Preparation and characterizations of thallium bromide single crystal for room temperature radiation detector use

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Abstract

Thallium bromide (TlBr) crystal of 8-mm-diameter, preferentially oriented in [1 1 0] direction has been prepared using a melt-based method without mechanical vibrations. Analyses on the crystal quality and growth process were made based on characterizations of X-ray diffraction, rocking curve, ultraviolet absorption and transmittance spectrum. Most section of the crystal exhibits crystalline perfection and low stress, and its bandgap was calculated to be 2.88 eV. Influence of ampoule diameter on crystal quality has been discussed. Resistivity of the material was measured to be over 10^{10} \Omega cm. Spectroscopic response of the fabricated detectors to 241Am shows 59.5 keV peak with the resolution of 38.27%.

1. Introduction

The selection of detecting material is greatly crucial to the performances of the radiation detector. Thallium bromide (TlBr) single crystal is a type of compound semiconductor with wide bandgap, which enables it to work under room temperature with low-noise signal. Its high atomic number (Tl: 81, Br: 35) and high density (7.56 g/cm³) benefit it with high detection efficiency [1] and high stopping power [2]. Furthermore, owing to its simple cubic crystal structure (CsCl type) and relatively low melting point (460 °C), it is convenient to grow TlBr crystal by melt-based method. Defections and imperfections in the single crystal may degrade performance of the detectors. Therefore, single crystal for detector use should be of low stress and crystalline perfection.

On account of the excellent physical attributes of TlBr crystal, it has been researched as a promising room temperature radiation detector material since 1990. Hitomi et al. [3,4] grew TlBr single crystal by traveling molten zone (TMZ) method. Owens et al. [5] utilized vertical Bridgman–Stockbarger method. They have also tried the hydrothermal method [6], but only small grains with the size 0.3–3 mm were obtained. The melt-based methods are relatively mature method [3–8], but mechanical vibrations due to movement of the heating element or the ampoule were inevitable in both the Bridgman method and the TMZ method, which may affect the crystal quality.

In the present work, an 8-mm-diameter TlBr single crystal, preferentially oriented in [1 1 0] direction, was prepared by a novel melt-based method with no mechanical vibrations. X-ray diffraction (XRD), X-ray rocking curve, ultraviolet (UV) transmission and UV absorption spectrum were used to characterize the crystal quality. To evaluate the crystal as radiation detector, resistivity and its spectroscopic response to the 241Am source have been measured.

2. Experimental procedure

2.1. Crystal growth and characterization

Three ampoules with inner diameters of 8, 10 and 15 mm were utilized, and their products were designated as P1, P2 and P3, respectively. The ampoules have been previously washed repeatedly with de-ionized water before use. Then, commercially...
available TlBr powder with purity over 98.5% was loaded in the ampoule. To avoid oxidation of the TlBr powder during the growth, the ampoules were vacuumized before they were sealed. The ampoule was loaded in the lower zone of a vertical single-zone pipe furnace that has a temperature profile with the shape of parabolic-like curve, as shown in Fig. 1. The temperature of material zone was first held at about 480–520 °C for 10 h. Then the temperature of furnace decreased with a cooling rate of 5 °C/h from 520 to 450 °C. Accordingly, the isothermal line of 460 °C, which is also the solid–liquid interface, elevated correspondingly as the set temperature value decreased, and the crystal grew gradually. Thus, mechanical motion of ampoule or heating element in Bridgman and TMZ methods was substituted. The average temperature gradient in the concerning zone, where the melt located, is 10–15 °C/cm. Then the temperature decreased by rate of 100 °C/h to room temperature. After the growth, the TlBr ingots could be separated easily with the ampoule.

To research the crystal quality and analyze factors in the growing course, ingots were sliced using a hacksaw with carborundum daubing, as shown in Fig. 2. Followed are careful surface treatments to flat the wafer surface. Abrasives of 5 μm in diameter and then 1 μm were used to polish physical defects. After that, wafers were etched in H₂O₂–HBr mixture for 1.5 min, followed by rinsed in ethanol. X-ray diffraction patterns and rocking curves were measured by a BRUKER AXS D8ADVANCE X-ray diffractometer. UV transmission and UV absorption spectrum were tested on the Lambda 35 ultraviolet–visible spectrophotometer.

2.2. Detector fabrication and characterization

The surface quality of the wafer affects the detector performance crucially, so the wafers were polished mechanically and...
chemically for the second time before detector fabrication. Platinum (Pt) electrodes of about 100 μm thickness were deposited by magnetron sputtering method on two sides of wafers of P1-1, P1-2, P1-3 and P1-4. Then aluminum wires were attached to the electrodes by silver conductive adhesive. The resulting devices were mounted on ceramic substrates. Measurements of the resistivity and spectroscopic performances were all taken under room temperature.

Resistance of the detectors was tested in a dark chamber using a KEITHLEY 6487 picoammeter/voltage source. The spectroscopic performances of the detectors were evaluated using conventional nuclear instruments, including an AC-coupled charge-sensitive preamplifier, an ORTEC linear amplifier and a multichannel analyzer. The final signals were sent to an oscillograph and a computer. The detectors were irradiated from cathode with a 241Am source for 300 s and the distance between the source and the detector was about 4 cm. The detectors were placed in an aluminum box to reduce electromagnetic interference in the environment while radiation detecting.

3. Results and discussion

3.1. General appearance observation

P1 was considered to be the ingot with the best crystal quality by comparing the appearances of P1, P2 and P3, as shown in Fig. 2. P1 is greenish yellow in color and of good transparency in the majority section. The isometric diameter part has a length of 10 mm and diameter of 8 mm, while the conical part is 20 mm in length as shaped by the ampoule. Owing to high viscosity of TlBr melt, bubbles were trapped in the beginning section of the conical part. The end section of P1 has an approximately flat surface and it is black and opaque, which shows the segregation of most impurities, consistent with the literature [9]. P2 and P3 show worse quality than P1, revealing opaque appearance, as well as surfaces concave to the air.

3.2. X-ray diffraction analysis

Fig. 3 presents the X-ray diffraction patterns of wafers (P1-1–P1-4) sliced from P1. For the four wafers, diffraction peaks of (110) plain are of the highest intensity, indicating that most part of the P1 sample is single crystal that preferentially orients in the [110] direction. The secondary diffraction peak of (110) plain, the (2 2 0) peak, is observed in the patterns, illustrating crystalline perfection of the crystal. Diffraction peaks of other planes, such as (210) and (211) planes, also can be observed with minor intensity, which explains the presence of some small crystal grains with different orientations in the sample.

The analyses above give a conclusion that large section of P1 ingot is single crystalline form oriented in [110] direction and with crystalline perfection. But there are some small crystal grains oriented in other direction existing in the ingot.

3.3. Rocking curve discussion

X-ray rocking curves of (110) plane for P1-1–P1-4 were measured, as shown in Fig. 4. Curves in Fig. 4a and b have
multi-peaks and relatively small full-width at half-maximum (FWHM) value, which indicate sub-crystalline structure and relatively less strains. While in Fig. 4c and d, the curves are single-peak forms with relatively larger FWHM, explaining low stress in the crystal [10].

The analyses of rocking curves and XRD patterns show that P1-3 and -4 have single crystalline form with crystalline perfection and better crystal quality of relatively low stress. They also demonstrate that in the growth process, crystallization begins from bottom tip of the ampoule orienting in the [110] direction. In the growth process, on account of segregation, impurities are accumulated to the end of the melt. Impurities may effectively reduce potential barrier of nucleation. Thus, additional nuclei based on impurities, which act as crystallization points are easy to form and sub-crystalline structures appeared. With stress releasing in the grain, new crystalline orientations appeared. Finally, a single crystal with sub-crystalline phase and impurities in the end section and has been acquired.

3.4. UV absorption and UV transmittance spectrum

The UV absorption and transmittance spectra of P1 wafers are shown in Fig. 5. In the transmission region of both the absorption and transmittance spectrum, it is obvious that P1-3 and -4 show better optical transmittance. Slight red shift due to impurities of wafers P1-1, P1-2 can be observed in the transmittance spectra. These indicate that end section of the ingot (P1-3 and -4) have higher pureness, coinciding with the XRD and X-ray rocking curve analysis that purer material insures better crystal quality.
The absorption edge of P1-3 is found to be at 431 nm in the absorption spectra shown in Fig. 4b. According to the equation $E_g = \frac{hc}{\lambda_0}$, bandgap of the TlBr crystal can be calculated to be approximately 2.88 eV.

3.5. Influence of ampoule diameter on crystal quality

The diameter of the ampoules is an important factor to the crystal quality, for it works on the heat conducting manner. This factor is researched by comparing appearances and XRD patterns of P1, P2 and P3. As described above, P1 has the best crystal quality, and also shows a black and flat-surface end section. Its ampoule inner diameter is 8 mm, which is smaller than other samples (10 and 15 mm).

Heat transportation drives crystal growth in a melt system. Under the growing temperature of TlBr crystal (460 °C), heat transportation is mainly by means of conducting. The flat end surface of P1 explains an axial heat conducting mechanism. Small ampoule diameter makes it easier to keep axial heat conducting rather than to lose heat in radial direction. Hence, crystal growth will orient in accordance with the grown crystal, instead of forming new nuclei on wall of the ampoule. Thus, it is crucial for single crystal growth that heat conducts only along the vertical axial direction and smaller ampoule diameter assures better crystal quality.

Moreover, while the crystal is growing, most impurity atoms are excluded from the TlBr crystal lattice. Therefore, impurities accumulated to the end of the melt, forming a black and opaque end of the sample. The purification effect is extremely distinct for impurities whose segregation coefficient is much smaller than 1 [9]. Thus, impurities are driven to the end of the ingot, and a black and opaque end formed as shown in Fig. 2.

3.6. Detector performance

The resistivities of the wafers were obtained by testing the currents of the detectors in a dark chamber under various bias voltages at room temperature. The voltage–current characteristic curves of the wafers are linear, and the resistivity of the crystal was calculated to be over $10^{10}\Omega \cdot \text{cm}$.

The detectors made from wafers of P1-2, P1-3 and P1-4 show signals resulted from radiation on the oscillograph. Nevertheless, only detector made from P1-4 (about 7 mm in diameter, and 700 μm in thickness) shows spectrum after the process of multichannel analyzer, as shown in Fig. 6a. For the $^{241}\text{Am}$ spectrum obtained from the prepared TlBr detector, a 59.5 keV peak can be seen with a relative resolution of 38.27% (FWHM=49.88 channels). The peaks of 11.9, 13.9, 17.8, 20.8 and 26.4 keV are mixed in the noise signal.

In Fig. 6b, a commercial CdZnTe detector's spectrum for $^{241}\text{Am}$ under the same test condition was also given for comparison. Better resolution of 9.47% for 59.5 keV and peak of 26.4 keV can be found. Oliveira et al. made TlBr detector with energy resolution of 27% for 59.5 keV peak under $^{241}\text{Am}$ radiation at room temperature [11]. The relatively worse resolution of the present detector made from P1-4 can be attributed to poor charge collection and hole trapping [6].

No signals can be found for detector made from P1-1 on the oscillograph, because it shows lower purity and worse crystal quality than any other sample. Although P1-2 and -3 show signals on the oscillograph when irradiated, no spectrum can be formed after process of the multichannel analyzer. The possible reason is that their count rates are not large enough to be acquired by the multichannel analyzer. In addition, the surface process may probably influence the detector performance.

Thus, the spectrum of prepared TlBr detector proves out that the crystal growth method utilized in the present work is feasible.
to obtain single crystal for room temperature radiation detector. But, the relatively larger resolution also suggests that efforts on enhancing the single crystal quality such as improving the temperature field, better temperature controlling and annealing process should be made in the future researches.

4. Conclusion

TlBr single crystal samples for radiation detector use are prepared by a low cost melt method without mechanical vibrations during the growth process. X-ray diffraction, rocking curve, UV absorption and transmittance spectrum are used to characterize the quality of acquired samples. Crystal with the best quality shows good transparency and uniform color of greenish yellow in appearance. Other characterizations illustrate its crystalline perfection and low stress. Bandgap calculated from the absorption edge is 2.88 eV. UV transmission spectra showed in accordance with the XRD and rocking curve analysis that purer section has better crystal quality. Ampoule with small inner diameter tends to yield crystal with good crystal quality.

Resistance of the single crystal was measured to be over $10^{10}\ \Omega\ \text{cm}$. The Obtained $^{241}\text{Am}$ spectrum of the TlBr detector shows 59.5 keV peak with resolution of 38.27%. Thus, feasibility of this method to grow TlBr single crystal for room temperature radiation detector was proved. Nevertheless, some key parameters in crystal growth process, such as temperature field, temperature controlling and annealing should be improved in future researches.

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References