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**Cadmium Zinc Telluride Selenide (CdZnTeSe) A Promising
Low Cost Alternative to Cadmium Zinc Telluride (CdZnTe)
for Medical Imaging and Nuclear Detector Applications**

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Cadmium Zinc Telluride Selenide (CdZnTeSe)

A promising low cost alternative to Cadmium
Zinc Telluride (CdZnTe) for medical imaging and
nuclear detector applications

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70 YEARS OF
DISCOVERY

A CENTURY OF SERVICE

Outline

- ❑ Room temperature semiconductor radiation detector
- ❑ State of the art CdZnTe detectors and its disadvantages
- ❑ New development of CdZnTeSe material
- ❑ Examples of medical applications

Scintillator vs semiconductor detectors

Indirect Conversion of Gammas to Electrons

Spread of light
reduces spatial
resolution

Direct Conversion of Gammas to Electrons

Compactness of
electric charge
enhances spatial
resolution

Generations of radiation detectors

- *Ge – High energy resolution, cryogenic cooling ($\sim 0.3\%$ at 662 keV)*
- *NaI Scintillators – Low energy resolution.*
- *CZT based hand held detector, fairly high energy resolution ($\sim 1\%$ resolution at 662 keV)*

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State-of-the-art: CdZnTe

❑ Today, cadmium zinc telluride (CZT) is the most advanced room-temperature semiconductor material for gamma-ray detection.

❑ However, CZT suffers from 3 major detrimental defects

- Non-unity segregation of Zn
- Crystal defect (sub-grain boundary) network
- High concentrations of Te inclusions/precipitates

(a) THM-grown CZT ingot cut along the length, (b) Zn concentration mapping and (c) Zn concentration along the length of the ingot.

Roy et al. *J. Crystal Growth* 347 (2012) 53.

X-Ray diffraction topography images showing $\sim 1 \text{ cm}^2$ areas of detector-grade CZT samples supplied by seven different vendors.

A. E. Bolotnikov et al. *J. Cryst. Growth* 379 (2013) 46.

- These issues cause low yield and high cost of CZT radiation detectors, limiting their applications.
- Researchers have tried to solve the issues by improving the crystal growth process and post-growth annealing, but have not mitigated all disadvantages.

Characterization Technique: X-ray Response Maps

Micro-scale X-ray Detector Response Mapping is a unique and powerful measurement technique to evaluate detector performance.

X-ray response maps can give information on:

1. **Detector polarization**
2. Local and global E-field non-uniformity
3. Extended defects
4. Electrode- and side-surfaces fabrication damage
5. Electrodes design
6. Non-uniformity of material

Effect of sub-grain boundary and their network on device response

X-ray topography and the high-resolution X-ray response map

X-ray topography and the high-resolution X-ray response map of pixelated device (sample dimensions: 20x20x2 mm³).

X-ray topography and the pulse height spectrum of Frisch-grid detector. Sample dimensions: 6x6x15 mm³.

A. E. Bolotnikov et al. J. Cryst. Growth 379 (2013) 46.

Effect of Te-inclusions/precipitates on device response

Planar detector $1.6 \times 1.0 \times 1.2 \text{ mm}^3$

30 keV V = 60 V

$400 \times 400 \mu\text{m}^2$

$200 \times 200 \mu\text{m}^2$

$100 \times 100 \mu\text{m}^2$

$50 \times 50 \mu\text{m}^2$

$20 \times 20 \mu\text{m}^2$

$10 \times 10 \mu\text{m}^2$

WBXDT images

X-ray response maps

Effect of Te-inclusions/precipitates on device response

FWHM (%) at 662 keV, of the cumulative effect of Te inclusions to energy resolution (after bi-parametric correction) versus their concentration calculated for 1-, 3-, 5-, 10-, and 20- μm inclusions. The detector's length is 15 mm.

A. E. Bolotnikov et al., *IEEE Trans. on Nucl. Science* 54, 821 (2007).

Size distribution and concentration of secondary phases for standard CZT from different vendors.

A. E. Bolotnikov et al., *IEEE Trans. on Nucl. Science* 57 (2010) 910.

Is it possible to develop new material to address the problems associated with today's CZT and at low cost?

From our past experience Se was found to be very effective in reducing sub-grain boundary networks and Te inclusions/precipitates. In addition, the Se segregation coefficient is near unity in the CdTe matrix.

The proposed new quaternary semiconductor $\text{Cd}_{1-x}\text{Zn}_x\text{Te}_{1-y}\text{Se}_y$ (CZTS) is expected to resolve these long-standing problems associated with CZT material. Hence, high-performance detector-grade CZTS material can be potentially produced at lower cost.

Roles of Se

- **Strong influence in modifying Zn segregation coefficient: better compositional homogeneity with increased Se concentration.**
- **Effective solution hardening in arresting sub-grain boundaries and their network with increased Se content.**
- **Decreased Te-inclusion/precipitate concentration with increased Se content.**

Growth and characterization

- ❑ CZTS ingots were grown by traveling heater method (THM) as well as vertical Bridgman Method (BM).
 - 6N purity CdZnTe and CdSe were used for synthesis of the CZTS compound.
 - 6N purity Te was used as solvent for THM growth.
- ❑ Although BM technique is being used for crystal growth, our main thrust is THM growth of CZTS for its following advantages:
 - Low-temperature growth
 - Less chance of incorporation of impurities from the crucible during growth
 - Less/no chance of ampoule explosion
 - Enhanced purity of the ingot
 - Fewer defects due to the lower growth temperature
- ❑ Crystals were cut and polished for various characterizations and detector fabrication and testing.

Optimizing THM-growth parameters

THM growth is highly sensitive to growth parameters.

- i. Width of Te-rich solution zone
- ii. Growth temperature
- iii. Temperature gradient near the growth interface

Schematic of growth interface shape *growth of large grain and single crystalline ingots.*
A) convex, B) concave and C) flat.

Flat interfaces are desired for seeded growth.

CZTS ingots

- We are focusing on THM-growth of 2-in diameter CZTS ingots with different elemental compositions:

$\text{Cd}_{0.9}\text{Zn}_{0.1}\text{Te}_{0.93}\text{Se}_{0.07}$ ingots:

40-mm diameter ingot grown by BM (undoped).

In-doped 52-mm diameter ingot grown by THM (fast cooled ingot).

$\text{Cd}_{0.9}\text{Zn}_{0.1}\text{Te}_{0.96}\text{Se}_{0.04}$ ingots:

40-mm diameter ingot grown by BM (undoped).

In-doped 52-mm diameter ingot grown by THM.

$\text{Cd}_{0.9}\text{Zn}_{0.1}\text{Te}_{0.98}\text{Se}_{0.02}$ ingots:

40-mm diameter ingot grown by BM (undoped).

In-doped 52-mm diameter ingot grown by THM.

Compositional distributions in CZTS

Composition of Zn and Se is fairly uniform throughout the ingot for $\text{Cd}_{0.9}\text{Zn}_{0.1}\text{Te}_{0.93}\text{Se}_{0.07}$. Especially the calculated band gap.

For 2% and 4% Se composition, the band gap of the ingots is fairly uniform within the experimental accuracy. It only decreases in a narrow region (< 1 cm) near the interface.

~90% of the ingot shows uniform band gap for both 2 and 4% Se composition).

On the contrary, for THM grown CZT, only about one third of the ingot shows uniform composition.

Zn and Se composition and the calculated band gap along the length of the THM-grown $\text{Cd}_{0.9}\text{Zn}_{0.1}\text{Te}_{0.93}\text{Se}_{0.07}$, $\text{Cd}_{0.9}\text{Zn}_{0.1}\text{Te}_{0.98}\text{Se}_{0.02}$ and $\text{Cd}_{0.9}\text{Zn}_{0.1}\text{Te}_{0.96}\text{Se}_{0.04}$ ingots: from top to bottom.

X-ray topographic analyses

a

b

c

a)- c): X-ray topographic pictures of THM-grown $\text{Cd}_{0.9}\text{Zn}_{0.1}\text{Te}_{0.93}\text{Se}_{0.07}$ sample and the corresponding optical photograph of the grains.

a

b

c

a

b

c

a) X-ray topographic, b) photograph of the polished sample in reflection mode and c) IR transmission picture of a THM-grown $\text{Cd}_{0.9}\text{Zn}_{0.1}\text{Te}_{0.98}\text{Se}_{0.02}$ sample. Dimensions: $8 \times 5.6 \times 2.5 \text{ mm}^3$ and $8.2 \times 7 \times 1.55 \text{ mm}^3$.

X-ray topographic picture and photograph of the polished sample. The surface area is $\sim 15 \times 10 \text{ mm}^2$.

Higher Se concentration is more effective in arresting sub-grain boundary.
No sub-grain boundary network was evidenced.

Sub-grain boundary network problem is alleviated for CZTS material.

Concentrations and size distribution of Te inclusions in CZTS

For both Bridgman and THM grown $\text{Cd}_{0.9}\text{Zn}_{0.1}\text{Te}_{0.93}\text{Se}_{0.07}$ ingots, concentrations of Te inclusions/precipitates were found **8-9 times** lower than in standard CZT.

PL map of CZTS 2-inch wafer

Room temperature photoluminescence (PL) map of $\text{Cd}_{0.9}\text{Zn}_{0.1}\text{Te}_{0.93}\text{Se}_{0.07}$ two inch wafer grown by THM. The map area is $4 \times 4 \text{ cm}^2$. Step size 2 mm.

Variation of the peak energy (peak 1) over the entire scan area, ΔE is ~ 2 meV, thus the composition and band gap are highly uniform over the $4 \times 4 \text{ cm}^2$ area.

Composition and band gaps are highly uniform for both 2% and 7% Se containing CZTS wafers.

Low temperature (7K) photoluminescence (PL) map of $\text{Cd}_{0.9}\text{Zn}_{0.1}\text{Te}_{0.98}\text{Se}_{0.02}$ two inch wafer grown by THM. The map area is $\sim 2.8 \times 3 \text{ cm}^2$. Step size 1 mm.

Variation of the peak energy (A^0,X and D^0,X) over the entire scan area, ΔE is ~ 1.5 meV, thus the composition and band gap are highly uniform over the $2.8 \times 3 \text{ cm}^2$ area.

Charge transport properties of THM-grown $\text{Cd}_{0.9}\text{Zn}_{0.1}\text{Te}_{0.98}\text{Se}_{0.02}$

Charge collection versus applied bias voltage

- ^{241}Am source
- Planar detector: $6.65 \times 5.75 \times 1.86 \text{ mm}^3$

- ^{241}Am source
- Planar detector: $5.65 \times 5.18 \times 2.8 \text{ mm}^3$
- Sample with more Te-inclusions/precipitations

In general the $\mu\tau$ product varies between $4.5\text{-}6 \times 10^{-3} \text{ cm}^2/\text{V}$.

Detector response of THM-grown $\text{Cd}_{0.9}\text{Zn}_{0.1}\text{Te}_{0.98}\text{Se}_{0.02}$

(a) Picture of the detector: $4.4 \times 4.4 \times 10 \text{ mm}^3$
 (b) Reflection mode microscopic scan
 (c) IR transmission image

I-V characteristics at room temperature. Inset: I-V for 0-1V.

Bias voltage: 1800V
Shaping time 3 micro sec.

Bias voltage: 2300V, (Frisch grid ~7mm long)
Shaping time 10 μs .

Bias voltage: 2300V, Shaping time 6 μs .

All the spectra are as-measured without any correction technique.

Detector response of THM-grown $\text{Cd}_{0.9}\text{Zn}_{0.1}\text{Te}_{0.98}\text{Se}_{0.02}$

*HV: -2300V,
Shaping time 10 μs*

All the spectra are as-measured without any correction technique.

CZTS virtual Frisch-grid detector

Device response of another virtual Frisch grid detector.

Resistivity: $2.6 \times 10^{10} \text{ ohm-cm}$

Left: Picture of the detector: $3.6 \times 3.4 \times 9.7 \text{ mm}^3$

Right: microscopic scan IR transmission image

Bias voltage: 1800V, Shaping time 6 micro sec (Frisch grid~3mm long)

All the spectra are as-measured without any correction technique.

CZTS virtual Frisch-grid detector

Device response of another virtual Frisch grid detector.

Bias voltage: 1800V, Shaping time 3 micro

Bias voltage: 1800 V, Shaping time 6 μs

All the spectra are as-measured without any correction technique.

**Bias voltage: 1800 V
Shaping time 6 μs**

Detector response of THM-grown $Cd_{0.9}Zn_{0.1}Te_{0.98}Se_{0.02}$ at different shaping

a

b

c

d

Response of VFG detector at different shaping time a) 2 μ sec, b) 3 μ sec, c) 6 μ sec and d) 10 μ sec.
The detector dimensions: 4.8x4.9x9.7 mm³. (Frisch grid~4mm long)

Detector response of THM-grown $\text{Cd}_{0.9}\text{Zn}_{0.1}\text{Te}_{0.98}\text{Se}_{0.02}$ under different bias voltage

The detector dimensions: $3.4 \times 3.4 \times 9.15 \text{ mm}^3$. (Frisch grid~3mm long)

In spite of moderate $\mu\tau$ value, the device is operating even at low voltages.

Detector quality at a glance

IR image

Dimensions: $4.4 \times 4.4 \times 10 \text{ mm}^3$
I at 500V : 1.77 nA
Resistivity : $1.2 \times 10^{10} \text{ ohm-cm}$
Resolution
at 662 keV : ~ 2%
FG length : 7mm

IR image

Dimensions: $3.4 \times 3.4 \times 9.15 \text{ mm}^3$
I at 500V : 0.57 nA
Resistivity : $1.5 \times 10^{10} \text{ ohm-cm}$
Resolution
at 662 keV : ~ 1.6%
FG length : 3mm

Detector qualities are comparable to good quality CZT available today.

IR image

Dimensions: $3.4 \times 3.6 \times 9.7 \text{ mm}^3$
I at 500V : 0.77 nA
Resistivity : $2.6 \times 10^{10} \text{ ohm-cm}$
Resolution
at 662 keV : ~ 1.3%
FG length : 3mm

IR image

Dimensions: $4.8 \times 4.9 \times 9.7 \text{ mm}^3$
I at 500V : 1.26 nA
Resistivity : $3 \times 10^{10} \text{ ohm-cm}$
Resolution
at 662 keV : ~ 1.9%
FG length : 4mm

All the charge transport characteristics and the detector responses are performed on as-grown THM CZTS ingots.

Advantages of CZTS

- Se was found to be very effective in:
 - i) arresting the sub-grain boundaries
 - ii) better compositional homogeneity and
 - iii) lowering the concentration of secondary phase
- High $\mu\tau$ value was obtained with required resistivity.
- CZTS looks promising and has potential to supersede presently available CZT in terms of quality and yield at lower cost of production.

Example 1: ProxiScan™ Gamma Camera

- **ProxiScan™**: A compact digital gamma camera capable of insertion into the rectum as a probe, bringing the detectors directly adjacent to the prostate gland for high-resolution localization and imaging of prostate cancer.
- FDA 510(k) granted and clinical trials were done.
- Commercialization by industrial partner.

Transaxial view of mid-base region

CZT detectors

ASIC

Right Base-mid

Left Base-mid

Right Apex

Left Apex

Patient Images

Example 2: SPECT Imaging

- CZT/CZTS is also good for whole-body SPECT imaging
 - Better image contrast
 - Higher spatial resolution
 - Higher efficiency
 - Enabling energy-resolved photon counting
- We are working on a new SPECT detector head for energy-independent SPECT imaging
 - 1.6-mm pixel CZT detector
 - New ASIC for signal readout

Prototype of SPECT detector head

Co-57 images

Summary

- ❑ We successfully developed CZTS – a new promising material for radiation detection to replace CdZnTe
 - High homogeneity
 - Less defects
 - Low cost
 - Comparable detector performance
- ❑ CZTS can be used in future equipment for medical imaging and nuclear detector applications

- ❑ BNL has unique R&D expertise in room-temperature semiconductor detectors and their broad-range applications
 - Material research
 - Circuit development
 - Instrument construction
- ❑ We welcome any collaboration on medical imaging and related technologies

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Thank you for your kind attention !