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BiI_3 single crystal for room-temperature gamma ray detectors

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ABSTRACT

BiI_3 single crystals were grown by the physical vapor transport method. The repeated sublimation of the starting material reduced impurities in the BiI_3 single crystal to sub-ppm levels. The detector was fabricated by depositing Au electrodes on both surfaces of the 100-μm-thick BiI_3 single crystal platelet. The resistivity of the BiI_3 single crystal was increased by post-annealing in an iodine atmosphere ($\rho = 1.6 \times 10^{11}\ \Omega$ cm). Pulse height spectroscopy measurements showed clear peaks in the energy spectrum of alpha particles or gamma rays. It was estimated that the mobility-lifetime product was $\mu_e\tau_e = 3.4\text{–}8.5 \times 10^{-6}$ cm^2/V and the electron–hole pair creation energy was 5.8 eV. Our results show that BiI_3 single crystals are promising candidates for detectors used in radiographic imaging or gamma ray spectroscopy.

1. Introduction

Radiation detectors, which can be classified as indirect conversion [1] and direct conversion [2] detectors, are widely used in medical, industrial, and astronomical applications. Indirect conversion detectors consist of a scintillation material coupled to the photodetector. The scintillation material absorbs the radiation and converts it into light, which is then detected and converted into an electrical signal by the photodetector. Direct conversion detectors use a semiconductor material, which absorbs the radiation and creates electron–hole pairs (carriers) depending on the absorbed energy. The electrical signal is then produced by moving these carriers toward the electrodes with the electric field applied by the external bias voltage circuit. Direct conversion detectors are more sensitive than indirect conversion detectors because the conversion efficiency, which means the ratio of the electrical signal to the absorbed radiation energy, is an order of magnitude higher than that of indirect detectors [3]. In addition, direct conversion does not suffer from light spread or scattering, which decreases the spatial resolution of the detector used in radiographic imaging. Several materials, such as CdTe, CdZnTe, TlBr, HgI_2, PbI_2, and BiI_3 have been investigated as semiconductor materials for room temperature radiation detectors [2,4,5]. Heavy metal iodides are considered promising materials because of their high atomic number and density, which makes them suitable for absorbing radiation [6]. BiI_3 is a semiconductor with an indirect band gap of 1.67 ± 0.09 eV [7] and a density of 5.8 g/cm^3, which are similar values to the other two heavy metal iodides [5]. BiI_3 is easy to use and handle because it does not contain toxic elements such as mercury or lead. However, the detection properties of BiI_3 single crystals reported previously [8–15] were inferior to those of HgI_2 [16] or PbI_2 [17]. For example, the BiI_3 single crystal grown by the physical vapor transport (PVT) method showed a response to an ^{241}Am radioactive source in the integral mode. However, it was not spectroscopic grade and the energy spectrum of ^{241}Am radioactive source could not be obtained because of problems with the charge transport in the crystal [12]. Although alpha particles from ^{241}Am radioactive source were detected and their energy spectrum was reported by using single crystals grown with the Bridgman method [9,10,13–15], the resistivity of crystals was lower than that of the PVT crystal [12] and gamma ray detection and energy spectra were not obtained. The number of electron–hole pairs created in the semiconductor for gamma ray detection is less than that for alpha particle detection because the energy of gamma rays is smaller than that of alpha particles. Therefore, gamma ray detection is more sensitive to crystal properties such as the dark current and charge transport. It is necessary to improve the crystal properties to achieve gamma ray detection. In this paper, we report the improvement of the properties of the BiI_3 single crystal by post-annealing in an iodine atmosphere and discuss its response to alpha particles and gamma rays.

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2. Experimental details

We used commercial BiI_3 powder (99.99%) as a starting material and purified it by repeated sublimation. BiI_3 powder (5 g) was placed in a quartz ampoule with a diameter of 10 mm, evacuated to less than 2.0×10^{-3} Pa, and sealed at a length of 250 mm. The ampoule was then heated at 350 °C in a horizontal tube furnace (Fig. 1). The BiI_3 powder sublimated, moved to the low-temperature side of the ampoule, and deposited on the ampoule wall at the end of the furnace, where the temperature gradient dropped sharply. The deposited BiI_3 was collected and this purification procedure was repeated twice before starting the single crystal growth process.

The purified BiI_3 (1 g) was placed in a quartz ampoule and it was sealed in the same way as for the purification, except that the ampoule was filled with argon gas at 60 kPa before sealing; the pressure of argon in the ampoule aids large crystal growth [11]. The ampoule was heated in the horizontal tube furnace and single crystal growth by the PVT method was carried out at a source temperature of 380 °C and a growth time of 120 h. Several single crystals were grown in the ampoule at the temperature of 200–250 °C. The crystals were hexagonal platelets, with sides 2–5 mm long and thicknesses of 25–150 μm.

Subsequently, a single crystal was annealed in an iodine atmosphere. A quartz ampoule 10 mm in diameter, in which the single crystal and iodine (99.999%, 70 mg) were placed, was evacuated to a pressure of 5.0×10^{-3} Pa and sealed at a length of 150 mm. The ampoule was heated in a muffle furnace at 150 °C for 2 h.

Au electrodes 1.5 mm in diameter and 50 nm thick were deposited on both sides of the single crystal (*c*-plane of the BiI_3 single crystal) by vacuum evaporation. Au wires with a diameter of 50 μm were attached to both electrodes with graphite paste and the detector was fabricated (Fig. 2).

The resistivity of the detector was measured by using an electrometer (6517A, Keithley). The response to alpha particles or gamma rays was measured by exposing the top electrode to ^{241}Am or ^{109}Cd radioactive source, respectively. The bottom electrode was positively biased by a DC bias supply (E6665, Clear Pulse). The pulse signals were amplified through a charge sensitive preamplifier (581K, Clear Pulse) and a shaping amplifier (4417, Clear Pulse), and they were analyzed by a multichannel analyzer (MCA8000, Amptek).

3. Results and discussion

The impurities in the commercial BiI_3 powder and the single crystal grown from purified BiI_3 analyzed by ICP-MS (Inductively Coupled Plasma Mass Spectrometry) are listed in Table 1. The repeated sublimation decreased the impurities to sub-ppm levels.

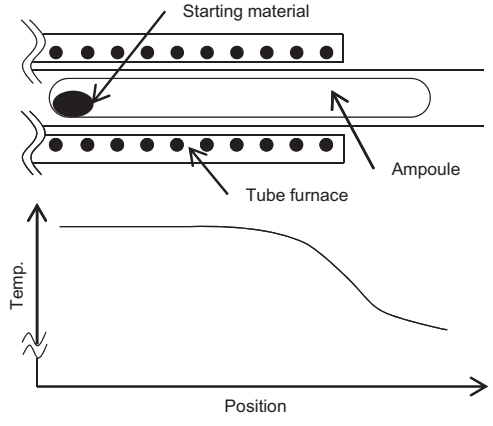

Fig. 1. Schematic diagrams of the horizontal tube furnace and its temperature gradient.

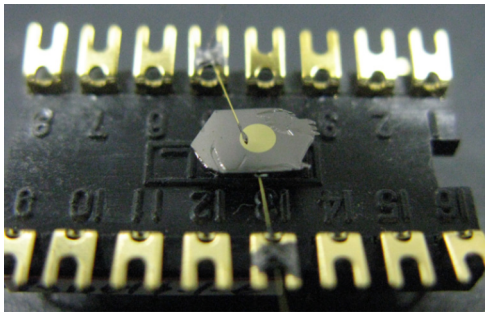

Fig. 2. BiI_3 detector connected with IC (Integrated Circuit) socket. Au electrodes 1.5 mm in diameter are deposited on both surfaces of the BiI_3 single crystal.

Table 1
Impurities in the commercial BiI3 powder and the single crystal grown from purified BiI3 powder analyzed by ICP-MS. The unit is ppm. <: under the detection limit, NA: not analyzed.

	Na	Fe	Ni	Cu	Zn	Ag	Pb
Commercial powder	< 1	< 0.4	< 0.3	2.5	3.4	< 0.1	5.7
Single crystal	< 1	< 0.4	NA	< 0.2	< 0.5	NA	0.1

The I–V characteristics of the BiI_3 single crystal with a thickness of 100 μm annealed in an iodine atmosphere (sample A) and with a thickness of 25 μm without iodine annealing (sample B) are shown in Fig. 3(a) and (b). The resistivity for sample A was 1.6×10^{11} Ω cm and 3.4×10^{9} Ω cm for sample B.

Fig. 4 shows the energy spectrum of the alpha particles (^{241}Am radioactive source) obtained from sample A. A clear peak was observed around 480 ch at a bias of 10 V. However, sample B did not show any response at a bias of 5 V, even though the crystal was thinner than sample A. The heavy metal iodides suffer from the depletion of iodine because of the high vapor pressure of iodine [18]. We expect that iodine annealing fills the iodine vacancies, which improves the resistivity and the carrier transport properties of sample A.

Fig. 5(a) shows the pulse shape of the response to the alpha particles obtained from sample A at a bias of 10 V recorded by a digital oscilloscope connected to a charge-sensitive preamplifier. Assuming that the interaction depth of an incident photon is very close to the cathode and hole contribution is negligible, the charge collection efficiency (CCE) as a function of time without detrapping effects is given by Hecht relation [19]

$$\mathrm{CCE} \equiv \frac{Q_e(t)}{Q_0} = \begin{cases} \frac{\tau_e}{t_e}\left\{1-\exp\left(-\frac{t}{\tau_e}\right)\right\} & \text{if } t < \left(1-\frac{x}{L}\right)t_e \\ \frac{\tau_e}{t_e}\left\{1-\exp\left(-\left(1-\frac{x}{L}\right)\frac{t_e}{\tau_e}\right)\right\} & \text{if } t \geq \left(1-\frac{x}{L}\right)t_e \end{cases} \quad (1)$$

$$t_e = \frac{L}{\mu_e E} \quad (2)$$

where Q_0 is the total number of carriers created by an incident photon, τ_e is the lifetime of an electron, L is the sample thickness, x is the interaction depth from the cathode, t_e is the transit time of an electron for $x=0$, E is the electric field, and μ_e is the electron mobility. By fitting Eq. (1) to experimental data in Fig. 5(a), we obtained $\mu_e\tau_e = 8.5 \times 10^{-6}$ cm^2/V ($\mu_e = 17.0$ cm^2/V s, $\tau_e = 0.50$ μs) and CCE = 60% ($t = t_e$) in the case of $x = 0$ (Fig. 5(b)). However, the sample thickness of 100 μm may not be thick enough to approximate x as 0. The penetration depth of the alpha particle can be estimated from Bragg–Kleeman rule [20]

$$\frac{R_1}{R_2} = \frac{D_2}{D_1}\sqrt{\frac{A_1}{A_2}} \quad (3)$$