the main energy spectra for the 122 keV line. As shown in Fig.7, the extracted $\mu\tau$ products for electrons were in the range from 1×10^{-3} to 2×10^{-3} cm^2/V. On the other hand, the $\mu\tau$ products for holes were one order of magnitude smaller than those for electrons. Both $\mu\tau$ products obtained here were in good agreement with the reported values [12], and were found to be independent of the growth rate.

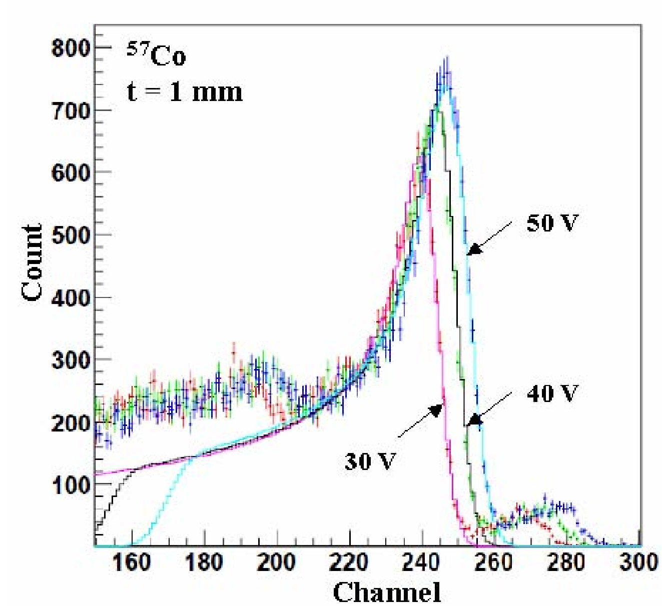

Fig. 6. Electrical field strength dependence of the energy spectra for the 122 keV line from ^{57}Co. Cross marks and solid lines represent measured spectra and calculated spectra, respectively.

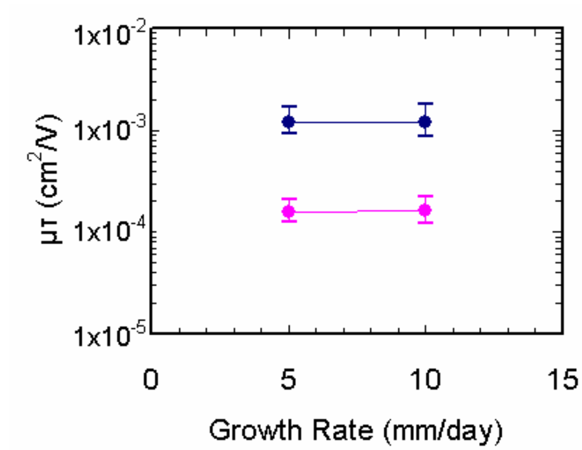

Fig. 7. $\mu\tau$ products for electrons and holes of 10 CdTe ohmic type detectors for each growth rate extracted by spectral fitting method for the 122 keV line from ^{57}Co..

B. Effect of THM growth rate on the CdTe detector performance

To clarify whether the deterioration of production yield due to THM growth rates occurs or not, we fabricated more than 200 Schottky type detectors for each growth rate. The acceptable detector performance was leakage current less than 10 nA at 500 V, and the energy resolution less than 4 % for 662 keV line from ^{137}Cs at 500 V. Fig. 8 shows the growth rate effect on yield of the leakage current and the energy resolution for two different single crystals grown with various growth rates less than the maximum growth rate mentioned previously. As shown in Fig. 8, the Schottky detector performance was also independent of the growth rate, and yield of the leakage current and energy resolution were on average above 90 %.

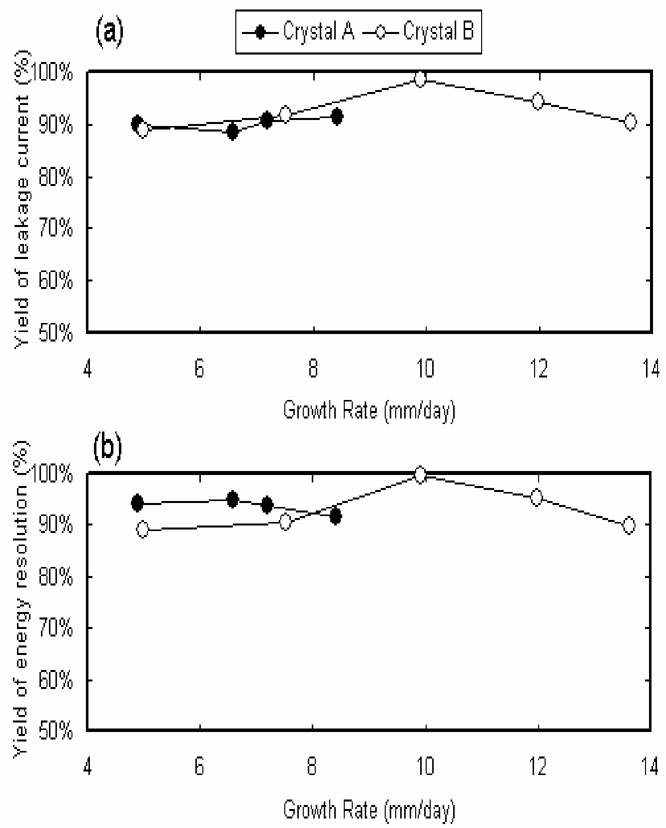

Fig. 8. Yield of the leakage current at 500 V and the energy resolution for the 662 keV line from ^{137}Cs at 500 V as a function of the growth rate.

From these results obtained here, it was concluded that the THM growth rate less than the maximum growth rate had no effect on the CdTe crystalline characteristics and the detector performance.

Taking advantage of the large volume CdTe single crystals, about 700,000 Schottky detectors with dimension of 4 mm× 7.5 mm× 1 mm were fabricated from 92 CdTe single crystal ingots for the research and development of the new Positron Emission Tomography (PET) system using CdTe detectors. Fig. 9 shows an example of the excellent uniformity of energy resolution among 36 CdTe single crystals. Fig 9 (a) shows the typical energy spectrum for the 662 keV line from ^{137}Cs. The histogram of the energy resolution among 226,110 Schottky detectors is shown in Fig. 9 (b). The average energy resolution and its standard deviation were 2.24 % and 0.48 %, respectively. This excellent uniformity of the detector quality is essential for the development of the new PET system with CdTe detectors.

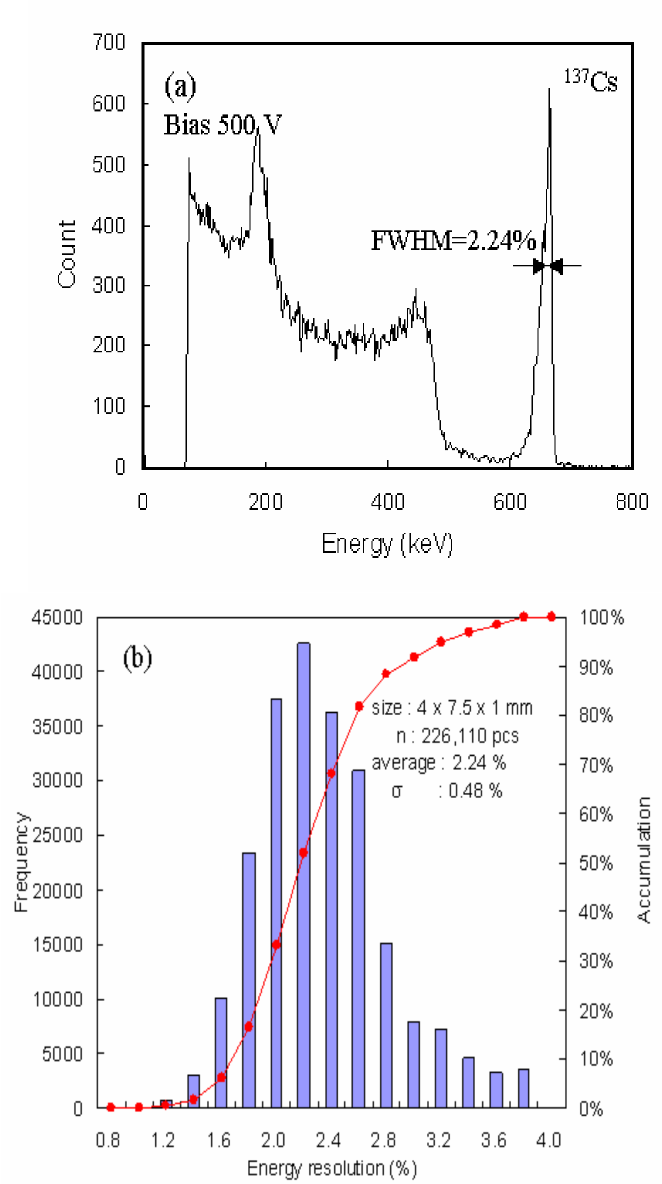

Fig. 9. (a) Typical energy spectrum of ^{137}Cs measured by In/CdTe/Pt Schottky detector at 500 V. (b) Histogram of the energy resolution for the 662 keV line from ^{137}Cs.

C. Next generation of THM-CdTe crystal growth technology

For the further improvement of productivity, our crystal growth development advances to the next generation in which the grown crystal diameter and length become 100 mm and 300 mm, respectively. Fig. 10 shows a state-of the-art THM-CdTe crystal growth technology. Fig.10 (a) shows the standard 75 mm diameter CdTe single crystal. In contrast to this, a newly developed 100 mm diameter crystal grown by THM is shown in Fig. 10 (b). When the development is completed, the 100 mm diameter ingots will produce a yield two times larger than the standard 75 mm diameter ingots. We will continue the intensive development of the huge 100 mm diameter CdTe single crystal.

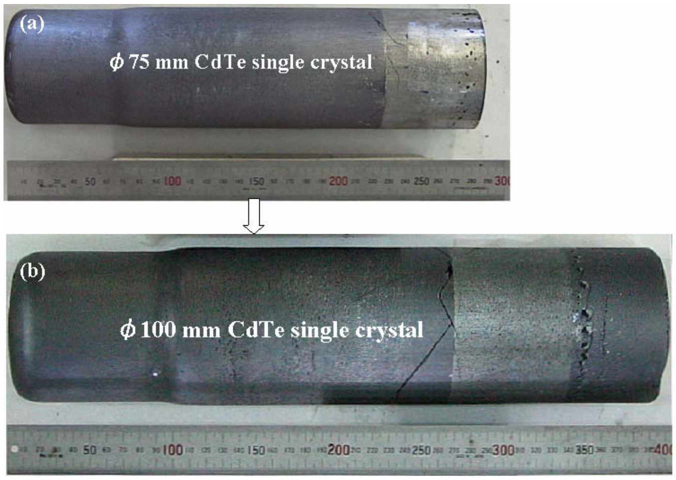

Fig. 10. (a) The standard 75 mm diameter CdTe single crystal and (b) a newly developed 100 mm diameter CdTe crystal grown by THM.

IV. Conclusions

To promote the applications of the CdTe radiation detectors in the medical imaging field, we investigated the effect of the THM growth rate on the 75 mm diameter CdTe crystalline quality and the detector performance.

The maximum growth rate for the single crystal growth was found to be approximately 15 mm/day which was three times greater than the conventional one. From the results of the investigation by IR transmission microscopy, it was found that there was no correlation between the behavior of Te inclusions and the THM growth rate 10mm/day or less. The Schottky detector performance was also revealed to be independent of the growth rate. Taking advantage of the increased growth rate of CdTe single crystals, a large amount of Schottky detectors were fabricated for the research and development of the new PET system. For the further improvement of productivity, the growth technology development of the 100 mm diameter CdTe single crystal is in progress.

References

[1] L. Verger, J. P. Bonnefoy, F. Glasser, and P. Ouvrier-Buffet, "New developments in CdTe and CdZnTe detectors for X and gamma-ray applications", *J. Electron. Mater.*, vol. 26, no. 6, pp. 738-744, 1997.

[2] R. Triboulet, Y. Marfaing, A. Cornet, and P. Siffert, “Undoped high-resistivity cadmium telluride for nuclear radiation detectors”, *J. Appl. Phys*., vol. 45, no. 6, pp. 2759-2765, 1974.

[3] R. Triboulet and Y. Marfaing, “CdTe Growth by Multipass THM and Sublimation THM”, *J. Cryst. Growth*, vo. 51, pp. 89-96, 1981.

[4] F. V. Wald and G. Entine, “Crystal growth of CdTe for gamma-ray detectors”, *Nucl. Instr. Meth.*, vol. 150, pp13-23, 1978.

[5] M. Funaki, T. Ozaki, K. Satoh, and R. Ohno, “Growth and characterization of CdTe single crystals for radiation detectors”, *Nucl. Instr. Meth.*, vol. A 436, pp. 120-126, 1999.

[6] M. Funaki, Y. Ando, R. Jinnai, A. Tachibana, and R. Ohno, “Development of CdTe detectors in Acrorad”, *International Workshop on Semiconductor PET*, 2007, unpublished.

[7] Y. Iwase, H. Takamura, K. Urata, and M. Ohmori, *Sensor and Actuators*, vol. A 34, pp31-36, 1992.

[8] T. Ozaki, Y. Iwase, Y. Takamura, and M. Ohmori, “Thermal treatment of CdTe surfaces for radiation detectors”, *Nucl Instr. Meth*., vol. A 380, pp141-144, 1996.

[9] C. Matsumoto, T. Takahashi, K. Takizawa, R. Ohno, T.Ozaki, and K. Mori, “Performance of a New Schottky CdTe Detector for Hard X-ray Spectroscopy”, *IEEE Trans. Nucl. Sci*., vol. 45, pp. 428-432, 1998.

[10] T. Takahashi, B. Paul, K. Hirose, C. Matsumoto, R. Ohno, T. Ozaki, K. Mori, and Y. Tomita, “High-resolution Schottky CdTe diode for hard X-ray and gamma-ray astronomy”, *Nucl. Instr. Meth*., vol. A 436, pp. 111-119, 1999.

[11] G. Sato, T. Takahashi, M. Sugiho, M. Kouda, T. Mitani, K. Nakazawa, Y. Odaka, and S. Watanabe, “Characterization of CdTe/CdZnTe detectors”, *IEEE Trans. Nucl. Sci.*, vol. 49, pp. 1258-1264, 2002.

[12] T. Takahashi and S. Watanabe, “Recent Progress in CdTe and CdZnTe Detector”, *IEEE Trans. Necl. Sci*., vol. 48, pp. 950-958, 2001.