TRANSACTIONS ON ELECTRICAL AND ELECTRONIC MATERIALS VOL. 10, NO. 1, FEBRUARY 25, 2009

Analysis of Photoluminescence for N-doped and undoped p-type ZnO Thin Films Fabricated by RF Magnetron Sputtering Method

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(Received January 15 2009, Accepted February 12 2009)

N-doped ZnO thin films were deposited on n-type Si(100) and homo-buffer layer, and undoped ZnO thin film was also deposited on homo-buffer layer by RF magnetron sputtering method. After deposition, all films were in-situ annealed at 800 °C for 5 minutes in ambient of O_2 with pressure of 10 Torr. X-ray diffraction shows that the homo-buffer layer is beneficial to the crystalline of N-doped ZnO thin films and all films have preferable c-axis orientation. Atomic force microscopy shows that undoped ZnO thin film grown on homo-buffer layer has an evident improvement of smoothness compared with N-dope ZnO thin films. Hall-effect measurements show that all ZnO films annealed at 800 °C possess p-type conductivities. The undoped ZnO film has the highest carrier concentration of $1.145\text{x}10^{17}$ cm^{-3}. The photoluminescence spectra show the emissions related to FE, DAP and many defects such as V_{Zn}, Zn_O, O_i and O_{Zn}. The p-type defects (O_i, V_{Zn}, and O_{Zn}) are dominant. The undoped ZnO thin film has a better p-type conductivity compared with N-doped ZnO thin film.

Keywords: P-type ZnO film, Homo-buffer layer, RF magnetron sputtering, Photoluminescence

1. INTRODUCTION

ZnO has a strong potential for various short-wavelength optoelectronic devices such as light emitting diodes(LEDs) and laser diodes(LDs), because of its wide band gap energy of 3.37 eV and large exciton binding energy of 60 meV at room temperature[1], which is one of the advantages over GaN. In order to exploit the potential offered by ZnO, both high-quality n- and p-type ZnO are necessary. N-type is easy to realize because ZnO occurs naturally as n-type conduction due to the presence of intrinsic donor defects, such as oxygen vacancies(V_o) and zinc interstitials(Zn_i). There have been many reports for growth of high quality n-type ZnO using group-III elements such as B, Al, Ga, and In as dopants[2,3]. However, the realization of p-type ZnO has been proven difficult and is thought to the bottleneck due to high self-compensation, low solubility of the dopant and deep acceptor level[4]. P-type doping in ZnO may be possible by substituting either group- I elements(Li, Na, K) for Zn sites or group-V elements (N, P, As) for O sites. Theoretically, N is the best dopant for p-type doping since it has nearly the same radius as O and is the shallowest acceptor in ZnO[5]. Further more, many N sources such as N_2, NO, N_2O and NH_3 have been studied. Among the available N sources, an easy getting, economical and non-toxic N_2 has been widely used in sputtering technique[6]. Factually, molecular N_2 is a n-type dopant and atom N is a p-type dopant. To realize the p-type doping, the separation of N_2 is necessary.

In this paper, N-doped ZnO thin films were deposited on n-type Si(100) and homo-buffer layer in the mixture of N_2 and O_2, and nominally undoped ZnO thin film was deposited in pure O_2 gas by RF magnetron sputtering method to compare their PL properties.

2. EXPEREMENTS

N-doped ZnO thin films were deposited on n-type Si(100) (about 20 Ωcm) and homo-buffer layer by RF magnetron sputtering method. Homo-buffer layer(about 70 nm) was deposited on the n-type Si(100) substrate in the mixture of O_2 and Ar with ratio of 1:4 at temperature of 100 °C, pressure of 15 mTorr, and RF power of 120 W for 30 minutes. Subsequently, the homo-buffer layers were in-situ annealed in pure O_2 gas ambient at 800 °C and 15 mTorr for 20 minutes. Ceramic ZnO (5N) was used as target. N-doped ZnO thin films were deposited on n-type Si(100) wafer and homo-buffer layer in the mixture of N_2 and O_2 with ratio of 3:2. Nominally undoped ZnO thin film was also deposited on homo-buffer layer in the ambient gas of pure O_2. Prior to deposition, the chamber was evacuated to below 10^{-6} Torr, and the substrate was cleaned ultrasonically first in acetone for 15 minutes, in methanol for 15 minutes, and in DI water for 5 minutes subsequently. After deposition, all ZnO thin films were processed with in-situ annealing. The details for deposition and annealing conditions of undoped and N-doped ZnO thin films are listed in Table 1.

In this work, N-doped ZnO thin film deposited on n-type Si(100), N-doped ZnO thin film deposited on homo-buffer layer, and undoped ZnO thin film were denoted as the sample A, sample B, and sample C respectively. The crystal orientation was examined by X-ray diffraction (XRD). The surface morphology of the N-doped ZnO thin films was characterized by atomic force microscopy (AFM). Hall-

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*Author to whom corresponding should be addressed: electronic mail: cbpark@wonkwang.ac.kr effect measurements were also carried out to evaluate the electrical properties of the ZnO films. The optical properties were studied by photoluminescence(PL) measurements.

Table 1. Conditions of RF magnetron sputtering to deposit ZnO thin films.

parameters	conditions
substrate	n-Si(100), buffer layer
target	ceramic ZnO (5N)
base pressure	below 10^{-6} Torr
working pressure	15 mTorr
growth temperature	450 °C
ambient gas	N_2:O_2=3:2 or pure O_2(5N)
RF power	210 W
deposition time	180 min(~900 nm)
annealing	ambient: O_2 (5N) pressure: 10 Torr temperature: 800 °C holding time: 5 min

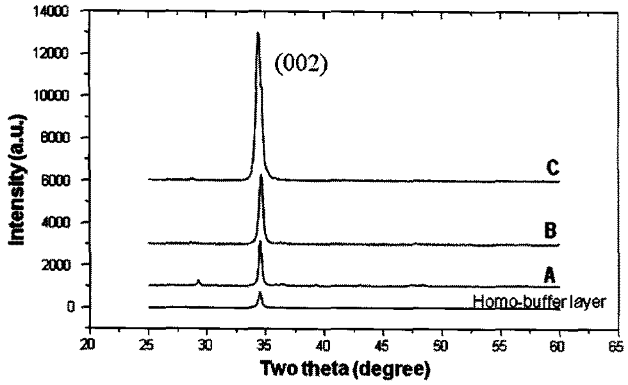

Fig. 1. XRD patterns of homo-buffer layer and sample A, B and C.

3. RESULTS AND DISCUSSION

Figure 1 shows that all ZnO thin films and homo-buffer layer have c-axis orientation, and two theta diffraction peaks of (002) are at about unstressed position of 34.44 ° which is the value of corresponding peak of bulk ZnO, implying that all ZnO thin films have not obvious internal stress[3]. The peak intensity of sample B(N-doped ZnO thin film deposited on homo-buffer layer) is greater than that of sample A(N-doped ZnO thin film deposited on n-type Si(100) wafer). Sample C(nominally undoped ZnO thin film) has the highest peak intensity. While the FWHMs of N-doped ZnO thin films become larger when they were deposited on homo-buffer layer. FWHMs of sample A, sample B and sample C are 0.286 °, 0.396 °, 0.502 °, respectively. This result is against common expectation that films grown on matched layers should have larger grain sizes than those on mismatched layers, which shows less FWHM(Full Width at Half Maximum) values for larger grains. One of the reasons is mismatched overlap of (002) peaks of the buffer layer and the film on it when the films grew[7].

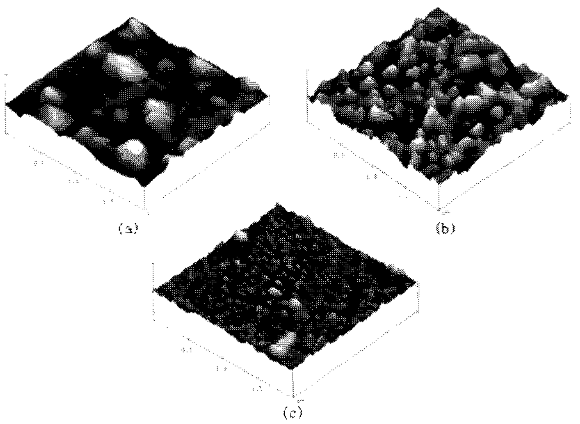

Fig. 2. AFM images of ZnO thin films deposited in different conditions. (a) sample A, (b) sample B, and (c) sample C.

Figure 2 shows AFM images of N-doped and undoped ZnO thin films deposited on n-type Si(100) or homo-buffer layer. The RMS roughness values of sample A, sample B, and sample C are 16.57, 19.86 and 5.37 nm, respectively, implying that undoped ZnO film grown on homo-buffer layer in pure O_2 has an evident improvement of smoothness compared with N-doped films. The corresponding average grain sizes are 109.38, 132.8 and 35.2 nm, respectively. Those results are not agree with those of grain sizes calculated by Scherrer's formula from FWHM values of (002)peaks of XRD spectra.

Table 2. Electrical properties of ZnO thin films deposited in different conditions. (Resistivity, hall mobility, and carrier concentration are denoted as R, μ, and n, respectively.)

sample	R (Ωcm)	μ (cm^2/Vs)	n (cm^{-3})	type
A	75.26	1054.6	7.84×10^{13}	p
B	72.20	91.5	9.46×10^{14}	p
C	0.0454	1201	1.145×10^{17}	p

The results of Hall-effect measurements are summarized in Table 2. All ZnO thin films deposited show p-type conductivities and high hall mobility. Sample A and sample B(N-doped ZnO thin films deposited on n-type Si(100) and on homo-buffer layer) have similar resistivity, but sample B has a higher hole concentration than sample A. Among all samples, sample C(undoped ZnO thin films on homo-buffer layer) has the highest hole concentration of 1.145×10^{17} cm^{-3} and mobility of 1201 cm^2/Vs, and the lowest resistivity of 4.54×10^{-2} Ωcm, implying that high-quality intrinsic p-type ZnO thin film could be obtained in O_2-rich ambient. N-doped p-type ZnO thin films show much less hole concentration than nominally undoped p-type ZnO thin film. This is because in N-doping process, most of N is doped in ZnO in a state of molecular N_2, which acts as a donor and makes p-type ZnO film hard to realize. However, the effect of homo-buffer layer on the electrical property of N-doped ZnO thin film can be seen. The homo-buffer layer promotes the hole concentration of N-doped ZnO thin film. However, the hole concentration is still too low to meet demand of p-n junction at which the hole concentration should be over 10^{17} cm^{-3}.

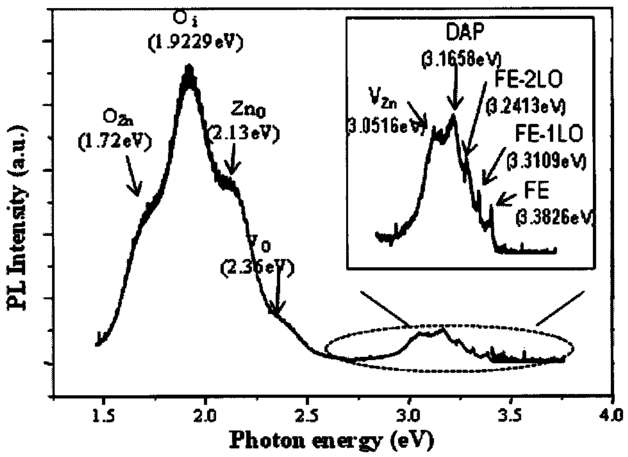

Fig. 3. PL spectrum at 10K of N-doped ZnO thin film deposited on n-type Si(100). The inset shows the PL details at the range of 2.65-3.75 eV.

Figure 3 shows PL spectrum of N-doped ZnO film deposited on n-type Si(100), revealing two peaks due to oxygen interstitial(O_i) and zinc vacancy(V_{Zn}), three shoulders due to oxygen antisite on zinc(O_{Zn}), zinc anti site on oxygen(Zn_O) and oxygen vacancy(V_O) in visible region. In the UV emission region, there are four explicit peaks, showing at the positions of 3.3826, 3.3109, 3.2413 and 3.1658 eV, ascribed to free exciton energy(FE), first and second LO phonon replicas(FE-1LO and FE-2LO) (according to C. Klingshirn's theoretic calculation, the LO phonon replica energy of ZnO is 72 meV)[8], and donor-acceptor pair transition(DAP) respectively.

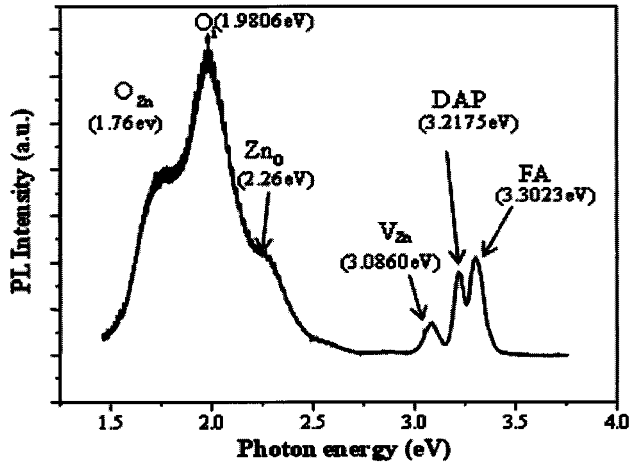

Fig. 4. PL spectrum at 10K of nominally undoped ZnO thin film deposited on homo-buffer layer.

Figure 4 shows PL spectrum of nominally undoped ZnO thin film deposited on homo-buffer layer. The peaks at 3.3023 and 3.2175 eV are attributed to the transition of free electron to acceptor level(FA) and donor-acceptor pair(DAP) respectively. The peaks at 3.0860 and 1.9806 eV are ascribed to zinc vacancy (V_{Zn}) and oxygen interstitial(O_i) respectively.

Comparison of Fig. 4 with Fig. 3 reveals similarity of two patterns at deep level defect emissions. The positions at 1.76, 1.9806, 2.26, and 3.0860 eV in Fig. 4 seem to correspond to those at 1.72, 1.9229, 2.13 and 3.0516 eV in Fig. 3. The concentration of Zn_O is inversely proportional to square root of oxygen partial pressure, but that of O_{Zn} is proportional to square root of oxygen partial pressure[9]. Therefore, at the condition of high oxygen partial pressure, the intensity related to Zn_O gets lower and that related to O_{Zn} gets higher as shown in Fig. 4 compared with those shown in Fig. 3. In addition, there is no oxygen vacancy(V_O) existed in undoped ZnO thin film, which leads to a better optical property in near band emission(NBE) region shown in Fig. 4[10]. According to either Fig. 3 or Fig. 4, the p-type defects(O_i, V_{Zn}, and O_{Zn}) are dominant. Moreover, there is no emission from zinc interstitial (Zn_i) which acts as a donor and should have the energy level of 2.9 eV, implying that there is no Zn_i in ZnO thin films, which means lack of n-type compensation caused by Zn_i. Therefore, all ZnO films in this study possess p-type conductivity.

4. CONCLUSION

In summary, the homo-buffer layers avail promoting microstructure of ZnO thin films. According to AFM, the smoothness of undoped ZnO thin film is improved significantly comparing with that of N-doped thin films. The PL spectra show the emissions related to FE, DAP and defects of V_{Zn}, Zn_O, O_i and O_{Zn}. Compared with N-doped ZnO thin film, the nominally undoped ZnO thin film has higher peaks in near band emission(NBE) region. The positions of O_{Zn} and Zn_O can be confirmed by comparison. The peak of p-type defect O_{Zn} also becomes higher, and the peak of n-type defect V_O disappears, which means the p-type conductivity of undoped ZnO thin film is better than N-doped ZnO thin film. So p-type carrier concentration of undoped ZnO thin film is higher than that of N-doped ZnO thin film.

ACKNOWLEDGMENTS

This research was supported by Wonkwang University in 2007.

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