Research Article

Narrowband, Visible-Blind UV-A Sensor Based on a $\text{Mg}_{0.52}\text{Zn}_{0.48}\text{O}$ Film Deposited by Radio-Frequency Sputtering Using a ZnO-Mg Composite Target

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A narrowband, visible-blind ultraviolet photodetector (PD) for UV-A is fabricated using a $\text{Mg}_{0.52}\text{Zn}_{0.48}\text{O}$ film that is formed on a quartz substrate by a radio-frequency sputtering technique using a ZnO-Mg composite target. The content of Mg in the film is controlled by varying the number of Mg chips on the ZnO plate. The fabricated PD has a metal-semiconductor-metal structure with interdigitated electrodes and exhibits a narrow 3 dB bandwidth of 26 nm with a peak response wavelength of 340 nm and a cut-off wavelength of 353 nm. Moreover, the peak responsivity of the PD increases linearly with the bias voltage up to 30 V, indicating that the device operates via a photoconductive gain mechanism.

1. Introduction

The application of wide bandgap semiconductors in various optical devices that operate in the blue or ultraviolet wavelength regions, such as laser diodes [1, 2], light-emitting diodes [3, 4], and photodetectors [5], has been widely studied. Ultraviolet photodetectors (UV-PDs) in particular have received much attention because of their potential use in combustion flame monitoring, pollution analysis, missile plume detection, chemical sensing, space communication, and ozone-layer monitoring.

Moreover, in recent years, the proportion of ultraviolet rays in the sunlight reaching the earth's surface has increased because of the increased ozone depletion. These rays may have adverse effects on the human body such as skin cancers, cataracts, and infections. As the sunlight passes through the atmosphere, nearly all of the UV-C (280–290 nm) and a part of the UV-B (290–320 nm) radiation are absorbed in the atmosphere. Therefore, the UV radiation reaching the earth's surface is largely composed of UV-A (320–400 nm) with a small UV-B component. High-performance and low-cost solid-state UV-A sensors are thus needed to measure this UV radiation in a convenient manner, and research into materials for use in UV sensors is expanding.

Recently, commercially available semiconductor UV-PDs are primarily fabricated using Si [6], but GaAs [7] and GaP [8] have also been studied. These UV-PDs, however, respond not only to UV light but also to visible light (i.e., 380–780 nm) because of their small bandgap energies. In many applications, simple and high precision measurement of UV light without optical filters, that is, visible-blind analysis, is preferred. To achieve visible-blind sensors, the cut-off wavelength for photosensitivity must be near 400 nm. Tsai et al. [9] reported visible-blind PDs fabricated using TiO_2 nanowires and n-ZnO/LaAlO₃ [10]. The TiO_2 nanowire had a cut-off wavelength of ca. 395 nm at a bias voltage of 5 V and was sensitive even for UV-B. The LaAlO₃ device had a cut-off wavelength of ca. 380 nm at a bias voltage of –2.5 V. However, the latter device suffered from constant sensitivity in the visible wavelength region as large as 40% compared to the peak responsivity in the UV-A region.

The alloy $\text{Mg}_x\text{Zn}_{1-x}\text{O}$ has received increasing attention as a wide bandgap material, because its bandgap can be tuned from 3.37 eV for wurtzite (ZnO) to 7.8 eV for rock salt (MgO) [11]. In fact, some optical devices have already been demonstrated using $\text{Mg}_x\text{Zn}_{1-x}\text{O}$ [12–15]. The $\text{Mg}_x\text{Zn}_{1-x}\text{O}$ films used in these optical devices have typically been

FIGURE 1: Schematic of the ZnO-Mg composite target.

FIGURE 2: Schematic of the $\text{Mg}_{0.52}\text{Zn}_{0.48}\text{O}$ UV-PD.

prepared via pulsed laser deposition (PLD) [16, 17]. However, because Mg and Zn species have different vapor pressures, it is difficult to control the Mg content in $\text{Mg}_x\text{Zn}_{1-x}\text{O}$ films prepared using this method; therefore, it is also difficult to adjust the bandgaps of the films to the visible-blind region. Consequently, films deposited using PLD typically become Mg-rich compared to the precursor target. Moreover, photoconductive UV-PDs fabricated with epitaxial $\text{Mg}_x\text{Zn}_{1-x}\text{O}$ films on sapphire substrates reported by Zhao et al. [14] and Yang et al. [15] suffered from rather large dark currents of $9\text{ }\mu\text{A}$ and 50 nA , respectively, which are inherent to photoconductive detectors.

Here we report the fabrication of a narrowband, visible-blind UV-A sensor with a $\text{Mg}_x\text{Zn}_{1-x}\text{O}$ film that is formed on a quartz substrate using a simple radio-frequency (RF) sputtering technique and a ZnO-Mg composite target. The current-voltage (I - V) characteristics of the PD in the dark and under xenon lamp irradiation are determined, and the responsivity spectra and bias dependence of the responsivity are also measured.

2. Materials and Methods

The $\text{Mg}_x\text{Zn}_{1-x}\text{O}$ thin films were deposited on synthetic quartz substrates using a simple RF sputtering technique. A ZnO-Mg composite target where Mg metal chips were placed on a ZnO plate was employed as the precursor target. The schematic of the ZnO-Mg composite target is shown in Figure 1. The diameters of the ZnO plate and Mg chips were 80 mm and 20 mm, respectively. The quartz substrate was degreased using organic chemicals before being placed on the sample holder of the parallel plate RF sputtering system. The distance between the substrate and the target was 55 mm. The deposition chamber was evacuated using an oil-diffusion pump to $3 \times 10^{-3}\text{ Pa}$ and Ar gas was introduced at a flow rate of 2.5 sccm. The Ar pressure was adjusted to 0.5 Pa during the sputtering deposition. The applied RF power was 100 W and the substrate temperature was 350°C during deposition. The Mg/Zn atomic ratio in the $\text{Mg}_x\text{Zn}_{1-x}\text{O}$ films was controlled by varying the number of Mg chips placed on the ZnO plate. After deposition, the samples were annealed at 600°C for 1 h in air after raising the annealing temperature at a rate of $1^\circ\text{C}/\text{min}$. The samples were then cooled down naturally to room temperature.

The surface morphology of the $\text{Mg}_x\text{Zn}_{1-x}\text{O}$ film was observed using a field-emission scanning electron microscope (SEM) (JEOL, JSM-7500F), while energy-dispersive X-ray spectroscopy (EDS) was used to determine the Mg content x in the $\text{Mg}_x\text{Zn}_{1-x}\text{O}$ film.

The schematic of the sputter-deposited $\text{Mg}_{0.52}\text{Zn}_{0.48}\text{O}$ UV-PD is shown in Figure 2. A gold film with a thickness of 300 nm deposited through a shadow mask onto the $\text{Mg}_{0.52}\text{Zn}_{0.48}\text{O}$ film via thermal evaporation served as the electrodes. The interdigitated electrode was $50\text{ }\mu\text{m}$ wide and 1.95 mm long with $50\text{ }\mu\text{m}$ spacing and occupied an area of $3 \times 3\text{ mm}^2$.

The I - V characteristics of the $\text{Mg}_{0.52}\text{Zn}_{0.48}\text{O}$ UV-PD were measured using a multichannel source-measure unit (YOKOGAWA, GS-820). A lock-in amplifier (Stanford Research, SR830) was employed for the spectral response measurements using a xenon arc lamp as the irradiation source.

3. Results and Discussion

Figure 3 shows an SEM image of an $\text{Mg}_{0.52}\text{Zn}_{0.48}\text{O}$ film deposited on the quartz substrate. Grains and boundaries can be seen in the SEM image, which implies that the $\text{Mg}_{0.52}\text{Zn}_{0.48}\text{O}$ thin film deposited on the quartz substrate via RF sputtering is polycrystalline.

Figure 4 shows the EDS spectrum of the $\text{Mg}_x\text{Zn}_{1-x}\text{O}$ film. The Mg content x in the $\text{Mg}_x\text{Zn}_{1-x}\text{O}$ film was determined to be 52% based on the EDS spectrum.

The I - V characteristics of the $\text{Mg}_{0.52}\text{Zn}_{0.48}\text{O}$ UV-PD measured in the dark and under Xe lamp illumination are shown in Figure 5. The I - V characteristics demonstrate a linear relationship, suggesting a photoconductive mechanism. The dark current was as little as 2.0 nA and the photocurrent was 507.4 nA at a bias voltage of 10 V. This dark-current value is smaller than that of visible-blind $\text{Mg}_x\text{Zn}_{1-x}\text{O}$

FIGURE 3: SEM image of an $\text{Mg}_{0.52}\text{Zn}_{0.48}\text{O}$ thin film. FIGURE 4: EDS spectrum of the $\text{Mg}_x\text{Zn}_{1-x}\text{O}$ thin film.

photoconductive detectors reported to date [14, 15] because of the high resistivity of the intrinsic $\text{Mg}_{0.52}\text{Zn}_{0.48}\text{O}$ film.

The responsivities (photocurrents) of the $\text{Mg}_{0.52}\text{Zn}_{0.48}\text{O}$ UV-PD for bias voltages from 0 to 30 V are shown as a function of wavelength in Figure 6. The device exhibited a peak response at a wavelength of 340 nm, which is in the UV-A region, with a 3 dB bandwidth of 26 nm and a cut-off wavelength of 353 nm. Therefore, the $\text{Mg}_{0.52}\text{Zn}_{0.48}\text{O}$ UV-PD fabricated in this study was narrowband, visible-blind, and suitable for sensing UV-A only. The UV/visible rejection ratio, defined here as the ratio of the photocurrent at 400 nm to that at 340 nm, was greater than two orders of magnitude. This value is comparable to or better than those obtained in the TiO_2 -based UV-A detector [9], the $\text{ZnO}/\text{LaAlO}_3$ UV-A detector [10], and the epitaxial MgZnO UV photoconductive detector [14].

Figure 7 shows the peak responsivity as a function of the applied bias voltage. As can be seen in the figure, a linear relationship existed at bias voltages up to 30 V, indicating that the device operated via a photoconductive gain mechanism without carrier-mobility saturation or a sweep-out effect, even up to a bias of 30 V [18].

4. Conclusions

A narrowband, visible-blind UV-PD for UV-A was fabricated with an $\text{Mg}_{0.52}\text{Zn}_{0.48}\text{O}$ film that was formed on a quartz

FIGURE 5: Dark and illuminated I - V characteristics of the $\text{Mg}_{0.52}\text{Zn}_{0.48}\text{O}$ UV-PD. The inset shows the I - V characteristics on a linear scale. FIGURE 6: Spectral responsivities of the $\text{Mg}_{0.52}\text{Zn}_{0.48}\text{O}$ UV-PD at different bias voltages.

substrate using a simple RF sputtering technique and a ZnO - Mg composite target. The content of the Mg was controlled by varying the number of Mg chips on the ZnO plate. The fabricated PD had a peak response at a wavelength of 340 nm with a 3 dB bandwidth of 26 nm and a cut-off wavelength of 353 nm and also exhibited a dark current as low as 2.0 nA, reflecting the high resistivity of the sputtered $\text{Mg}_{0.52}\text{Zn}_{0.48}\text{O}$ film. Moreover, the peak responsivity of the PD increased linearly with bias voltages up to 30 V, indicating that the device operated via a photoconductive gain mechanism.

FIGURE 7: Peak responsivity versus bias voltage of the $\text{Mg}_{0.52}\text{Zn}_{0.48}\text{O}$ UV-PD.

Conflict of Interests

The authors declare that there is no conflict of interests regarding the publication of this paper.

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References

- [1] S. Nakamura, M. Senoh, S.-I. Nagahama et al., “InGaN-based multi-quantum-well-structure laser diodes,” *Japanese Journal of Applied Physics, 2: Letters*, vol. 35, no. 1, pp. L74–L76, 1996.
- [2] S. Itoh, S. Taniguchi, T. Hino et al., “Room temperature laser operation of wide band-gap II-VI laser diodes,” *Materials Science and Engineering B*, vol. 43, no. 1–3, pp. 55–59, 1997.
- [3] H. Amano, M. Kito, K. Hiramatsu, and I. Akasaki, “P-type conduction in Mg-doped GaN treated with low-energy electron beam irradiation (LEEBI),” *Japanese Journal of Applied Physics, 2: Letters & Express Letters*, vol. 28, no. 12, pp. L2112–L2114, 1989.
- [4] A. Tsukazaki, M. Kubota, A. Ohtomo et al., “Blue light-emitting diode based on ZnO,” *Japanese Journal of Applied Physics, 2: Letters*, vol. 44, no. 20–23, pp. L643–L645, 2005.
- [5] A. BenMoussa, A. Soltani, U. Schühle et al., “Recent developments of wide-bandgap semiconductor based UV sensors,” *Diamond and Related Materials*, vol. 18, no. 5–8, pp. 860–864, 2009.
- [6] M. Razeghi and A. Rogalski, “Semiconductor ultraviolet detectors,” *Journal of Applied Physics*, vol. 79, no. 10, pp. 7433–7473, 1996.
- [7] R. D. Baertsch and J. R. Richardson, “An Ag-GaAs Schottky-Barrier ultraviolet detector,” *Journal of Applied Physics*, vol. 40, no. 1, pp. 229–235, 1969.
- [8] R. Mientus, R. Wolf, B. Kloth, M. Protsch, and A. N. Pikhtin, “A highly UV-selective Schottky-barrier photodiode based on a Ag-GaP contact,” *Surface and Coatings Technology*, vol. 116–119, pp. 711–715, 1999.
- [9] T.-Y. Tsai, S.-J. Chang, W.-Y. Weng et al., “A visible-blind TiO_2 nanowire photodetector,” *Journal of the Electrochemical Society*, vol. 159, no. 4, pp. J132–J135, 2012.
- [10] D. S. Tasi, C. F. Kang, H. H. Wang et al., “N-ZnO/LaAlO₃/p-Si heterojunction for visible-blind UV detection,” *Optics Letters*, vol. 37, no. 6, pp. 1112–1114, 2012.
- [11] M. W. Williams and E. T. Arakawa, “Optical properties of single-crystal magnesium oxide,” *Journal of Applied Physics*, vol. 38, no. 13, pp. 5272–5276, 1967.
- [12] H. Zhu, C. X. Shan, B. H. Li, Z. Z. Zhang, B. Yao, and D. Z. Shen, “Deep-ultraviolet light-emitting device realized via a hole-multiplication process,” *Applied Physics Letters*, vol. 99, no. 10, Article ID 101110, 2011.
- [13] Z. G. Ju, C. X. Shan, D. Y. Jiang et al., “ $\text{Mg}_x\text{Zn}_{1-x}\text{O}$ -based photodetectors covering the whole solar-blind spectrum range,” *Applied Physics Letters*, vol. 93, no. 17, Article ID 173505, 2008.
- [14] C. Y. Zhao, X. H. Wang, J. Y. Zhang et al., “Ultraviolet photodetector fabricated from metal-organic chemical vapor deposited MgZnO,” *Thin Solid Films*, vol. 519, no. 6, pp. 1976–1979, 2011.
- [15] W. Yang, R. D. Vispute, S. Choopun, R. P. Sharma, T. Venkatesan, and H. Shen, “Ultraviolet photoconductive detector based on epitaxial $\text{Mg}_{0.34}\text{Zn}_{0.66}\text{O}$ thin films,” *Applied Physics Letters*, vol. 78, no. 18, pp. 2787–2789, 2001.
- [16] M. Brandt, M. Bonholzer, M. Stölzel et al., “Electrical transport in strained $\text{Mg}_x\text{Zn}_{1-x}\text{O}$:P thin films grown by pulsed laser deposition on ZnO(000-1),” *Physica Status Solidi (B) Basic Research*, vol. 249, no. 1, pp. 82–90, 2012.
- [17] S. Heitsch, G. Benndorf, G. Zimmermann et al., “Optical and structural properties of MgZnO/ZnO hetero- and double heterostructures grown by pulsed laser deposition,” *Applied Physics A: Materials Science and Processing*, vol. 88, no. 1, pp. 99–104, 2007.
- [18] A. Rogalski, *Infrared Detectors*, CRC Press, New York, NY, USA, 2011.