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Optical properties of three sectors in a zinc-oxide single crystal grown under hydrothermal process

Shigeaki Sugimura [a,*], Haruyuki Endo [b], Yasube Kashiwaba [b,c], Eiichi Sato [d]

[a] New Materials Department, Tokyo Denpa Co., Ltd, 82-5, Ueno, Ichinohe-aza, Ichinohe-machi, Ninohe-gun, Iwate 028-5312, Japan
[b] Iwate Industrial Research Institute, 3-35-2 Iiokashinden, Morioka, Iwate 020-0852, Japan
[c] Iwate University, 4-3-5 Ueda, Morioka, Iwate 020-8551, Japan
[d] Iwate Medical University, 2-1-1 Nishitokuta, Yahaba, Iwate 028-3694, Japan

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ABSTRACT

We evaluated photoluminescence, radioluminescence, transmittance, and decay time at room temperature at each sector of zinc oxide (ZnO) single crystals grown utilizing the hydrothermal process. The −c-sector wafer, grown on the oxygen face of the *c*-plane seed crystal, has a short decay time and a high light yield and shows properties different from those of other sectors. We also fabricated a radiation sensor by combining the −c-sector chip cut from a wafer and a multipixel photon counter (MPPC). X-rays were detected using sensor with high sensitivity. At room temperature, typical decay time for the −c sector at the near band edge was 700 ps, and the range of relative light yield was thirty- to forty-times larger than that of the +c sector. Therefore, the properties of the −c-sector wafer at the near band edge will be suitable for high-speed radiation sensors in the near future.

1. Introduction

Zinc oxide (ZnO) is a promising material because of its many attractive properties including a large exciton binding energy of 60 meV for light-emitting diodes (LEDs) [1,2], the same lattice structures for epitaxial substrates [3,4], high transparency in visible light for transparent electronics [5], high-sensitive ultraviolet (UV) sensors [6], fast scintillators with short decay times below 1 ns [7,8], and large piezoelectric-constant materials. Among these applications, the fast scintillator is the most expected applications for use in novel photon sensors or X-ray CT systems [9], and many researchers have been studying the optical properties of ZnO films [10], ceramics [11], and single crystals [12,13].

It is known that the light yield of pure ZnO is quite low [13]. However, the decay time is very short, and ZnO is an attractive material for making scintillation devices. Due to the relative ease of production, various studies on metal-doped ZnO ceramics have been carried out [14–16]. However, single crystals are suitable because of their high uniformity, high density, and high transparency.

In 1990, we developed an autoclave with a platinum (Pt) liner for producing quartz crystals with low impurity content and high crystallinity. By means of the unique hydrothermal process, we have been developing ZnO single crystals with low impurity content and high crystallinity for the past decade. Next, we succeeded in producing large-dimension ZnO single crystals for various applications in 2004 [17].

The multipixel photon counter (MPPC, Hamamatsu Photonics) is a high-sensitive photoelectric sensor consisting of arranged avalanche photodiodes (APD) operated in Geiger mode, and has an excellent photon-counting capability with a peak-sensitive wavelength of 440 nm and a time resolution of 10 ns [18]. Therefore, novel high-speed radiation sensors will be realized in the near future by combining a ZnO crystal and MPPC.

In the present research, we measured the scintillation properties of three sectors in the ZnO crystal. Next, we selected the −c-sector chip as a ZnO scintillator with a short decay time and a high light yield. Finally, we developed a ZnO/MPPC radiation sensor using the −c chip and measured the X-ray response.

2. As-grown ZnO single crystals

A hydrothermal process is a way for growing crystals on seed crystals at high temperature in a high-pressure solution, in other words, a supercritical state. In our process, ZnO single crystals are grown on all planes of seed crystals as shown in Fig. 1. Specifically, the properties of the +c, m, and −c sectors are obviously different. For example, the +c- and m-sectors are transparent, but the −c sector is colored (pale yellowish green) owing to the

* Corresponding author. Tel.: +81 195 31 1621; fax: +81 195 31 1904.
E-mail address: sugimura@tew.co.jp (S. Sugimura).

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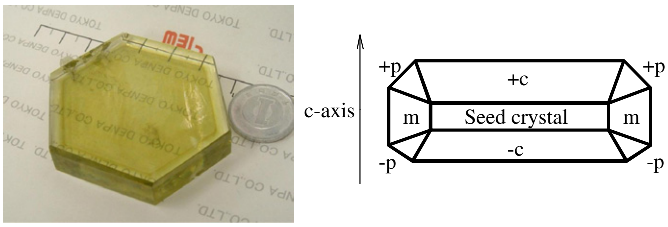

Fig. 1. Photograph and cross-section drawing of a ZnO single crystal grown under the hydrothermal process.

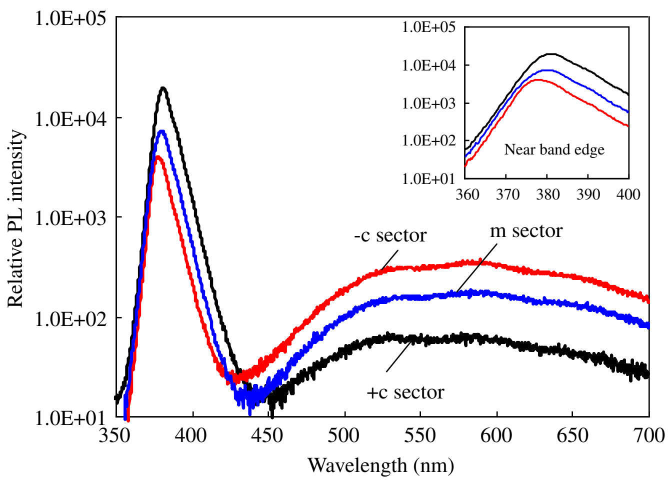

Fig. 2. Photoluminescence spectra from 1.0-mm-thick ZnO single crystals excited by He–Cd laser of 325 nm in wavelength at room temperature (RT).

crystal involving metal impurities caused by the polarity to the *c*-axis. Representative impurities of the $-$c sector are aluminum (Al) and ferrum (Fe) and the typical densities of both are 1.0×10^{17} atoms/cm^3 as determined by secondary ion mass spectroscopy. The density of the $-$c-sector wafer is two orders of magnitude higher than those of the +c- and m-sector wafers. As a result, the resistivity of the +c sector is higher than that of the $-$c sector. However, the difference of the scintillation properties of the sectors grown under the hydrothermal process has not been researched yet.

3. Characteristics of ZnO crystals

As a preliminary evaluation, we measured photoluminescence (PL), radioluminescence (RL), and transmittance without reflection of 1.0-mm-thick sections of the +c-, $-$c-, and m-sector wafers. Fig. 2 shows the PL spectra of these wafers. The measurement was carried out using a 325-nm-wavelength He–Cd laser with an excitation power density of 0.7 W/cm^2 at room temperature (RT). By expanding the PL spectra at the near band edge of these wafers, we could find a remarkable difference between the +c-, $-$c-, and m-sector wafers. The peak position at the near band edge of the $-$c-sector wafer was around 378 nm and was shifted to a short wavelength by at least 2 nm compared with those of +c- and m-sector wafers, as shown in the inset of Fig. 2.

Fig. 3 shows RL spectra and transmittance without reflection spectra at RT. In the RL measurement, the distance from the shutter of the X-ray source to both samples was 0.03 m, and we employed an X-ray generator (RIX-52, R-TEC) and a photonic multichannel analyzer (Hamamatsu Photonics, PMA-12). The

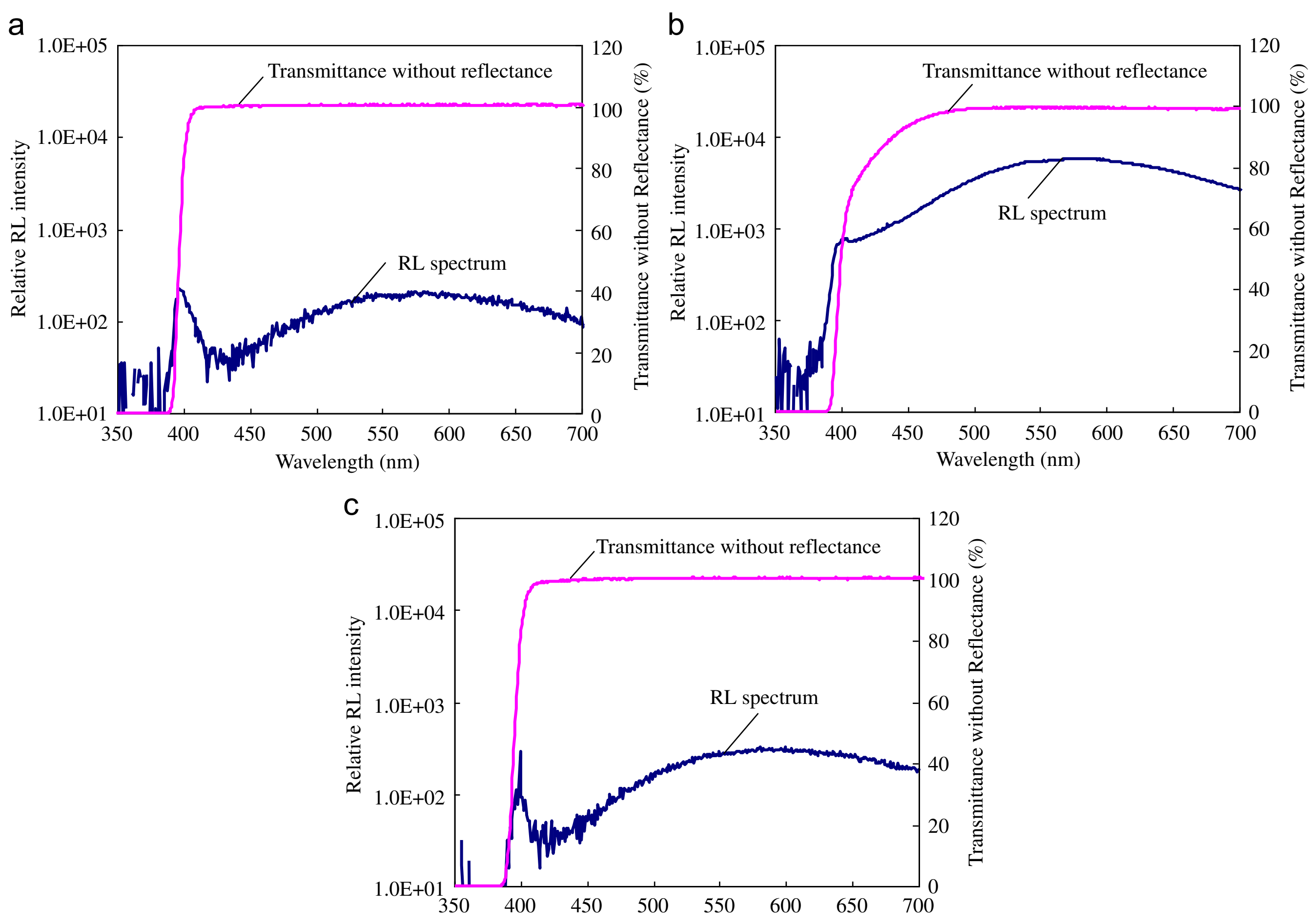

Fig. 3. Radioluminescence spectra and transmittance spectra without reflection at RT. (a) 1.0-mm-thick +c-sector ZnO, (b) 1.0-mm-thick $-$c-sector ZnO, and (c) 1.0-mm-thick m-sector ZnO.