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

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Abstract. Magnesium (Mg) diffusion behavior on the band modulation of MgxZn1-xO/ZnO metal-semiconductor-metal photodetectors (MSM-PDs) was studied. As the annealing temperature increases, Mg atoms diffuse from MgxZn1-xO 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 MgxZn1-xO and the ZnO layer, respectively. When the annealing temperature is raised to 900 °C, the MgxZn1-xO/ZnO bi- layer becomes homogenized into a single MgxZn1-xO layer, leading to only one detection band with a wavelength region of 280-340 nm. In the photoluminescence measurement, the as-deposited MgxZn1-xO/ZnO bi-layer demonstrates two distinct emission peaks located at about 340 and 400 nm for the absorption of the MgxZn1-xO and ZnO layers, whereas only one emission peak of 355 nm was observed in the 900 °C-annealed MgxZn1-xO/ZnO bi-layer.

## 1 Introduction

ZnO and  $Mg_{x}Zn_{1-x}O$ -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-bandgap material, MgO (7.8 eV), the tunable bandgap material of  $Mg_XZn_{1-x}O$ , 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  $Mg_XZn_{1-x}O$  material because  $Mg^{+2}$  has a very similar ionic radius to that of  $Zn^{+2}$  [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  $Al_xGa_{1-x}N$ 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  $Mg_xZn_{1-x}O$  materials, the

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

The photoluminescence (PL) was investigated by annealing the  $Mg_XZn_{1-x}O/ZnO$  bilayer, which tuned the Mg composition [27]. Dual-band  $Mg_XZn_{1-x}O$  UV-PDs were fabricated by employing two  $Mg_XZn_{1-x}O$  layers with different Mg compositions [28]. The Mg atomic reconstruction was observed in p-type interface (ZnO on Zn-polar MgZnO), but not in n-type interface (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  $Mg_XZn_{1-x}O/ZnO$  bi-layer was studied. We found that by increasing the annealing temperature of the  $Mg_XZn_{1-x}O/ZnO$  bi-layer, one could modulate the detection band of the fabricated MSM-PDs from two bands into one band.

# 2 Experiments

ZnO and Mg<sub>X</sub>Zn<sub>1-x</sub>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 Mg<sub>X</sub>Zn<sub>1-x</sub>O film. Then, the Mg<sub>x</sub>Zn<sub>1-x</sub>O/ZnO bi-layers were annealed at various temperatures between 700 and 900 °C for 2 h, which forced the Mg atom to diffuse from Mg<sub>x</sub>Zn<sub>1-x</sub>O/znO bi-layer was also prepared for comparison. MSM-PDs were fabricated by evaporating Au electrodes on the Mg<sub>x</sub>Zn<sub>1-x</sub>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 Mg<sub>x</sub>Zn<sub>1-x</sub>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 varioustemperature-annealed Mg<sub>X</sub>Zn<sub>1-x</sub>O/ZnO bi-layer are shown in Fig. 1. Clearly, the current increases with annealed temperature because the sheet resistance of the Mg<sub>X</sub>Zn<sub>1-x</sub>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 Mg<sub>x</sub>Zn<sub>1-x</sub>O layers decreased from 179 M $\Omega$ / $\Box$  and 189 M $\Omega$ / $\Box$  for the as-deposited films to 0.6 K $\Omega$ / $\Box$  and 100 K $\Omega$ / $\Box$  for the ones annealed at 900 °C.



Fig. 1. Dark I-V characteristics of the fabricated MSM-PDs with as- deposited and various-temperature- annealed Mg<sub>X</sub>Zn<sub>1-X</sub>O/ZnO bi-layer



**Fig. 2.** Responsivity versus wavelengths for the MSM-PDs with as-deposited and various-temperature-annealed MgxZn1- xO/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  $Mg_XZn_{1-x}O/ZnO$  bi-layer biased at 10 V is shown in Fig. 2. It is interesting that the MSM-PDs with as-deposited and 700–800 °C annealed  $Mg_XZn_{1-x}O/ZnO$  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 °C annealed  $Mg_XZn_{1-x}O/ZnO$  bi-layer, meaning these MSM-PDs has only one detection band, III.

In the MSM-PDs with as-deposited and 700–800°C annealing, the sharp increasing band of region I, wavelength region of 360–400 nm, originated from the absorption of ZnO layer. However, the sharp increasing band of region II comes from the absorption of the Mg<sub>x</sub>Zn<sub>1-x</sub>O layer, having a wavelength region of 280–320 nm. In contrast, the absorption band of ZnO disappears and only one absorption band is observed in the MSM-PDs with 900 °C

annealed Mg<sub>X</sub>Zn<sub>1-x</sub>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<sub>x</sub>Zn<sub>1-x</sub>O layer with Mg content (x value) less than 0.3 for the as-deposited Mg<sub>x</sub>Zn<sub>1-x</sub>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  $Mg_XZn_{1-x}O/ZnO$  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, shown in Fig. 3(b),

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 Mgdiffusion 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  $Mg_XZn_{X-1}O$  / 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  $Mg_XZn_{1-x}O$  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  $Mg_XZn_{1-x}O/ZnO$  bi-layer is completely mixed into one  $Mg_XZn_{1-x}O$  layer owing to the diffusion of Mg atoms from  $Mg_XZn_{1-x}O$  to the underlying ZnO layer. PL measurement show that there are two emission peaks in the as-deposited and 700–800 °C annealed  $Mg_XZn_{1-x}O/ZnO$  bi-layer. However, only one emission peak was found in the 900°C annealed  $Mg_XZn_{1-x}O/ZnO$  bi-layer. Equations should be centred and should be numbered with the number on the right-hand side.

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