CdTe and CdZnTe Detectors I

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Development of THM Growth Technology for CdTe Radiation Detectors and the Applications

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ABSTRACT

4 Nines (99.99%) Cd and Te were purified to the semiconductor grade 6 Nines ~ 7 Nines purity materials by the distillation and the zone melting processes, in order to be used for the growth of CdTe single crystal. The CdTe single crystal of 100 mm in diameter and 18kg in weight was successfully grown by the traveling heater method (THM). The shape of the growth interface had the key role for the single crystal growth. The distribution of the Te inclusion size was measured by IR microscopy. The uniformity of mobility-lifetime products and energy resolution in the wafer were also evaluated. The CdTe X-ray flat panel detector (FPD) was developed using the THM grown CdTe single crystal wafer. The CdTe pixel detectors with 100 μm pixel pitch were flip-chip bonded with the C-MOS readout ASIC and lined up on the print circuit board to cover the active area of 77 mm x 39 mm. The evaluation results showed that the CdTe X-ray FPD is promising as the imager for the non-destructive testing.

INTRODUCTION

Thanks to the large atomic number (48-52) and the wide band gap (1.5 eV), CdTe was recognized as a prospective material for the room temperature radiation detector in 1970s [1-2]. Since then, various types of growth methods have been attempted, i.e. Te-rich solution growth method, Traveling Heater method (THM), Bridgman method, High Pressure Bridgman method, Vapor Phase growth method and so on.

In case of the THM growth, CdTe crystal is grown from the Te-rich solution at much lower temperature than the melting point (1092°C). Due to this low temperature growth and the impurity gettering effect of the Te-solution, THM has the advantage to grow the higher purity crystal, where the purity is very important for obtaining the larger mobility-lifetime products. On the other hand, it had been believed that "THM can grow only the small diameter crystals (10~20 mm) at very small growth rate, so that it isn't suitable for the production". Although this limit was not based on the theoretical reasons, the improvement of productivity was really crucial as the industrial process.

20 years ago, we started the development of CdTe THM growth technology. The crystal diameter was 32mm and the grown single crystal showed the very good energy resolution and found to be very uniform throughout the crystal [3]. The step by step scale-up of the crystal diameter (32 mm, 50 mm [4] and 75 mm [5]) has been needed with increase in the demand of the large quantity and the low cost in market. Although we could recently produced 700,000 of CdTe detectors in a year by using 75mm diameter crystal, more productivity is still the strong demand in many applications.

Concerning the application of CdTe detectors, the X-ray FPD is an application with interest, as it can be used for the medical instruments, non-destructive testing devices, security, food inspection and so on. For this kind of imaging applications, the wafer size and the uniformity are very important.

In this paper, our recent development of 100 mm diameter CdTe single crystal growth technology by THM and X-ray FPD were discussed.

EXPERIMENT

Purification of raw materials

Commercial 4 Nines grade Cd and Te were purified to the semiconductor grade 6 Nines~7 Nines purity materials by the distillation and the zone melting processes. The distillation was repeated twice for the purification of Cd, the distillation followed by the zone melting were carried out for the purification of Te.

The raw materials were distilled in the high purity graphite containers with evaporation and condensation sections under the high purity hydrogen flow. The distillation yield was kept at about 80%, for both Cd and Te.

The distilled Te was then purified by zone melting in the high purity hydrogen atmosphere. The tail 20% part was removed due to the impurity accumulation by the zone refining process. The material purity was analyzed by glow discharge mass spectrometry (GDMS).

THM growth of 100mm diameter CdTe and the characterization

Prior to the THM process, a CdTe poly-crystal ingot and Te solution alloy were synthesized in the quarts ampoules for the THM growth. For Cl doping of the THM crystal, Te-solutions were doped with appropriated amount of $CdCl_2$. Then the CdTe single crystal seed, the solution alloy and the CdTe poly-crystal ingot were charged into the quarts THM ampoule and the ampoule was evacuated and sealed.

The prepared THM ampoule was set in the THM furnace so that the Te-solution part is located at the middle of the furnace. Then the crystal growth was carried out with raising the furnace temperature and pulling the ampoule downward slowly. The growth rate of 3mm/day~7mm/day was used in this work. The schematic diagram of the THM growth was shown in figure 1.

In order to investigate the growth interface shape during the growth, the furnace was rapidly cooled to room temperature and the growth interface part was cut along the growth axis. For the characterization of Te inclusion, CdTe wafer was observed by infrared (IR) microscopy and the size distribution was studied. The mobility-lifetime ($\mu\tau$) products were also measured using the "$\mu\tau$ model" spectral fitting method [6]. Schottky type detectors [7] with dimension of 4 mm x 4 mm x 1mm were fabricated from the 100 mm diameter wafer and the uniformity of energy resolutions was investigated.

X-ray Flat panel detector

The ohmic type pixel electrodes with 100 μm pitch and the Schottky continuous electrode were fabricated on the each side of the 1 mm thick CdTe single crystal wafer, then the wafer was

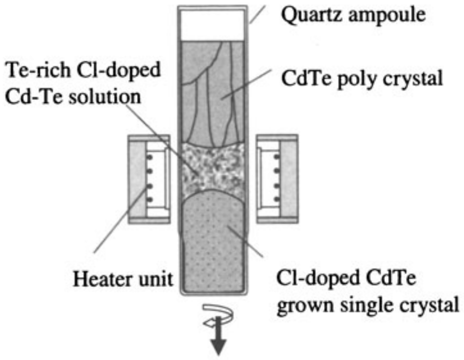


Figure 1. Schematic diagram of CdTe THM growth

cut into a couple of individual detector, which size is 12.9 mm x 25.7 mm. The pixel CdTe detector was Flip-Chip bonded with the C-MOS readout ASIC. They were lined up on the print circuit board to form the flat panel with the dimension of 77 mm x 39 mm. The spatial resolution was evaluated by the test chart image. The result was compared with the CsI:Tl flat panel. The detail was described elsewhere [8].

RESULTS and DISCUSSION

The purification of Cd and Te

The picture of purified Cd (distillation twice) and Te (distillation followed by zone refining) was shown in figure 2. The GDMS analytical results of Cd and Te at each purification steps were shown in table I.

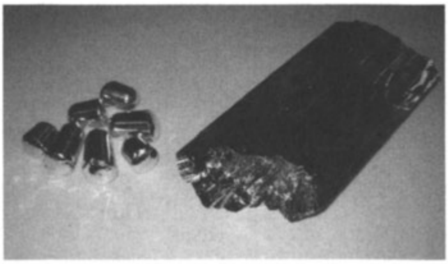


Figure 2. The purified Cd (left) by distillation and Te (right) by distillation and zone melting

For Cd purification, the major impurities of raw 4Nine Cd were Cu, Ag, Tl and Pb, with the impurity level of a few ppm in weight base. All these impurity elements are effectively removed by the first distillation and the sum of the detected impurities was 0.059 ppm, resulting that the distilled Cd was 7 Nine grade material. However, still S, Cl, Ti, Cr, Fe, Cu, Pb were detected at ~10 ppb level. These elements could be removed below the detection limit by the second distillation except for Zn, which seems to be harmless element for CdTe radiation detector.

On the other hand, the distillation of 4Nine Te removed Al, Cl, Fe, Co, Ni, Ir, Pb below the detection limits and Cu was reduced by one order, while there was almost no effect on Se. After the distilled Te was purified by zone melting process, only Si and Se were detected. The origin of Si was probably the quarts boat for zone melting. Se was reduced by one third. The sum of the detected impurity was 0.41 ppm.

As described above, the commercial 4N grade Cd and Te were purified to the semiconductor grade materials by coupling distillation and zone refining process.

Table I. GDMS analytical result of each step of the purification process
The heavy element, which was not detected in the raw material, was excluded from the table.

element	GDMS Analytical result (weight ppm)					
	Cd			Te		
	4N Raw material	Distillation once	Distillation 2times	4N Raw material	Distillation	Distillation +Zone melting
Na	0.005	<0.001	<0.001	0.005	0.002	<0.001
Mg	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001
Al	<0.001	<0.001	<0.001	0.03	<0.001	<0.001
Si	0.008	<0.001	0.003	<0.001	0.009	0.01
P	<0.001	<0.001	<0.001	0.006	0.02	<0.001
S	0.38	0.02	<0.005	0.009	0.008	<0.001
Cl	0.003	0.005	<0.001	0.35	<0.01	<0.01
K	<0.005	<0.005	<0.005	<0.05	<0.05	<0.05
Ca	<0.005	<0.005	<0.005	<0.05	<0.01	<0.01
Sc	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001
Ti	<0.001	0.001	<0.001	<0.001	<0.001	<0.001
V	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001
Cr	<0.001	0.003	<0.001	<0.001	<0.001	<0.001
Mn	<0.005	<0.005	<0.005	<0.001	<0.001	<0.001
Fe	0.02	0.02	<0.005	0.006	<0.001	<0.001
Co	0.01	<0.001	<0.001	0.002	<0.001	<0.001
Ni	0.12	<0.001	<0.001	0.39	<0.001	<0.001
Cu	7.2	0.003	<0.001	2.0	0.17	<0.001
Zn	0.02	<0.001	0.01	<0.005	<0.005	<0.005
Se	<0.002	<0.002	<0.002	1.6	1.4	0.4
Ag	4.1	<0.05	<0.05	<0.01	<0.01	<0.01
W	0.01	<0.001	<0.001	<0.001	<0.001	<0.001
Re	0.003	<0.001	<0.001	<0.001	<0.001	<0.001
Ir	<0.001	<0.001	<0.001	0.24	<0.001	<0.001
Hg	0.02	<0.005	<0.005	<0.001	<0.001	<0.001
Tl	1.8	<0.001	<0.001	<0.001	<0.001	<0.001
Pb	3.8	0.007	<0.001	0.02	<0.001	<0.001
Bi	0.01	<0.001	<0.001	<0.001	<0.001	<0.001

THM growth of 100 mm diameter CdTe

The picture of the grown CdTe single crystal ingot of 100 mm diameter was shown in figure 3. The total length and the weight were about 390 mm and 18 kg, respectively. We believe that this is the largest THM grown CdTe single crystal that has ever been reported. When we developed CdTe THM growth in 1992, the ingot diameter and weight were only 32mm and 600g, which was also the largest at that time. The crystal weight became 30 times in 17 years, increasing the productivity dramatically.

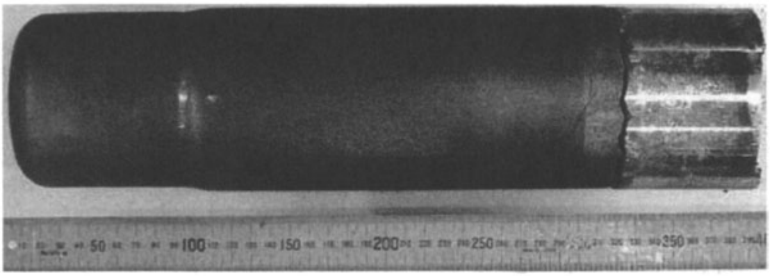


Figure 3. CdTe ingle crystal ingot grown by THM.

As new grains were generated during the crystal growth at the early stage of this work, the grown crystal became a poly-crystal and the thorough improvement of the growth condition was necessary for the the single crystal growth.

Observing the cross section at growth interface was classical approach but had been the most effective way to improve the single crystal yield through our scale-up experience. The cross sectional view of the growth interface at conventional growth condition was shown in figure 4. As a whole, the growth interface was convex to the solution zone, but a partially concave part existed. Below this point, a newly generated grain boundary was found. This growth interface is the primarily the result of the temperature profile, so that the improvement of thermal condition was carried out to obtain the complete convex shape of the growth interface.

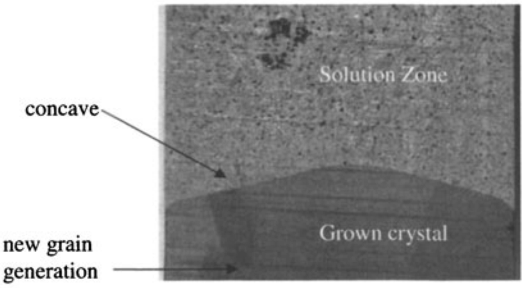


Figure 4. The cross sectional view of the growth interface before optimization of the growth

The effect of growth interface was shown in figure 5. Before the improvement, the growth interface at the initial growth stage included the partial concave part, as already described and seen in right hand side of figure 5. While that at the final growth stage was completely round and convex shape. Probably due to the incomplete convex shape at the initial stage, the grown CdTe crystal includes the grain boundaries close to the wafer edge. On the other hand, the growth interface at the initial growth stage was improved by the change of thermal environmental condition as seen in left side of the figure 5. The interface shape became a complete round and convex shape during the whole growth period. The grown crystal was confirmed to be the single crystal.

Improved growth condition Conventional growth condition

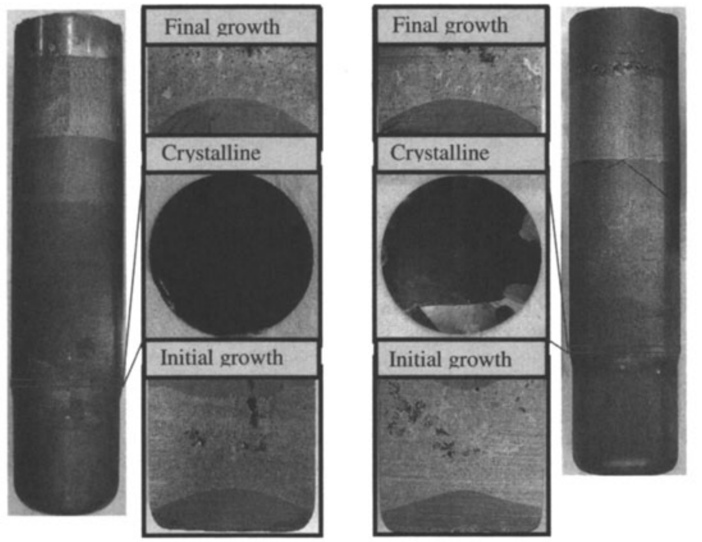


Figure 5. The effect of thermal environmental condition improvement on the crystalline quality

Characterization of the grown crystal

The distribution of the Te inclusion size measured by IR microscopy was shown in figure 6. It was found that there were two groups in the distribution. The smaller one was the diameter less than 7 μm and about two third of the Te inclusions were in this group. The larger group was the diameter between 10 μm and 20 μm and the average size was roughly 15 μm. This inclusion size were still acceptable for the X-ray imaging detector with 100 μm pixel pitch, described later.

Concerning the transport properties, the map of the μ-τ products in the 4 inch wafer were shown in figure 7. The average μ-τ products for electrons and holes were 2.5×10^{-3} cm^2/V and 5.0×10^{-4}, respectively. The standard deviations of the μ-τ products both for electrons and holes were less than 10% of the average, showing the very good homogeneity within the wafer.

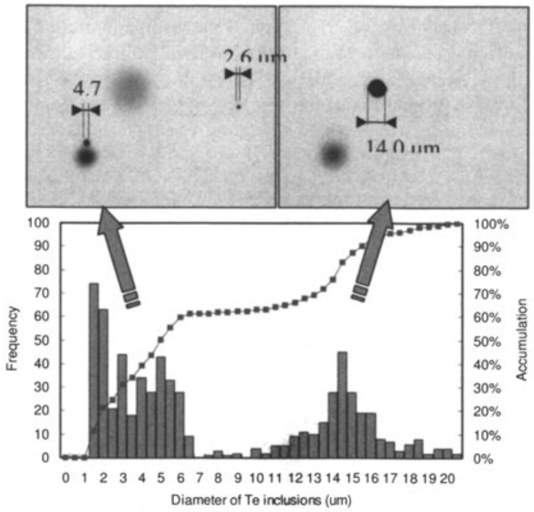
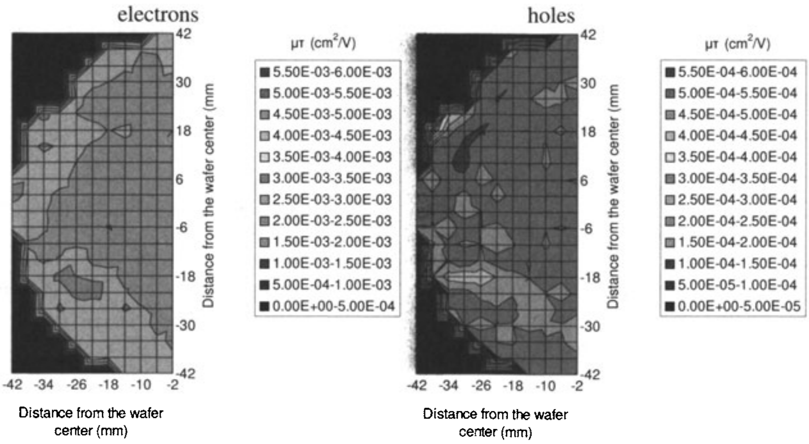


Figure 6. Size distribution and IR image of the Te-inclusion



Average : 2.5 x 10^{-3} cm^2/V
Std.Dev. : 9.80 %

Average : 5.0 x 10^{-4} cm^2/V
Std.Dev. : 8.47 %

Figure 7. Mapping data of μ-τ products in the wafer

The Schottky detectors with dimension of 4 mm x 4 mm x 1 mm were fabricated and the energy spectra of the ^{57}Co were measured. The typical spectrum and the FWHM of the 122 keV peak was mapped in the figure 8. The average of the FWHM and the standard deviation were 5.3keV and about 6% of the average, respectively. This uniformity of the detector performance is very important for the mass production of the detector and for the large area imaging detector.

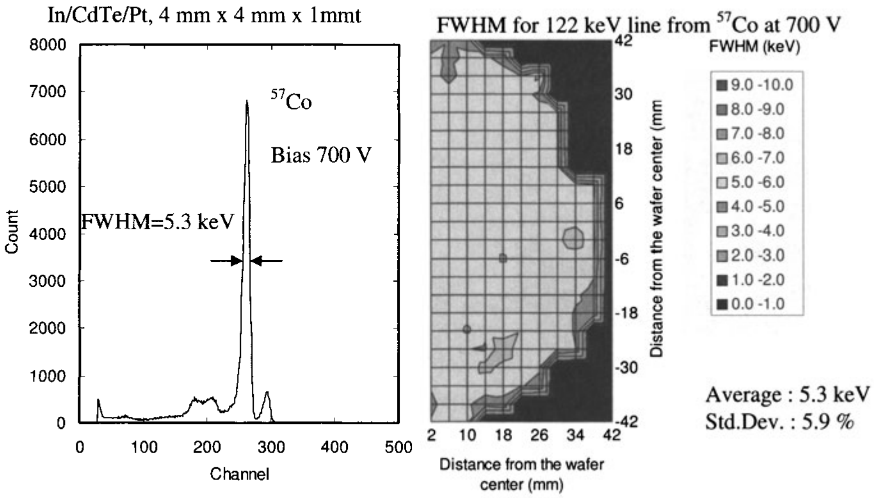


Figure 8. The typical energy spectrum of the Schottky detector (left) and the FWHM mapping in the wafer.

CdTe X-ray flat panel detector

A couple of pixel detectors with the dimension of 12.9 mm x 25.7 mm were simultaneously fabricated on a single crystal CdTe wafer as shown in figure 9. Then the wafer was diced into the individual detector. The CdTe detector was flip-chip bonded with C-MOS readout ASIC, to fabricate the CdTe-ASIC hybrid module, shown in figure 10. Nine pieces of the hybrid were die bonded on the print circuit board to fabricated the flat panel detector with the active area of 39mm x 77 mm as shown in figure 11. The detail of the FPD fabrication was described elsewhere [8].

The spatial resolution of the CdTe FPD was evaluated by taking the image of the resolution chart pattern as shown in figure 12. The image taken by the commercial CsI:Tl flat panel with the same pixel pitch was also shown for comparison. The 5 line pair pattern was clearly seen by the CdTe X-ray FPD. On the other hand, the same pattern taken by the CsI:Tl flat panel was blurred probably due to the diffusion of the emitted light in the CsI:Tl scintillator layer.

In order to assess the potential of the CdTe FPD as the imager for non-destructive testing, many kinds of objects were imaged by the CdTe FPD. Figure 13 shows the image of a USB