DOE-I Final Report

Project Number: DE-FG02-07ER84766

Project Title: Annealing as Grown Large Volume CZT Single Crystals for Increased Spectral Resolution
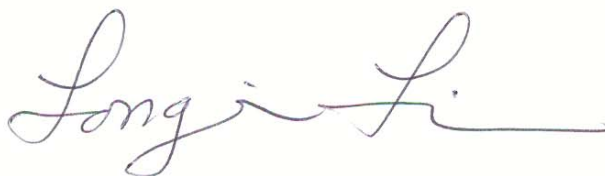
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I INTRODUCTION

The spectroscopic performance of current large-volume Cadmium 10% Zinc Telluride, $Cd_{0.9}Zn_{0.1}Te$, (CZT) detectors is impaired by cumulative effect of tellurium precipitates (secondary phases) presented in CZT single-crystal grown by low-pressure Bridgman techniques[1]. This statistical effect may limit the energy resolution of large-volume CZT detectors (typically 2-5% at 662 keV for 12-mm thick devices). The stochastic nature of the interaction prevents the use of any electronic or digital charge correction techniques without a significant reduction in the detector efficiency.   This volume constraint hampers the utility of CZT since the detectors are inefficient at detecting photons >1MeV and/or in low fluency situations.

During the project, seven runs CZT ingots have been grown, in these ingots the indium dopant concentrations have been changed in the range between 0.5ppm to 6ppm. The I-R mapping imaging method has been employed to study the Te-precipitates. The Te-precipitates in as-grown CZT wafers, and after annealing wafers have been systematically studied by using I-R mapping system (home installed, resolution of 1.5µm).   We employed our I-R standard annealing CZT (Zn=4%) procedure or two-steps annealing into radiation CZT (Zn=10%), we achieved the "non"-Te precipitates (size < 1µm) CZT n+-type with resistivity $>10^{9-10}$ Ω-cm. We believe that the Te-precipitates are the p-type defects, its reducing number causes the CZT became n+-type, therefore we varied or reduced the indium dapant concentration during the growth and changed the Te-precipitates size and density by using different Cd-temperature and different annealing procedures.

We have made the comparisons among Te-precipitates size, density and Indium dopant concentrations, and we found that the CZT with smaller size of Te-precipitates is suitable for radiation uses but non-Te precipitates is impossible to be used in the radiation detectors, because the CZT would became un-dopant or "intrinsic" with non radiation affection (we have studied before).

We used 3 weeks' annealing time for 3-5 mm thickness CZT wafres, if the thickness increased to 10-15mm, the annealing time would be increased to many months, which is very unpractical and very difficult to control the CZT property.

We have obtained as-grown CZT by using adding the extra Cd before growth, which showed the smaller size of Te-precipitates and excellent radiation performance. These CZT has very high $\mu\tau(e) >1x10^{-2}cm^2/V$, $\rho>2x10^{10}$ Ω-cm, and the thickness could be up to 80-100mm. The energy resolution of the detector (thickness>10mm) at 662 keV is about 1.2% without any correction [2] and according to Aquila, the 0.5-0.8% resolution at 662 keV would be expected by using appropriated electronic correction.

II. EXPERIMENT

During the phase-I, using MVB technique we have grown seven 2"-diameter CZT ingots, such as 07-1, In=5.6ppm; 07-2, In=6ppm; 07-3, In=2ppm; 07-4: In=1ppm; 07-5, In=4.3ppm; 07-6, In=0.5ppm and 07-7: In=5ppm.

We have cut 40-piece wafers of $10x10x5mm^3$ from each ingot, and these wafers have been lapped with 15µm then 5µm powder. Each piece from each ingot will be roughly

polished using 1μm polishing solution. These pieces have been inspected by I-R mapping system to check the As-grown CZT. The rest of wafers have been etched by using 2% B_2 in Methanol solution for 3 minutes then cleaned by D.I. water. The wafers would be dry on clean bench. Put one or two wafers from each ingot into the quartz tube as shown in figure 1, (each tube would be placed six wafers, the Cd will be put in another side the tube. The tubes will be sealed one by one under vacuum (mechanical pump only). We have two annealing furnaces, each furnace have three tubes in. The CZT and Cd temperatures can be measured by thermal couples, and they could be controlled manualy. Annealing procedure:

- Two-step: step 1 (CZT temp, at 800°C) for 48hr.
  Step 2 (CZT temp. at 700°C) for 21 days
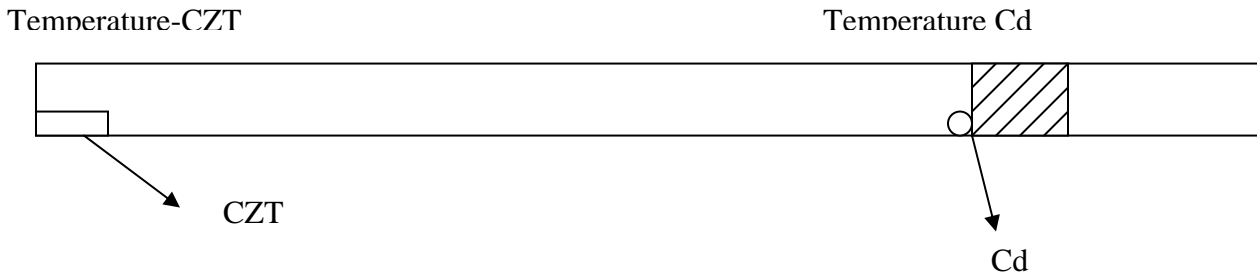- One-step: (CZT temp. at 700°C) for 21 days or at 600°C for 30 days

Temperature-CZT   Temperature Cd

Figure 1, CZT annealing schematic

After annealing, we opened the tubes and take the wafers out of tubes then do lapping and polishing down to 1 μm. The polished wafers could be checked the Te-precipitates by I-R mapping system. We will use them to re-polishing and etching by 2% B_2 in Methanol solution for 3-minite, the both sides surfaces could be covered by Gold thin layers (700A) using the thermal evaporator for electrical and radiation measurement.

III. RESULTS

Table 1, and 2, showed the measurement results of CZT wafers were from Indium dopant concentration with 2ppm and 1ppm ingot respectively after two-step annealing.

Table 1, CZT3-07-03, In =2ppm

Sample No	1*	2	3	4 *	5	6 *
Cd °C	623	611	548	563	583	599
ρ x10^{9}Ω-cm (-1 to +1V)	2.5	4.0	4.0	0.8	1.0	0.5
"Turn on" Voltage	-25/15	-20/15	+/- 15V	-30/1	+/- 15	-7 /20
Te ppt size, μm(Max.)	<10	<10	<10	<10	<10	<10
Te ppt density (/cm^3)	<100	<100	<100	<100	<100	<100
$\mu\tau$(e), 10x^{-3} cm^2/V	NPA	NPA	PA	NPA	NPA	NPA

PA = photoactive at 10V bias
NPA = not photoactive at 10V bias

* had contact with molten Cd on CZT surface appears leakage

Table 2, CZT2-07-04, In =1ppm

Sample No	1	2	3	4	5	6
Cd °C	555	584	530	603	610	637
ρ x10^9 Ω-cm (-1 to +1V)	3.5	3.5	5.5	0.13	4.3	1.0
"Turn on" Voltage	±25	±25	±25	±25	±25	±25
.Te ppt size (max), μm	<10	<10	<10	<10	<10	<10
Te ppt density (/cm^3)	<100	<100	<100	<100	<100	<100
μτ(e), 10x^{-3} cm^2/V	PA	PA	PA	PA	PA	PA

Figure 2, and figure 3, left and right showed the CZT wafers' Te-precipitates as-grown and after two-step annealing on the 2ppm and 1mmp indium doping concentration respectively. It is clear that the Te-precipitates couldn't be seen after annealing.
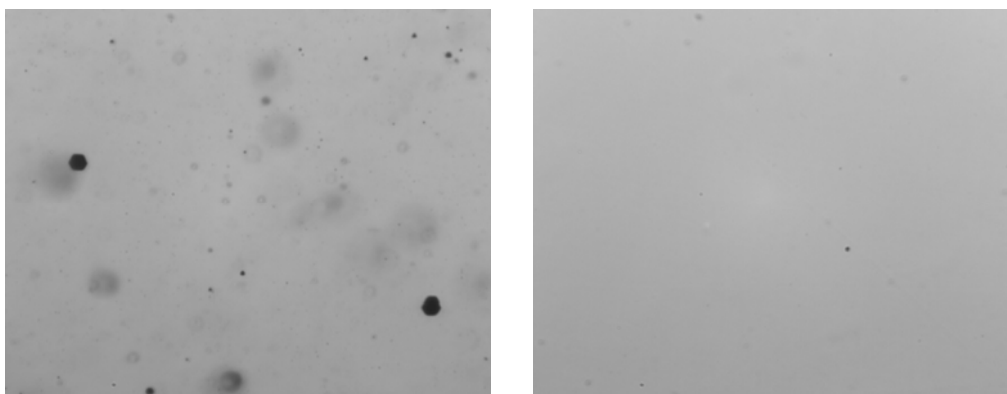

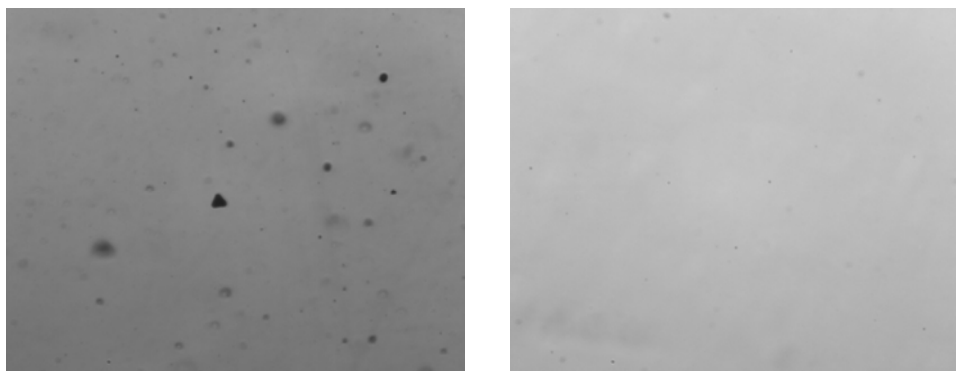Figure 2, CZT2-07-03 before and after two-step annealing

Figure 3, CZT2-07-04 before and after two-step annealing

Figure 4, and 5, showrd the distribution of Te-precipitates in the as grown CZT2-07-03 (2ppm) and CZT-07-04 (1ppm) respectively. The program Image J is an instrument for image analyses. It allows transforming a grayscale image into binary image and calculates the areas of each object of the same faze as well as the fraction of all objects of this faze in the image. We used this program for the analyses of infrared images of CZT

crystals. Provided with the data of all precipitates' sizes in each image we could draw the distribution of tellurium precipitates by their size.
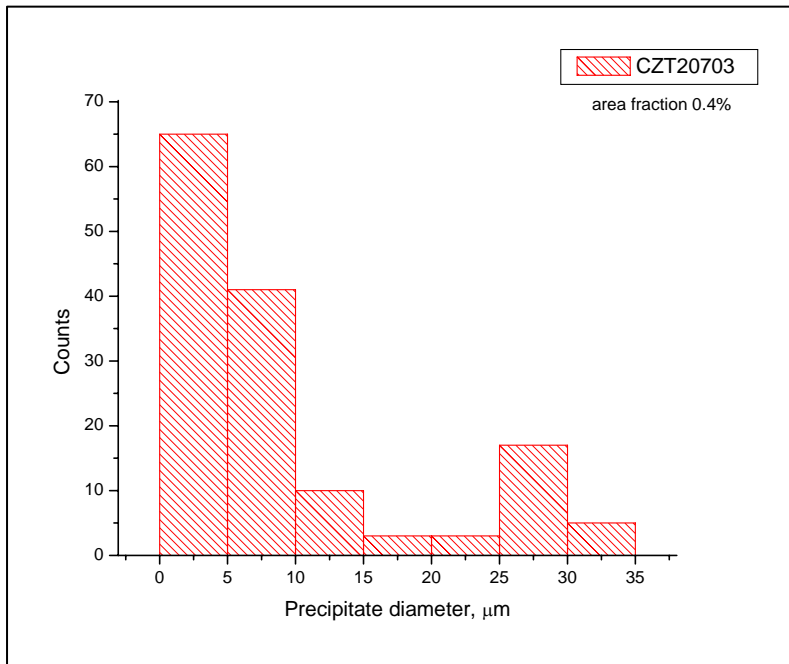
4, Distribution of Te-precipitates in the as grown CZT2-07-03
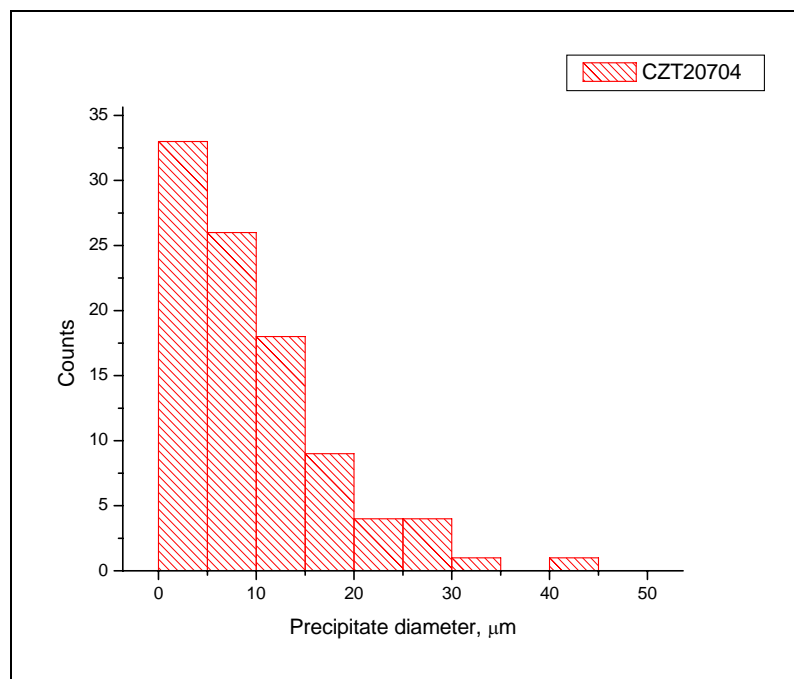
5, Distribution of Te precipitates in the as grown CZT2-07-04
   Te-precipitates distribution by size.

In these annealing wafers, non Te-precipitates could be found, so the distributions couldn't be measured either.
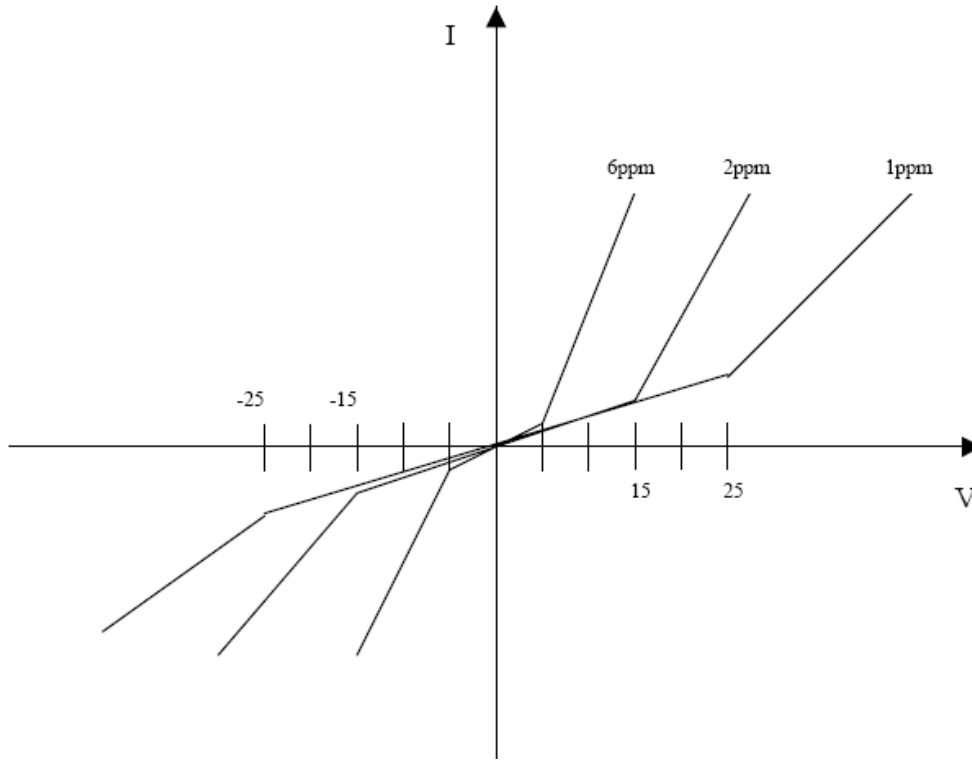

Figure 6, Two-step annealing. I-V curves for CZT with different In doping concentrations

Figure 6, is the schematic of Two-step annealing. I-V curves for CZT with different In doping concentrations, and it shows the bias applied on the detectors are increasing when reducing the Indium doping. We expect that the higher bias voltage would happen when the indium doping concentration is close to zero or intrinsic in another words, undoping, which is impossible in our experiment.
We established a one-step annealing to intend to reduce the size of Te-precipitates only, which the first higher temperature step annealing has been taken away.

Table 3, CZT2-07-03, In=2%

Sample No	1	2	3	4	5	6
Cd °C/CZT °C	440/600	460/600	480/600	510/700	530/700	549/700
ρ x$10^9\Omega$-cm (-1to+1V)	1.0	0.9	3.9	2.1	5.9	N/A
"Turn on" Voltage, V	-16/14	-2/18	-6/20	-14/20	± 8	N/A
Te ppt size (max), μm	10	20	10	12	12	N/A
$\mu\tau$(e), $10x^{-3}$cm^2/V	PA	PA	PA	PA	PA	N/A

Table 4, CZT2-07-04, In=1%

Sample No	1	2	3	4	5	6
Cd °C/CZT °C	440/600	460/600	480/600	510/700	530/700	549/700
ρ x10^9 Ω-cm (-1 to +1V)	5.7	0.9	1.7	1.6	2.3	5.2
"Turn on" Voltage, V	±15	±15	-15/20	-8/15	±15	±15
Te ppt size, μm (max)	15	12	12	12	7	12
$\mu\tau$(e), 10x^{-3} cm^2/V	PA	PA	PA	PA	PA	PA

Table 5, CZT2-07-06, In=0.5%

Sample No	1	2	3	4	5	6
Cd °C/CZT°C	440/600	460/600	480/600	510/700	530/700	549/700
ρ x10^9 Ω-cm (-1 to +1V)	5.2	0.9	1.0	1.5	5.3	5.2
"Turn on" Voltage, V	-25/1	-5/12	-10/15	-7/15	±20	±15
Te ppt size (max), μm	8	17	12	9	6	6
$\mu\tau$(e), 10x^{-3} cm^2/V	PA	PA	PA	PA	PA	PA

Table 3, 4 and 5 showed the measurement results of the wafers with In=2ppm, 1ppm and 0.5ppm respectively.

Figure 7-1, Te-precipitates using I-R mapping, CZT annealing temp. 600°C
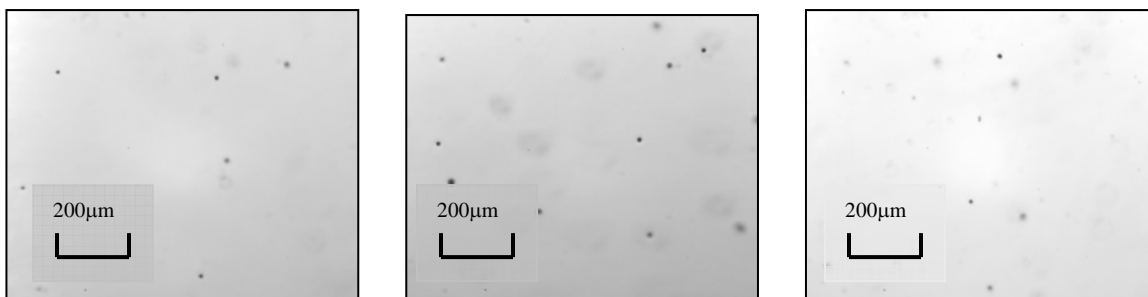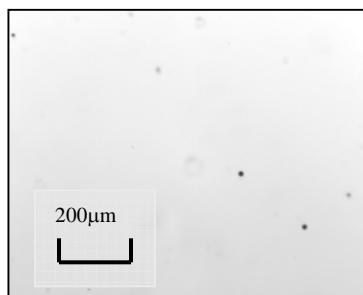

Cd source temp.440 °C   Cd source temp.460 °C   Cd source temp.480 °C

Figure 7-2, Te-precipitates using I-R mapping, CZT annealing temp. 700°C

Cd source temp.530 °C

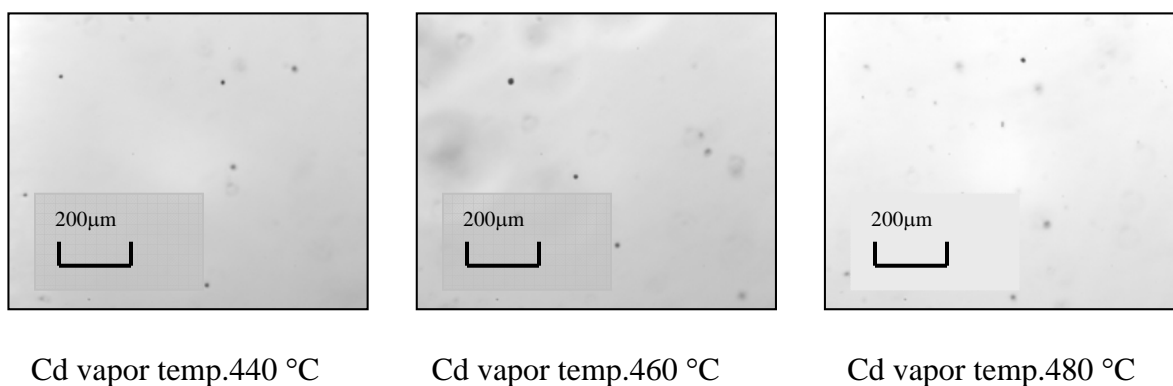Figure 8, Te-precipitates using I-R mapping, CZT (In=1ppm) annealing temp. 600°C

200μm   200μm   200μm

Cd vapor temp.440 °C   Cd vapor temp.460 °C   Cd vapor temp.480 °C

Figure 9-1, Te-precipitates using I-R mapping, CZT (In=0.5ppm) annealing temp. 600°C

200μm   200μm   200μm

Cd vapor temp.440 °C   Cd vapor temp.460 °C   Cd vapor temp.480 °C
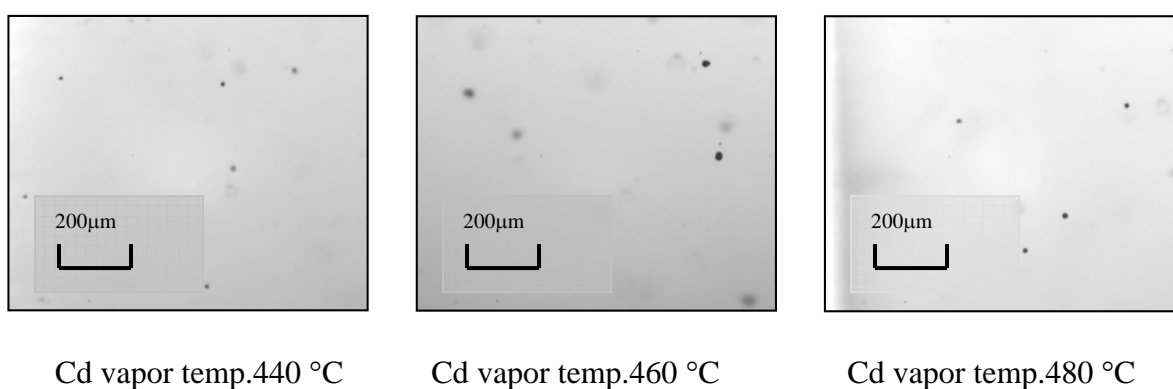
Figure 9-2, Te-precipitates using I-R mapping, CZT(In=0.5ppm) annealing temp. 700°C

Cd vapor temp.510 °C   Cd vapor temp.530 °C   Cd vapor temp.549 °C
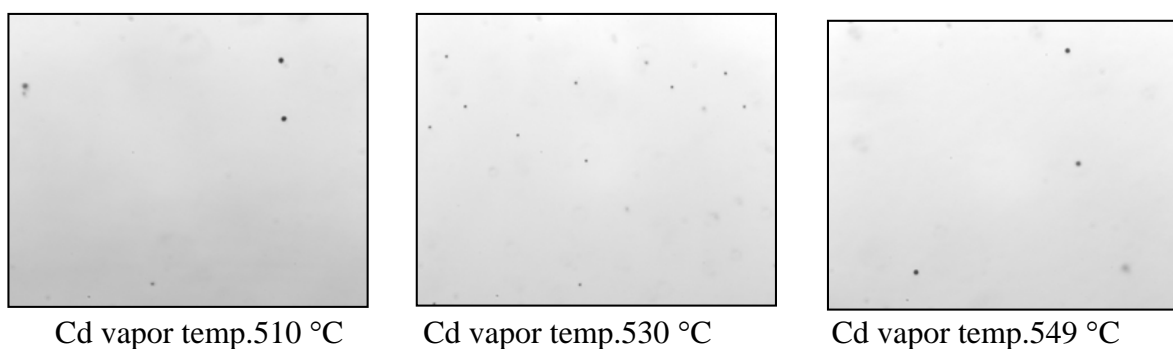
Figure 7-1, 7-2 showed the CZT (In=2ppm) Te-precipitates annealing at 600°C and 700°C respectively with different Cd vapor pressures, the figure 8 showed the CZT (In=1ppm) Te-precipitates annealing at 600°C and the figure 9-1 and 9-2 showed the

CZT (In=2ppm) Te-precipitates annealing at 600°C and 700°C respectively with different Cd vapor pressures. We found that the Te-precipitates are smaller than that of as-grown. The figure 10 is the Te-precipitates distribution of as-grown CZT (In=0.5ppm) and figure 11 shows the distribution after its one-step annealing for three weeks. It is clear that the Te-precipitates (seen in figure 11 compared with figure 10) the larger size of Te-precipitates have been reduced significantly.
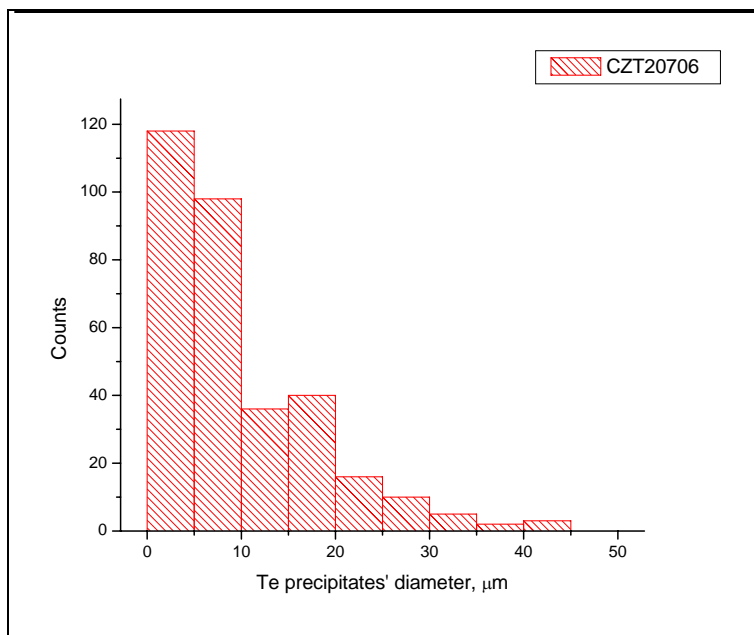
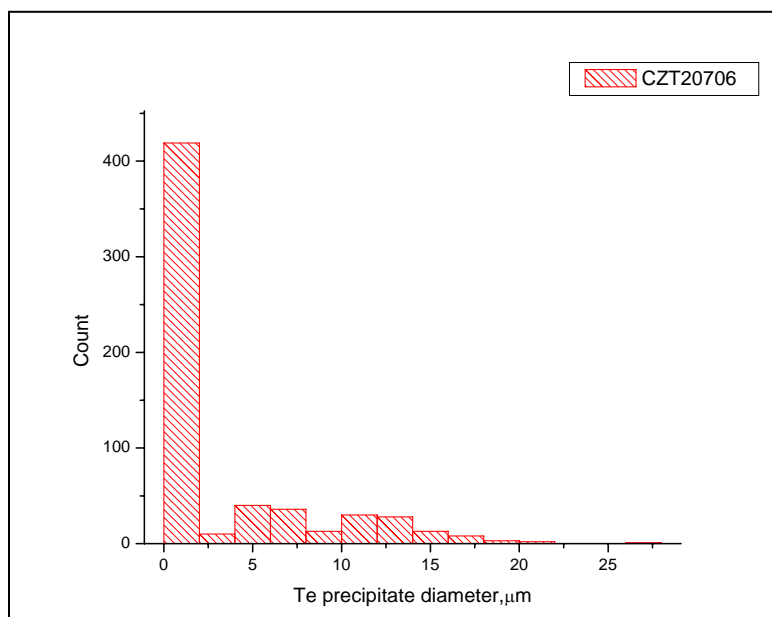Figure 10, Distribution of Te precipitates in the as grown CZT2-07-06

Figure 11, Distribution of Te precipitates in the annealed CZT2-07-06, CZT at 700°C

IV. ADDING EXTRA Cd BEFORE CZT GROWTH

The annealing procedures of one-step and two-step could reduce the Te-precipitates size or density, but they are not very practical, therefore we believe that the " adding extra Cd before growth " is a better way to reduce the Te-precipitates size and to improve the detector performances. The detector's thickness could be as thick as 100mm unlike Redland's 5mm. Figure 12 showed the $\mu\tau(e)$ has the optima number of Te-precipitates size (here is 7μm) at In=10ppm, of course at any indium concentration, we can found the different optimal Te-precipitates size number at different indium dopping concentration. Among them we can obtain the best growth condition, Produce the best as-grown CZT ingots, if we can be supported.
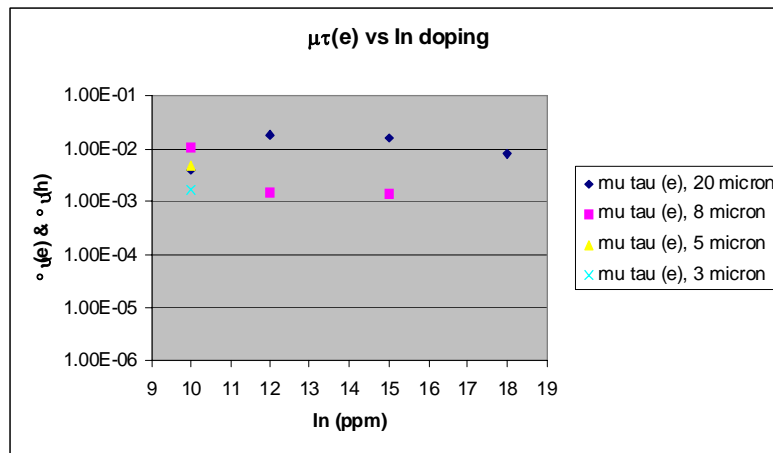

Figure 12 $\mu\tau(e)$ vs. In dopant. When the Te-ppts size was~7 μm at indium=10ppm, the $\mu\tau$ (e) was the highest, 1.2×10^{-2} cm^2/V. We expect that the $\mu\tau$ (e) related with Te precipitates size and density, the CZT purity, and the indium dopant level.
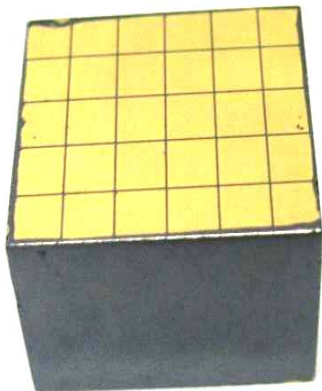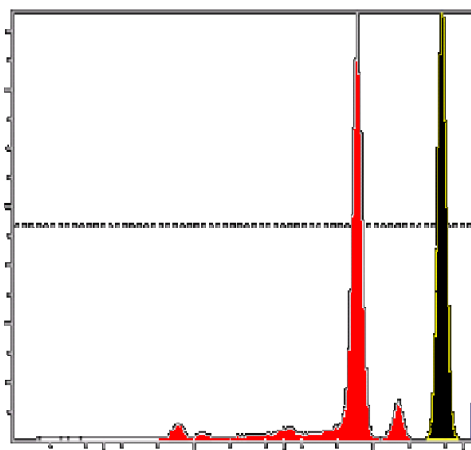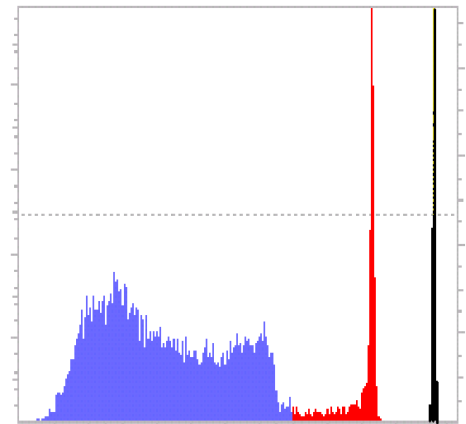

Figure 13
15x13x10mm3
detector

3.25% FWHM resolution at 122 keV
Also visible are peaks from the 136 keV Co-57 gamma-ray and tungsten K X-rays at 59 and 67 keV due to fluorescence of the collimator

1.26% FWHM resolution at 662 keV

Compton edge occurs at 478 keV.

Figure 13 showed the pixellated detector ($15x13x10mm^3$), its Te-precipitates have been reduced down to 12μm from 20-30μm (original) by using adding extra Cd and FWHM resolution at 122 keV is 3.25% and **FWHM resolution at 662 keV is 1.26%** respectively. This work has been done between Yinnel and Aquila. According Aquila, If the appropriated electrical correction has been applied, the resolution could be 0.5-0.8% at 662keV, and the detector working energy can be expanded to **3mV.**

V. CONCLUSION
Yinnel has successfully achieved the CZT with non Te-precipitates or less and smaller Te-precipitates as we wished by two-step and one-step annealing respectively. We found that unlike I-R substrate of HgCdTe, the annealing is not good idea for making perfect and thicker CZT radiation. We believe that "adding extra Cd before growth" is the better way to reduce the Te-precipitates size and to improve the radiation performances.

VI. REFERENCE
1. Aleksey Bolotnikov, IEEE 2006
2. Aquila Tech, Inc. report to Yinnel, March, 2008

VII. ACKNOLEGEMENT