A Study on the Optical Property of Al-N-codoped p-type ZnO Thin Films Fabricated by DC Magnetron Sputtering Method

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Abstract : In this study, high-quality Al-N doped p-type ZnO thin films were deposited on n-type Si (100) wafer or Si coated with buffer layer by DC magnetron sputtering in the mixture of N_2 and O_2 gas. The target was ceramic ZnO mixed with Al_2O_3 (2 wt%). The p-type ZnO thin film showed higher carrier concentration $2.93\times10^{17}cm^{-3}$, lower resistivity of 5.349 Ωcm, and mobility of 3.99 $cm^2V^{-1}s^{-1}$, respectively. According to PL spectrum, the Al donor energy level depth (E_d) of Al-N codoped p-type ZnO film was reduced to about 51 meV, and the N acceptor energy level depth (E_a) was reduced to 63 meV, respectively.

Key Words : P-type ZnO film, Buffer layer, DC magnetron sputtering, Photoluminescence, Acceptor/donor level

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]. 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 vacancy (V_o) and zinc interstitial (Zn_i). However, the realization of high-quality p-type ZnO thin films is still a bottleneck due to high self-compensation, low solubility of the dopant and deep acceptor level [2]. 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. But molecular N_2 is difficult to be seperated and acts as donors. According to codoping theory, the solubility is enhanced, and acceptor level is made shallower, which is beneficial to the fabrication of p-type ZnO thin films. In this study, it was confirmed that both acceptor level and donor level were made shallower.

2. Experiments

Al-N codoped ZnO films were fabricated on Si coated with buffer layer (buffer layer/Si) by DC magnetron sputtering. All Si substrates were ultrasonically cleaned in acetone, methanol, and then DI water sequentially. Later they were dried by N_2 gas. The ceramic ZnO mixed with 2 wt% Al_2O_3 was selected as a sputtering target. The details for deposition and annealing Al-N codoped ZnO films are listed in Table 1. X-ray diffraction (XRD), Hall Effect in Van der Pauw configuration and photoluminescence (PL) were conducted to evaluate the microstructure, electrical and optical properties, respectively.

Table 1. The sputtering conditions for Al-N codoped ZnO thin films.

parameters	conditions
target	$ZnO:Al_2O_3$
substrate	buffer layer/Si
base pressure	below 10^{-6} Torr
working pressure	15 mTorr
DC power	340 V, 0.1 A
growth temperature	450 ℃
ambient gas (N_2+O_2)	N_2: 20%, 40%, 60%, 80%
growth time	120 min

3. Results and discussion

XRD patterns of Al-N codoped ZnO thin films fabricated in different N_2 fractions on buffer layer/Si (denoted as sample BS1, BS2, BS3, and BS4) are shown in fig. 1. Two theta diffraction (002) peaks lie at the position smaller than the unstressed position of 34.44° (dotted line), implying that the c-axis crystal lattice constant of Al-N codoped ZnO is lager than that of bulk ZnO. The crystallinity becomes worse with increasing N_2 fraction.

The electrical property is listed in table 2. The conduction type was changed from n-type to p-type with increasing N_2 fraction, implying that more atom N is incorporated into ZnO films. The p-type film shows higher hole concentration of $2.93\times10^{17}cm^{-3}$.

PL spectrum of the p-type film (sample BS4) is shown in fig. 2. The p-type film shows deep defect levels at 1.67, 2.36, 2.59, and 2.95 eV and near band edge levels at 3.374 and 3.323 eV. The peaks of 3.373 and 3.323 eV are ascribed to the transition of free electrons in the conduction

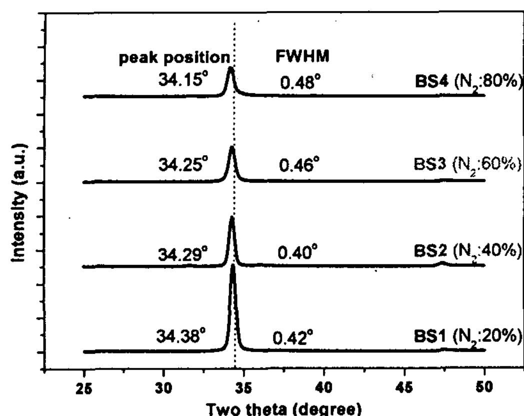

Fig. 1. XRD patterns of Al-N codoped ZnO thin films fabricated on buffer layer/Si in different N_2 fractions.

band to acceptor level (FA) and donor-acceptor pair (DAP), respectively. The samll peaks ranged from 3.17 eV to 3.27 eV are related to Al-N-uncoupled DAPs. The peak energy difference between DAP and FA is the depth of donor level (E_d), and the difference between FA and bandgap energy of ZnO (~3.437 eV at low temperature [3]) is the depth of acceptor level (E_a). So, according to calculation, the donor (Al) and acceptor (N) levels are 51 and 63 meV, respctively. Theoretically, the Al donor level in Al-doped ZnO film is 65 meV, and the N acceptor level in N-doped ZnO film is 100 meV [4]. In this study, Al donor level and N acceptor level were reduced by 14 meV and 37 meV, respectively, which is beneficial to the formation of p-type conduction.

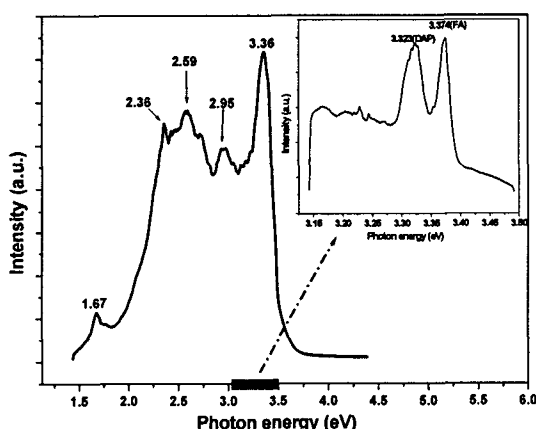

Fig. 2. PL spectrum of Al-N codoped p-type ZnO thin film fabricated in N_2 fraction of 80%. The inset shows the PL details at the range of 3.15~3.75 eV.

Table 2. Electrical property of Al-N codoped ZnO thin films fabricated in different N_2 fractions .(Resistivity, hall mobility, and carrier concentration are denoted as n, μ, and R, respectively.)

sample	n (cm^{-3})	μ ($cm^2V^{-1}s^{-1}$)	R (Ωcm)	type
BS1	--	--	--	--
BS2	$1.19x10^{16}$	142	3.689	n
BS3	$3.38x10^{15}$	53.7	30.7	n
BS4	$2.93x10^{17}$	3.99	5.349	p

4. Conclusion

In this study, high quality Al-N codoped p-type ZnO thin film was fabricated on buffer layer/Si with ZnO:Al_2O_3 (2 wt%) target in N_2 fraction of 80% by DC magnetron sputtering method. The p-type film shows high hole concentration of $2.93x10^{17}cm^{-3}$. All films show unidirectional growth along the crystal c-axis, but the crystallinity became worse with increasing N_2 fraction. The p-type film shows fine PL spectrum. According to PL spectrum, the donor and acceptor levels were made shallower to 51 meV and 63 meV, respectively, which is beneficial to the formation of p-type conduction and improvement of hole concentration.

Acknowledgments

This research was supported by Wonkwang University in 2009.

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