

# Properties of Melt-Grown ZnSe Solid-State Radiation Detectors

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## Abstract

Zinc Selenide (ZnSe) crystals grown using the High Pressure Bridgman (HPB) technique were used to fabricate solid-state radiation detectors measuring  $10 \times 10 \times 2 \text{ mm}^3$ . Sputtered platinum and gold contacts were applied to polished detector blanks. Voltage versus current characteristics were determined for the devices at 25°C. Pulse height spectra were obtained using  $^{241}\text{Am}$  and  $^{109}\text{Cd}$  at both 25°C and 150°C with applied bias of 9000 V/cm. Current versus temperature was measured over the temperature range of 30°C to 150°C. Performance was measured at energies of 22.1 and 59.5 keV over a temperature range of -70°C to 170°C. Current versus dose rate was measured with 662 keV gamma irradiation. A value of the Mobility-Lifetime product ( $\mu\tau$ ) for electrons was estimated. Time and temperature dependence of photo-peak position using Pulse Height Analysis (PHA) was studied.

## I. INTRODUCTION

Of the II-VI semiconductors, only Cadmium Telluride (CdTe) and Cadmium Zinc Telluride (CdZnTe) have been developed as practical, room temperature, solid state radiation detectors. A useful operating temperature of these detectors is limited, however, to approximately 70°C and storage temperatures above 100°C can cause irreversible damage. Zinc Selenide (ZnSe), a II-VI semiconductor with a room temperature band gap of 2.7 eV, compared to CdTe at 1.47 eV, should have a potential to operate at lower bias currents and higher temperatures. Other workers have fabricated detectors from Cadmium Zinc Selenide ( $\text{Cd}_{0.7}\text{Zn}_{0.3}\text{Se}$ ) using the Temperature Gradient Solution Zoning technique[1]. Our work details preliminary results obtained with detectors fabricated from ZnSe crystals produced from the HPB growth technique. The results of this work focus on the possibility of using ZnSe detectors for high temperature applications.

## II. EXPERIMENTAL DETAILS

### A. Crystal Growth

ZnSe was grown in a High Pressure Bridgman (HPB) furnace at eV Products. High purity, pre-reacted ZnSe pieces

were placed in a 90 mm diameter graphite crucible. The ampoule, under a 100 atm. over pressure, was heated to 1600°C and dropped at 1 mm/hour from the melt zone.

### B. Material Characterization

The resulting 90 mm diameter x 130 mm long ingot was sliced using a diamond inside diameter saw to produce both <111> oriented single crystal and randomly oriented polycrystalline slices 2 mm thick. The pieces were inspected for visible twinning. The following methods were used to characterize representative samples:

1. Double Crystal Rocking Curves (DCRC) were generated using  $\text{CuK}_\alpha$  radiation, conditioned using a <111> InSb first crystal. Spot size was 2 mm x 2 mm.
2. X-ray topographs were produced using  $\text{CuK}_\alpha$  radiation conditioned with an asymmetrically cut silicon crystal operating in the magnification mode.

### C. Detector Fabrication

Blanks 10mm x 10mm in area were inspected for defects and polished on six sides with 1  $\mu\text{m}$  alumina grit followed by 0.25  $\mu\text{m}$  diamond grit. Direct Current sputtering was used to apply platinum or gold contacts on the two large area faces of each detector, producing a Metal-Semiconductor-Metal arrangement (MSM).

### D. Detector Characterization

All performance tests were conducted on detectors without protective coatings or atmospheres on exposed surfaces:

1. Pulse Height Analysis (PHA) was conducted using an eV Products 550/5093 pre-amplifier and a Canberra 2020 spectroscopy amplifier. Elevated temperature PHA studies were performed by heating the detectors in a brass test fixture with a Be entry window. The apparatus was arranged to keep the preamplifier near room temperature.
2.  $\mu\tau$  for electrons at 25°C was estimated using the photo-peak position method. 59.5 keV gamma radiation was directed to the negative contact of a biased detector. Photo-peak position versus bias voltage was fitted to the Hecht relationship[2]

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3. Current measurements at  $\leq 1100$  volts bias were made with a Keithley 237 high voltage source/measure instrument. A Keithley 417 electrometer was used to measure voltage drop across a  $1\text{ G}\Omega$  resistor in series with the detector under test to determine detector currents at  $> 1100$  volts bias.

4. DC current versus  $^{137}\text{Cs}$  dose rate measurements were performed at  $25^\circ\text{C}$  using a Keithley 237 high voltage source/measure instrument and a calibrated  $^{137}\text{Cs}$  test facility<sup>2</sup> Dose rate was varied by placing the detector at calibrated distances from the source.

### III. RESULTS AND DISCUSSION

#### A. Crystal Quality

The DCRC of Fig. 1, with a Full Width Half Maximum (FWHM) of 160 arc-seconds, is indicative of poor crystalline quality. Likewise the X-ray topograph of the same sample (Fig. 2) indicates 2 variants of dense striation indicating heavy dislocation densities. ZnSe undergoes a phase transformation just below the melting point from a hexagonal to cubic structure[3]. This transformation may be largely responsible for degradation of crystallinity.

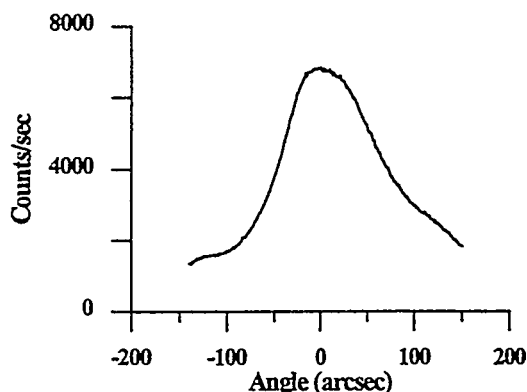


Fig. 1 DCRC of typical ZnSe sample (HPB3-9-1), FWHM = 160 arcsec.

#### B. Dark Current Characteristics

Fig. 3 shows the current versus voltage characteristic for a typical  $10\text{mm} \times 10\text{mm} \times 2\text{mm}$  detector at  $25^\circ\text{C}$ . In order to investigate if the Pt contacts form a barrier with the ZnSe at room temperature, a device was irradiated with 14 keV X-rays at 55 Rad/hour with 0 volts applied bias. The resultant current was  $-3 \times 10^{-12}$  amps compared to  $2.1 \times 10^{-11}$  amps when biased at +5 volts with the same irradiation. This implies the existence of a barrier and non-ohmic contacts. The formation of an injecting contact between gold and ZnSe has been reported by others[4]. It is possible that the Pt contact

forms an injecting contact in this case. Fig. 4 shows the current versus temperature characteristic of the same detector with an applied bias of 1000 volts.



Fig. 2 X-ray topograph of ZnSe sample HPB3-9-1

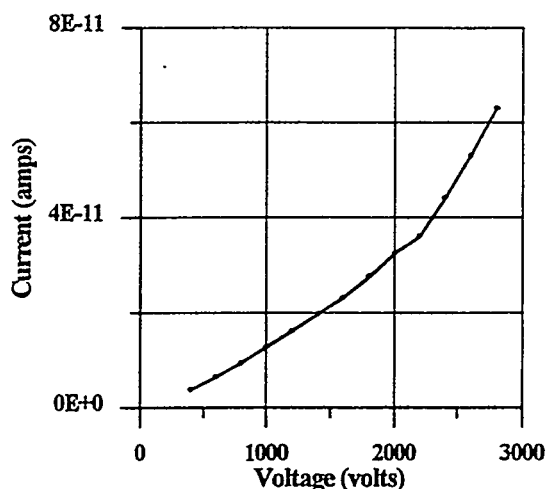


Fig. 3 Current vs. voltage characteristic of ZnSe detector.

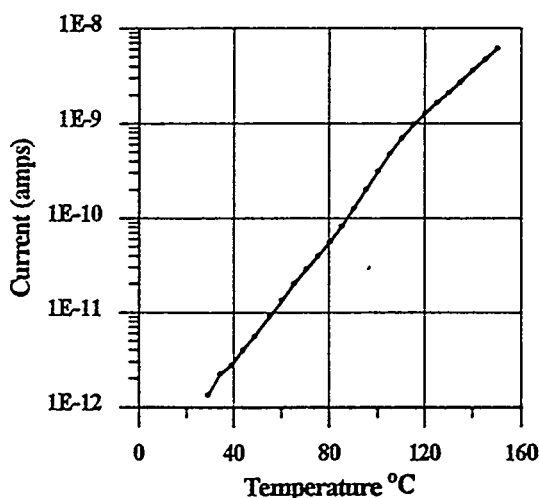


Fig. 4 Current vs. temperature characteristic of ZnSe detector. Bias = 1000 volts.

<sup>2</sup> We would like to acknowledge The Project Manager, Nuclear Biological Defense Systems, United States Army, for use of their radiation dosimeter test facility

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### C. Pulse Height Spectrum Analysis

At room temperature the best conditions for PHA were determined to be 900-1000 V/mm bias, and 1.5  $\mu$ s shaping time. PHA spectra for typical detectors at 25°C (Fig. 5a, b) exhibited 6 keV energy thresholds and resolutions of approximately 50%. Some detectors exhibited resolutions of 25% at 22.1 keV (Fig. 6) and 35% at 130°C. At 160°C, the energy threshold increased to approximately 17 keV (Fig. 5c,d). Shaping times of 0.25  $\mu$ s were more desirable at temperatures greater than 150°C due to increased current noise. Evaluation at temperatures above 175°C was precluded by a breakdown of the detector signal. It was not determined if the breakdown occurred within the detector, the mounting, or BNC connectors used in the connection to the preamplifier.

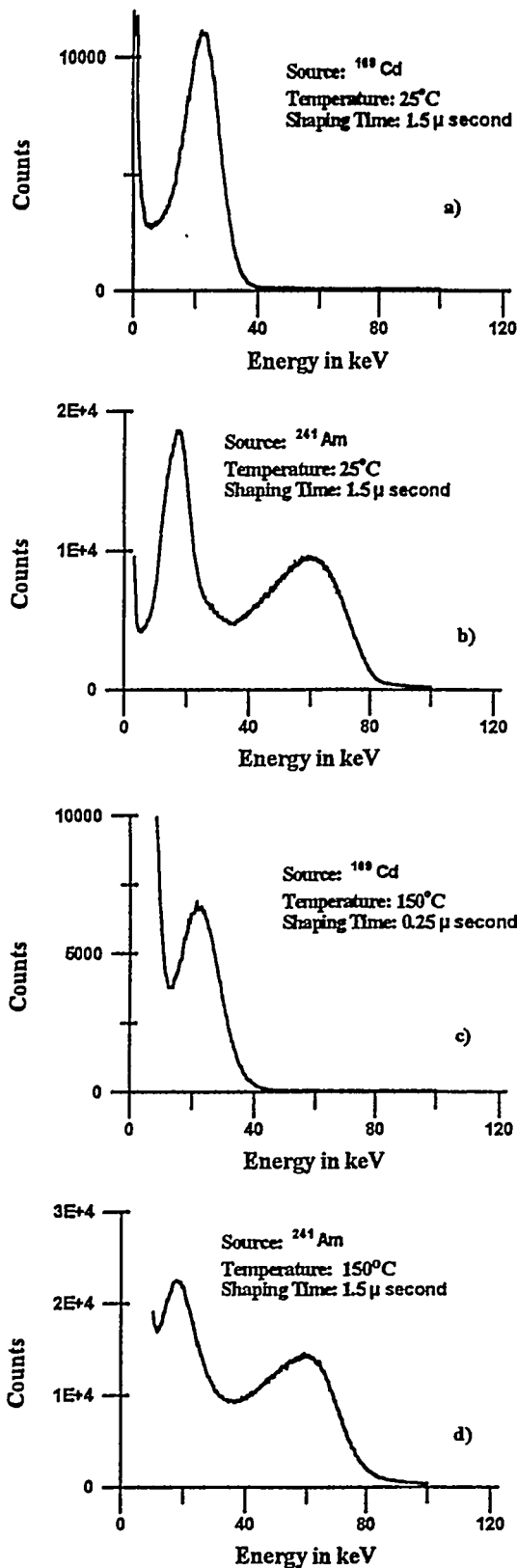


Fig. 5. a,b,c,d PHA analysis of detector at 25°C and 150°C

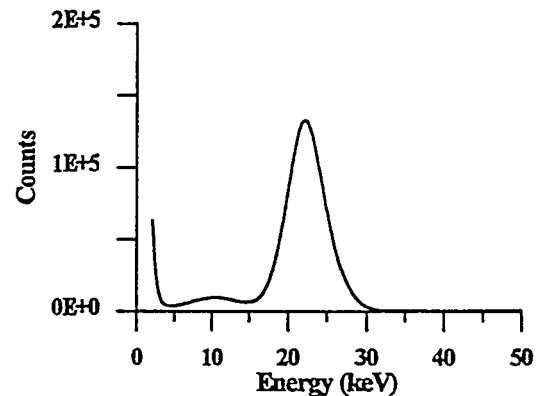


Fig. 6 Spectrum of device with 25% resolution at 22.1 keV. Bias = 2000V, shaping time = 1.5 usec, T = 25°C

Photo-peak position versus energy for a typical detector at 125°C is summarized in Fig. 7. Higher energy peaks were not included because centroid determination was ambiguous. Detectors exhibited energy linearity between 18 and 32 keV.

Photo-peak position is a function of both temperature and elapsed time after application of bias. The photo-peak position remained constant in the range of -70°C to 100°C and decreased by approximately 31% at 150°C when measured at a constant shaping time of 1.5  $\mu$ s (Fig. 8). At 40°C, photo-peak position decreased for a period of approximately  $10^3$  seconds after bias was applied (Fig. 9). At temperatures above 100°C the time to reach stable operation decreased, but over long periods of time at elevated temperatures, the decrease continued slowly (Fig. 10). It is suspected that oxidation of the edges of the detector played a role in this long term degradation. When the detector edges were cleaned with acetone after the detector had been at high temperature for a long period of time, the photo-peak positions returned to the same channels occupied before the heating cycle.

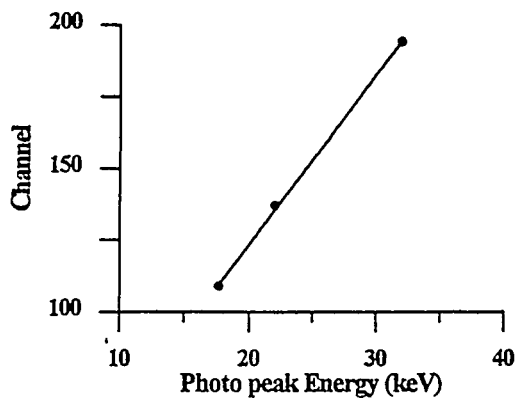


Fig. 7 Photo-peak energy vs. photo-peak position.  $T = 125^{\circ}\text{C}$ , Photo-peak energies:  $^{241}\text{Am}$ , 17.7 keV;  $^{109}\text{Cd}$ , 22.1 keV;  $^{137}\text{Cs}$ , 32.1 keV.

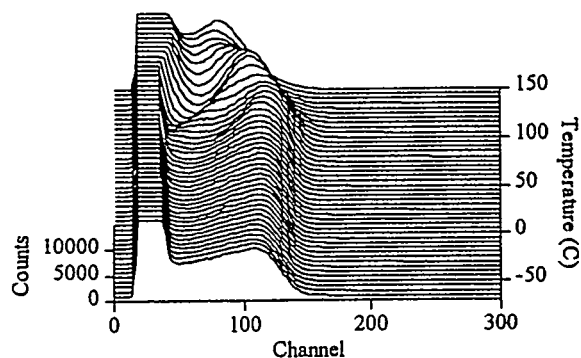


Fig. 8 Photo-peak position :  $-70^{\circ}\text{C}$  to  $150^{\circ}\text{C}$ , Bias = 1000 V, Shaping time =  $1.5 \mu\text{sec}$ .

#### D. $\mu\tau$ For Electrons

Fitting the Hecht equation to the 59.5 keV gamma photo-peak position data yielded an estimate of  $\mu\tau$  for electrons at  $25^{\circ}\text{C}$  of  $4 \times 10^{-5} \text{ cm}^2/\text{Volt}$ .

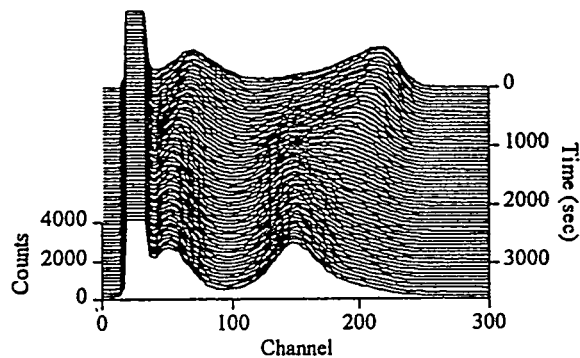


Fig. 9. Photo-peak position:  $T = 40^{\circ}\text{C}$ , Bias = 1000 V at  $t > 0 \text{ sec}$ , Shaping time =  $1.5 \mu\text{sec}$ .

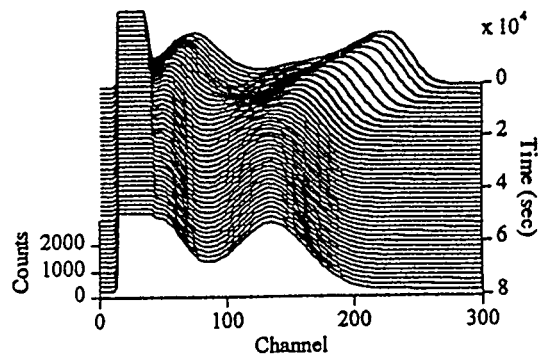


Fig. 10 Photo-peak position:  $T = 100^{\circ}\text{C}$ , Bias = 2000 V at  $t > 0 \text{ sec}$  Shaping time =  $1.5 \mu\text{sec}$ .

#### E. Current Mode Operation

A 10mm x 10mm x 2mm detector biased at 5 volts was irradiated with 662 keV  $\gamma$ -rays at dose rates of 30, 60 and 120 Rad/hour. Fig. 11 shows detector current vs. time at  $25^{\circ}\text{C}$ . At  $t = 0 \text{ sec}$ , a mechanical shutter on the radiation source was opened. Response time for the detector to reach a steady state current was on the order of 10 sec while sensitivity was approximately 1 picoamp/rad/hour. At a bias of 1000 volts, sensitivity was increased by a factor of  $10^3$ , but the response time is too large for practical applications. (Fig. 12)

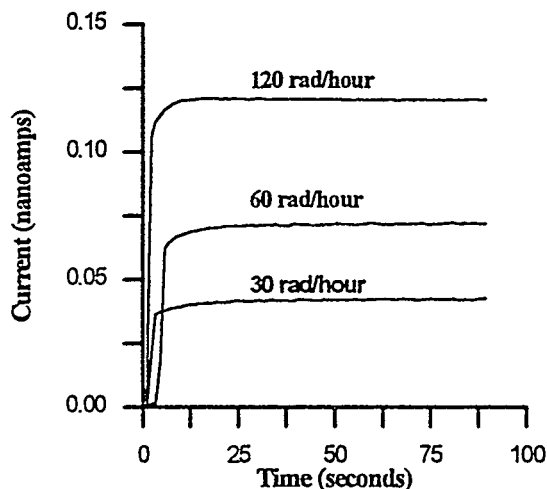


Fig. 11 Current vs. time for various dose rates of 662 keV gamma irradiation. bias = 5 volts

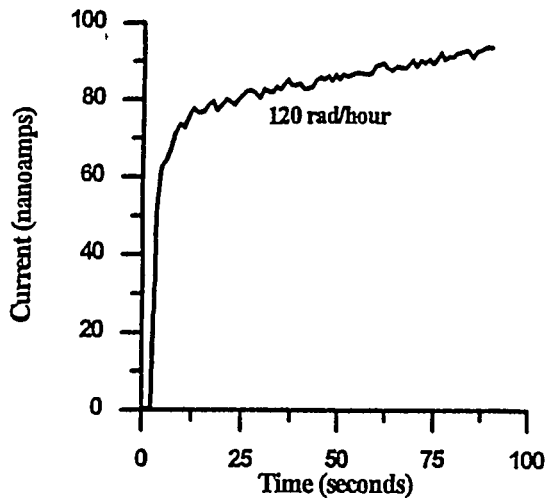


Fig. 12 Current vs. time for various dose rates of 662 keV gamma irradiation. Bias = 1000 Volts, dose = 120 Rad.

#### IV. CONCLUSIONS

In this paper, we have discussed the possibility of using the II-VI compound semiconductor, ZnSe, for a high temperature ( $25 \leq T \leq 160^\circ\text{C}$ ) x-ray or  $\gamma$ -ray detector. Various properties have been measured and photo-peaks were observed at both 22 and 60 keV over an extended temperature range. Time and temperature dependence of photo-peak position using PHA were measured for various detectors. The details of this behavior are not understood, but some polarization has been observed below  $50^\circ\text{C}$ . Gold contacts were found to be more stable during temperature cycling, and crystals with visible twins appeared to have higher resolution photo-peaks. Further studies are underway to elucidate these novel detectors for various applications.

#### V. REFERENCES

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