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Growth of PBI_2 single crystals from stoichiometric and Pb excess melts

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Abstract

We have successfully grown high-purity and -quality PbI_2 single crystals by the vertical Bridgman method. The rocking curves of four-crystal X-ray diffraction (XRD) show 120 arcsec in full-width at half-maximum (FWHM). The photoluminescence (PL) spectra at 7.8 K show the resolved intensive exciton emission line and the weak DAP emission band. The deep-level emissions are not observed. The measurement of the electrical and radiographic properties show that Leadiodide (PbI_2) single crystal has a resistivity of $5 \times 10^{10}\,\Omega\,cm$ and imager lag is 8 s, respectively. In order to improve the controllability of crystal growth, PbI_2 single crystals were also grown from a lead (Pb) excess PbI_2 source. The experimental results show very good reproducibility. In addition, the growth models of crystal are proposed, and the growth mechanism is discussed.

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1. Introduction

Lead iodide (PbI_2) is a potential material for fabricating X-ray and γ-ray detectors operating at room temperature due to its high atomic number ($Z_{Pb} = 82$, $Z_I = 53$), wide-band gap energy (2.4 eV) and high density ($D = 6.2\,g/cm^3$) [1,2]. However, there are some remaining problems to solve. The two main problems are low mobility of charge carriers and image lag property. These disadvantages are thought to be related to residual impurities, structural defects and their interaction during crystal growth [3]. Since the purity and crystallinity determine the performance of a detector, it is important to purify PbI_2 material and to prepare high-quality PbI_2 single crystal.

In our previous study [4], in order to prepare high-purity PbI_2 single crystals, the starting material, iodine (I), has been purified by the sublimation method, and the PbI_2 polycrystal has been purified by the normal freezing method. The purification effect of these methods has been confirmed by evaluating the impurity concentration in the ingot by glow discharge mass spectrometry (GDMS) analysis. In the present study, high-purity and -quality PbI_2 single crystals are grown using the above purified PbI_2 by the vertical Bridgman method. In order to improve the reproducibility of crystal growth, PbI_2 single crystals were also grown from a lead (Pb) excess PbI_2 source. The grown PbI_2 single crystal is evaluated with X-ray diffraction (XRD), low-temperature photoluminescence (PL) spectra, current–voltage (I–V) characteristics and radiographic properties. In addition, the growth mechanism of crystal is discussed.

2. Experimental procedure

In order to grow high-purity PbI_2 single crystals, quartz tubes with an inner -diameter of 12 mm were carefully cleaned [5]. After the quartz tube was shaped by H_2–O_2 flame, the shaped ampoule was vacuum-baked at 1373 K for 20 h. We have proved that the commercially available PbI_2 is unsuitable for growing high-purity crystal [4]. In the present study, the purified PbI_2 polycrystal is used as starting material. About 20 g PbI_2 was charged into the

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ampoule, which was then sealed in vacuum. Two kinds of starting materials were used to grow PbI_2 single crystals. One is purified PbI_2 by the normal freezing method, another is Pb-excess purified PbI_2. The amount of Pb excess is in the range of 3–5 g.

All PbI_2 single crystals were grown by the unseeded vertical Bridgman method. The ampoule charged with PbI_2 was directly raised to 693 K, and kept there for more than 20 h in order to guarantee complete melting, homogenization and breaking of possible melt complexes; then the ampoule was descended at a rate of 2.0 mm/h. The temperature gradient near the interface where the PbI_2 crystal started solidifying was 5 K/cm. The grown PbI_2 ingot crystals were cleaved into wafers for the characterization.

The PbI_2 shows many crystal structures and the most common structures are 2 H and 4 H [6]. These crystals with different structures show differences in XRD peak positions and in PL spectra [7]. In order to determine the crystal structure of grown PbI_2 crystal, an XRD pattern was measured using Philips X'pert. In order to evaluate the crystal quality, the rocking curve was measured with four-crystal XRD using a PHILIPS MRD 1880/HR apparatus having 3 kW Cu radiation source. PL spectra were measured at 7.8 K under excitation by the 325 nm line from a He–Cd laser. The sample was mounted on a holder in a strain-free manner, and the spectra were dispersed with a 1 m spectrometer and detected by a thermoelectrically cooled MOS image sensor. The whole system was controlled by a computer, which also served for data displaying, analysis and storage. All samples were measured on the cleaved surface (0 0 1) without any surface treatment.

In order to measure the electrical properties, an electrode with an outer diameter of 4 mm and thickness of 30 nm, and a gate electrode with an outer-diameter of 12 mm, inner-diameter of 11 mm and thickness of 30 nm were deposited on the PbI_2 wafer surface. Chromium (Cr) was employed as the electrode material. *I–V* characteristics were measured using Pico-Ampere meter (6487 type) made by KEITHLEY Co. Ltd. The radiographic properties were measured using an X-ray source from an X-ray generator made by Hamamatsu Photonics Co. Ltd.

3. Results and discussion

Fig. 1 represents the photographs of PbI_2 crystals grown by the vertical Bridgman method using purified PbI_2 in our laboratory [4]. Fig. 1(a) shows PbI_2 crystal in the growth ampoule, and Fig. 1(b) shows a PbI_2 wafer cleaved along the (0 0 1) plane. PbI_2 ingot in Fig. 1(a) appears to be translucent, with a reddish orange color. Its surface is smooth and the structural defects such as precipitates, inclusions, lamella-shaped twins and micro-twins cannot be observed. In order to evaluate the crystal, the wafer is cleaved from PbI_2 ingot along the (0 0 1) plane shown in Fig. 1(b). The cleaved plane shows a transparent mirror surface.

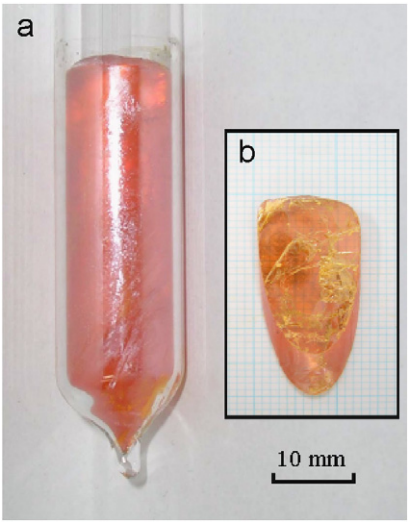

Fig. 1. Photographs of PbI_2 single crystals grown by vertical Bridgman method. (a) PbI_2 single crystal in growth ampoule; (b) PbI_2 wafer cleaved along (0 0 1) direction.

In order to determine the crystal structure and to evaluate the crystal quality of grown PbI_2, XRD and rocking curve were measured, and the results are shown in Fig. 2. The XRD spectrum shown in Fig. 2(a) demonstrates that the grown PbI_2 crystal is a single crystal, and it has the hexagonal crystalline pattern with a 2 H type crystal structure. Fig. 2(b) shows the rocking curve of the (0 0 1) diffraction peak from PbI_2 wafer. Its full-width-at-half-maximum (FWHM) is 120 arcsec. To our knowledge, this is the first time we report the FWHM value of PbI_2 single crystal.

Fig. 3 shows the PL spectra measured at 7.8 K on the cleavage (0 0 1) plane. Two main emission peaks can be observed. One is located at 2.495 eV and the other at 2.420 eV. The peak at 2.495 eV has been identified to be exciton (EX) emission by its reflective spectrum shown in the inset. Another peak at 2.420 eV can be attributed to the donor-acceptor pair (DAP) emission [8]. On the other hand, we do not observe any peaks in the deep emission region below 2.3 eV. This suggests that the PbI_2 single crystal grown in the present study has a high quality.

The dark current is an important parameter for X-ray detectors. Therefore, we prepared an X-ray detector using grown PbI_2 single crystal and measured its characteristics of dark *I–V*. Fig. 4(a) represents the results of the dark current as a function of the applied bias voltage. This detector shows a less than 15 pA/mm^2 dark current in the measured bias range where we obtained higher than 14.3 $mC/R/cm^2$ sensitivity. The resistivity value is $5 \times 10^{10}\,\Omega$ cm. Meanwhile, we also measured the radiographic properties of this detector. The measured condition is that the current density decreases to 1% of the applied value after the X-ray stops radiating the sample. The measured result shows an image lag of 8 s shown in Fig. 4(b). Although the above