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Optical and electrical properties of phosphorus-doped ZnMgTe bulk crystals grown by Bridgman method

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Phosphorus-doped $Zn_{1-x}Mg_xTe$ crystals with Mg concentration x of 0 to 0.33 have been grown by vertical Bridgman method. The lattice constant, transmissivity and band-gap energy as a function of x have been determined. The linear relation has been found between the lattice constant or band-gap energy and x. The number of precipitates in $Zn_{1-x}Mg_xTe$ single crystals seems to be less than that in ZnTe grown from VGF method. The p-type $Zn_{1-x}Mg_xTe$ ($x \le 0.19$) crystals with carrier concentration of ~10^{17} cm^{-3} were obtained independent of x.

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1 Introduction ZnTe shows a direct transition-type band gap of 2.26 eV at room temperature, and is expected to be as a useful material for purely green light emitting diodes (LED). We have already succeeded phosphorus (P) doped ZnTe of good quality by Bridgman method [1], which is simple and leads to low cost. By using these conductive p-type substrates, we have demonstrated purely green LED of ZnTe by means of thermal diffusion process of Al [2,3]. The ternary $Zn_{1-x}Mg_xTe$ mixed crystals are useful materials as a cladding layer and a transparent substrate for ZnTe based pure green LED, because they have wider band gap than ZnTe [4]. Therefore, it is significant to investigate growth and characterization of conductive p-type $Zn_{1-x}Mg_xTe$ crystals for improving the performance of the ZnTe LED. With respect to bulk growth of $Zn_{1-x}Mg_xTe$ crystals, several investigations have so far been carried out mainly using Bridgman technique [5–10]. However, there are only a few works [5,6] on P-doped $Zn_{1-x}Mg_xTe$ bulk crystals that are very important for fabricating ZnTe based LEDs. In the previous study [6], we have described the characterization of the P-doped $Zn_{1-x}Mg_xTe$ single crystals from Bridgman ingots by measuring composition Mg and photoluminescence spectra mainly that are an important step to realize ZnTe based LED with high performance. Furthermore, the specific contact resistance have been investigated for electroless Pd electrode, which acts an excellent ohmic contact for p-type ZnTe [11], in order to obtain reliable electrical properties for P-doped $Zn_{1-x}Mg_xTe$. As for the photoluminescence spectra at 4.2 K, P-doped $Zn_{1-x}Mg_xTe$ ($0 \le x \le 0.19$) crystals are characterized by a bound exciton emission due to neutral P acceptor and a P acceptor related free-to-bound transition emission. No significant deep emissions in the wavelength range longer than 580 nm were observed. The appearance of the excitonic emission indicates that the crystalline quality is good. Thus, P gives a useful dopant for preparing conductive p-type substrates, similar to the case of P-doped ZnTe [2]. Then further characterization should be done for the P-doped bulk crystals.

In this study, we focus mainly on the characterization of lattice constant, transmissivity and band-gap as a function of x which will provide fundamental data for considering lattice mismatch between

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$Zn_{1-x}Mg_xTe$ substrate and ZnTe epitaxial layer, the LED structure and so on. Furthermore, we describe precipitates and electrical properties of the P-doped $Zn_{1-x}Mg_xTe$ single crystals from Bridgman ingots as characterization of *p*-type substrates for epitaxial growth.

2 Experimental P-doped $Zn_{1-x}Mg_xTe$ crystals were grown by vertical Bridgman method. Te-rich growth condition was adopted with 5 at.% deviation from stoichiometry to decrease the melting point. As an dopant source, 0.02 at.% P was added into the sources. A pyrolitic boron nitride (pBN) crucible was employed to reduce the strong reaction of Mg with the quartz tube at high temperatures. The pBN crucible containing sources was doubly sealed in quartz ampoule at a vacuum level of 5×10^{-7} Torr. The details of the sealing process are described in the previous report [1,6]. The maximum temperature of the one-zone furnace was set to 1150 °C. The crystal growth was started with a downward rate of 25 mm/day. The temperature gradient around solid-liquid interface was about 10 °C/mm.

The grown P-doped $Zn_{1-x}Mg_xTe$ ingots were sliced into wafers and then lapped for optical and electrical characterizations. The composition of Mg was estimated by energy dispersive X-ray (EDX) analysis. The crystal structure and the lattice constant were determined by powder X-ray diffraction (XRD) analysis. The optical property was evaluated by measurement of transmissivity together with the cathodoluminescence (CL) measurement. The band-gap energy (E_g) was obtained from CL spectra at room temperature. Observation of the precipitates in grown crystals was performed by the optical microscope. The electrical properties were analyzed using AC Hall measurement system (TesiTest8300 (LN)). The Hall measurements were performed at room temperature. The electroless Pd plating was used as an electrode, which gives ohmic contact for measuring the electrical properties of P-doped $Zn_{1-x}Mg_xTe$ [6].

3 Results and discussion P-doped $Zn_{1-x}Mg_xTe$ crystals with the composition of Mg between 0 and 0.33 were successfully prepared by vertical Bridgman method. As described previously [6], it was confirmed that the crystal structure of all samples is zinc blend type from the powder XRD measurement. Figure 1 shows the Mg composition (x) dependence of the lattice constant (a) of zinc blend type P-doped $Zn_{1-x}Mg_xTe$ determined from the powder XRD measurement. Almost linear relationship between x and a is obtained, which indicates that Vegard's law is valid in this ternary alloy system. The variation of x with a is described by the proportional equation;

$$a = 6.1026 + 0.36\,x. \quad (1)$$

In Fig. 2, the transmissivity spectra of P-doped $Zn_{1-x}Mg_xTe$ wafer are shown for the various x. The transparent region is enlarged towards shorter wavelength side with increasing x, which is corresponding to the band-gap widening with increasing x. P-doped $Zn_{1-x}Mg_xTe$ wafer with at least more than $x = 0.1$ filter out pure green light (550 nm). Thus P-doped $Zn_{1-x}Mg_xTe$ ($x \geq 0.1$) wafers are expected to be effective in preventing a self-absorption effect as a transparent substrate for ZnTe based LED.

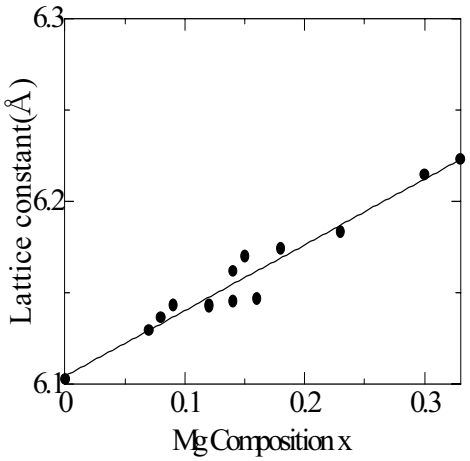

Fig. 1. Lattice constant of P-doped $Zn_{1-x}Mg_xTe$ as a function of Mg composition x.

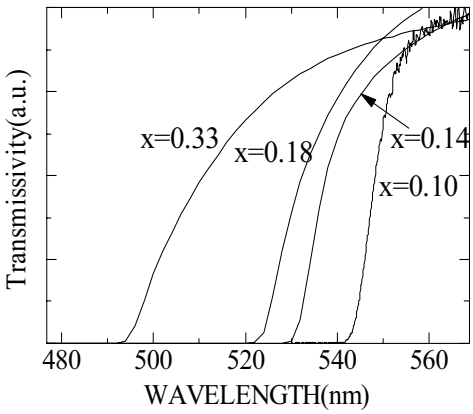

Fig. 2. Transmissivity spectra of P-doped $Zn_{1-x}Mg_xTe$ wafer.

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In Fig. 3, the room temperature CL spectra of P-doped $Zn_{1-x}Mg_xTe$ are shown for various x. The band edge emissions are clearly observed with no significant deep emissions. As the x increase, the emission peak shifts towards shorter wavelength side, which is due to the increase in E_g with increasing x.

Figure 4 shows the relationship between x and E_g of P-doped $Zn_{1-x}Mg_xTe$ estimated from the CL peak energy. As shown in the same figure, E_g linearly increases with increasing x. From a quadratic least-square fitting, band-gap bowing parameter of P-doped $Zn_{1-x}Mg_xTe$ ($x \leq 0.33$) is negligible and the linear variation can be described by the equation;

$$E_g = 2.26 + 0.96\,x \quad \text{(R.T.)}. \qquad (2)$$

The fact that two luminescence peaks, i.e. a bound exciton emission due to neutral P acceptor and a P acceptor related free-to bound transition emission, shifts towards shorter wavelength with increasing x [6] will be explained well by the behaviour of band gap energy on x.

Figure 5 shows the typical surface micrograph of P-doped $Zn_{1-x}Mg_xTe$ wafer observed by an optical microscope. It was pointed out that Te precipitates with a size of a few μm are introduced into the as-grown ZnTe crystals grown from the melt, e.g. the vertical gradient freezing (VGF) method [12,13], which is prevent the fabrication of the devices with high performance and reliability. For present as-grown P-doped $Zn_{1-x}Mg_xTe$ wafer, as shown in Fig. 5, the precipitates with a diameter of few μm are not almost observed. The number of the precipitates in P-doped $Zn_{1-x}Mg_xTe$ is much less than that in ZnTe grown from VGF method. Then we are able to prepare substrates of good quality for epitaxial growth.

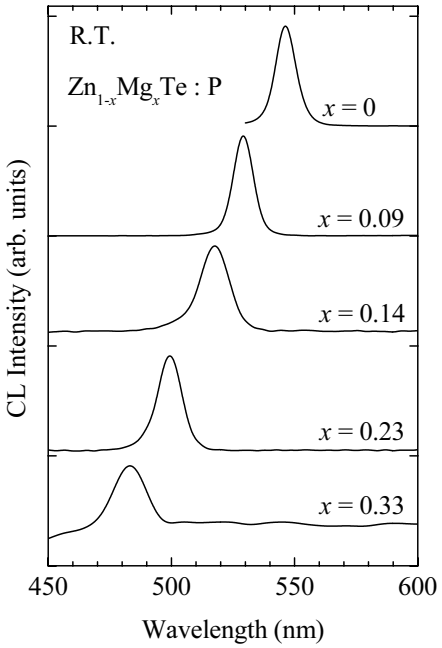

Fig. 3. CL spectra of P-doped $Zn_{1-x}Mg_xTe$ at room temperature.

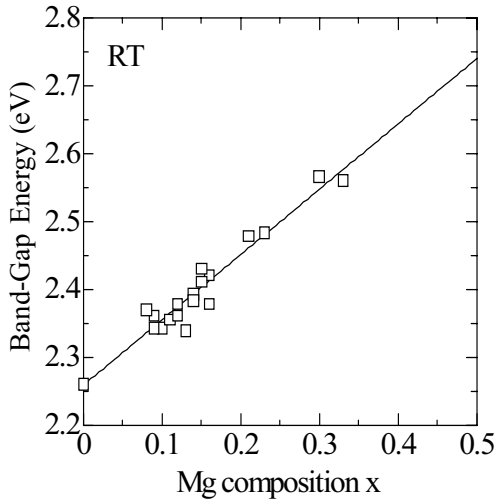

Fig. 4. Band-gap energy of P-doped $Zn_{1-x}Mg_xTe$ at room temperature as a function of Mg composition x.

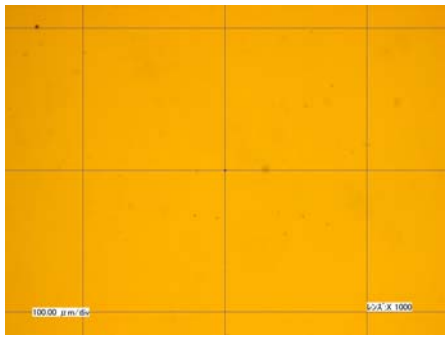

Fig. 5. Typical surface micrograph of P-doped $Zn_{1-x}Mg_xTe$ wafer.

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The Hall measurement was performed by the van der Pauw method with electroless Pd electrode. In Fig. 6, the carrier concentration and the resistivity of P-doped $Zn_{1-x}Mg_xTe$ at room temperature are plotted as a function of x. By the use of P as a dopant, conductive p-type $Zn_{1-x}Mg_xTe$ ($x \le 0.19$) crystals with carrier concentration of ~10^{17} cm^{-3} were obtained independent of x.

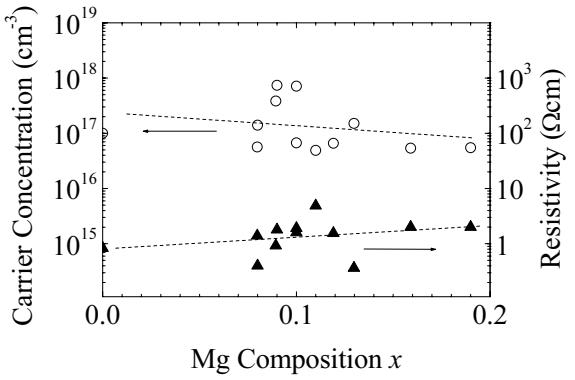

Fig. 6. Carrier concentration and resistivity of P-doped $Zn_{1-x}Mg_xTe$ at room temperature as a function of Mg composition x.

4 Conclusion Through this experiment, P-doped $Zn_{1-x}Mg_xTe$ crystals with Mg concentration x of 0 to 0.33 were successfully prepared by vertical Bridgman method. The lattice constant, transmissivity and band gap as a function of x have been determined. The linear relation was found between the lattice constant or band-gap energy and x. The number of the precipitates in P-doped $Zn_{1-x}Mg_xTe$ is much less than that in ZnTe grown from VGF method. The precipitates with a diameter of few μm are not almost observed. These mean usefulness as substrates of good quality for epitaxial growth. Conductive p-type $Zn_{1-x}Mg_xTe$ crystals for LED application were obtained. These results will pave the way for fabricating ZnTe based LED with high performance.

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