Evaluation of monocrystalline ZnSe as a high-temperature radiation detector

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Abstract
This work presents the investigation of wide-band gap semiconductor ZnSe used as a radiation detector utilizing X-ray radiation sources to evaluate its operation over a wide temperature range. The results of an experimental investigation into the electrical and spectrometric properties of monocrystalline ZnSe are shown. Undoped monocrystalline ZnSe has an extremely low leakage current over a wide temperature range of up to 167 °C. Spectrometric measurements of X-rays with a $^{57}$Co point source show that there is a range of optimal values for the bias voltages applied to the ZnSe samples that allow the influence of the noise to be minimized and simultaneously give a counting efficiency close to some maximum value which is different for different temperatures. For the particular ZnSe sample explored, this range is from 500 V (2000 V/cm) to 750 V (3000 V/cm) in a temperature range from 20 °C to 130 °C. Under these conditions and with a low energy threshold of approximately 35-40 keV, the maximal noise count rate can be reduced to approximately 10 cps. The obtained results allow us to conclude that monocrystalline ZnSe has the potential to be effectively used as a radiometric detector of gamma and X-ray radiation in a wide temperature range up to at least 130 °C.

Keywords: X-ray, ZnSe, semiconductor, radiation, high temperature, detector.

1. Introduction
Nowadays solid-state radiation detectors are in widespread use, but one limitation on them is that they need to be operated at low or close to room temperatures [1-6]. Conversely, inorganic scintillators [1-2] and detectors based on semiconductors with energy gaps between 1.4 eV and 1.9 eV, such as CdTe, CZT, AlGaAs or GaAs [3-6], can be operated in a wide temperature range up to approximately 100 °C, but they usually require additional cooling in order for them to operate at higher temperatures. This cooling requirement is one of the main limitations for effective industrial application of these detectors. Increasing the upper operational temperature limit of solid-state radiation detectors to about 200 °C would expand the boundaries of their applications in industries such as metallurgy (thickness measurements of hot-rolled products [7]), petroleum (integrity inspection of oil-wells and boreholes [8]), nuclear energy, and many other fields of science and technology where the high temperature solid-state detectors are needed. This improvement is also more difficult for scintillation detectors than for semiconductors because in addition to scintillators with good temperature behaviour and luminescence quantum yield [9], high-temperature light detectors, such as photomultipliers, photodiodes or photo resistors with appropriate light spectral sensitivity is required. The increase in temperature of any semiconductor leads to an exponential increase in the probability of the thermal generation of additional charges in its valance and conduction bands. These additional charges are the primary causes for the leakage current when a bias voltage is applied to it. The leakage current depends strongly on the concentration of...
impurities, the band gap and the type of electrical contacts. From a physical point of view the semiconductors with the greater values of the band gap have the smaller probabilities of thermal charge generation. For example, the wide-gap semiconductor ZnSe has a band gap of 2.8 eV (300 K) and good absorption efficiency for X-ray and gamma photons (\( \rho = 5.26 \text{ g/cm}^3 \)) and it is a good example of a dense and wide-gap semiconductor with properties close to the dielectrics. The physical features of the crystal structure of ZnSe allows for single crystals to be grown with a large bulk volume (\( \Delta V > 50 \text{ cm}^3 \), [10, 11]), which is a significant advantage over wide-band gap semiconductors such as SiC, GaN/ InGaN and diamond [12-14]. In this work we show the results of experimental investigations into the electrical and spectrometric properties of undoped monocrystalline ZnSe samples in a wide temperature range from 20 °C to 167 °C in order to estimate the efficiency of the use of this semiconductor as a high temperature detector of ionizing radiation.

2. Experimental Methods

The samples under study consisted of undoped ZnSe crystals that have been grown in a highly clean environment to obtain crystals with a minimum concentration of impurities and a maximum specific resistance between \( 10^{13} - 10^{14} \text{ Ohm-cm} \). To study conductivity, multilayer metal contacts were sputtered on the crystals with the resistive method, and conductors were soldered to these contacts. The quality of the contacts was verified by measuring the volt-ampere characteristics of the induced X-ray conductivity (XRC) and the intrinsic conductivity of the samples. The distance between the electrodes was 5 mm (Figure 1 (a)) and 2.5 mm (Figure 1 (b)). A bias voltage up to 1000 V was supplied to one electrode with the other electrode grounded through a nanoampere meter (Figure 1 (a)). The measurement error of the voltage did not exceed ±1 V, and the measurement error of the current did not exceed ±3% (for currents > 10 pA). The measurements were performed within a temperature range of 20 °C to 167 °C (293-440 K). The conductivity of the ZnSe samples was analysed through excitation with different X-ray sources. Initially, X-ray irradiation was achieved by radiation from an X-ray tube (Re - anode, 20 kV, 5-25 mA, distance to the sample of 150 mm) through a cryostat beryllium window. The maximal energy flux of the generated X-rays was of 0.42 mJ/s·cm² in the sample plane at the accelerating potential of 20 kV and tube current of 25 mA. Subsequently, a \(^{57}\text{Co}\) point source was used to investigate the spectrometric properties of ZnSe samples. This source has the dominant X-ray emission line at 122 keV (85.6%). Schematics for the X-ray measurements with ZnSe samples are shown in Figure 1. The temperature of the ZnSe samples was maintained at two constant levels of 22 °C and 134 °C (295 K and 407 K) to measure the volt-ampere characteristics; the temperature was varied linearly with a speed of 0.15 K/s to measure the temperature dependence of the dark conductivity. A charge-sensitive preamplifier CPS10 developed by “FAST ComTec” was used in the spectrometric measurements to detect the charge pulses produced in the ZnSe sample by the absorbed X-rays from a point source \(^{57}\text{Co}\) (1.47 MBq).
The integration time of the CPS10 is 140 μs, and the gain is 1.4 V/pC. The estimated amplitude of the noise fluctuation in the output of the CPS10 was approximately ±5 mV. A digital scope Rigol DS2202 was used to control the output signal from the preamplifier. The CPS10 was directly connected to the analogue input of a Canberra DSA-1000 multichannel analyser. The digitised spectrometric data was transferred from the multichannel analyser to a PC through a USB interface. The spectrometric measurements were performed at different temperatures of the ZnSe sample from 20 °C to 130 °C (293-403 K).

3. Electrical properties of the undoped monocrystalline ZnSe samples

The conductivity of doped and undoped ZnSe samples has been studied for a long time [28, 32]. ZnSe can be easily doped with Al, Ga or In (shallow donors), which provide n-type conductivity in a wide temperature range above the liquid helium temperature. Undoped ZnSe with high optical quality has low intrinsic (dark) conductivity (as shown in Figure 2). The deep donors with high energy levels (ΔET) ranging from 0.9 eV to 1.1 eV within the band gap are responsible for this low intrinsic conductivity. These values of ΔET were found using the following relation:

\[ i_\text{D}(T) \sim e^{-\frac{\Delta E_T}{kT}} \]  

As shown in Figure 2, the dark current in ZnSe is about 200 pA at a temperature of 423 K (150 °C, 330 V/cm) and the estimated concentration of deep donors is approximately \(10^{13}\) cm\(^{-3}\). The specific resistance of the ZnSe sample is approximately \(10^{14}\) Ohm·cm at room temperature. These characteristics are better than those of wide-band gap semiconductors such as CdZnTe or GaAs [17, 18]. The maximal integrated current of induced XRC on the ZnSe samples is approximately 0.5 μA with utilizing an X-ray tube (20 kV/25 mA) and an applied electric field strength of 330 V/cm at room temperature; however, the induced XRC decreases with heating of the ZnSe sample up to 97 °C (370 K in Figure 3) and then slowly increases with the applied bias voltage. These measurements allow calculating the effective resistance of the ZnSe sample irradiated by X-rays: \(R_{XRC} = \frac{U_{bias}}{i_{XRC}}\). These dependences, measured at different values of the electric field strength, are shown in Figure 3. The increase of XRC at higher temperatures (or decrease of the sample resistance) does not depend on the
dark conductivity of ZnSe, because as shown in Figures 2 and 3, the dark current is much less than the current from XRC.

Fig. 2. The temperature dependence of the dark current of monocrystalline ZnSe for an electric field strength of 330 V/cm.

Fig. 3. The temperature dependence of the effective resistance of one ZnSe sample at X-ray irradiation for different electric field strengths: 30 V/cm (1), 160 V/cm (2) and 10^3 V/cm (3).

As shown in Figure 3, the temperature dependence of the XRC of ZnSe depends on the bias voltage applied. Because the radiation level of the X-ray tube was the same for each measurement, we can assume that the temperature dependence of the XRC can be explained through the increase in the lifetimes of the charge carriers generated in the crystal at greater temperatures, and this increase is enough to compensate for the decrease in the mobility of the charge carriers caused by scattering on the phonons. This phenomenon may be explained in two ways: 1) the significant decrease in the localisation time of the electrons and holes in the
deep traps at temperatures above 370 K [33] that also may depend on the electric field strength value due to Poole-Frenkel effect [34]; 2) the decrease in the probability of the recombination of free charge carriers with charge carriers localised in the traps. The volt-ampere characteristics (VACs) of the investigated ZnSe samples are not linear under X-ray irradiation. The VACs can be well approximated by a power function such as

\[ i_{\text{XRC}}(U) \sim U^\alpha \]

where \( U \) is the bias voltage and \( \alpha \) changes from 1.4 at 22 °C (295 K) to 1.08 at 134 °C (407 K). The degree of nonlinearity of the VACs depends on the type and concentration of the traps in the crystal [32, 34]. Figure 4 shows two VAC functions of one ZnSe sample measured at different temperatures and at the same X-ray tube radiation level. The VACs of the dark conductivity of ZnSe can only be measured accurately at high temperatures (above 350 K) and also has a nonlinear dependence on the bias voltage with power of \( \alpha \approx 1.12 \) (300 K) because of the Poole-Frenkel effect [34]. However, this effect is not dominant for the X-ray irradiation of ZnSe. The nonlinearity of the VACs for X-ray irradiation is greater at low temperatures; however, at these temperatures the traps become deeper [33], and at large enough irradiation levels, the filled deep traps can create an additional space charge in the crystal, especially in the electrical contact regions. This effect is partially confirmed by the slow increase in the XRC current of (~ 10 s) after beginning the irradiation with the X-ray tube, but this phenomenon needs additional investigation.

![Fig. 4. The VACs of one ZnSe sample measured at the same radiation level of X-ray tube and at the different temperatures: 22 °C (1) and 134 °C (2).](image)

Thus, the investigation into the X-ray induced conductivity of monocrystalline ZnSe samples shows that this semiconductor can be used as an integral X-ray sensor over a wide temperature range and that the benefit and advantage of ZnSe over widespread semiconductors such as Si or CZT is greater at higher temperatures.

4. Spectrometric properties of ZnSe at different temperatures

Investigation into the spectrometric properties of the ZnSe sample with bias voltages up to 1000 V (4000 V/cm) shows that ZnSe has a small charge collection efficiency, which is insufficient for reconstruction of the primary spectrum of the detected radiation but is
sufficient for radiometric measurements with effective noise discrimination in a wide
temperature range at least up to 130 °C. The amplitude spectra of the detector noise and X-
rays from the source $^{57}$Co measured at different temperatures in the range of 20 °C up to
130 °C are shown in Figures 5 and 6. The low energy threshold was approximately 25 keV
(channel 48).

![Image](image1.png)

Fig. 5. The amplitude spectra of the detector noise measured at temperatures of 20 °C (1) and
of 130 °C (2) and an electric field strength of 4000 V/cm.

![Image](image2.png)

Fig. 6. The amplitude spectra of X-rays from $^{57}$Co measured at temperatures of 20 °C (1),
55 °C (2), 92 °C (3) and 130 °C (4) and an electric field strength of 4000 V/cm. The noise
spectra measured separately were extracted.

The counting efficiency (the integral of the spectrum over all energy range) of ZnSe sample
for the detection of X-rays or noise was found to depend significantly on the bias voltage.
These dependences, measured at different temperatures, are shown in Figure 7 (X-ray
irradiation) and Figure 8 (noise measurements). A low energy threshold of approximately 35-
40 keV (channel 58) was used to filter the noise counts that is primarily concentrated in a restricted energy range up to this value.

Fig. 7. The dependence of the X-ray count rate (without noise) of one ZnSe sample on the electric field strength in the sample at different temperatures: 20 °C (1) and 130 °C (2). A $^{57}$Co source was used.

Fig. 8. The dependence of the noise count rate of one ZnSe sample on the electric field strength in the sample at different temperatures: 20 °C (1) and 130 °C (2).

As can be seen in Figures 5 and 8 the intensity of noise count rate depends appreciably not only on the temperature but also on the electric field strength that may be explained by high-frequency discharges in the crystal that create high amplitude noise pulses which are detected as a continuous spectrum (it is shown in Figure 5). As shown in Figures 7 and 8, there is a range of optimal values for the bias voltages of the ZnSe samples that minimise the influence of noise and simultaneously have a counting efficiency close to the maximum value. For the ZnSe sample explored, this range is 500 V (2000 V/cm) to 750 V (3000 V/cm) in the
temperature range from 20 °C to 130 °C. Under these conditions and with a low energy threshold of approximately 35-40 keV the noise count rate is about 10 cps. The dependence of the noise count rate for different values of the low energy threshold is shown in Figure 9 for different temperatures.

![Figure 9](image.png)

Fig. 9. The dependence of the noise count rate of one ZnSe sample on the low energy threshold at different temperatures of 20 °C (1) and 130 °C (2) and an electric field strength of 3200 V/cm.

As can be seen in Figure 7, at higher temperatures and for electric field strengths above 2000 V/cm, the counting efficiency is greater than at lower temperatures. This phenomenon may be caused by the deep traps in ZnSe. The localisation time for any charge trap decreases at higher temperatures [33] and may also depend on the electric field strength in the crystal caused by the Poole-Frenkel effect [34], which influences the charge collection efficiency for the charges generated by absorbed X-ray photons.

5. Conclusions

Temperature measurements of the dark conductivity of monocrystalline ZnSe samples show that specially undoped ZnSe has an extremely low dark conductivity of approximately 200 pA at the temperature of 150 °C (423 K, 330 V/cm), and the estimated concentration of deep donors is approximately $10^{13}$ cm$^{-3}$. Therefore, the specific resistance of the investigated ZnSe samples is approximately $10^{14}$ Ohm·cm at room temperature. These characteristics are better than those of wide-gap semiconductors such as CdZnTe or GaAs [17, 18]. Two methods for the measurement of X-rays were used to investigate the charge response of ZnSe under different conditions: the integral method and the pulse method (in spectrometric mode).Integral measurements with ZnSe of X-rays generated by an X-ray tube show that the volt-ampere characteristics depend on the temperature and can be easily calibrated with power functions. Spectrometric measurements of X-rays with a $^{57}$Co point source show that a range of optimal values for the bias voltages of the ZnSe samples allow the influence of the noise to be minimised and simultaneously give a counting efficiency close to the maximum measured value. For the ZnSe sample explored, this range is from 500 V (2000 V/cm) to 750 V (3000 V/cm) in a temperature range from 20 °C to 130 °C. Under these conditions and with a low
energy threshold of approximately 35-40 keV, the maximal noise count rate can be reduced to approximately 10 cps. The obtained results allow to assume that monocrystalline ZnSe can be effective used as a radiometric detector of gamma and X-ray radiation in a wide temperature range up to at least 130 °C.

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References