New Semiconductor Materials for Radiation Detectors

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Outline

Overview of new compound semiconductor detector materials

Summary of recent Radiation Hardness measurements

Material development and characterisation:
- material growth: impurities, stochiometry, compensation
- electrical properties: band gap, charge transport, trapping, hole tailing
- uni-polar devices
- device fabrication: contact technologies, material availability

Single Crystal and Polycrystalline Materials

Future prospects and challenges
New semiconductor materials

New semiconductor materials research has been driven by both Particle Physics, and non-PP research programmes:

Examples of new materials include:

- Radiation Hard silicon detectors, eg. oxygenated silicon
- Crystalline compound semiconductors, eg. CdZnTe, CdTe, for medical X-ray imaging and nuclear medicine
- High purity epitaxial materials, eg. SiC, GaAs
- Polycrystalline CVD materials, eg. diamond
- Large area “polycrystalline” materials; a-Si, CdTe, HgI$_2$

Non-PP application areas driving these materials include:

- Medical and Synchrotron X-ray Imaging
- Nuclear Medicine - gamma cameras
- Astronomy - X-ray and Compton telescopes
- Customs and Security applications
## Material Properties

Summary of some material properties:

<table>
<thead>
<tr>
<th></th>
<th>Z</th>
<th>$E_G$ (eV)</th>
<th>W (eV/ehp)</th>
<th>$\rho_i$ at RT (Ω)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Si</td>
<td>14</td>
<td>1.12</td>
<td>3.6</td>
<td>$\approx 10^4$</td>
</tr>
<tr>
<td>Ge</td>
<td>32</td>
<td>0.66</td>
<td>2.9</td>
<td>50</td>
</tr>
<tr>
<td>InP</td>
<td>49/15</td>
<td>1.4</td>
<td>4.2</td>
<td>$10^7$</td>
</tr>
<tr>
<td>GaAs</td>
<td>31/33</td>
<td>1.4</td>
<td>4.3</td>
<td>$10^8$</td>
</tr>
<tr>
<td>CdTe</td>
<td>48/52</td>
<td>1.4</td>
<td>4.4</td>
<td>$10^9$</td>
</tr>
<tr>
<td>CdZn$_{0.2}$Te</td>
<td>48/52</td>
<td>1.6</td>
<td>4.7</td>
<td>$10^{11}$</td>
</tr>
<tr>
<td>Hgl$_2$</td>
<td>80/53</td>
<td>2.1</td>
<td>4.2</td>
<td>$10^{13}$</td>
</tr>
<tr>
<td>TlBr</td>
<td>81/35</td>
<td>2.7</td>
<td>5.9</td>
<td>$10^{11}$</td>
</tr>
<tr>
<td>Diamond</td>
<td>6</td>
<td>5</td>
<td>13</td>
<td>$&gt;10^{13}$</td>
</tr>
</tbody>
</table>

Also: SiC, PbI$_2$, GaSe
Empirical band gap relation

The relationship between band gap and ehp creation energy appears to lie in two distinct regions:

\[ \varepsilon = 2.67E_g + 0.87 \text{eV} \]

\[ \varepsilon = 2.91E_g - 1.93 \text{eV} \]
# Material Properties (2)

Material properties relevant to tracking detectors:

<table>
<thead>
<tr>
<th>Material</th>
<th>ehp created per keV</th>
<th>Density (g/cm³)</th>
<th>ehp created in 300µm</th>
<th>μτₑ/ℏ (cm²/V)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Si</td>
<td>280</td>
<td>2.33</td>
<td>32,200</td>
<td>0.4 / 0.2</td>
</tr>
<tr>
<td>Ge</td>
<td>350</td>
<td>5.33</td>
<td></td>
<td>0.8 / 0.8</td>
</tr>
<tr>
<td>InP</td>
<td>240</td>
<td>4.79</td>
<td></td>
<td>10⁻⁵ / 10⁻⁵</td>
</tr>
<tr>
<td>Si-GaAs</td>
<td>230</td>
<td>5.32</td>
<td>53,000</td>
<td>10⁻⁵ / 10⁻⁶</td>
</tr>
<tr>
<td>CdTe</td>
<td>225</td>
<td>5.85</td>
<td>50,000</td>
<td>10⁻³ / 10⁻⁴</td>
</tr>
<tr>
<td>CdZn₀.₂Te</td>
<td>200</td>
<td>6.0</td>
<td></td>
<td>10⁻³ / 10⁻⁴</td>
</tr>
<tr>
<td>Hgl₂</td>
<td>240</td>
<td>6.4</td>
<td></td>
<td>10⁻⁴ / 10⁻⁶</td>
</tr>
<tr>
<td>TlBr</td>
<td>170</td>
<td>7.5</td>
<td></td>
<td>10⁻⁴ / 10⁻⁵</td>
</tr>
<tr>
<td>Diamond</td>
<td>80</td>
<td>3.51</td>
<td>11,850</td>
<td>10⁻⁶ / 10⁻⁶</td>
</tr>
</tbody>
</table>
Most compound semiconductors show relatively poor hole mobility

The corresponding drift velocity for holes is often low:
Radiation Damage effects in compound semiconductors

The underlying radiation damage mechanisms are similar for most semiconductor materials:

- displacement of lattice atoms $\Rightarrow$ interstitials and vacancies
- nuclear interactions $\Rightarrow$ eg. neutron capture and transmutation
- secondary damage from displace lattice atoms $\Rightarrow$ eg. defect clusters from cascade processes

In compound semiconductors these phenomena are generally not well investigated.

Most of the existing work concentrates on cosmic ray damage for imaging arrays in space.

Crystalline CdTe, CdZnTe and Hgl$_2$ have been studied at up to $10^{12}$ cm$^{-2}$ (protons) and $10^{15}$ cm$^{-2}$ (neutrons):

Radiation Hardness of CdZnTe and HgI₂

A summary of the literature shows the following trends:

**CdZnTe**
- 200 MeV protons: >25% gain shift in strip detectors after $5 \times 10^9$ p/cm²
- Moderated neutrons: significant degradation after $7 \times 10^{10}$ n/cm²
- Thermal neutron activation of $^{113}$Cd produces gamma lines from $10^{10}$ n/cm²
  
  A. Cavallini et al, NIM A458 (2001) 392-399

**HgI₂**
- 10 MeV Protons: no $\Delta E$ loss up to $10^{12}$ p/cm²
- 8 MeV neutrons: no $\Delta E$ loss up to $10^{15}$ n/cm²
  
  $\Rightarrow$ More studies of HgI₂ are needed

Spectra from CdZnTe show:
- reduction in CCE
  ⇒ significant recombination of holes by $10^{13}$ n/cm$^2$
- peak widths unchanged
Materials Development and Characterisation

A range of issues need to be addressed in the development of new semiconductor materials:

- material quality
  - commercial growth techniques: large area, thick material
  - availability of whole wafers, uniformity, stochiometry
  - impurities: resistivity and compensation mechanisms

- electrical properties
  - band gap, ehp creation energy
  - charge transport and trapping: “hole tailing”
  - leakage current

- device fabrication
  - contact technologies, barrier heights
  - passivation
  - read-out technology: eg. flip-chip bonding or CMOS
  - novel electrode structures: unipolar detectors
Material Quality in CdZnTe

High Pressure Bridgeman CdZnTe is the new material of choice for medium resolution X-ray and gamma ray detection. Material suffers from mechanical defects - and is effectively polycrystalline. Monocry stalline pieces are hand selected from wafers - so whole wafer availability is very poor. Eg. typical price is 2500 euro for a pixel array 15 x 15 x 2mm.
Te precipitates in CdZnTe

CdZnTe is grown Te rich, and tends to tellurium precipitates and tellurium oxides

SEM image of Pt contact region in CdZnTe, showing tellurium precipitates formed at the contact interface:

X-ray spectra

(a) Cd, Te peaks

(b) Pt peak

(c) Te peak
Whole Wafer Uniformity

Single crystal materials can also exhibit non-uniform electrical properties across wafers:

- thermal stress induced during growth
- non-uniform defect or impurity concentrations
- local variations in traps and resistivity

Contact-less whole-wafer inspection methods are required to assess wafer quality prior to device fabrication:

For example:

- Sub band-edge (IR) microscopy
- Room temperature photoluminescence mapping
- Contact-less bulk resistivity measurement
Photoluminescence microscopy is used as a non-contacting technique to study the uniformity of defects in semiconductor wafers.

For example, does Fe-doped SI InP suffer from the same defect non-uniformity as SI GaAs?

We use a room temperature wafer-scanning technique, with a 25 mW HeNe laser focussed to 50-100 µm spot size.

A GaAs-PMT (sensitive to 930 nm) detects the luminescence after passing through a monochromator ($\Delta \lambda = \pm 2$ nm). Very weak signals are extracted using a digital lock-in amplifier.
Room temperature PL on Indium Phosphide

PL emission of MASPEC wafer

response/ A

6e-10
5e-10
4e-10
3e-10
2e-10
1e-10
0

wavelength/ nm

650 700 750 800 850 900 950 1000

Material uniformity shows no growth-related structures - but some surface damage due to mechanical polishing.
PL comparison with GaAs

PJ Sellin et al, NIM A460 (2001) 207-212

Growth-related defect distribution in SI GaAs (EL2)
Resistivity mapping of GaAs wafers

Contact-less resistivity mapping using the Time Dependent Charge Method has been pioneered at Freiburg.

The wafer forms a capacitor dielectric where the time dependence of the discharge depends on the resistivity.

Compensation in compound semiconductors

Bulk compound semiconductor materials often have a high residual impurity concentration ⇒ conducting material

- Eg. bulk GaN and InP are both n-type: $n_e \sim 10^{18}$ and $\sim 10^{15}$ cm$^{-3}$ respectively, due to residual donor impurity concentration

- For Semi Insulating (SI) material at $10^6$-$10^8$ Ωcm, requires residual donor concentration to be reduced by $>10^6$

In InP compensation is achieved using Fe as a deep acceptor: 0.65 eV below the conduction band edge.

In GaN compensation is by Mg as an acceptor

Undoped GaAs is SI due to a native EL2 defect acting as a deep donor
Unipolar charge sensing in CdZnTe

CdZnTe suffers from poor mobility-lifetime products for holes, due partly to low hole mobility inherent in compound semiconductors. In a planar detector, this causes:

- depth dependent pulse heights when $\mu \tau_e$ and $\mu \tau_h$ differ strongly
  \( \Rightarrow \) asymmetric photopeaks in gamma ray spectra
  \( \Rightarrow \) poor energy resolution

- low CCE when either $\lambda_e$ or $\lambda_h$ (or worse, both) are significantly less than the detector thickness
  \( \Rightarrow \) small signals, poor S/N for tracking detectors

Spectroscopy performance of CdZnTe is greatly improved using a detector geometry that is only sensitive to electrons:
The Frisch grid is a classic solution to incomplete charge collection of ions in gas detectors.

The grid provides an electrostatic shield ⇒ movement of carriers in the region between the cathode and grid produce minimal signal.

Pulses give full amplitude signals providing the electrons can travel the distance from the grid to the anode.
An analogous semiconductor version of the Frisch grid was proposed in CdZnTe detectors.

Inter-digitated strip electrodes with slightly different bias at A and B achieve this effect:
⇒ weighting potential for A tends towards 1 (at A) and 0 (at B)
⇒ electron drifting towards A induces signals $q_A$ and $q_B$
⇒ the subtracted signal is only sensitive to electron movement close to the strip electrodes
Small pixel effect in CdZnTe

A similar effect to the Frisch grid is realised in pixel detectors by the ‘small pixel effect’:

- For small pixels, where \( \frac{\text{pixel pitch}}{\text{thickness}} < 0.1 \), the weighting field at each electrode is maximised close to the pixel electrode (anode).

- Along the pixel axis, the weighting field has the form:

\[
E_{Wj}(z) = \left(\frac{D}{2}\right)^2 \sum_{k=-\infty}^{\infty} \frac{1}{\left[(z + 2kL)^2 + \left(\frac{D}{2}\right)^2\right]^{\frac{3}{2}}}
\]

- The small pixel effect was first applied to CdZnTe pixel detectors by Barrett and Barber.


- Signal risetimes improve \(~10x\), but still \(~100\)ns.

![Graph showing weighting field for different pixel pitches](image)
Other single crystal materials

Other bulk materials show promise for single element radiation detectors, but are not yet ready for commercial use:

**Gallium Nitride**

Single crystals of GaN have been developed in Warsaw

Grown in liquid Ga with N\textsubscript{2} over pressure:
20 kbar and 1700 °C

Undoped
⇒ n-type at 10\textsuperscript{19} cm\textsuperscript{-3}, p ~ 10\textsuperscript{-3}-10\textsuperscript{-2} Ωcm

Grown with 0.5% Mg
⇒ semi insulating, p ~ 10\textsuperscript{4}-10\textsuperscript{6} Ωcm

SI material has residual concentration of ~10\textsuperscript{16} cm\textsuperscript{-3} - very poor charge transport

S. Porowski, J Cryst Growth 189/190 (1998) 153-158

GaN single crystal (1mm grid)
**Thallium Bromide**

TlBr has been extensively developed for use as optical windows in the millimetre wavelength region.

Use of TlBr is currently limited for radiation detectors

TlBr has a high density, high atomic number (81, 35) and wide bandgap (2.68 eV) - similar stopping power to BGO

The material is very soft, melting at 480 °C

New growth techniques since 1992 have produced high purity materials:
- mu-tau products are similar to Hgl₂
- electron and hole lifetimes are >1μs, better than CdTe

Currently, no contact technologies exist to allow bonded pixel detectors

TlBr spectroscopy

Spectra obtained from TlBr detectors fabricated from single crystals grown by the horizontal Travelling Molten Zone method

Each detector 3mm² in area and 570 mm thick
400V bias was applied at room temperature

Single crystal Fe-doped InP is readily available in whole wafers with good uniformity. MASPEC wafer doped InP exhibits $\mu\tau$ values >50x greater than commercial AXT material. CAS material is ~10x better performance than AXT.
Gamma ray spectroscopy at 59 keV

$^{241}\text{Am}$ 59 keV $\gamma$ rays

$V = -300\text{V}$, $T = -50\text{C}$

Channel number

Counts

0 500 1000 1500 2000 2500

0 50 100 150 200 250 300

In escape peak

Photopeak 59 keV

Pulser

H. El-Abbassi, P. Sellin, NIM A466 (2001) 47-51
Semi insulating GaAs has been studied unsuccessfully for use as a possible radiation hard tracking detector:

- The electron transport is killed by the native EL2 defect
- Non uniform and unstable electric fields prevent reliable operation

Recently an ESA funded programme has developed 400µm thick epitaxial GaAs

This is high purity non-compensated GaAs, with residual defect concentrations $<10^{12}$ cm$^{-3}$

Polycrystalline Materials

Some promising materials are truly polycrystalline, and have the potential for large area sensors:

- CVD diamond, supplied as free-standing films with thickness of typically 50 - 300 µm
- Polycrystalline amorphous silicon, CdTe and HgI₂

CVD diamond has been studied extensively by the HEP community:
- excellent radiation hardness
- minimal leakage currents, low noise
- robust technologies for contacts and bonding
- charge signal per MIP is low
- charge trapping can cause CCE <100%
- cost for large area detectors
IBIC imaging of diamond with 2 MeV protons

The Surrey University microprobe performs Ion Beam Induced Charge (IBIC) imaging with a 1 micron resolution 6 MeV proton beam.

IBIC maps show ‘hot spots’ at electrode tips due to concentration of the electric field.
Close-up scans of strip tips

- Scans as a function of bias voltage, zoomed around the tip of one electrode.
- ‘hot’ crystallites build up in density with increasing bias.
- Electric field initially concentrates at the edges of the electrodes.

Simultaneous SEM and CL images show the morphology of a small region of a diamond strip detector.

The large crystallite is ~120µm wide by ~150µm high, and is positioned centrally between two electrodes.

The IBIC data clearly follows the morphology of the grain and shows charge transport terminating at the grain edges.
Intra-crystallite charge collection efficiency

IBIC system records a full pulse height spectrum at each pixel in the image.
Pulse height spectra vs. bias voltage

100% CCE is observed within a single large crystallite that lies between two electrodes.

We see no evidence for gain mechanisms giving >100% CCE.
Large Area detector technologies

a-Si arrays pioneered by dpiX, are now replacing film in medical X-ray radiography systems
- typical pitch 127 - 392 µm
- active areas up to 30x40 cm²
Large area polycrystalline CdTe detectors have recently been developed by LETI, Grenoble (M. Cuzin et al, NIM A380 (1996) 179-182).

These have been extensively tested at CERN as beam monitors, with excellent radiation hardness: (E. Rossa et al, CERN-SL-2000-068 BI)

eg. $10^{13}$ Gy at ~ 200 keV photons, equivalent to $10W/mm^2$

Polycrystalline devices have particular charge transport properties:
- short lifetimes, limited by small crystallite sizes
- ohmic contacts - operating as photoconductors
- relatively high mobilities
- high bulk resistivity

Both GaAs and CdTe have been fabricated at LETI:

CdTe MOCVD:
- Mobility $\mu_e$: 100 cm$^2$/Vs
- Lifetime $\tau_e$: <10 ps
- Resistivity: $10^7$-$10^{10}$ $\Omega$cm

(bulk: $1000$ cm$^2$/Vs)

(bulk: 0.1 $\mu$s)

(bulk: $>10^9$ $\Omega$cm)
Pulse height spectra from polycrystalline CdTe

Measured pulse heights are limited by short charge drift lengths in the polycrystalline material - improved signal magnitudes are seen with a fast linear amplifier.

CdTe detector test with MIPS
sample ref 172/ 470 microns
(Integrating Amplifier: D. Meier Set-up)

edouard.rossa@cern.ch
Polycrystalline CdTe radiation hardness

Response after $10^{16}$ n cm$^{-2}$ dose is almost unchanged:

400 µm thick detector, 400V bias
Polycrystalline Mercuric Iodide HgI$_2$

Single crystal HgI$_2$ is attractive for gamma ray imaging due to high atomic number (80, 53) with $\rho \sim 10^{13}$ $\Omega$cm

Electron $\mu\tau \sim 10^{-4}$ cm$^2$/V, but hole $\mu\tau$ is $\sim 10^{-6}$ cm$^2$/V

Polycrystalline HgI$_2$ offers a low cost large area detector material, fabricated by screen printing of ceramic:

- electron $\mu\tau \sim 10^{-7}$ cm$^2$/V
- (cf. diamond $\mu\tau \sim 10^{-6}$ cm$^2$/V, selenium $\mu\tau \sim 10^{-5}$ cm$^2$/V)

Evaporated material gives better charge transport, and shows columnar growth similar to CVD diamond

Beam tests with HgI$_2$ strip detectors

Polycrystalline HgI$_2$ contained in a ceramic binder has been screen printed glass substrates patterned with electrode strips

- Beam tests have been made at CERN:
  - strip pitch 275 µm, large inter-electrode gap of 135 µm
  - strip length 1 cm
  - thickness 600 µm
- Mean pulse height of
  ~4500 electrons
- Signal reduced to
  ~3500 electrons
  after $5 \times 10^{14}$ n/cm
- New evaporated layers
  give ~10x better signal output

Conclusions

- Good progress has been made with a number of new wide bandgap compound semiconductor detector materials in the last 5-10 years.
- Material availability and quality still limit single crystal materials.
- Polycrystalline materials (CdTe, HgI$_2$) show great potential for large area, radiation hard, devices.
- These materials are also of interest for direct application to CMOS pixel detectors.
- Radiation hardness measurements are incomplete, and more high dose characterisation is required.
- A wide range of semiconductor physics characterisation techniques need to be applied to understand charge transport and defect mechanisms better in these materials.
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Radiation detector development is carried out within the Radiation Imaging Group, part of the Department of Physics

Academic Staff:
Dr Ed Morton
Dr Paul Sellin
Dr Walter Gilboy

The group members currently include
6 postdoctoral Research Associates
8 postgraduate PhD students
Research Activities

Development of new semiconductor materials for X-ray and gamma ray detectors:
- Cadmium Zinc Telluride (CdZnTe)
- Gallium Arsenide (GaAs)
- Other wide bandgap materials (CdTe, InP)
- Diamond radiation sensors
- Pixel detectors for medical and space imaging

Ion beam and implantation techniques
- detector characterisation with nuclear microprobes
- device fabrication with ion implantation
- RBS and PIXE material characterisation

Related research topics:
- X-ray microtomography and diffraction imaging
- digital neutron / gamma radiation monitors
- large volume Germanium detectors for nuclear spectroscopy
Facilities in the Group

Semiconductor detector laboratories:
- Optical and electrical characterisation (PICTS, DLTS, PL, Raman)
- Detector mapping systems using microfocus lasers and collimated radioisotopes

Ion Beam accelerator lab:
- new 6 MeV proton, 3 MeV alpha particle accelerator
- sub micron resolution nuclear microprobe for detector imaging
- implantation and damage studies

Device Fabrication: semiconductor clean room, photolithography

Device simulation: 3D device modelling (Silvaco), MCNP, EGS4, Geant

X-ray laboratory: X-ray sources 50-200 keV, Philips Fluorex
  monoenergetic X-ray source, image intensifiers, X-ray µ–CT

Radiation Physics: >130 sources including:
- Am:Be neutron sources (up to 18 GBq)
- $^{60}$Co ‘hot spot’ irradiator (1.9 TBq), ~2.5 kGy per day