

# Band-modulation of MgZnO/ZnO Metal-semiconductor-metal Photodetectors

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**Abstract.** Magnesium (Mg) diffusion behavior on the band modulation of Mg<sub>x</sub>Zn<sub>1-x</sub>O/ZnO metal-semiconductor-metal photodetectors (MSM-PDs) was studied. As the annealing temperature increases, Mg atoms diffuse from Mg<sub>x</sub>Zn<sub>1-x</sub>O into the underlying ZnO layer, which modulates the detection band of the fabricated MSM-PDs from two distinct bands into one band. For the annealing temperature lower than 900 °C, two detection bands were achieved located in the wavelength region of 280–320 nm and 360–400 nm, attributed to the absorption of the Mg<sub>x</sub>Zn<sub>1-x</sub>O and the ZnO layer, respectively. When the annealing temperature is raised to 900 °C, the Mg<sub>x</sub>Zn<sub>1-x</sub>O/ZnO bi-layer becomes homogenized into a single Mg<sub>x</sub>Zn<sub>1-x</sub>O layer, leading to only one detection band with a wavelength region of 280–340 nm. In the photoluminescence measurement, the as-deposited Mg<sub>x</sub>Zn<sub>1-x</sub>O/ZnO bi-layer demonstrates two distinct emission peaks located at about 340 and 400 nm for the absorption of the Mg<sub>x</sub>Zn<sub>1-x</sub>O and ZnO layers, whereas only one emission peak of 355 nm was observed in the 900 °C-annealed Mg<sub>x</sub>Zn<sub>1-x</sub>O/ZnO bi-layer.

## 1 Introduction

ZnO and Mg<sub>x</sub>Zn<sub>1-x</sub>O-based ultraviolet (UV) photodetectors (PDs) have been continuously studied because the ZnO material has many advantages, including a wide band gap (3.37 eV), high transparency (>80%) in the visible wavelength region, high exciton binding energy (60 meV), and non-toxicity [1,8]. By mixing ZnO with another wide-direct-band-gap material, MgO (7.8 eV), the tunable bandgap material of Mg<sub>x</sub>Zn<sub>1-x</sub>O, which can modulate the detection wavelength of PDs by varying Mg content, can be formed [9-11]. In addition, no significant lattice distortion is found in the Mg<sub>x</sub>Zn<sub>1-x</sub>O material because Mg<sup>+2</sup> has a very similar ionic radius to that of Zn<sup>+2</sup> [12].

Although GaN and Al<sub>x</sub>Ga<sub>1-x</sub>N materials have been employed in various PDs, expensive and high-temperature technology was required to grow the GaN and Al<sub>x</sub>Ga<sub>1-x</sub>N materials, including molecular beam epitaxy and metal organic chemical vapor deposition systems. In contrast, ZnO and Mg<sub>x</sub>Zn<sub>1-x</sub>O materials can be grown using low-cost and low-temperature techniques, including radio-frequency (RF) magnetron sputtering and hydrothermal methods [13,14]. As opposed to pure ZnO or Mg<sub>x</sub>Zn<sub>1-x</sub>O materials, the

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$\text{Mg}_x\text{Zn}_{1-x}\text{O}/\text{ZnO}$  bi-layer heterostructure is a promising technological platform as evidenced heterojunction field-effect transistor, multi-quantum-well (MQW) light-emitting diodes, MQW-PDs, and optoelectronic devices with superlattice, as well as two-dimensional electron gas (2DEG) structures [15].

Previously, many  $\text{Mg}_x\text{Zn}_{1-x}\text{O}/\text{ZnO}$  heterojunction UV-PDs were fabricated [16-120]. As compared to the MSM-PDs without the  $\text{Mg}_x\text{Zn}_{1-x}\text{O}$  capping layer, the PDs with the  $\text{Mg}_x\text{Zn}_{1-x}\text{O}/\text{ZnO}$  bi-layer presented higher dark current, photocurrent, and photoresponsivity due to the shielding of ambient oxygen, defect, and surface states passivation by the  $\text{Mg}_x\text{Zn}_{1-x}\text{O}$  capping layer [21]. The  $\text{Au}/\text{Mg}_x\text{Zn}_{1-x}\text{O}/\text{ZnO}$  PDs had larger responsivity than  $\text{Au}/\text{ZnO}/\text{Mg}_x\text{Zn}_{1-x}\text{O}$  PDs [22]. By varying the applied bias voltage, the detection wavelength of the  $\text{Mg}_x\text{Zn}_{1-x}\text{O}/\text{ZnO}$  MSM-PDs could be modulated from a single to a dual wavelength [23].  $\text{MgZnO}/\text{ZnO}$  bi-layer with 2DEG behavior was investigated [24-26].

The photoluminescence (PL) was investigated by annealing the  $\text{Mg}_x\text{Zn}_{1-x}\text{O}/\text{ZnO}$  bi-layer, which tuned the Mg composition [27]. Dual-band  $\text{Mg}_x\text{Zn}_{1-x}\text{O}$  UV-PDs were fabricated by employing two  $\text{Mg}_x\text{Zn}_{1-x}\text{O}$  layers with different Mg compositions [28]. The Mg atomic reconstruction was observed in p-type interface (ZnO on Zn-polar  $\text{MgZnO}$ ), but not in n-type interface ( $\text{MgZnO}$  on Zn-polar ZnO) due to the different polarity of the interface [29]. The Mg atomic reconstruction was not caused by thermal diffusion, instead by the asymmetry of energy scales.

In this work, the Mg thermal diffusion behavior on the MSM-PDs with the  $\text{Mg}_x\text{Zn}_{1-x}\text{O}/\text{ZnO}$  bi-layer was studied. We found that by increasing the annealing temperature of the  $\text{Mg}_x\text{Zn}_{1-x}\text{O}/\text{ZnO}$  bi-layer, one could modulate the detection band of the fabricated MSM-PDs from two bands into one band.

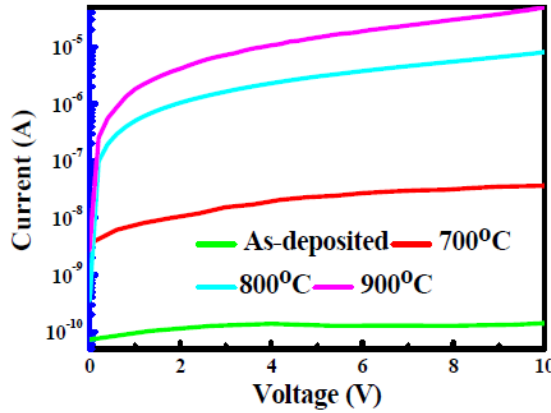
## 2 Experiments

ZnO and  $\text{Mg}_x\text{Zn}_{1-x}\text{O}$  layers with a thickness of 250 nm were deposited consecutively on a sapphire substrate using an RF magnetron sputtering system with a substrate temperature of 200 °C in a 10-mTorr Ar atmosphere. X-ray photoelectron spectroscopy showed the Mg content being 0.3 in the as-deposited  $\text{Mg}_x\text{Zn}_{1-x}\text{O}$  film. Then, the  $\text{Mg}_x\text{Zn}_{1-x}\text{O}/\text{ZnO}$  bi-layers were annealed at various temperatures between 700 and 900 °C for 2 h, which forced the Mg atom to diffuse from  $\text{Mg}_x\text{Zn}_{1-x}\text{O}$  to the underlying ZnO layer. The as-deposited (not annealed)  $\text{Mg}_x\text{Zn}_{1-x}\text{O}/\text{ZnO}$  bi-layer was also prepared for comparison. MSM-PDs were fabricated by evaporating Au electrodes on the  $\text{Mg}_x\text{Zn}_{1-x}\text{O}$  surface in an interdigitated pattern. Inter-diffusion behavior of Mg atoms was studied by absorption, PL, and secondary ion mass spectrometry (SIMS) measurements. Current–voltage ( $I$ – $V$ ) characteristics were recorded using a Keithley 2400 source meter, and the photoresponse was measured with a monochromator by illuminating the samples from the  $\text{Mg}_x\text{Zn}_{1-x}\text{O}$  side with a 300-W Xe arc lamp.

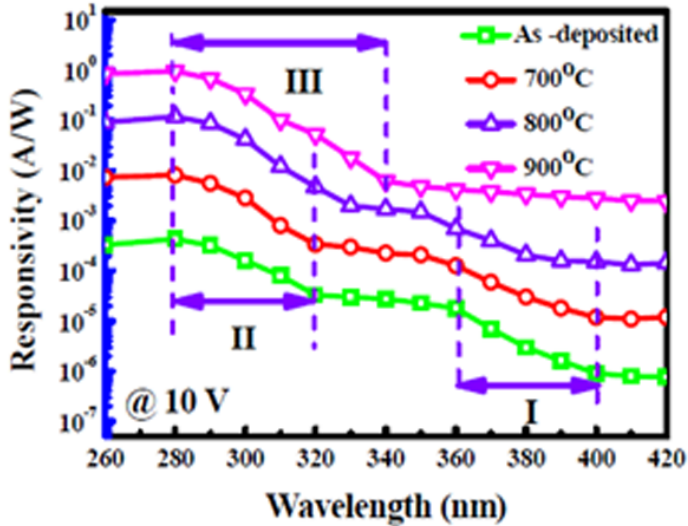
## 3 Results and discussions

Dark  $I$ – $V$  characteristics of the fabricated MSM-PDs for the as-deposited and various-temperature-annealed  $\text{Mg}_x\text{Zn}_{1-x}\text{O}/\text{ZnO}$  bi-layer are shown in Fig. 1. Clearly, the current increases with annealed temperature because the sheet resistance of the  $\text{Mg}_x\text{Zn}_{1-x}\text{O}$  and ZnO layers was reduced by the thermal energy of the annealing process. With increasing annealing temperature, the sheet resistance of the ZnO and  $\text{Mg}_x\text{Zn}_{1-x}\text{O}$  layers decreased

from  $179 \text{ M}\Omega/\square$  and  $189 \text{ M}\Omega/\square$  for the as-deposited films to  $0.6 \text{ K}\Omega/\square$  and  $100 \text{ K}\Omega/\square$  for the ones annealed at  $900^\circ\text{C}$ .



**Fig. 1.** Dark  $I$ - $V$  characteristics of the fabricated MSM-PDs with as-deposited and various-temperature-annealed  $\text{Mg}_x\text{Zn}_{1-x}\text{O}/\text{ZnO}$  bi-layer



**Fig. 2.** Responsivity versus wavelengths for the MSM-PDs with as-deposited and various-temperature-annealed  $\text{Mg}_x\text{Zn}_{1-x}\text{O}/\text{ZnO}$  bi-layer biased at 10-V voltage

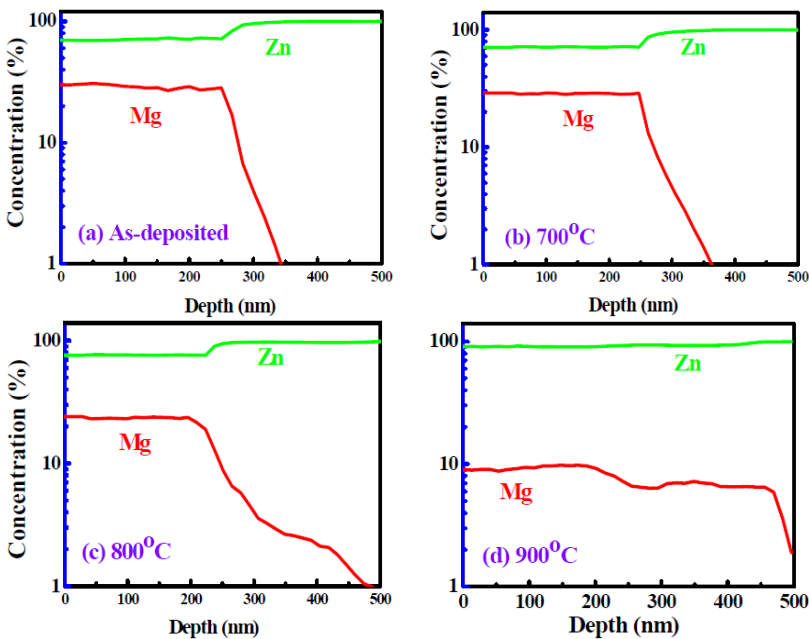
The plot of responsivity versus wavelength for the MSM-PDs with as-deposited and various-temperature-annealed  $\text{Mg}_x\text{Zn}_{1-x}\text{O}/\text{ZnO}$  bi-layer biased at 10 V is shown in Fig. 2. It is interesting that the MSM-PDs with as-deposited and  $700$ – $800^\circ\text{C}$  annealed  $\text{Mg}_x\text{Zn}_{1-x}\text{O}/\text{ZnO}$  bi-layer demonstrate two sharp increasing bands in responsivity, that is; the MSM-PDs have two detection bands, I and II. In contrast, only one sharp increasing band is observed in the MSM-PDs with  $900^\circ\text{C}$  annealed  $\text{Mg}_x\text{Zn}_{1-x}\text{O}/\text{ZnO}$  bi-layer, meaning these MSM-PDs has only one detection band, III.

In the MSM-PDs with as-deposited and  $700$ – $800^\circ\text{C}$  annealing, the sharp increasing band of region I, wavelength region of  $360$ – $400 \text{ nm}$ , originated from the absorption of ZnO layer. However, the sharp increasing band of region II comes from the absorption of the  $\text{Mg}_x\text{Zn}_{1-x}\text{O}$  layer, having a wavelength region of  $280$ – $320 \text{ nm}$ . In contrast, the absorption band of ZnO disappears and only one absorption band is observed in the MSM-PDs with  $900^\circ\text{C}$

annealed  $Mg_xZn_{1-x}O/ZnO$  bi-layer. This absorption band has a wavelength region of 280–340 nm, which is shorter than the absorption region (360–400 nm) of ZnO. Thus, the one absorption band (280–340 nm) is an absorption result of the  $Mg_xZn_{1-x}O$  layer with Mg content ( $x$  value) less than 0.3 for the as-deposited  $Mg_xZn_{1-x}O$  [10,11, 30].

More evidence of Mg inter-diffusion can be observed in the SIMS depth profile of the as-deposited and various temperature annealed  $Mg_xZn_{1-x}O/ZnO$  bi-layers, shown in Fig. 3. It is clear that the top  $Mg_xZn_{1-x}O$  and bottom ZnO layers are present in the as-deposited  $Mg_xZn_{1-x}O/ZnO$  bi-layer with Mg concentration of about 30%, shown in Fig. 3(a). The sharp interface between  $Mg_xZn_{1-x}O$  and ZnO leads two detection bands in the MSM-PDs with the as-deposited  $Mg_xZn_{1-x}O/ZnO$  bi-layer, shown in Fig. 2. No significant Mg diffusion is seen in the 700 °C annealed  $Mg_xZn_{1-x}O/ZnO$  bi-layer, shown in Fig. 3(b), which causes a similar responsivity between the MSM- PDs with as-deposited and 700 °C annealed  $Mg_xZn_{1-x}O/ZnO$  bi-layer, also shown in Fig. 2.

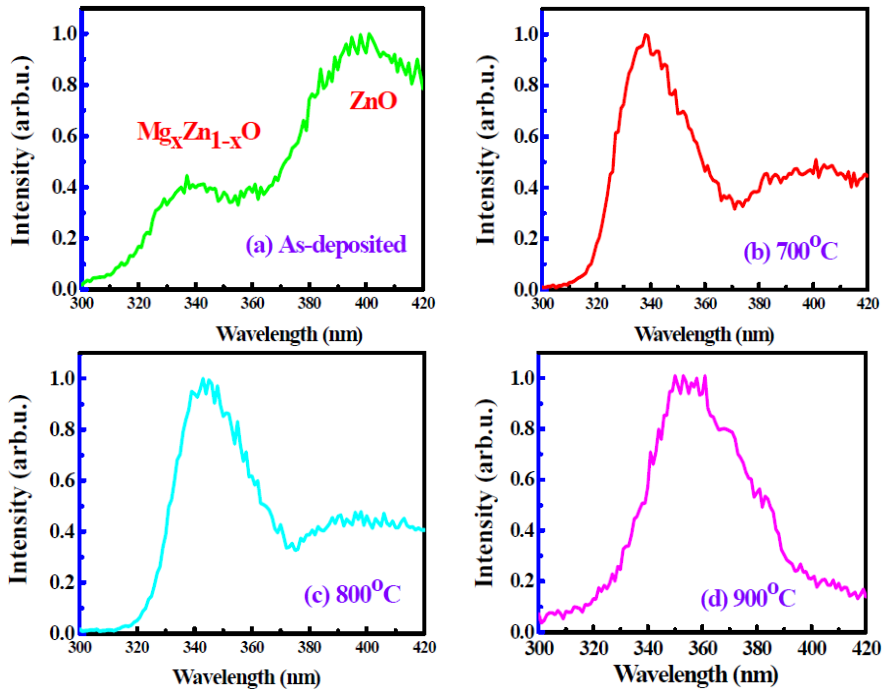
Whereas a significant Mg diffusing, from top  $Mg_xZn_{1-x}O$  into the underlying ZnO layer, is present in the 800 °C annealed  $Mg_xZn_{1-x}O/ZnO$  bi-layer, shown in Fig. 3(c). The Mg diffusion results in decreased Mg concentration from ~30% for the as-deposited (Fig. 3(a)) to ~23% for the 800 °C annealed  $Mg_xZn_{1-x}O/ZnO$  bi-layer, shown in Fig. 3(c). The decrease in Mg concentration causes a red-shift of the  $Mg_xZn_{1-x}O$  absorption edge; the Mg atom also diffuses into the underlying ZnO layer, generating a blue-shift of the ZnO absorption edge. On further increasing the annealing temperature to 900 °C, the  $Mg_xZn_{1-x}O/ZnO$  bi-layer gets homogenized into a single  $Mg_xZn_{1-x}O$  layer with ~8% Mg distributed almost uniformly as shown in Fig. 3(d), leading to only one detection band in the 900 °C annealed MSM-PDs, shown in Fig. 2.



**Fig. 3.** SIMS depth profile of the as-deposited and various temperature annealed  $Mg_xZn_{1-x}O/ZnO$  bi-layer

The normalized PL spectra of the as-deposited and various-temperature-annealed  $Mg_xZn_{1-x}O/ZnO$  bi-layer are shown in Fig. 4. The as-deposited  $Mg_xZn_{1-x}O/ZnO$  bi-layer

demonstrates two distinct peaks located at about 340 and 400 nm for the emissions of the  $Mg_xZn_{1-x}O$  and ZnO layers, respectively, as shown in Fig. 4(a). PL is maintained at almost the same peak wavelengths in the 700 °C annealed  $Mg_xZn_{1-x}O/ZnO$  bi-layer, shown in Fig. 4(b). It is a fact that no significant Mg diffusion is observed in the SIMS depth profile of Fig. 4(b). However, compared to the as-deposited  $Mg_xZn_{1-x}O/ZnO$  bi-layer, the annealed  $Mg_xZn_{1-x}O/ZnO$  bi-layer reveals a larger emission peak in  $Mg_xZn_{1-x}O$  than that in ZnO.



**Fig. 4.** Normalized PL spectra of the as-deposited and various-temperature-annealed  $Mg_xZn_{1-x}O / ZnO$  bi-layer

This is because the crystalline property of the  $Mg_xZn_{1-x}O$  film is largely improved after annealing due to the full width at half maximum being drastically reduced from  $0.54^\circ$  to  $0.36^\circ$  for the as-deposited and 700 °C annealed  $Mg_xZn_{1-x}O$  layers, respectively.  $Mg_xZn_{1-x}O$  is the top layer, and the incident light is illuminated from the  $Mg_xZn_{1-x}O$  side in the PL measurement. When raising the annealing temperature to 800°C, the emission wavelength of  $Mg_xZn_{1-x}O$  is red-shifted and that of the ZnO is blue-shifted, due to the Mg diffusing across  $Mg_xZn_{1-x}O/ZnO$  interface, shown in Fig. 4(c). On further increasing the annealing temperature to 900°C, only one PL peak occurs at about 355 nm, due to the completely homogenized  $Mg_xZn_{1-x}O$  layer generated, as shown in Fig. 4(d).

## 4 Conclusions

The tunable detection band of MSM-PDs with  $Mg_xZn_{1-x}O/ZnO$  bi-layer was fabricated. By varying the annealing temperature from 700 to 900 °C during fabrication, we can modulate the detection band of the fabricated MSM-PDs from two bands into one band. When the annealing temperature is lower than 900 °C, two distinct detection bands were

achieved due to the absorption of  $\text{Mg}_x\text{Zn}_{1-x}\text{O}$  and the underlying ZnO layers. When the annealing temperature was raised to 900 °C, only one detection band was observed in the NSM-PDs. This is because the  $\text{Mg}_x\text{Zn}_{1-x}\text{O}/\text{ZnO}$  bi-layer is completely mixed into one  $\text{Mg}_x\text{Zn}_{1-x}\text{O}$  layer owing to the diffusion of Mg atoms from  $\text{Mg}_x\text{Zn}_{1-x}\text{O}$  to the underlying ZnO layer. PL measurement show that there are two emission peaks in the as-deposited and 700–800 °C annealed  $\text{Mg}_x\text{Zn}_{1-x}\text{O}/\text{ZnO}$  bi-layer. However, only one emission peak was found in the 900°C annealed  $\text{Mg}_x\text{Zn}_{1-x}\text{O}/\text{ZnO}$  bi-layer. Equations should be centred and should be numbered with the number on the right-hand side.

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