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Characteristics of ZnO Schottky photodiode and effects of high-energy proton irradiation

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We fabricated a Pt/ZnO Schottky photodiode based on single-crystal substrates grown by the hydrothermal growth method. We measured the electrical properties and the spectral responsivity in UV region. The responsivity was 0.1 W/A and there was a sharp cutoff wavelength corresponding to the band gap of ZnO. The fabricated diode can be used as a visible–blind sensor. We also investigated the performance of the diode for the incidence of X-rays and observed the signal obtained. We demonstrated the potential of the ZnO device for ionizing radiation.In addition, we investigated the effects of irradiating the photodiode with high energy protons. For a sample irradiated with $\sim 10^{15}$ protons/cm^2, the dark currents were observed to increase by a factor of 10. Moreover, the behavior of the forward currents significantly changed. In the current–voltage measurement 2 months after irradiation, the dark current decreased to the same level as that before irradiation. This behavior of the dark current may indicate that the defects generated by proton irradiation had been annihilated.

1 Introduction Zinc oxide (ZnO) has excellent properties in terms of its thermal, mechanical, and chemical stability, and it has been recently applied to optoelectric devices in the UV region, as well as to high-power and high-speed electronic devices [1–5]. Particularly for UV sensing, a ZnO photodiode with high sensitivity and responsivity is desired in various fields such as environmental monitoring, flame detection, and optical transmission. Various studies have been conducted to improve the performance optimizing surface treatment, device structure, and the growth method of crystals [6–8]. In this study, we have fabricated a Pt/ZnO Schottky photodiode using single-crystal substrates grown by the hydrothermal growth method, and investigated their electrical properties and spectral responsivity in the UV region.

Because of its high density and high threshold voltage, it is also interesting to apply ZnO to ionizing radiation sensors, which can be utilized in the fabrication of energy spectrometers and imaging devices. Then, we investigated the feasibility of the diode as an X-ray sensor. In addition, ZnO is expected to have high tolerance for damage caused by the incidence of high-flux radiations. Because radiation sensors are often used in harsh radiation environments, it is important to understand the particle irradiation effect. The effects of irradiation of high-energy electrons and heavy ions have been investigated from various viewpoints [9–13], and the results of these studies have suggested that ZnO may have high radiation tolerance. In addition, the radiation induced effects were found to depend on the crystal growth method. Because the effects of the damage depend on the type and energy of the irradiating particles as well as on structure of the device, the treatment process, and the operating conditions, it is necessary to perform the irradiation test to confirm the radiation hardness of ZnO. In this study, the fabricated diode was irradiated with a high-energy proton beam and characterization was subsequently repeated.

2 Experimental

2.1 Diode sample We used a single crystal ZnO substrate with a size $10 \times 10 \times 0.5\,\mathrm{mm}^3$, which was grown by the hydrothermal growth method [14, 15]. In this study, we fabricated photodiodes with two types of substrates with different resistivities: $\sim$2000 Ω cm and $\sim 10^{10}$ Ω cm. Hereafter, the photodiode samples with the lower and the higher substrates are designated as "type-I" and "type-II" sample, respectively. A 3-nm-thick Pt electrode was deposited on the ZnO surface to form the Schottky contact. A 50-nm-thick Al-doped ZnO film, a 20-nm-thick Ti film, and a 50-nm-thick Au film were deposited as ohmic electrodes. The Pt Schottky electrode of this diode is UV transparent; therefore, the diode may be operated as a UV photodiode. After depositing the electrodes, the diode was diced into 1.0 mm square chips, and each chip was bonded on a stem using silver paste. The area of the Schottky electrode was 0.00625 cm^2. Figure 1 shows the cross-sectional view of the diode chip. Note that we fabricated special samples for the proton irradiation test. The detailed specification of the diode is described later.

2.2 Characterization of the diode We measured the current–voltage (I–V) characteristics of the diodes using a semiconductor characterization system (Keithley SCS-4200). Diode parameters such as dark current, breakdown voltage, and the Schottky barrier height were investigated in the measurement.

The spectral responsivity was measured in the wavelength ranging from 250 to 600 nm. The measurement system consisted of a Xe arc lamp, a monochrometer, and an I–V transfer amplifier (Keithley; 428-PROG). The photocurrent for each wavelength was measured at intervals of 2 min without any irradiation to avoid possible contributions by persistent current.

The output signal from the diode irradiated with X-rays was analyzed to investigate its performance as a radiation sensor. The number of charge carriers generated by incident radiations depends on how much energy is deposited in the depletion layer. Therefore, we may make the width of the depletion layer as large as possible to obtain a large electric signal. In principle, the width of the depletion layer W is expressed as follows:

$$W = \sqrt{\frac{2\varepsilon_s}{qN_D}(V_{bi} - V)} \quad (1)$$

where ε_s is the relative dielectric constant, q is the electron charge, N_D is the donor density associated with the resistivity of the substrate, V_{bi} is the built-in potential, and V is the applied bias voltage. This equation indicates the use of a high-resistivity substrate is effective in expanding the depletion layer. Because X-rays have a high probability of penetrating the material and they have relatively small energy deposition, we used a diode with a higher-resistivity substrate (i.e., type-II) for X-ray measurements, where the width of the depletion layer could be made thicker with a reasonable applied voltage. An X-ray tube with a tungsten target (R-TEC CORPORATION; RXG-0152-955) was used for these measurements. The diode sample was placed in the shielding box at a distance of 50 cm from the X-ray source. The pulsed X-ray was irradiated and the signal from the sample was amplified and shaped (Clear Pulse; 580 K, 4419HI) with a 2 μs shaping time; the signal was then analyzed by a multi-channel analyzer (Princeton Gamma-Tech Instruments; MCA8000). Figure 2 shows the X-ray irradiation setup.

We investigated the effects of irradiating the diode with high energy protons. For the proton irradiation test, we prepared special samples fabricated using substrates with a resistivity of $\sim$1000 Ω cm and thickness of 0.6 or 1.2 mm. The diode chip was bonded onto an FR-4 PCB. The irradiation test was conducted at CYRIC, Tohoku University, using a 20 MeV proton beam with a current of $\sim$100 nA. In this test, the irradiation fluence for the samples ranged from 10^{13} to 10^{15} protons/cm^2. Before irradiation of the samples, an Al foil was exposed to the beam and the radioactivity of the foil was measured by an imaging plate to obtain the beam profile. The proton fluences on the diode were determined by the beam current and the profile. The *I–V* characteristics were measured pre- and post-irradiation by an ultra-high resistance meter (ADVANTEST; R8340); and the dark currents, the breakdown voltage, and the behavior of the forward currents were investigated to evaluate the effects of particle irradiation. The *I–V* measurement was performed 1 and 2 months after irradiation to investigate any change in the characteristics with time. The samples were maintained in a dry cabinet in the air-conditioned laboratory, where the temperature was controlled at $\sim$20 °C for the duration of the experiment.

3 Results and discussion The *I–V* characteristics of the type-I and type-II samples are shown in Fig. 3. For the

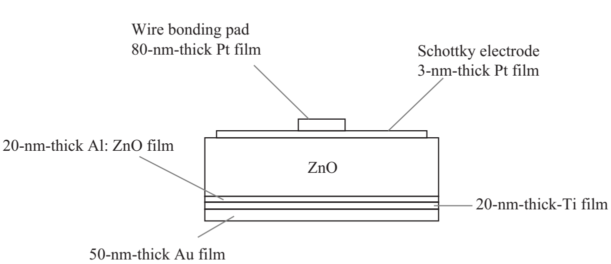

Figure 1 Cross-sectional view of the Pt/ZnO Schottky diode.

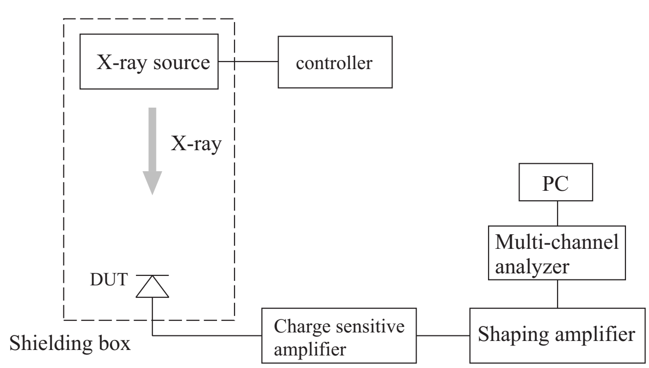

Figure 2 X-ray irradiation and signal readout system.

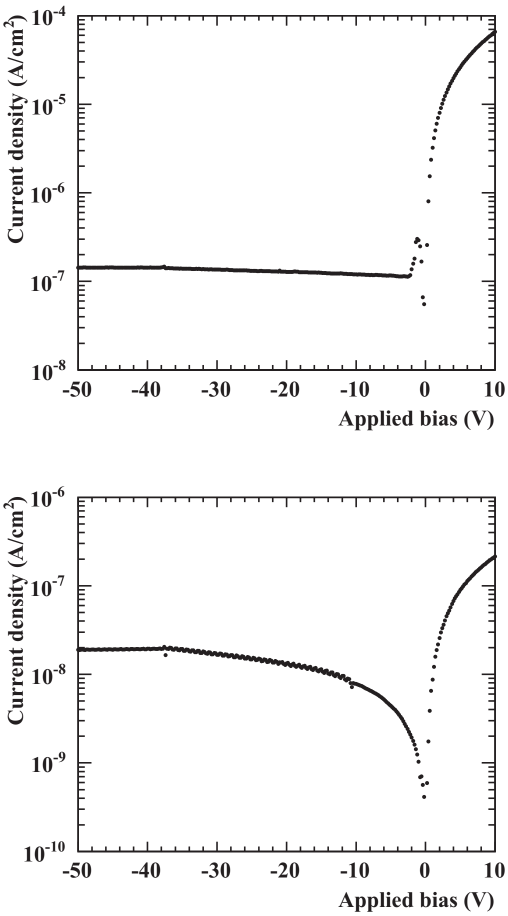

Figure 3 *I–V* characteristics of the type-I (top) and type-II (bottom) diodes.

type-I sample, the dark current was reasonably suppressed to be typically of the order of 100 nA/cm^2 and the breakdown voltage was less than −50 V. On the other hand, the *I–V* characteristics for the type-II sample showed an Ohmic-like behavior and the forward currents were very small. Because the type-II diode has a significantly high resistance, the forward currents do not flow easily for these applied biases. The Schottky barrier heights were derived to be 0.8 eV for type-I and 1.1 eV for type-II. Schottky barrier height strongly depends on the preparation and condition of the ZnO material. The measurements have been performed by various groups and the barrier height of the Pt/ZnO contact was reported to be 0.4–0.9 eV [16–20].

Figure 4 shows the responsivity of the type-I sample for UV light. The responsivity was 0.1 W/A and there is a sharp cutoff wavelength corresponding to the band gap of ZnO. The responsivity of the sensitive UV region is larger by two magnitude than that of the wavelength above the cut-off. The fabricated diode can be used as a visible–blind sensor.

Figure 5 shows the spectra of the signal charge generated by X-ray irradiation when different voltages are applied to the X-ray tube. In the measurement, a bias voltage of −50 V was applied to the sample. It was assumed that the sample

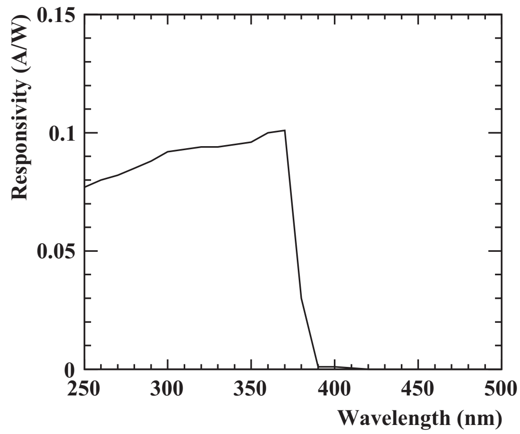

Figure 4 Responsivities of the type-I diodes.

was fully depleted at this bias voltage considering the resistivity of the substrate and Eq. (1). The signal intensity increased and the tail of the spectrum further shifted with an increase in the tube voltage. We did not observe clear signals in the spectra when we shielded the sample from the X-ray. It was suggested that the fabricated diode was sensitive to X-rays and appeared to be capable of operating as an energy spectrometer. As mentioned above, the type-II sample had high resistivity and the current in the diode was too small to enable to easy identification of the peaks of the characteristic X-rays of the tungsten target in the X-ray tube.

Figure 6 shows the *I–V* characteristics before and after proton irradiation at fluences of 5.1×10^{13} protons/cm^2 and 3.1×10^{15} protons/cm^2. In principle, high energy proton irradiation causes atomic displacement in the crystal, and the intrinsic defects affect the electrical properties of the device. For the sample irradiated with a fluence of 5.1×10^{13} protons/cm^2, neither the reverse dark currents or the breakdown voltage significantly changed. For the sample with a fluence of 3.1×10^{15} protons/cm^2, the reverse current increased by a factor of ∼10 in the measurement a month after irradiation. The slope of the forward current became

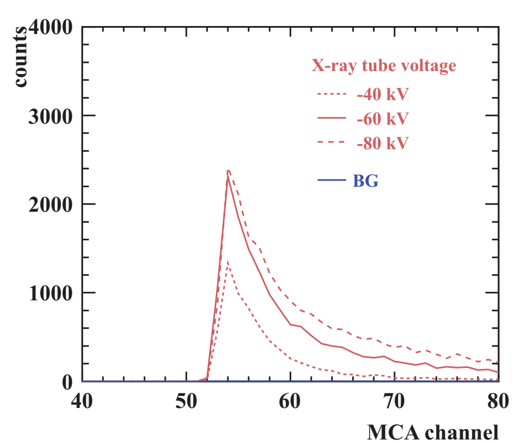

Figure 5 Signal charge distribution measured by the MCA for X-rays emitted from the X-ray tube for voltages of 40, 60, and 80 kV.

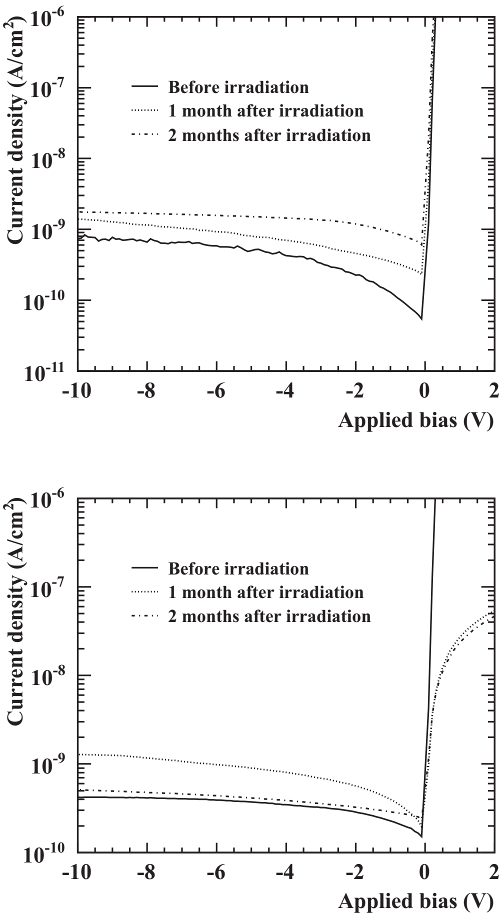

Figure 6 *I–V* characteristics of the diode before and after irradiation of the proton beam. The fluences are 5.1×10^{13} protons/cm^2 (top) and 3.1×10^{15} protons/cm^2 (bottom).

less steep, and this may indicate the forming interface state. In the *I–V* measurement 2 months after irradiation, the dark current decreased to the same level as that before irradiation. The samples were maintained at room temperature for the duration of the experiment. This behavior of the dark current may indicate that the defects generated by proton irradiation had been annihilated. Such behavior has been observed in other experiments involving ZnO diodes [9, 21]. To clarify the effects as well as the relaxation behavior, it is necessary to perform the test under various conditions and quantitatively evaluate the properties from various viewpoints.

4 Summary We fabricated a Pt/ZnO Schottky photodiode using single-crystal substrates grown by the hydrothermal growth method. The photodiode showed a good performance in UV sensing. The output signals from the diode were analyzed for the incidence of X-rays, and we demonstrated the potential of the ZnO-based device for ionizing radiation. We also examined the radiation-induced damage by irradiating with a high energy proton beam. No significant change in the electrical properties of the diode was observed for fluences up to $\sim 10^{13}$ protons/cm^2. However, the radiation hardness of ZnO needs to be investigated by further studies under various conditions.

References

[1] C. Periasamy and P. Chakrabarti, Curr. Appl. Phys. **11**, 959–964 (2011).
[2] Z. Z. Zhang, Z. P. Wei, Y. M. Lu, D. Z. Shen, B. Yao, B. H. Li, D. X. Zhao, J. Y. Zhang, X. W. Fan, and Z. K. Tang, J. Cryst. Growth **301–302**, 362–365 (2007).
[3] A. N. Aleshin, I. P. Scherbakov, V. N. Petrov, and A. N. Titkov, Org. Electron. **12**, 1285–1292 (2011).
[4] H. Endo, M. Sugibuchi, K. Takahashi, S. Goto, S. Sugimura, K. Nane, and Y. Kashiwaba, Appl. Phys. Lett. **90**, 121906 (2007).
[5] E. Sato, S. Sugimura, H. Endo, Y. Oda, A. Abudurexiti, O. Hagiwara, A. Osawa, H. Matsukiyo, T. Enomoto, M. Watanabe, S. Kusachi, S. Sato, A. Ogawa, and J. Onagawa, Appl. Radiat. Isotopes **70**, 336–340 (2012).
[6] V. K. Dwivedi, P. Srivastava, and G. V. Prakash, J. Semicond. **34**, 033001 (2011).
[7] N. K. Hassan, M. R. Hashim, and N. K. Allam, Sens. Actuators A **192**, 124–129 (2013).
[8] F. Zahedi, R. S. Dariani, and S. M. Rozati, Sens. Actuators A **199**, 123–128 (2013).
[9] E. Gür, C. Coskun, and S. Ruzemen, J. Phys. D: Appl. Phys. **41**, 105301 (2008).
[10] E. Gür, H. Asil, C. Coskun, S. Tuzemen, K. Meral, Y. Onganer, and K. Serifogul, Nucl. Instrum. Methods B **266**, 2021–2026 (2008).
[11] A. Y. Azarov, A. I. Titov, P. A. Kareseov, S. O. Kucheyev, A. Hallen, A. Y. Kuznetsov, B. G. Svensson, and A. P. Pathak, Vacuum **84**, 1058–1061 (2010).
[12] F. Tuomisto, D. C. Look, and G. C. Farlow, Physica B **401–402**, 604–608 (2007).
[13] A. Burlacu, V. V. Ursaki, V. A. Skuratov, D. Lincot, T. Pauporte, H. Elbelghiti, E. V. Rusu, and I. M. Tiginyanu, Nanotechnology **19**, 215714 (2008).
[14] E. Ohshima, H. Ogino, I. Niikura, K. Maeda, M. Sato, M. Ito, T. Fukuda, J. Cryst. Growth **260**, 166–170 (2004).
[15] K. Maeda, M. Sato, I. Niikura, and T. Fukuda, Semicond. Sci. Technol. **20**, S49–S54 (2005).
[16] S. H. Kim, H. K. Kim, and T. Y. Seong, Appl. Phys. Lett. **86**, 022101 (2005).
[17] M. S. Oh, D. K. Hwang, J. H. Lim, Y. S. Choi, and S. J. Park, Appl. Phys. Lett. **91**, 042109 (2007).
[18] L. J. Brillson, H. L. Mosbacker, M. J. Hetzer, Y. Strzhemechny, D. C. Look, G. Cantwell, J. Zhang, and J. J. Song, Appl. Surf. Sci. **254**, 8000–8004 (2008).
[19] L. J. Brillson and Y. Lu, J. Appl. Phys. **109**, 121301 (2011).
[20] S. J. Pearton, D. P. Norton, K. Ip, Y. W. Heo, and T. Steiner, Prog. Mater. Sci. **50**, 293–340 (2005).
[21] C. Coskun, D. C. Look, G. C. Farlow, and J. R. Sixelove, Semicond. Sci. Technol. **19**, 752–754 (2004).