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Growth of Nitrogen-Doped $Mg_xZn_{1-x}O$ for Use in Visible Rejection Photodetectors

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Improvement in the Schottky behavior of metal (Au) contacts with $Mg_{0.01}Zn_{0.99}O$ and $Mg_{0.01}Zn_{0.99}O$:N thin films were observed by treating the films with hydrogen peroxide (H_2O_2) (dipping of samples in H_2O_2 at 100 °C for 3 min). Contacts formed on untreated film showed Ohmic behavior in the current-voltage (I-V) measurements. The H_2O_2 treatment led to a smooth surface morphology for the films and resulted in Schottky contact of Au fabricated on the treated films with barrier heights of 0.82 ∼ 0.85 eV. The absolute current density at a reverse bias of 3 V was 1 ∼ 6 × 10^{-6} A/cm^2 for Au contacts on H_2O_2-treated films. The treated films showed lower electron concentration than the untreated films due to removal of the relatively high conducting top layers of the thin films. A metal-semiconductor-metal (MSM) detector was fabricated using a $Mg_{0.05}Zn_{0.95}O$:N film and was characterized for its spectral response.

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I. INTRODUCTION

Solar-blind ultraviolet photodetectors for control of environmental, flame detection, ultraviolet rays-A (UV-A) and UV-B dosimeters are increasing the research efforts to develop more efficient adaptations for wavelength of ultraviolet rays [1]. ZnO presents advantage of having a large exciton binding energy (60 meV), which is beneficial for operating ZnO devices at a high temperature. Until the present time, there have been only a few works on ZnO-based Schottky photodetectors [2,3]. ZnO grown by using Metalorganic chemical vapor deposition (MOCVD) tends to have n-type conductivity due to intrinsic defects, such as oxygen vacancy and interstitial zinc, and contains hydrocarbon impurities originating from metalorganic precursors. Typical electron concentrations of MOCVD-grown ZnO are 10^{17} ∼ 10^{20} cm^{-3} [4]. In terms of rectifying Schottky contacts, it has been reported that metals having a large work function such as Au, Ag and Pt form Schottky barriers of 0.6 ∼ 0.8 eV on n-ZnO while the barrier height is not correlated with the obvious difference in the work functions [5,6]. These reports claimed that the interface defect states play a major role in determining the Schottky characteristics of metal contacts. Recently, it has been reported that a surface treatment using hydrogen peroxide (H_2O_2) could improve the rectifying contact quality by increasing the Schottky barrier height, decreasing the reverse bias leakage-current, and achieving of an ideality factor approaching unity.

This paper reports on the effect of H_2O_2 treatment for improving the surface of $Mg_{0.01}Zn_{0.99}O$ and $Mg_{0.01}Zn_{0.99}O$ films, leading to Schottky behaviors of Au contacts on these films. A MSM Schottky-type UV detector using $Mg_{0.05}Zn_{0.95}O$:N as an n-type layer and Pt as a Schottky contact was fabricated and was evaluated for its spectral response.

II. EXPERIMENTS

$Mg_xZn_{1-x}O$ films were grown on a-plane (11-20) sapphire substrates using diethylzinc (DEZn) and bis-ethylcycropentadienylmagnesium ($EtCp_2Mg$). The details of the growth system are available in a previous paper [7]. The films were grown at a total gas pressure of 0.01 Torr, a substrate temperature of 600 °C, an oxygen flux of 10 sccm, a nitrogen flux of 4 sccm, a radio-frequency output of 30 W, and a hydrogen carrier flux of 46 sccm. The molar fraction of magnesium of the

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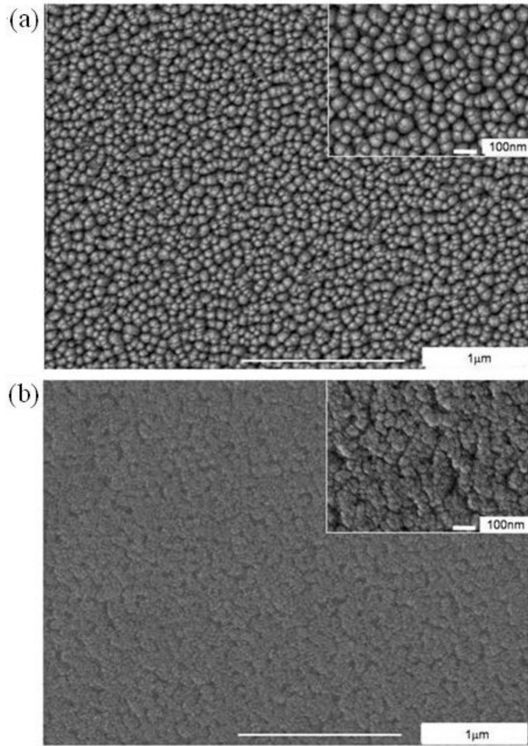

Fig. 1. FESEM images of $Mg_{0.01}Zn_{0.99}O$:N surfaces (a) untreated and (b) with H_2O_2-treatment.

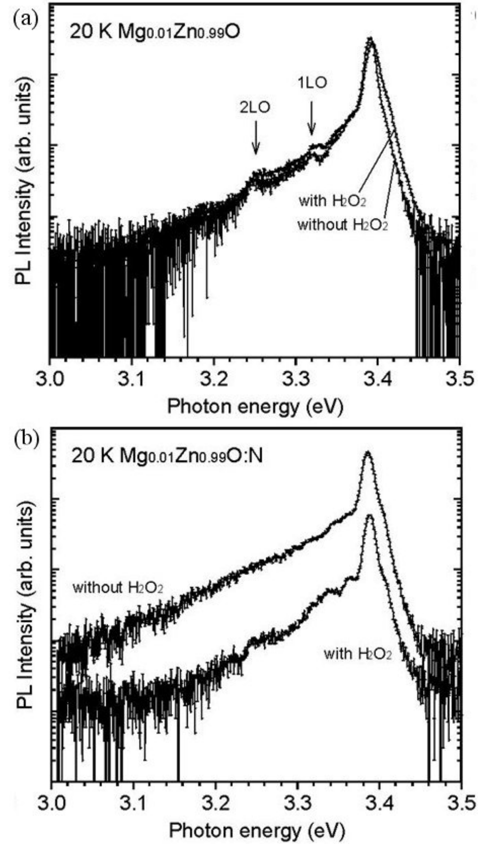

Fig. 2. Photoluminescence spectra taken at 20 K: (a) undoped $Mg_{0.01}Zn_{0.99}O$ film either with or without H_2O_2 treatment and (b) nitrogen-doped $Mg_{0.01}Zn_{0.99}O$ film with and without H_2O_2 treatment.

$Mg_xZn_{1-x}O$ film was $x = 0.01$, as estimated from the optical bandgap.

The optical transmission spectra were recorded on an UV-VIS-NIR scanning spectrometer at wavelength from $200 \sim 700$ nm. The optical bandgap energies were determined from a plot of $(\alpha h\nu)^2$ as a function of the photon energy ($h\nu$). The relationship between the magnesium molar fraction and the bandgap of $Mg_xZn_{1-x}O$ film has been reported in a previous paper [8]. Photoluminescence (PL) measurements were carried out using a He-Cd laser (325 nm) at 20 K. The morphology of the films was analyzed by a field emission scanning electron microscopy (FESEM).

Prior to the metal deposition, the samples were cleaned in organic solvents (acetone and methanol), rinsed in de-ionized water, and dried by a nitrogen stream. Then, samples were dipped in a H_2O_2 solution at 100 °C for 3 min. Au contacts having contact area of 2.16×10^{-3} cm^{-2} and a thickness of 100 nm was formed by thermal evaporation through shadow mask under turbo molecular pump vacuum at around 1×10^{-6} Torr. The Ohmic contacts were made by indium. Schottky properties were examined by capacitance-voltage C-V measurements and current-voltage I-V characteristics at room temperature. Hall-effect measurement was done at room temperature by a Van der Pauw configuration. A UV photodetector was designed and fabricated using an interdigital (IDT) metal-semiconductor-metal (MSM) structure. For the IDT structure, the fingers were 2-μm wide and 250-μm long, with a 2-μm gap. Platinum was used to form the Schottky contact in this detector.

III. RESULT AND DISCUSSION

Figure 1 shows FESEM images of the $Mg_{0.01}Zn_{0.99}O$:N film (thickness: 1 μm) grown directly on sapphire substrates. The as-grown film had a vertically aligned columnar growth with respect to the sapphire (11-20) substrate (Figure 1(a)). These columns had a length about 1 m and an average diameter of about 60 nm. On the other hand, the H_2O_2 treated film showed a smooth surface (Figure 1(b)) with grains having diameters of about 10 nm. The overall smoothness of the $Mg_{0.01}Zn_{0.99}O$:N surface was improved by the H_2O_2 treatment.

Figure 2 shows PL spectra of $Mg_{0.01}Zn_{0.99}O$ and $Mg_{0.01}Zn_{0.99}O$:N films with and without H_2O_2 treatment taken at 20 K. The spectrum of the $Mg_{0.01}Zn_{0.99}O$ film without H_2O_2 treatment exhibited emission peaks at 3.391 eV and shoulders on the lower energy side (Fig-

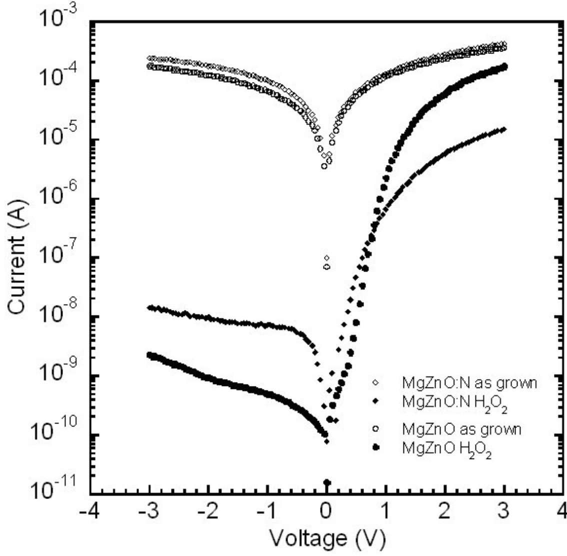

Fig. 3. *I-V* characteristics of Au/ $Mg_{0.01}Zn_{0.99}O$ (:N)/In diodes. Open circles and squares show *I-V* for diodes deposited on untreated films whereas solid circles and squares illustrate *I-V* for diodes deposited on H_2O_2-treated films.

ure 2(a)). The shoulders are assigned to the longitudinal optical (LO) phonon replicas of the main peak of 3.391 eV, associated with 1-LO of 3.321 eV and 2-LO of 3.251 eV, respectively. The origin of the peak at 3.391 eV is not clear for the present. However, the maximum peak can be attributed to neutral donor bound exciton emission because the Hall-measurement indicated n-type conductivity for undoped $Mg_{0.01}Zn_{0.99}O$ film and its optical bandgap (3.32 eV) at room temperature was close to that of ZnO (3.28 eV) [9, 10]. For the H_2O_2-treated sample, the luminescence maxima at 3.393 eV dominated the spectrum; a new and weaker UV emission peak located at 3.411 eV, compared to the sample without H_2O_2-treatments was attributed to free exciton emission of $Mg_{0.01}Zn_{0.99}O$ [10, 11]. The shoulders at a low energy side were assigned to the LO phonon replicas of the main peak of 3.393 eV, associated with 1-LO of 3.323 eV and 2-LO of 3.253 eV, respectively. For both of the N-doped $Mg_{0.01}Zn_{0.99}O$ samples with and without H_2O_2 treatment (Figure 2(b)), the luminescence maxima at 3.385 eV dominated the spectrum with a low energy tail due to overlapping of bound excitons emissions and the satellite band of free excitons, and the DAP transition and its LO phonon replicas [11, 12]. After H_2O_2 treatment, the intensity of the PL spectrum was decreased whereas the structure of the spectrum remained the same. N-doped samples exhibited n-type conductivity by Hall-effect measurements.

The current-voltage characteristics for the Au metal contacts are shown in Figure 3. The samples without H_2O_2 treatment showed the linear *I-V* characteristics expected for Ohmic contacts. In contrast, the samples treated with H_2O_2 exhibited a rectifying behavior.

Table 1. Schottky barrier heights (Φ_B) and ideality factors (n) for Au Schottky contacts, and electron concentrations (N) of the films.

Sample no.	doping	treatment	Φ_B (eV)	n (···)	$N(\mathrm{cm}^{-3})$ (C-V)	N(Hall) (cm^{-3})
1	NID	as-grown	···	···	···	2.42×10^{18}
2	NID	H_2O_2	0.85	3.4	2.42×10^{18}	···
3	N-doped	as-grown	···	···	···	1.47×10^{18}
4	N-doped	H_2O_2	0.82	3.0	2.11×10^{16}	···

The absolute current density at a reverse bias of 3 V was 1×10^{-6} A/cm^2 in the case of the H_2O_2-treated $Mg_{0.01}Zn_{0.99}O$ film and was 6×10^{-6} A/cm^2 in the case of the H_2O_2-treated $Mg_{0.01}Zn_{0.99}O$:N film. The forward current was fitted by considering thermionic emission as being the dominant current transport process.

$$I = I_s\left[\exp\left(\frac{e(V_a - IR_s)}{nk_BT}\right) - 1\right] \tag{1}$$

where, e is the elementary charge, V_a is the applied voltage, R_s is the series resistance of the diode, n is the ideality factor, T is the absolute temperature, k_B is Boltzmann's constant and I_s is the saturation current, which can be expressed as

$$I_s = AA^*T^2\exp\left(-\frac{\Phi_B}{kT}\right) \tag{2}$$

Eq. (2) contains the contact area A, the effective Richardson constant A^*, having a theoretical value for ZnO of $A^* = 32$ A/cm^{2}K^2 and the effective barrier height B at zero bias. From the data, Φ_B was obtained as 0.85 eV for an Au contact deposited on a H_2O_2-treated $Mg_{0.01}Zn_{0.99}O$ and as 0.82 eV for $Mg_{0.01}Zn_{0.99}O$:N. The ideality factors were 3.4 for $Mg_{0.01}Zn_{0.99}O$ and 3.0 for $Mg_{0.01}Zn_{0.99}O$:N, suggesting that the transport mechanism was dominated by surface recombination and/or trapped states at deep levels rather than by thermionic emission.

Table 1 summarizes the Schottky characteristics and the electron concentrations for $Mg_{0.01}Zn_{0.99}O$ (:N). The electron concentration of sample 4 was estimated to be 2.11×10^{16} cm^{-3}, which was lower than that of the undoped sample 2. This was due to compensation of residual electron states by nitrogen acceptors. The lower carrier concentrations obtained for treated samples (Table 1) was due to the removal of a relatively high conducting layer on the thin films. Besides, the higher carrier concentration for H_2O_2-untreated samples was possibly overestimated in Hall-calculations due to a trapping of mobile carriers at the grain boundary, thereby reducing their mobility [13]. The untreated film (Figure 1(a)) had exhibited a preferential columnar growth. Since the atoms at the grain boundary of the column structure are disordered, there are a large number of defects due to

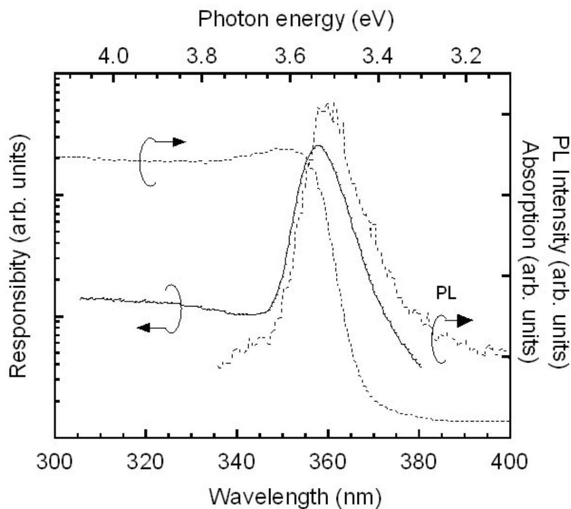

Fig. 4. AC photoresponse from the MSM photodetector fabricated on nitrogen-doped $Mg_{0.05}Zn_{0.95}O$. The photoresponse spectrum was compared with the absorption spectrum and the photoluminescence spectrum of the $Mg_{0.05}Zn_{0.95}O$:N film measured at room temperature.

incomplete atomic bonding, thereby reducing their Hall-mobility.

Finally, we fabricated a MSM detector using a $Mg_{0.05}Zn_{0.95}O$:N film. Platinum was used to form the Schottky contact in this detector. Platinum has a large work-function (5.6 eV) compared with Au (5.1 eV). Therefore, Pt Schottky performance was expected to be a better Schottky contact than Au. The $Mg_{0.05}Zn_{0.95}O$:N film had an optical band gap of 3.48 eV at room temperatures as calculated from the absorption coefficient. A strong wide peak was observed in the spectral response of the photodetector, as shown in Figure 4. This peak was centered at 357 nm, had a FWHM of 8 nm, and had a relative height of more than one order of magnitude over the higher energy response plateau. A room-temperature PL emission centered at 359 nm was observed for the $Mg_{0.05}Zn_{0.95}O$:N film and the near-band-edge emission and absorption were attributed to free exciton recombination emission. As a result, the MSM detector with $Mg_{0.05}Zn_{0.95}O$:N had a strong excitonic absorption near band edge.

IV. CONCLUSION

$Mg_{0.01}Zn_{0.99}O$ and $Mg_{0.01}Zn_{0.99}O$:N films having n-type conductivity with low carrier concentrations were realized for possible applications in photodetectors. Surface treatment using H_2O_2 was used to improve the surface conditions for forming Au Schottky contacts with barrier heights of 0.82 $\sim$ 0.85 eV in the case of the H_2O_2-treated surfaces. H_2O_2-treatment is thought to modify the Fermi level pinning for Schottky metal contacts. Treatment also resulted in a lowering of the carrier concentration due to the removal of a relatively high conducting top layer of the thin films. The lowest concentration among the experimental samples was 2.11×10^{16} cm^{-3} in the case of the H_2O_2-treated $Mg_{0.01}Zn_{0.99}O$:N film. A MSM detector was fabricated using a $Mg_{0.05}Zn_{0.95}O$:N film and showed a peak response at 357 nm.

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