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Growth and properties of new ZnSe(Al,O,Te) semiconductor scintillator

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Abstract

The zinc selenide crystals were grown in graphite crucibles by Bridgman–Stockbarger method in vertical compression furnace under argon pressure of 5×10^6 Pa. The grown ZnSe(Al,O,Te) single crystals were annealed in a Zn vapor at 1290 K for 24 h. An X-ray diffractometer (XRD) was used to investigate the structural properties of the zinc selenide single crystals. The lattice constants of the ZnSe single crystals were obtained from XRD data. After annealing it in a Zn vapor at 1290 K, it is found that the lattice constant decreases. From the absorption spectra, the band gap energies of the ZnSe single crystals were calculated by a linear fitting process. The band gap energy of the ZnSe(Al,O,Te) single crystal decreases more than that of the ZnSe single crystal. The maximum wavelength of the radioluminescence of the ZnSe(Al,O,Te) scintillator excited by X-ray was 606 nm, which was well matched with the response wavelength of the Si photodiode. The energy resolution of the annealed ZnSe(Al,O,Te) scintillator was 13.9% when it was exposed to ^{137}Cs γ-ray. Its size was $10 \times 10 \times 1$ mm^3. The afterglow level of the annealed ZnSe(Al,O,Te) scintillator after 5 ms was 0.014%. The luminescence decay time of the annealed ZnSe(Al,O,Te) scintillator has two exponential components with 4 and 12 μs time constants. The charged particle and the low energy gamma ray can be detected successfully with the annealed ZnSe(Al,O,Te) scintillator. It was investigated that the ZnSe(Al,O,Te) scintillator can be used for the security inspection system.

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Keywords: ZnSe; Semiconductor scintillator; XRD; Pulse height spectrum; Afterglow

1. Introduction

A^{II}–B^{VI} compound semiconductor has various physical properties such as piezoelectricity, photo-electricity, luminescence, and scintillation. But single crystals of the A^{II}–B^{VI} compound semiconductors were not used as scintillator and radiation sensor because they have low transmittance and a recrystallization. But recently they can be used as the radiation sensor due to the advance of the single crystal growth technique (Lee et al., 2006; Schotanus et al., 1992).

Scintillators based on ZnSe crystals are not hygroscopic. Their light output is higher and afterglow level after 10 ms is lower than that of CsI(Tl) (Ryzhikov et al., 1993). Scintillators based on ZnSe crystals are quite acceptable for their use in X-ray introscopy detectors because their radiation stability is relatively good and their light output is higher than the oxide scintillators ($CdWO_4$, $Bi_4Ge_3O_{12}$, Gd_2SiO_5) used on similar purposes (Kwak et al., 2005; Ryzhikov et al., 2005).

The ZnSe scintillators based on the A^{II}–B^{VI} compound semiconductor doped with various activators were investigated (Ryzhikov et al., 2001a, b).

In our work, the ZnSe single crystals based on the A^{II}–B^{VI} compound semiconductors were grown by a modified Bridgman–Stockbarger technique. The doping and annealing effects of the ZnSe single crystal were observed and discussed. It was also investigated the physical and the scintillation properties of the ZnSe single crystals such as X-ray diffraction (XRD), transmittance, radioluminescence, afterglow, light output, pulse height spectrum, and decay time.

2. Experimental procedure

Doped and un-doped ZnSe single crystals were grown by a modified Bridgman–Stockbarger technique with a narrow zone

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heater in a vertical compression furnace under argon atmosphere. Graphite crucible was used. During growth, the inert gas pressure P of Ar was $\sim 5 \times 10^6$ Pa and the crystallization rate was $2 \sim 5$ mm/h. The raw materials were ZnSe polycrystals of 5 N offered by ELMA Inc. After growth, thermal treatment on the ZnSe crystal was carried out at 1290 K for 24 h in sealed quartz tube containing Zn vapor. In our study, the size of the ZnSe specimen was $10 \times 10 \times 1$ mm^3.

The crystal structures and lattice parameters of the single crystals were characterized by the XRD method using Cu Kα radiation (Rigaku, D/MAX 2100H, Japan).

The pulse height spectrum was measured with the gamma energy radioactive isotopes, ^{241}Am (59.6 keV) and ^{137}Cs (662 keV). The PMT R1307 (Hamamatsu) was used to measure the pulse height spectrum of the ZnSe(Al,O,Te) scintillator.

In order to obtain the decay time of the ZnSe(Al,O,Te) scintillator at room temperature, a pulsed Nd:YAG laser was employed as an excitation source. The repetition rate of the pulsed laser was 10 Hz with a 6 ns duration.

3. Result and discussion

Fig. 1 shows XRD patterns of un-doped and doped ZnSe crystals. It is found that ZnSe cross-section shows preferred orientation of (2 2 0) direction.

There are no new observable phases when doping and annealing in Zn condition; this means that doping and annealing do not change the cubic structure of ZnSe.

However, the doping and annealing in Zn condition have shifted the position of (2 2 0) peak. The lattice constant a of cubic structure ZnSe were calculated according to Bragg's Law

$$2d \sin\theta = m\lambda. \tag{1}$$

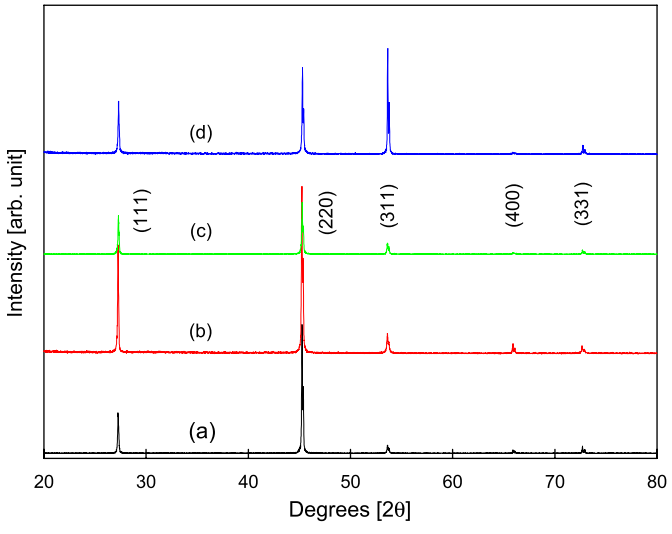

Fig. 1. XRD patterns of ZnSe single crystals (a) as-grown ZnSe(pure), (b) as-grown ZnSe(Al,O,Te), (c) annealed ZnSe(pure), and (d) annealed ZnSe(Al,O,Te).

Table 1
The lattice parameter a of as-grown and annealed ZnSe single crystals

	As-grown		Annealed	
	(2 2 0) peak (2θ)	a (Å)	(2 2 0) peak (2θ)	a (Å)
ZnSe(pure)	45.258	5.659	45.271	5.654
ZnSe(Al,O,Te)	45.244	5.662	45.305	5.651

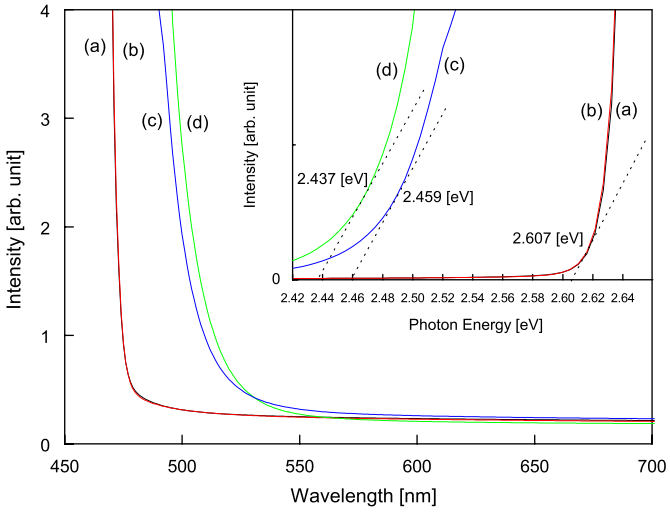

Fig. 2. Absorption spectra of ZnSe single crystals (a) as-grown ZnSe(pure), (b) annealed ZnSe(pure), (c) as grown ZnSe(Al,O,Te), and (d) annealed ZnSe(Al,O,Te).

For cubic structure of ZnSe, lattice constant a is given by

$$\frac{1}{d_{hkl}^2} = \frac{h^2 + k^2 + l^2}{a^2}, \tag{2}$$

where d is plane-spacing, λ is X-ray wavelength of 1.5405 Å. The calculated lattice constants a are listed in Table 1.

With the doped impurities (Al, O, Te), the lattice constant a was changed from 5.659 to 5.662 Å. With the annealing in Zn condition, the lattice constant a was changed insignificantly. When impurity is doped to ZnSe, impurities replaced the vacancies of Se, Zn ion or remained as an interstitial. When impurities are placed as an interstitial ion, the atoms can be rearranged and placed on the equilibrium state due to the Coulomb interaction between Zn^{2+} and Se^{2-} ions; so the lattice constant a will increase. However, after annealing, lattice constant a was decreased. Because the ion radius of O is 0.66 Å, which is smaller than that of Se ion, 1.14 Å, the inter-atomic distance of Zn–O will become shorter compared to the bonding length of Zn–Se. Al impurities follow the same mechanism. As a result, the lattice constant will decrease after annealing.

Fig. 2 shows the absorption spectra of the ZnSe and ZnSe(Al,O,Te) crystals by annealing. Assuming the absorption coefficient α corresponding to the direct band gap of the zinc blend structure, a plot of $[\alpha * (h\nu)]^2$ versus the photon energy $h\nu$ yields in the sharp absorption edge by linear fit.