Scintillation and Dosimetric Properties of Cu-Doped Zinc Oxide Thin Films*

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Basic photoluminescence (PL), scintillation and thermoluminescence (TL) properties of Cu-doped ZnO thin films deposited by the Liquid Phase Epitaxy (LPE) method are reported. When the films were excited with 280 nm LED, the emission band was detected at 510 nm wavelength. This emission originated from the recombination between neutral shallow donor levels related to oxygen vacancy and the $t^2$ energy level of excited Cu$^{2+}$ ($d^9$) acceptor. The PL quantum efficiency was estimated to be about 3%. The pulse height spectra recorded under $^{241}$Am alpha-ray irradiation indicated that the Cu-doped film had scintillation light yield greater than that of Bi$_4$Ge$_3$O$_{12}$ (BGO) commercial scintillator. [DOI: 10.1380/ejssnt.2014.275]

Keywords: Zinc oxide; Luminescence; Copper

I. INTRODUCTION

Scintillating materials are widely used in spectroscopic studies and detection of high energy photons (X-rays and gamma-rays) and charged particles. The scintillation detectors are commonly used in nuclear and particle physics research, medical imaging, diffraction, non-destructive testing, nuclear treaty verification and safeguards, nuclear non-proliferation monitoring, and geological exploration. Such detecting systems are formed through coupling of a scintillator with a photodetector such as photomultiplier tube (PMT) or photodiode that are necessary for converting the scintillation photons into an electrical pulse. Important requirements for the scintillators used in such applications include high light yield, high detection efficiency, low cost and availability in large volume.

Blue-green luminescence properties of zinc oxide (ZnO) were well studied for its application as a phosphor in electroluminescence displays and light-emitting diodes (LED) [1–3]. The luminescence bands of ZnO originate from free excitons, donor-acceptor pairs relating to vacancies of oxygen, interstitial zinc atoms and impurities in the crystal. Various types of ZnO based scintillators have been examined in the past, and it was found that scintillation light yield of ZnO is relatively low compared to other scintillating materials. Recently, the scintillation properties of undoped, In-, Ga-, and Mg-doped ZnO thin films produced by the Liquid Phase Epitaxy (LPE) technique were reported. These reports indicated promising properties of ZnO including fast response and relatively high light yield when the specimens were excited with X-rays and alpha-rays [4–7]. Therefore, the idea of this report was to evaluate basic photoluminescence (PL), scintillation, and thermoluminescence (TL) properties of Cu-doped ZnO thin films grown by the LPE method and to examine their performance for alpha-ray detection.

II. EXPERIMENTAL

The 0.3 mol% Cu-doped ZnO thin films were produced by the liquid phase epitaxy (LPE) method. High purity ZnO and CuO powders were used as film-forming starting materials. The growth of the films was performed from the flux contained PbO and PbF$_2$ as a flux. An undoped ZnO single crystal grown by the hydrothermal method by Tokyo Denpa Corporation was used as a substrate. The starting materials were loaded into the crucible, overheated until complete melting and homogenization, and then the melt was cooled down to growth temperature. The substrate rotation of 60 rpm was applied. The LPE processes were performed in air atmosphere. The growths were completed by separating the substrates from the melt.

The transmittance spectra of the Cu-doped and undoped ZnO films were examined with a V-670 spectrometer (JASCO) and compared. The spectra were recorded in the wavelength range from 190 to 2500 nm.

The PL spectra of the films were measured using a Quantaurus-Tau spectrometer (Hamamatsu) at room temperature (RT). In these measurements, the LED emitting at wavelength of 280 nm was used as an excitation source, and the scintillation light from the films was detected by a V-670 spectrometer. All these measurements were also performed at RT. The monitored emission wavelength was set to be 520 nm.

For the examination of the alpha-rays detection performance, the radio luminescence (RL) spectra were also evaluated using a $^{241}$Am 5.5 MeV alpha-rays sealed source. The films were placed directly on the surface of the sealed source, and the scintillation light from the films was detected by a V-670 spectrometer (JASCO). All these measurements were also performed at RT. Similar set-up was used for characterization of both undoped and Cu-doped films to compare the spectra.

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The pulse height spectra obtained under alpha-rays irradiation from $^{241}$Am 5.5 MeV source were used to evaluate scintillation light yield of the Cu-doped ZnO films. BGO single crystal was used as a reference scintillator (with light yield of 8600 ph/MeV and decay time of 300 ns [8]). For the evaluation, the samples were optically coupled with photomultiplier tube (PMT, R7600U, Hamamatsu) using optical grease (OKEN 6262A), and high voltage of 600 V was supplied to PMT. The electric pulse signals were fed into a preamplifier (ORTEC 113), a shaping amplifier (CLEAR-PULSE 4479), a multichannel analyzer (Anapect 8000A), and finally to the personal computer for data analysis. In these measurements, it was necessary to optimize the value of the shaping time in order to efficiently detect the pulse signals caused by the scintillation photons. Thus, we could estimate the maximum performance of the samples. The shaping time was 100 µs for the Cu-doped ZnO, and it was 2.0 µs for the BGO crystal as optimum value considering the decay times of the samples. The scintillation light yield was calculated from the number of relative peak channels and the quantum efficiency of the PMT (30-40% at 400-500 nm wavelength range).

Finally, the TL glow curves were recorded using TL-2000 thermoluminescence dosimeter and FP8600 spectrofluorometer (nano Gray). The films were irradiated with X-rays at a rate of 15 Gy. Thereafter, the glow curves were recorded in the temperature interval of 330-720 K with constant rate of heating (1 K s$^{-1}$).

### III. RESULTS AND DISCUSSION

Figure 1 illustrates general view of polished undoped and 0.3% Cu-doped films. The films are colorless and transparent under visual observation. This observation corresponded well to their transmittance spectra illustrated in Fig. 2. According to the spectra, small red-shift of the absorption edge resulting from Cu-doping was observed at 380-400 nm. Also, the films demonstrated transmittance exceeding 70% in the wavelength range from 420 to 2500 nm. The PL spectra of undoped and Cu-doped films excited at 280 nm are illustrated in Fig. 3. In the case of undoped film, sharp emission peak was detected at 380 nm that was caused by free exciton. Additionally, the intrinsic emission band associated with some lattice defects present in undoped ZnO films was observed at wide wavelength range from 450 to 650 nm. However, the spectrum of the Cu-doped films was completely different. In later case, the free exciton emission band disappeared, and the emission intensities at 450-650 nm range increased with Cu-doping level. To understand the origin of this emission, the decay times of the Cu-doped and undoped films were compared. The results are illustrated in Fig. 4. Using exponential fitting of the experimental data, the decay times were calculated to be about 24 and 2300 ns for undoped films and 21500 ns for Cu-doped ones, respectively. The origin of the green emission band observed for the Cu-doped films is expected to be different from the intrinsic emission. Similar result has been reported in Refs. [9–11]. Thus, it was suggested that the green emission band of the Cu-doped films was result of recombination between neutral shallow donor levels (oxygen vacancy) and the $t^2$ energy level of excited Cu$^{2+}$ ($d^9$) acceptor [9–11]. Generally, Zn$^{2+}$ cation is substituted by Cu$^{2+}$ cation according to the formula of (Cu$_x$, Zn$_{1-x}$)O.
FIG. 4: Decay time profile of undoped and Cu-doped ZnO films recorded under excitation of the samples with 280 nm LED.

FIG. 5: Radioluminescence spectra of undoped and Cu-doped ZnO films recorded under excitation of the samples with 241Am alpha-rays.

Because the ionic radius of Cu$^{2+}$ (~0.73 Å) is close to that of Zn$^{2+}$ (~0.74 Å). Thus, Cu$^{2+}$ cations substituting Zn$^{2+}$ donate two electrons for the bond formation and are in a neutral state with respect to the Cu$^{2+}$ lattice (3d$^9$). In this case, the Cu$^{2+}$ (3d$^9$) are expected to form a deep accepter levels, which are spaced 0.17-0.19 eV away from the bottom of the conduction band [12, 13].

Based on the results of the photoluminescence measurements, the scintillation properties of the films irradiated with 241Am 5.5 MeV alpha-rays were also inspected. The resulting RL spectra are presented in Fig. 5. These spectra indicated that Cu-doped films exhibit an intense emission band at 520 nm similar to that in PL spectra (Fig. 3). In addition, the emission peak caused by free excitons was also observed at 400 nm. However, the peak intensities for the Cu-doped ZnO were very low compared with those of undoped ZnO. This is result of formation of the donor-acceptor pairs relating neutral shallow donors and Cu$^+$ accepter by Cu-doping, and it may change the scintillation process. To examine the scintillation light yield under alpha-rays excitation, the 241Am 5.5 MeV alpha-rays irradiated pulse height spectra were also plotted. The spectra for the Cu-doped film together with that for the BGO are shown in Fig. 6. The Cu-doped film demonstrated alpha-rays peak at 500 ch and that of BGO appeared at 350 ch. Taking into account the peak channel number for the samples and quantum efficiency of PMT, the scintillation light yield of the Cu-doped ZnO film was found to be approximately 140% compared to that of BGO.

Finally the TL properties of the films observed under X-ray irradiation at a rate of 15 Gy were evaluated. The TL glow curves of undoped and Cu-doped films are illustrated in Fig. 7. Both TL peaks were not very clear. Thus, it was expected that numbers of trapped levels for the free electrons and the holes associated with some lattice defects were very low as a result of high structural quality of the films discussed above.

FIG. 6: Pulse height spectra of Cu-doped ZnO film and BGO commercial crystal recorded under excitation of the samples with 241Am alpha-rays.

FIG. 7: Thermoluminescence glow curves of undoped and Cu-doped ZnO films.

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IV. CONCLUSIONS

Basic PL, scintillation, and TL properties of Cu-doped ZnO thin films grown by the LPE method were reported. The PL spectrum recorded for the specimens excited with 280 nm LED demonstrated intense emission band at 450-650 nm. This band was associated with recombination between neutral shallow donor levels related to oxygen vacancy and the $t^2$ energy level of excited Cu$^{2+}$ ($d^9$) acceptor. Similarly, in the RL spectra obtained under alpha-rays excitation, the intense green emission band that corresponds to the donor-acceptor recombination was observed. The scintillation light yield of the Cu-doped ZnO films was estimated to be about 140% compared to that of BGO when the $^{241}$Am 5.5 MeV alpha-ray irradiated. The Cu-doped ZnO was found to be excellent scintillating material for alpha-rays detection with high scintillation light yield.

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