

# Preparation and Performance of CdZnTe Ray Detector

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## ABSTRACT

$\gamma$ -ray and x-ray detectors made by  $\text{Cd}_{1-x}\text{Zn}_x\text{Te}$  alloy can gain high energy resolution and detect efficiency at room temperature due to its high atomic number, large energy gap and high density, which were well-developed recently. By well controlled of Cadmium partial pressure and compensatory doping technique,  $\Phi 90$  mm  $\text{Cd}_{1-x}\text{Zn}_x\text{Te}$  alloy obtained successfully ( $\rho \geq 10^{11}$   $\Omega \cdot \text{cm}$ ) by an improved-Bridgman method.  $3 \text{ mm} \times 3 \text{ mm} \times 3 \text{ mm}$  CZT detector was made at Kunming Institute of Physics, which has energy resolution of 3.52% (FWHM) at room temperature when detect 59.54 KeV  $\text{Am}^{241}$   $\gamma$ -ray source.

## 1. Introduction

As a technical branch of experimental nuclear physics, X-ray detector plays an important role in the development of nuclear physics. With the development of national economy, science and technology, compound semiconductor detector can work at room temperature  $\gamma$  Nuclear radiation detector with high detection efficiency and good energy resolution can be used in various detectors and spectrometers in astronomy, medicine, industry, military and other fields [1-3].

Cadmium zinc telluride ( $\text{Cd}_{1-x}\text{Zn}_x\text{Te}$ ) crystal (hereinafter referred to as CZT when x value is not specifically referred to) is a new solid solution compound semiconductor developed from cadmium telluride (CdTe) crystal. CdTe as an X-ray and  $\gamma$  Ray detector materials has been widely studied since the 1970s. But its resistivity is too low to work at room temperature. Therefore, it is assumed that adding a certain amount of Zn into CdTe can contin-

uously adjust the lattice constant between 0.6100 nm ~ 0.6428 nm, so as to adjust the lattice constant, increase the band gap and improve the resistivity. At the same time, the introduction of Zn increases the lattice strength and stacking staggered energy, reduces the dislocation density and the possibility of forming twins, so as to make up for the deficiency of CdTe crystal performance, CdZnTe crystal was developed.

Cadmium zinc telluride ( $\text{Cd}_{1-x}\text{Zn}_x\text{Te}$ ) crystal is a new type of room temperature ternary compound semiconductor nuclear radiation detector material with excellent performance. It has high resistivity (about 1011  $\Omega/\text{cm}$ ), large atomic number (48, 30, 52), high density (about 6  $\text{G}/\text{cm}^3$ ) and large band gap width. With the different content of Zn, the band gap width changes continuously from 1.4 eV (near infrared) to 2.26 eV (green light). X-ray at room temperature  $\gamma$  The ray energy resolution is good, and its energy range is 10K eV-6m eV. Compared with CdTe,

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CD1 xznxte crystal has wider band gap, so it has higher resistivity than CdTe, smaller leakage current at room temperature and higher energy resolution, so it is more popular<sup>[4]</sup>.

## 2. CD1 Xznxte Crystal Growth

CdZnTe is a pseudo binary compound semiconductor material composed of CdTe and ZnTe. It has a sphalerite structure (as shown in Figures 1 and 2). The melting point varies from 1092 °C to 1295 °C due to the content of Zn. Due to the factors unfavorable to crystal growth such as high growth temperature, low thermal conductivity, strong ionic property and low stacking fault energy, it is difficult to grow CdZnTe crystal with good repeatability and high yield.

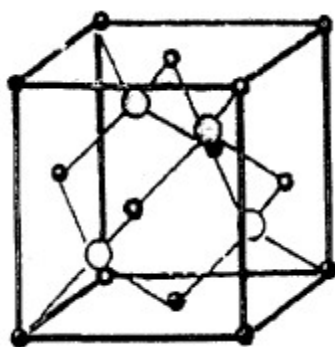


Figure 1. Structure of sphalerite

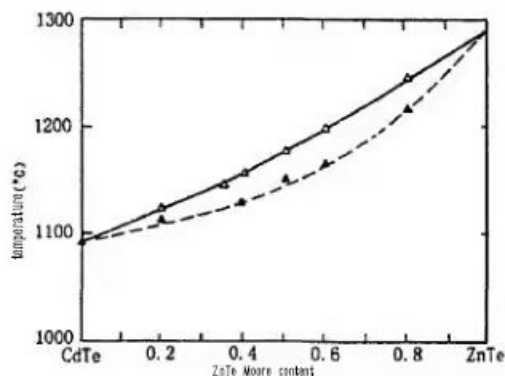


Figure 2. CZT pseudo binary phase diagram

At present, the commonly used methods include vertical gradient solidification method (VGFM), mobile heater method (THM), high pressure Bridgeman method (HPB), physical vapor transport (PVTM), horizontal Bridgeman method (HBM) and vertical Bridgeman method (VBM). The above methods have their own advantages and disadvantages<sup>[5]</sup>. At present, we mainly use the improved Bridgeman method to grow CZT crystals. It is a common melt growth method. Its growth process is actually a com-

pound melt composed of Cd, Te and Zn, which decreases slowly in a temperature field with a certain temperature gradient and crystallizes continuously due to local super-cooling nucleation.

For the ray detector, the material of the detector is required to have high resistivity (greater than 1010 Ω·cm) and small leakage current. The high Cd vacancy concentration in the crystal is the main reason for the reduction of infrared transmittance and resistivity. At the same time, the defect complex composed of vacancy, dislocation, Te deposition and impurities can play the role of donor or acceptor in the crystal, Affect its electrical properties and produce large leakage current<sup>[6,7]</sup>. In order to improve the photoelectric performance of materials, in order to improve the performance, we improve the purity of raw materials, strictly operate and reduce the pollution of foreign impurities in the process. The unique Cd pressure control technology, the optimization of preset seed crystal process and in-situ heat treatment technology are used to compensate doping (such as Cl doping). Appropriate wafer annealing can reduce the size and density of Te precipitation in the crystal. Specific measures are as follows:

(1) Additional Cd source growth to maintain the Cd vapor pressure balance of the growth system. The Cd vapor pressure near the growth temperature is obtained from the relationship between CD1 xznxte, alloy component partial pressure and component X, and the additional amount of Cd is obtained in combination with the ampoule volume.

(2) Slow growth and slow cooling reduce the possibility of Te inclusion or Te precipitation in the crystal. A slower growth rate and a lower interfacial temperature gradient are used to grow single crystals.

(3) Improve the purity of raw materials, strictly operate and reduce the pollution of foreign impurities in the process. The raw materials Cd, Zn and Te are further purified by secondary evaporation and zone dissolution process, and the purity can reach 7 N ~ 8 N. During synthesis, the temperature oscillates to eliminate the free gas in the melt. Finally, high purity CZT single crystal raw materials were obtained.

(4) Targeted compensation doping (such as Cl doping) can further improve the resistivity of crystal materials.

Now we have successfully grown the crystal diameter Φ 90 mm, resistivity ρ CD1 xznxte crystal ≥ 1011 Ω·cm. Infrared transmittance: > 60%, dislocation density: EPD < 1 × 10<sup>4</sup> cm<sup>-2</sup>. Half peak width of X-ray diffraction: FWHM: 10 ~ 20 arcsec. Inclusions and sedimentary facies: particles less than 10 μm and quantity less than 2 × 10<sup>4</sup> cm<sup>-2</sup>. The X-ray morphology image is uniform and the lattice structure is relatively complete.



Figure 3. Growing  $\Phi$  90mm CD1 xznxte crystal

### 3. Detector Preparation Process

The preparation process of CdZnTe detector is: material selection - wafer processing - electrode fabrication - passivation - packaging.

In the preparation process of CdZnTe detector, the leakage current is the main source of noise for the detector. The surface leakage current formed by the surface conductive layer and the influence of electrode injection or blocking on the bulk leakage current are two important problems that seriously reduce the detection efficiency<sup>[8]</sup>. In addition, the internal electric field distribution and the composite centers in the body and near the surface are the factors affecting the current collection efficiency and leakage current. Therefore, the preparation process of the detector needs to be optimized. The specific manufacturing process of the detector is as follows:

(1) Select the selected CdZnTe material according to the designed size (3 mm  $\times$  3 mm  $\times$  3 mm) physical cutting;

(2) SiC (9) for  $\mu\text{m}$ , 3  $\mu\text{m}$ ) After mechanical grinding of the abrasive, use diamond suspension (1  $\mu\text{m}$ ) Mechanical polishing;

(3) After polishing, the polished CZT wafer was chemically treated with 5% br + methanol (BM) and 2% br + 20% lactic acid + ethylene glycol (LB), and the corroded wafer was rinsed in methanol to remove the residual BR on the surface;

(4) Au electrodes were plated on both sides of the sample by magnetron sputtering;

(5) The non electrode sidewall of the sample was chemically passivated with koh-kcl and NHF/H<sub>2</sub>O<sub>2</sub> aqueous solution.

(6) Assemble the detector on the prepared ceramic base for packaging.

The purpose of corrosion is to make the crystal surface clean, uniform and high finish. To achieve these, we must

carefully select the type, concentration, corrosion time and temperature of the corrosion solution. Generally, br-ch30h solution is used for corrosion. After repeated experiments, the best corrosion condition of the wafer is determined as follows: use 5% bromomethyl alcohol solution as the corrosion solution and corrosion at 300 K for 30 s. When the wafer is corroded by bromomethanol for 30 seconds, the detector shows better I-V curve performance, and the resistivity of the detector is increased by 1-2 orders of magnitude compared with other corrosion times. This is because appropriate bromomethanol corrosion can remove the surface strain layer formed in the machining process and reduce the influence of surface defects and impurities. However, the corrosion solution is non-uniform corrosion, which will cause the deviation of stoichiometric ratio on the wafer surface (generally rich in TE). The interface layer can also form excessive leakage current in the device. For example, ch3chohco2h (lactic acid) + br-hoch2chzoh (ethylene glycol) corrosion solution can reduce this effect. After the wafer is corroded by bromine methanol, bromine removes the surface damage layer to make the surface smooth. If it is corroded again by lactic acid, the crystal surface will be more smooth. Further reduce the surface leakage current.

In the process of manufacturing semiconductor devices, it is inevitable to encounter the problem of metal semiconductor contact. Because semiconductor devices have to lead out electrodes or need to be connected with external circuits, even if the materials used have excellent properties, if there is no suitable contact, the performance of the device will be degraded. At least one of the two electrodes of the detector is designed to block contact, which can reduce leakage current and improve energy resolution. For high resistance materials, if the two electrodes are designed as ohmic contact, the response speed of the detector can be significantly improved, and the electrical performance test of high resistance materials is also inseparable from ohmic contact. Therefore, good ohmic contact is a necessary condition to ensure the normal operation of semiconductor devices.

We experimented with Au, in and C as contact materials, using the combination of c-czt-c, au-czt-au, au-czti-n and in CZT in, considering only from the work function,  $\Phi_{\text{In}} < \Phi_{\text{CZT}}, \Phi_{\text{Au}} > \Phi_{\text{CZT}}, \Phi_{\text{C}} > \Phi_{\text{CZT}}$ , c-czt-c and Au CZT Au can theoretically form single hole injection, Au CZT in is double injection or no injection, and in CZT in is single electron injection. From the I-V characteristics, single injection will form the space charge limiting current of  $i-v^2$  relationship. We first consider that as a p-type semiconductor, the metal with high work function is easy to form ohmic contact with it. Among Au, in and Al as electrode materials, AU

has the largest work function. Therefore, we use the method of vacuum evaporation of Au and appropriate diffusion treatment to form ohmic contact.

After CdZnTe surface is treated with absolute ethanol and bromine containing corrosive solution, it is difficult to obtain a fresh surface without oxidation. Improper surface treatment will also aggravate the surface oxidation, which will affect the performance, yield and reliability of the device. For the detector, it is required to strictly control the surface of the material, so that the surface has uniform chemical ratio, no crystal defects, little surface oxidation and other surface contamination. Various charged particles adsorbed on the semiconductor surface and movable ions, fixed charges, trap charges, etc. in the semiconductor surface oxide layer can lead to the formation of surface space charge region, so as to increase the surface leakage current, change the electric field distribution in the surface layer, reduce the performance and stability of the detector, and obtain a detector with good and stable performance, A stable passive film shall also be deposited on the wafer surface. We passivate the wafer made above with koh-kcl and NHF/H<sub>2</sub>O<sub>2</sub> aqueous solution to form a film with high resistivity on the wafer surface, which can effectively reduce the surface leakage current. At the same time, after forming a thin layer, it can effectively saturate the hanging bond on the wafer surface, so as to prevent surface pollution.

## 4. Performance Test

We tested the performance of the prepared CdZnTe detector in the following aspects:

### 4.1 Resistivity

According to the working principle of photoconductive device, two important factors affecting the performance of detector are material resistivity and trap concentration. The higher the resistivity of the detector material, the smaller the leakage current, and the lower the noise of the detector. Defects in the crystal will become carrier traps or recombination centers. Carrier traps will capture photogenerated carriers and form space charges, which will reduce the electric field intensity of the detector depletion layer and reduce the working stability of the detector. When the concentration of recombination center in the crystal is high, it will shorten the lifetime of photogenerated carriers, reduce the mobility Lifetime product of carriers, reduce the collection efficiency of photogenerated carriers, and reduce the energy resolution of the detector. And the performance of nuclear radiation detector becomes worse with the extension of time. Therefore, studying the electrical properties of CZT crystal and measuring

its resistivity and trap concentration are important experimental means to evaluate the properties of materials.

We use Keithley 8002a high resistance tester to test the resistance of CdZnTe detector, and its resistance is  $5.1 \times 10^{10} \Omega$ , the resistivity is 1.5 calculated according to the size of the detector  $\times 10^{11} \Omega \cdot \text{cm}$ .

### 4.2 I-V Characteristics

A good current voltage characteristic (I-V characteristic) is a necessary condition for a high-quality detector. The leakage current of the detector is the main source of its noise. It directly affects the energy resolution and sensitivity in ray measurement. It is one of the important parameters of the detector.

The leakage current of detectors prepared under different process conditions varies greatly. Under the condition of adding working bias voltage and avoiding light, the current flowing in the detector when no particles are incident is called the leakage current of the detector. There are three main sources of leakage current: body leakage current, diffusion leakage current and surface leakage current. I-V characteristic is a simple method to judge the preparation process and the quality of finished products. In the experiment, we first judge whether the surface treatment is successful according to the leakage current at room temperature. When the leakage current is small. Then it is judged by the straight line fitting of I-V characteristic curve good or bad contact.

In the process of making semiconductor devices, it is inevitable to encounter the problem of metal semiconductor contact<sup>[9-11]</sup>. If both electrodes are designed as ohmic contact, the response speed of the detector can be significantly improved, and the electrical performance test of high resistance materials is also inseparable from ohmic contact. It can be seen from the I-V test curve in Figure 4 that the CZT electrode made by this method realizes ohmic contact.

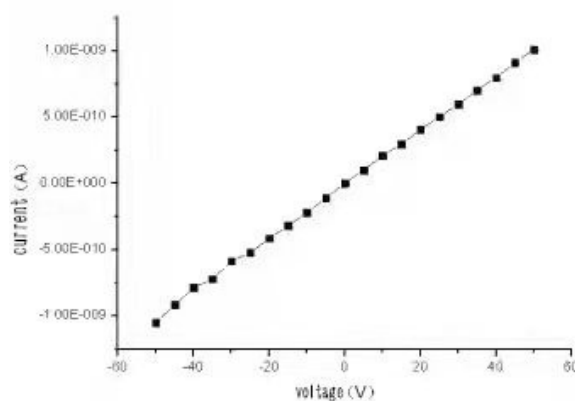


Figure 4. I-V characteristics under Au CZT Au contact

### 4.3 Energy Spectrum Response and Resolution

For an ideal detector, the pulse height generated by each X-ray with determined energy should be equal. For single energy rays, all pulse counts shall be on the same track number. In the actual detection process, the role of ray and crystal is more complex. Part of the incident photons do not exchange energy with the crystal completely, but directly pass through the detector; Some photons are scattered due to Compton effect; Some photons produce secondary radiation in the detector. These factors will increase the statistical fluctuation of the number of carriers produced by the ray, widen the spectral line of the energy spectrum and affect its resolution. In addition, the current fluctuation in the detector is also caused by the capture of carriers by traps and the recombination of electron hole pairs, which affects the resolution.

The resolution of the detector includes three aspects: spatial resolution, time resolution and energy resolution. Spatial resolution refers to the resolution of array multi-channel detector to spatial solid angle, which is usually expressed by linewidth that can distinguish a certain distance. In this study, only single channel detector is discussed, and the problem of spatial resolution is not involved. Time resolution refers to the time difference between two signals that the detector can distinguish. It requires the detector to have short response time and afterglow time.

Energy resolution is an important parameter to char-

acterize the performance of detector, which refers to the ability to separate spectral lines with similar energy. It is often measured by the half height width or relative linewidth of the spectral line. One definition method is to express the energy resolution by the ratio of the half height width of the spectral peak to the energy of the spectral peak. Namely  $ER = \frac{FWHM}{E_{peak}}$ .

DC coupled preamplifier with working bias voltage of 300V is adopted for am241  $\gamma$ . As shown in Figure 5, the main peak position of 59.54 keV is 250.42 channels, the half width of 59.54 keV peak is 8.83 channels, and  $FWHM = 2.10$  keV (resolution is 3.52%).

### 4.4 Polarization Effect and Stability

II-VI compound semiconductor materials are considered to be prone to polarization effect when making detectors. This effect is due to the internal electric field generated by the charge accumulated in the detector, which weakens the external electric field. With the extension of bias time, the resolution and detection efficiency of the detector gradually decrease<sup>[12,13]</sup>. We kept the detector working for a long time and observed the energy spectrum response after 2 hours. It was found that there was no obvious polarization effect and the detector worked stably. At the same time, we retested the same detector after being stored in an ordinary laboratory environment for 6 months, and its performance did not change significantly.

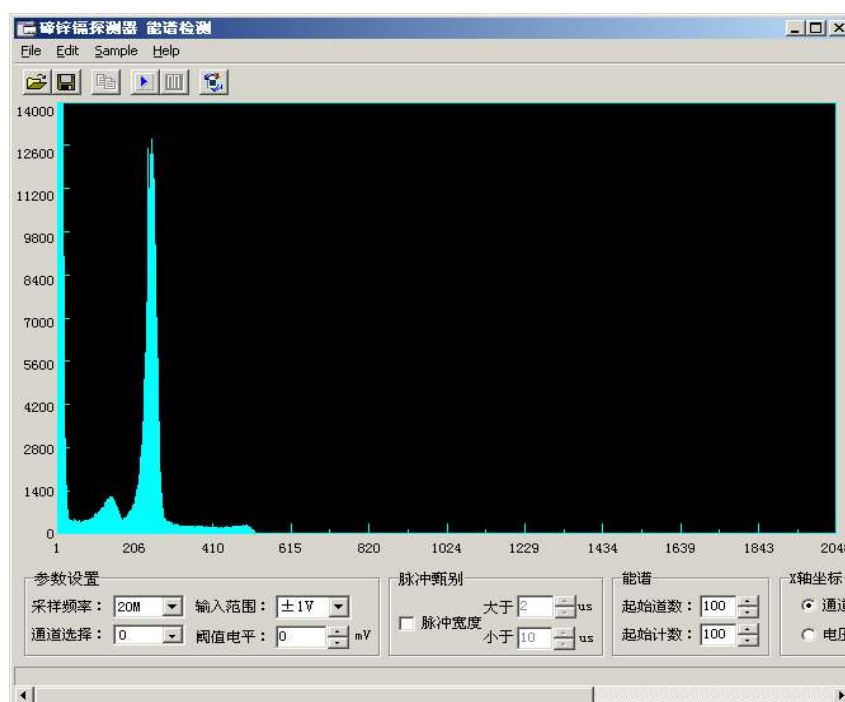


Figure 5. Energy spectrum response test of CZT detector to am241

## 5. Conclusions

CZT crystals were grown by improved Bridgman method. Large size CZT crystals were grown by using Cd pressure control technology, optimization of preset seed crystal process and in-situ heat treatment technology ( $\Phi$  90 mm), high resistivity ( $\rho \geq 1011 \Omega \cdot \text{cm}$ ). A ray detector with no polarization effect, stable performance and good energy spectrum resolution is prepared by using a unique detector preparation process. The test results show that the detector has met the requirements of practical application.

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