# Fabrication of a Pt/Mg<sub>x</sub>Zn<sub>1-x</sub>O/ZnO Schottky barrier photodiode utilizing a field plate structure

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#### Abstract

We demonstrated fabrication of a Pt/Mg<sub>x</sub>Zn<sub>1-x</sub>O/ZnO Schottky barrier photodiode (SBD) utilizing a field plate structure toward realization of a high gain avalanche photodiode for feeble ultraviolet ray detection. A Mg<sub>x</sub>Zn<sub>1-x</sub>O film on a c-ZnO substrate was grown by the molecular beam epitaxy method. The interface between the Mg<sub>x</sub>Zn<sub>1-x</sub>O film and the ZnO substrate was investigated using transmittance electron microscopy (TEM). Fabricated Pt/Mg<sub>x</sub>Zn<sub>1-x</sub>O/ZnO SBD showed over -500 V of breakdown voltage in a reverse biased condition.

#### 1. Introduction

ZnO and bandgap modulated  $Mg_xZn_{1-x}O$  are a promising metal oxide semiconductor for optical and electronic device applications because of the large exiton binding energy of 60 meV, direct transition, easiness to control the bandgap in a wurtzite structure [1], and capability for production large amounts of zinc and magnesium. Therefore, a nanostructured film and its applications such as an ultraviolet light-emitting diode [2], high electron mobility transistor [3] and photodiodes [4-6] have been extensively studied. There have been many reports on photodetectors because photodetectors can be fabricated by a Schottky barrier photodiode or photoconductor without p-type ZnO. However, there has been no report on large breakdown voltage and avalanche gain in Pt/Mg\_xZn\_1.xO Schottky barrier photodiodes.

In this report, a  $Mg_xZn_{1-x}O$  film on a c-ZnO substrate grown by the molecular beam epitaxy (MBE) method and fabrication of  $Pt/Mg_xZn_{1-x}O/ZnO$  SBD are described. The deposited  $Mg_xZn_{1-x}O$  has a band gap of 4.31 eV with a wurtzite structure and good lattice match with the c-ZnO substrate. In addition, fabricated the  $Pt/Mg_xZn_{1-x}O/ZnO$ SBD have a relatively low forward current and large breakdown voltage.

## 2. Experiment

### 2-1 Mg<sub>x</sub>Zn<sub>1-x</sub>O thin film preparation

Figure 1 shows a schematic cross-sectional view of a Pt/ Mg<sub>x</sub>Zn<sub>1-x</sub>O/ZnO SBD. A Mg<sub>x</sub>Zn<sub>1-x</sub>O film was deposited by using a plasma-assisted MBE system (Universal Systems; UMB-200). Elemental Zn (6N), Mg (4N) and oxygen (6N5) were used as sources. The composition ratio of Mg and Zn was controlled by the temperature of an Mg-K cell and the temperature of a Zn-K cell for bandgap modulation. An n-type (0001) ZnO substrate (Tokyo Denpa Co., Ltd.,  $\rho = 17.6 \ \Omega \cdot cm$ ,  $10 \times 10 \times 0.5 \ mm^3$ ) was used for  $Mg_x Zn_{1-x}O$  film deposition. The ZnO substrate has a 0.5° off-angle to the m-axis direction and was annealed for desorption of lithium used as a mineralizer from ZnO. After annealing, the ZnO substrate was polished by chemical mechanical polishing.

The process for  $Mg_xZn_{1-x}O$  film deposition was as follows. First, the ZnO substrate was set in the deposition chamber and heated to 850°C for 30 minutes. After thermal cleaning, the temperature was decreased to 400°C and then the  $Mg_xZn_{1-x}O$  buffer layer was deposited for 5 minutes at the Mg-K-cell temperature of 350°C and the Zn-K-cell temperature of 300°C with oxygen plasma (O<sub>2</sub> = 1.5 sccm, rf-power = 300 W). Next, the ZnO substrate was heated to 750°C and the  $Mg_xZn_{1-x}O$  film was deposited for 90 minutes. The thickness of the film was approximately 0.3 µm.

Figure 2 shows transmittance and reflectance spectra of the deposited Mg<sub>x</sub>Zn<sub>1-x</sub>O film. In Fig. 2, some fringes are shown by interference between the surface of Mg<sub>x</sub>Zn<sub>1-x</sub>O and ZnO. A small peak based on free exiton appeared in the short wavelength range. We estimated the band gap energy consisting of free exiton energy (4.25 eV) and binding energy (0.06 eV) to be 4.31 eV. Figure 3 shows an X-ray diffraction pattern of (a) a 2Theta-Omega scan of ZnO (0002) and  $Mg_xZn_{1-x}O$  (0002) and (b)  $Mg_xZn_{1-x}O$  (0002) rocking curve (XRC) measured by an X-ray diffractometer (Cu  $k\alpha_1$ , Bruker; D8 discover). As shown in Fig 3(a), only a single phase Mg<sub>x</sub>Zn<sub>1-x</sub>O (0002) peak appeared; however, full-width at half-maximum value (FWHM) of Mg<sub>x</sub>Zn<sub>1-x</sub>O (0002) in the Fig. 3(b) was 107 arcsec. This relatively large FWHM value compared with our previous value of 40 arcsec was attributed to aging degradation of the surface condition of the ZnO substrate that was manufactured in 2013.





Fig. 1. Schematic cross-sectional view of the  $Pt/Mg_xZn_{1-x}O/ZnO$  SBD.

Fig. 2. Transmittance and reflectance spectra of the  $Mg_xZn_{1-x}O$  film deposited on the ZnO substrate.



Fig. 3. (a) 2Theta-Omega scan of ZnO (0002) and  $Mg_xZn_{1-x}O$  (0002), (b)  $Mg_xZn_{1-x}O$  (0002) rocking curve.



Fig. 4. (a) An optical microscope image of fabricated  $Pt/Mg_xZn_{1-x}O/ZnO$  SBD, (b) a TEM image of a cross-sectional view at the edge of the field plate portion.

# 2-2 Fabrication of a Pt/Mg<sub>x</sub>Zn<sub>1-x</sub>O/ZnO SBD

First, a 300-nm-thick SiO<sub>2</sub> film was deposited on the  $Mg_xZn_{1,x}O$  film by using a ternary cathode oblique incidence magnetron sputtering system (ULVAC, Inc.; MPS-3000) for a field plate structure. Next, a Pt/Ti (20 nm/ 20 nm) electrode was formed by a lift-off process for an adhesive layer, and an SiO<sub>2</sub> film was etched by buffered HF solution for forming a contact hole. Then a semitransparent 3-nm-thick Pt film was deposited in a square region as a Schottky electrode on the surface of the  $Mg_xZn_{1-x}O$  and Pt/Ti film and a ring-shaped 80-nm-thick Pt film for a boding pad was deposited using a lift-off process. The square-shaped window for UV-C light detection was 500 um in width. A 43-nm-thick SiO<sub>2</sub> film was deposited mainly on the Pt semitransparent film for a single layer anti-reflection coating at the wavelength of 250 nm. Finally, a 50-nm-thick Al-doped ZnO film, a 20-nm-thick Ti film and an 80-nm-thick Au film were deposited on the O-face of the ZnO substrate for an ohmic electrode.

Figure 4(a) shows an optical microscope image of fabricated  $Pt/Mg_xZn_{1-x}O/ZnO$  SBD, (b) a TEM image of a cross-sectional view at the edge of the field plate portion. Figure 4(b) shows that a field plate structure consisting of Pt and SiO<sub>2</sub> was clearly formed. However, the Pt film was slightly thin at the edge of SiO<sub>2</sub> because the SiO<sub>2</sub> step form was overhang. On the other hand, a lattice-matched  $Mg_xZn_{1-x}O$  thin film and ZnO substrate interface was clearly observed. From this result, high breakdown voltage based on the field plate and good internal quantum efficiency due to no occurrence of recombination in the interface between the  $Mg_xZn_{1-x}O$  film and the ZnO substrate are expected.

Current-voltage (*I-V*) characteristics of fabricated  $Pt/Mg_xZn_{1-x}O/ZnO$  SBD were measured using a semiconductor characterization system (Keithley; 4200-SCS with pre-amp), a high-voltage source-measure unit (Keithley; 2400) and a manual probing system (HiSOL; HMP-400).

The inset of Figure 5(a) shows the I-V characteristics at low voltage measured by a semiconductor characterization system. The ideality factor n of the diode and the saturation current density  $J_s$  in the inset of Fig. 5(a) were calculated by the thermionic emission theory [7] to the measured values to be 1.97, and  $3.0 \times 10^{-10}$  A/cm<sup>2</sup>, respectively. We also investigated the I-V characteristics at high reverse voltage as shown in Fig. 5(a). Breakdown voltage was observed at -380 V and typical breakdown voltage was over -500 V, which exceeds the measurement limitation of this measurement setup. The high breakdown voltage was achieved by a low density of defects in both the Mg<sub>x</sub>Zn<sub>1-x</sub>O film and ZnO substrate and the field plate structure, and therefore a depletion layer reached the bulk of the ZnO substrate through the  $Mg_xZn_{1-x}O$  film, and applied reverse voltage acted on both the Mg<sub>x</sub>Zn<sub>1-x</sub>O film and the ZnO substrate. Figure 5(b)shows the spectral responsivity of the fabricated photodiode measured using a Xe-arc lamp and a monochromator (JASCO; IUV-25) and a semiconductor characterization system. A high responsivity was obtained in the wavelength range from 250 nm to 300 nm, which is in agreement with the bandgap 4.31 eV shown in Fig.1. Maximum responsivity was 0.031 A/W at the wavelength of 280 nm.



Fig. 5. (a) *I-V* characteristics of the Pt/Mg<sub>x</sub>Zn<sub>1-x</sub>O/ZnO SBD in reverse bias voltage. The inset shows the low voltage-range characteristics, (b) Spectral responsivity.

#### **3.** Conclusions

A Pt/Mg<sub>x</sub>Zn<sub>1-x</sub>O/ZnO SBD was fabricated on a Zn-face of a ZnO substrate. The ideality factor of the photodiode was 1.97, and the maximum responsivity was 0.031 A/W at a wavelength of 280 nm. High breakdown voltage of up to -500 V was obtained.

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