PL Property of Al-N Codoped p-type ZnO Thin Films Fabricated by DC Magnetron Sputtering

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High-quality Al-N doped p-type ZnO thin films were deposited on Si and buffer layer/Si by DC magnetron sputtering in a 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 films showed a carrier concentration in the range of $1.5x10^{15}$~$2.93x10^{17}$ cm^{-3}, resistivity in the range of 131.2~2.864 Ωcm, mobility in the range of 3.99~31.6 $cm^2V^{-1}s^{-1}$, respectively. It was easier to dope p-type ZnO films on Si substrates than on buffer layer/Si. The film grown on Si showed the highest quality of photoluminescence (PL) characteristics. The Al donor energy level depth (E_d) of Al-N codoped ZnO films was reduced to about 50 meV, and the N acceptor energy level depth (E_a) was reduced to 63 meV.

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

1. INTRODUCTION

ZnO has attracted substantial interest in the area of photoelectronic devices for the potential high performance of light-emission properties, because ZnO has a large exciton binding energy of 60 meV and direct wide electron energy bandgap of 3.37 eV at room temperature (RT). It is pivotal to grow high quality p-type ZnO films to implement light-emitting devices based on ZnO material. Many approaches (with various dopants) have been used to fabricate high quality p-type ZnO films[1-7]. In theory, group I and group V elements can be used as acceptor dopants for mono-doping in ZnO, and N is the best dopant of group V elements[8]. However, it is difficult to obtain high quality p-type ZnO using mono-doping with these elements. Hydrogen is affiliated to group I elements and acts as a donor in ZnO[9]. Because of the electron compensation induced by interstitial zinc (Zn_i) and oxygen vacancy (V_O), low acceptor solubility and deep acceptor levels, it is difficult to obtain p-type ZnO using the mono-doping method with group I and group V elements as dopants. T. Yamamoto et al. proposed the theory of codoping group V and III elements with a ratio of 2:1 (which can increase acceptor solubility and make acceptor levels shallower) to solve the problems of p-type doping in ZnO[10,11]. The feasibility of codoping theory has been proven through experiments[12-15]. Magnetron sputtering is often used to grow thin films for the ease of operation and is also used to grow p-type ZnO films. DC and RF magnetron sputtering have been used to grow intrinsic p-type ZnO films[16] and doped p-type ZnO films[17-21]. According to codoping theory, deep acceptor and donor levels can be made shallower, and the low solubility of acceptors in ZnO is enhanced by reducing Madelung energy. To date, explicit evidence of improving the deep acceptor level (i.e. making it shallower by codoping) cannot be seen in the literature. When ceramic ZnO is used as the sputtering target, it is hard to fabricate p-type ZnO films in the mixture of N_2 and O_2 gas by RF magnetron sputtering, despite the high crystallinity shown in X-ray diffraction (XRD) spectra. This study confirmed that both acceptor levels and donor levels were made shallower.

2. EXPERIMENT

Al-N codoped ZnO films were fabricated on Si and Si coated with a buffer layer (buffer layer/Si) by DC magnetron sputtering. All Si substrates were ultrasonically cleaned sequentially in acetone, methanol, and then DI water. 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 buffer layer and Al-N codoped ZnO films are listed in Table 1. In-situ annealing was carried out on the buffer layer templates to decrease resistivity and promote crystallinity. The annealing gas, temperature, pressure, and time were O_2, 800 °C, 15 mTorr and 20 min, respectively. XRD, Hall Effect in Van der Pauw configuration and photoluminescence (PL) were conducted to evaluate the microstructure, electrical, and optical properties.

3. RESULTS AND DISCUSSION

Figure 1 shows that all films have c-axis orientation. 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

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Table 1. Growth conditions of a homo-buffer layer template and Al-N codoped ZnO films.

Buffer layer		Al-N codoped ZnO thin film	
parameters	conditions	parameters	conditions
target	ZnO (5N)	target	AZO (5N)
substrate	n-type (100)Si	substrate	n-(100)Si, buffer layer/Si
base pressure	$7x10^{-6}$ Torr	base pressure	$7x10^{-6}$ Torr
working pressure	15 mTorr	working pressure	6, 15 mTorr
RF power	120 W	DC power	340 V x 0.1 A
growth temperature	100 °C	growth temperature	450 °C
ambient gases	$Ar:O_2$=4:1(5N)	ambient gases	$N_2:O_2$=1:4,2:3,3:2,4:1
pre-sputtering time	10 min	pre-sputtering time	10 min
growth time	30 min (70 nm)	growth time	120 min (570 nm)

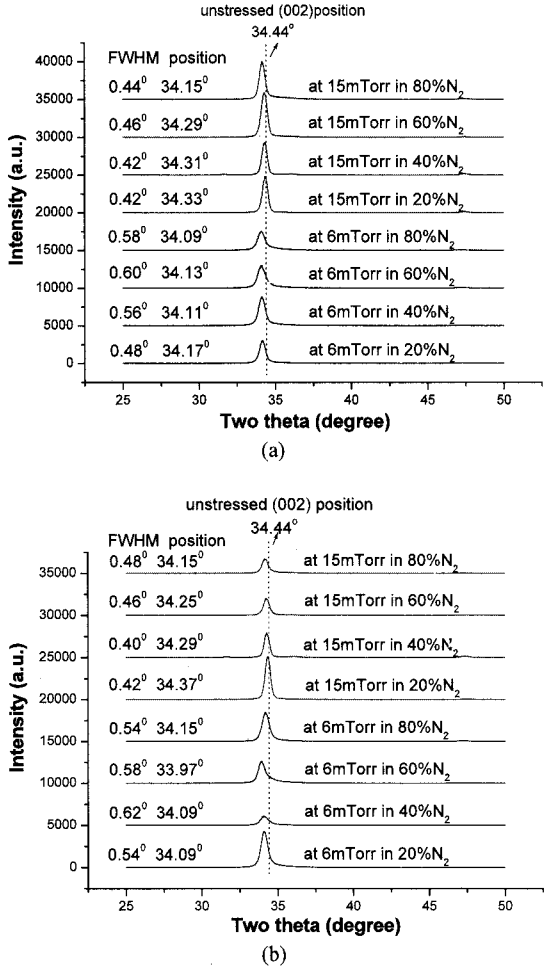

Fig. 1. XRD patterns of Al-N codoped ZnO thin films deposited on (a) Si, (b) buffer layer/Si in different N_2 fractions.

film is larger than that of the single crystal bulk ZnO. This is a result of the molecular N_2 doping in ZnO[22]. The position of (002) peaks shows that the films grown at 15 mTorr show a closer crystal c-axis lattice constant to the corresponding lattice constant of bulk ZnO than other films. The peak positions of films grown at 6 mTorr lie at the lower positions than those at 15 mTorr in the same N_2 fraction, implying the incorporation of more molecular N_2 in films grown at 6 mTorr. The FWHMs of (002) peaks at 6 mTorr are larger than those at 15 mTorr, indicating that average grain sizes of the films grown at 6 mTorr are smaller than those at 15 mTorr. Figure 1(a) shows that the intensity of the (002) peak of ZnO films grown on Si substrates at the 15 mTorr is higher than that at 6 mTorr. Figure 1(b) shows the (002) peak intensity of films deposited on buffer layer/Si, not showing evident changes compared with Fig. 1(a). Usually, a buffer layer is beneficial to the crystallinity and microstructure of ZnO film, but in the case of Al-N codoped ZnO films deposited by DC magnetron sputtering in this study, the buffer layer does not show the improvement of the ZnO microstructure via XRD spectra.

The films were measured by the Hall Effect in Van der Pauw configuration to evaluate the electrical properties. Table 2 lists the electrical property for the films grown at 15 mTorr in different N_2 fractions. Sample S1, BS1, and BS3 had high resistivity (>1 $x10^5$ Ωcm) which was beyond the measurement range of the Hall effect analyser and the measurements of their electrical properties were not possible. All Al-N codoped ZnO films on Si substrates show p-type conduction. When the films were grown on a buffer layer/Si, the conduction type was changed from n-type to p-type with an increasing N_2 fraction in ambient conditions. The p-type film (BS4) grown on buffer layer/Si shows the highest hole concentration of $2.93x10^{17}$ cm^{-3} and low hole mobility of 3.99 $cm^2V^{-1}s^{-1}$. The n-type film (BS2) grown on buffer layer/Si shows a low electron concentration of $1.19x10^{16}$ cm^{-3} and a high mobility of 142 $cm^2V^{-1}s^{-1}$.

Three films (sample S2, S3, and S4) grown on Si at 15 mTorr show p-type conduction and the changing tendencies of the electrical properties are shown in Fig. 2. The p-type film (S3) grown in N_2 fraction of 60 % shows the highest hole concentration of $9.35x10^{16}$ cm^{-3} and the lowest resistivity of 2.864 Ωcm and moderate mobility of 23.3 $cm^2V^{-1}s^{-1}$. The hole concentration was reduced and resistivity was increased for p-type ZnO film grown on Si when it was fabricated in N_2 fraction of 20 % or 80 %.

PL spectra of sample BS2, BS4, and S4 at 6 K are shown in Fig. 3(a), (c), and (e), respectively. The corresponding high-resolution spectra near the band edge (3.15-3.5 eV) are shown in Fig. 3(b), (d) and (f), respectively. The n-type film (BS2) grown on buffer layer/Si in N2 fraction of 40 % shows many deep defect levels at 1.69, 1.77, 2.09, and 2.73 eV (Fig. 3(a)) and near the band edge levels at 3.363 and 3.304 eV (Fig. 3(b)). The peaks of 3.363 and 3.304 eV are

Table 2. Electrical properties of Al-N codoped ZnO films grown on Si and buffer layer/Si substrates at 15 mTorr in different N_2 fractions.

sample	substrate	condition (N_2 fraction)	type	concentration (10^{16} cm^{-3})	mobility ($cm^2V^{-1}s^{-2}$)	resistivity (Ωcm)
S1	Si	20 %	--	--	--	--
S2	Si	40 %	p	0.15	31.6	131.2
S3	Si	60 %	p	9.35	23.3	2.864
S4	Si	80 %	p	8.82	22.6	3.128
BS1	Buffer layer/Si	20 %	--	--	--	--
BS2	Buffer layer/Si	40 %	n	1.19	142	3.689
BS3	Buffer layer/Si	60 %	--	--	--	--
BS4	Buffer layer/Si	80 %	p	29.3	3.99	5.349

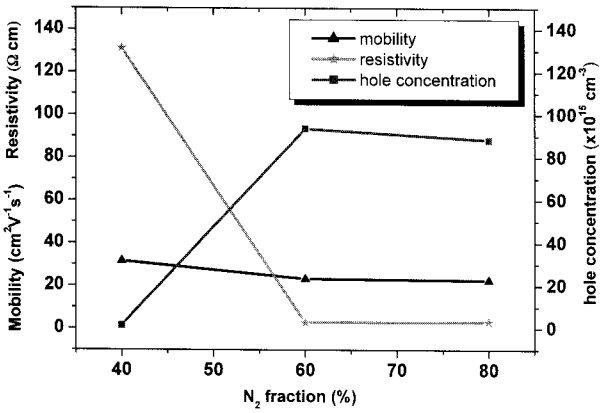

Fig. 2. Electrical property of Al-N codoped ZnO thin films deposited on Si at 15 mTorr in different N_2 fractions.

attributed to the transition of excitons bound to the neutral donor (D^oX) and transition of donor-acceptor pair (DAP) respectively. The p-type film (BS4) grown on buffer layer/Si in N2 fraction of 80 % shows deep defect levels at 1.67, 2.36, 2.59, and 2.95 eV (Fig. 3(c)) and near band edge levels at 3.374 and 3.323 eV (Fig. 3(d)). The peaks of 3.374 and 3.323 eV are attributed to the transition of free electrons in the conduction band to acceptor level (FA) and DAP respectively. The p-type film (S4) grown on Si in N_2 fraction of 80 % shows deep defect levels at 1.66, 2.36, 2.57, and 2.76 eV (Fig. 3(e)) and near band edge levels at 3.366 and 3.316 eV (Fig. 3(f)). The peaks of 3.366 and 3.316 eV are attributed to FA and DAP respectively. The small peaks ranged from 3.17 to 3.27 eV and are related to Al-N-uncoupled DAPs as shown in Fig. 3(b), (d) and (f).

The emission energy of DAP at low temperature is

$$h\nu = E_g - E_a - E_d + \frac{e^2}{4\pi\varepsilon r} \quad (1)$$

where, E_g, E_a, E_d, e, ε and r are energy bandgap, acceptor level to valence band maximum, donor level to conduction band minimum, electron charge, permittivity, and distance between the acceptor and donor, respectively. According to the formula (1), the emitting energy hν increases with decreasing distance r. Suppose that the donor density exists in the given range for all films, the higher the acceptor concentration is, the shorter the distance is. Thereby, the photon energy emitting from DAP of the film with high acceptor concentration is increased. The hole concentration of the film (S4) on Si is lower than that of the film (BS4) on buffer layer/Si. The emissions from FA and DAP of the film (BS4) on the buffer layer are larger than the corresponding emissions from that (S4) on Si.

The emission energy of FA at low temperature is

$$h\nu = E_g - E_a \quad (2)$$

The peak energy difference between DAP and FA is the depth of donor level (E_d). The donor levels of sample BS4 and S4 are 51 meV and 50 meV, respectively. M. Grundmann et. al claimed that the depth of Al donor level in Al-doped ZnO is 65 meV[23]. In this study, the Al donor level was reduced by 15 meV. The DAP and FA peaks of the film (BS4) with higher hole concentration(Fig. 3(d)) have a blue shift compared to that (S4) with lower hole concentration (Fig. 3(f)). This may be caused by the enlargement of bandgap in the film with high internal stress[24].

Excitons bound to neutral acceptors (A^oX) are usually shown in the photon energy range of 3.3-3.5 eV[25,26]. In this study, the peaks of 3.366 and 3.374 eV are beyond this range. So the two peaks in this study are not attributed to the recombination of A^oX. The peak of 3.366 eV of the film on the buffer layer and 3.374 eV of the film on Si may be attributed to the recombination of free electrons in the conduction band and holes at the acceptor level (FA). The bandgap energy of ZnO at low temperature is about 3.437 eV[27]. According to formula (2) and the value of ZnO bandgap energy, the acceptor levels of sample BS4 and S4 are 63 meV, and 71 meV, respectively, less than 100 meV[28]. In this study, Al donor level and N acceptor level were reduced by 15 meV and 37 meV, respectively, which is beneficial to the formation of p-type conduction.

4. CONCLUSION

$Li[Ni_{0.2}Li_{0.2}Mn_{0.6}]O_2$ cathode powder was synthesized via the microwave assisted sol-gel process. The XRD study of the material has confirmed that an O3 layered structure formed during a microwave treatment that followed a heating process. The electrochemical test of the sample has shown that it has a high discharge capacity and stable cyclic

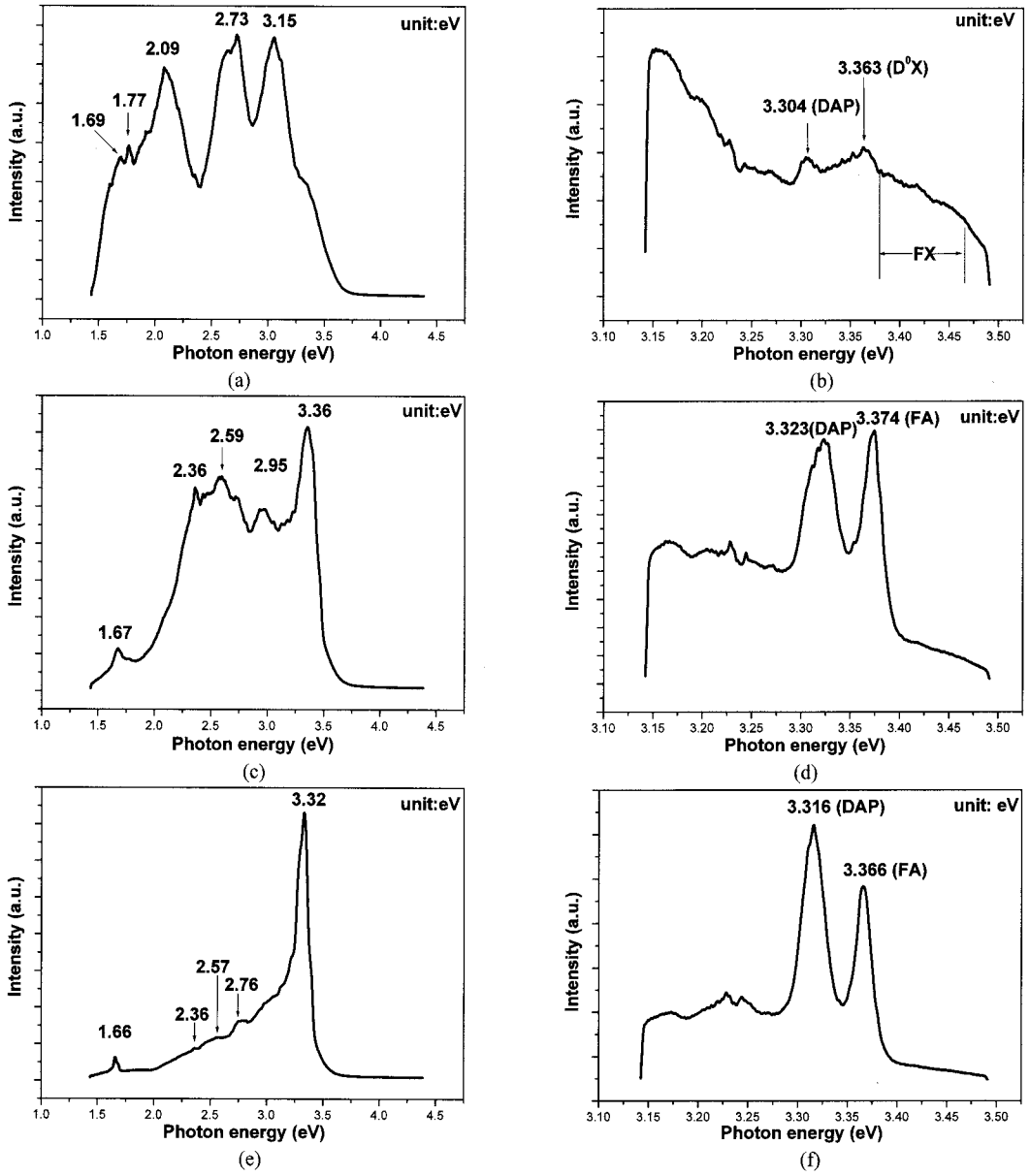

Fig. 3. PL spectra at 6 K in full regions of Al-N codoped ZnO films deposited at 15 mTorr on Si and buffer layer/Si substrates in a different N2 fraction. (a) buffer layer/Si, N_2:40 %, (c) buffer layer/Si, N_2:80 %, and (e) Si, N_2: 80 %, and their corresponding high-resolution spectra near the band edge are shown in (b), (d) and (f), respectively.

properties. The discharge capacity of the sample electrode was ~230 $mAhg^{-1}$ at the specific current of 40 mAg^{-1} (0.2 C rate) in the voltage range of 2.0~4.8 V. It was saturated to ~200 $mAhg^{-1}$ after 30 cycles. The discharge capacity decreased to ~140 $mAhg^{-1}$ at 6 C (1200 mAg^{-1}) rate, but the cyclic performance did not deteriorate at a high C rate.

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