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# V-I Curves of p-ZnO:Al/n-ZnO:Al Junction Fabricated by RF Magnetron Sputtering

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## Abstract

Al-doped p-type ZnO films were fabricated on n-Si (100) and homo-buffer layers in pure oxygen at 450 $^0$C by RF magnetron sputtering. Target was ZnO ceramic mixed with 2 wt% $Al_2O_3$. XRD spectra show that the Al-doped ZnO thin films have ZnO crystal structure and homo-buffer layers are beneficial to Al-doped ZnO films to grow along c-axis. Hall Effect experiments with Van der Pauw configuration show that p-type carrier concentrations are ranged from $1.66 \times 10^{16}$ to $4.04 \times 10^{18}$ cm$^{-3}$, mobilities from 0.194 to 2.3 cm$^2$V$^{-1}$s$^{-1}$ and resistivities from 7.97 to 18.4 Ωcm. P-type sample has density of 5.40 cm$^{-3}$ which is smaller than theoretically calculated value of 5.67 cm$^{-3}$. XPS spectra show that O1s has O-O and Zn-O structures and Al2p has only Al-O structure. P-ZnO:Al/n-ZnO:Al junctions were fabricated by magnetron sputtering. V-I curves show that the p-n junctions have rectifying characteristics.

**Key Words** : p-ZnO:Al/n-ZnO:Al junction, p-type ZnO:Al, V-I curve, Rectifying characteristic

## 1. INTRODUCTION

ZnO has be intensively investigated for its potential application of highly efficient light emitting since it has large direct energy bandgap of 3.37 eV at and large exciton binding energy of 60 meV. Heavily doped ZnO with In and Al could be used as transparent conducting oxides[1,2]. Recent investigations on this material have gotten important progress and even light emitting diodes (LEDs) have been made[3-6]. Although great progress of study on this material has been taken place, a tough bottleneck of getting high-quality p-type ZnO hinders the development of LEDs based on this material. Group I elements are used as acceptors to dope p-type in ZnO[7,8]. Group V elements are more popular to be used to dope p-type in ZnO[9-12] and nitrogen seems to be the best acceptor choice of group V elements since nitrogen has nearly the same radius as oxygen and is the shallowest acceptor in ZnO [13]. Some large radius elements, such as As and Sb, show unexpected fairish effects of p-type dopants in ZnO[14,15], which is theoretically explained as a complex acceptor model of $X_{Zn}$-$2V_{Zn}$ (X=As, Sb)[16], or a cluster model of $X_{Zn}$-$4V_{Zn}$[17]. A hint could be gotten that it is a salutary attempt to find other appropriate elements which act as complex acceptors like as the models above and even group Ⅲ elements should not be excluded. If Al-doped ZnO is grown under $O_2$-rich condition, many Zn vacancies ($V_{Zn}$) should occur due to the strong bonding of Al-O. In the present study we have grown highly Al-doped ZnO thin films under the condition of $O_2$-rich ambient and obtained Al-doped p-type ZnO films. We have fabricated p-ZnO:Al/n-ZnO:Al junctions which show rectifying characteristic.

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## 2. EXPERIMENT

Al-doped ZnO films were prepared in $O_2$ on homo-buffer layers and n-(100) Si respectively by an RF magnetron sputtering. The buffer layers were fabricated on Si in the mixture of $O_2$ and Ar with ratio of 1:4 at 100 $^{0}$C and 15 mTorr with ZnO ceramic as target by RF magnetron sputtering and then were annealed in-situ at 800 $^{0}$C and 15 mTorr of $O_2$ for 20 min. Al-doped ZnO films were grown in oxygen at 450 $^{0}$C and 15 mTorr for 180 min by RF magnetron sputtering and annealed in oxygen at 10 Torr and 600 $^{0}$C and 800 $^{0}$C respectively. ZnO ceramic mixed with 2 wt% $Al_2O_3$ is as target. Samples are denoted as Wx. W=B or S means that the substrate is a buffer layer template or a silicon wafer and x=0, 1 or 2 means that the Al-doped ZnO film is as-grown, 600 $^{0}$C- or 800 $^{0}$C-annealed one. The ZnO:Al films were tested with X-ray diffraction (XRD) to investigate the films' microstructure, Hall effect in Van der Pauw configuration to analyze the films' electrical properties and X-ray photoelectron spectroscopy (XPS) to observe the films' chemical properties. Homo p-n junctions were fabricated and their V-I curves were done.

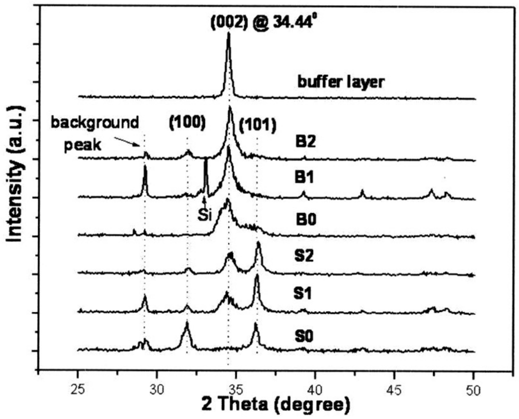

Fig. 1. XRD spectra of ZnO:Al and buffer layer (background peaks were attributed to paste which fastened samples on XRD holder. Due to samples being cut too small, the paste was exposed to x-ray and showed its XRD peaks on XRD patterns of samples).

Table 1. Conduction type, carrier concentration, carrier mobility and resistivity of Al-doped ZnO films.

| sam. | type | con./ $10^{18}$cm$^{-3}$ | mob./ cm$^{2}$V$^{-1}$s$^{-1}$ | resist./ Ωcm |
|---|---|---|---|---|
| S0 | p | 0.0166 | 2.03 | 18.4 |
| S1 | n | 8.99 | 0.161 | 4.32 |
| S2 | n | 2.45 | 1.98 | 1.29 |
| B0 | - | - | - | - |
| B1 | p | 4.04 | 0.194 | 7.97 |
| B2 | n | 4.0 | 1.15 | 1.35 |

## 3. RESULTS AND DISCUSSION

Figure 1 shows that except S0 the XRD spectra of the buffer layer and the ZnO:Al films exhibit (002) peak of $2\Theta$ angle at $34.44^{0}$ which is the value of corresponding peak of bulk ZnO. All (100) and (101) peaks are consist with the positions at which the corresponding peaks of bulk ZnO are, implying that all films haven't inner stress. As annealing temperature goes up to 600 and 800 $^{0}$C (002) peak appears and gets higher, implying that annealing temperature makes the films recrystallize along c-axis. The films grown on buffer layers and high annealing temperatures are beneficial to ZnO:Al films growth along c-axis. Comparing the spectrum of buffer which is without Al-doping with the spectra of ZnO:Al films, we can conclude that Al in films is adverse for films to grow along c-axis although annealing processing and buffer layer improve the crystallization of ZnO:Al films along c-axis to some extension. We also measured the density of a p-type sample on Si and found that the p-type sample has density of 5.40 gcm$^{-3}$ which is smaller than theoretically calculated value of 5.67 gcm$^{-3}$. Low density of Al-doped p-type ZnO is attributed to zinc vacancies in the film, which makes the film p-type.

Table 1 shows that as-grown film on Si shows p-type with carrier concentration of 1.66x$10^{16}$ cm$^{-3}$. While annealing process is set at 600 $^{0}$C and

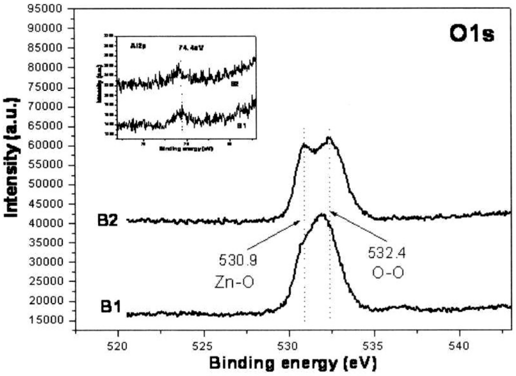

**Fig. 2.** XPS spectra of O1s with Al2p spectra in inlet of sample B1 and B2.

800 $^0$C, the type converts to n-type. The electrical properties of the as-grown film on buffer layer can't be tested due to high resistivity. But the 600 $^0$C annealed film on buffer layer shows p-type and high carrier concentration of $4.04 \times 10^{18}$ cm$^{-3}$. As annealing temperature goes to 800 $^0$C the film on buffer layer covert back to n-type again. It is known that at Zn-rich condition ZnO with 2 wt% $Al_2O_3$ as sputtering target shows high electron concentration of $10^{21}$ cm$^{-3}$ and low resistivity of $10^{-3}$ ~ $10^{-4}$ Ωcm[18]. In this study all n-type films show low electron concentration and a little high resistivity due to oxygen-rich condition. This is because at oxygen-rich condition strong bonding strength of Al-O makes Zn vacancies which is origin of p-type in ZnO films. Under 700 $^0$C diffusion temperature Al is hard to diffused in silicon[19]. So p-type conductivity shown in samples is attributed to p-type ZnO:Al films. As for annealing at high temperature (for films on Si at 600 $^0$C and 800 $^0$C, and for films on buffer layer at 800 $^0$C) some atomic oxygen escapes from the films, making films convert to n-type.

Figure 2 shows XPS spectra of O1s with spectra of Al2p in inset. It can seen through Gaussian fitting that two peaks appear at about 530.7 and 532.3 eV respectively. 530.7 eV is attributed to $O^{2-}$ ion in stoichiometric ZnO. 532.3 eV is attributed to loosely bound oxygen $O^{2-}$ ions in films and at surfaces of films[3], indicating presence of Zn vacancies in Al-doped films. The p-type sample (B1) shows that intensity of 532.3 eV peak is higher than that of 530.7 eV peak while for the case of n-type sample (B2) the two peaks show same intensity, which implies that p-type film shows more Zn vacancies. Binding energy peaks of Al2p are both at 74.4 eV that is the value of the case of Al-O bonding in $Al_2O_3$[6]. But we can confirm from XRD patterns that in all films $Al_2O_3$ phase does not exist. In metal Al the peak of Al2p appears at 72.2 eV, implying that all Al is at Al-O bonding state.

Figure 3 shows that Al-doped ZnO p-n homo-junctions have rectifying characteristics, which imply that Al-doped ZnO can be with p-type conduction. Sample A and B are with p-type thicknesses of about 200 and 400 nm respectively. The n-type films were fabricated by RF magnetron sputtering in argon gas at 200 $^0$C and 15 mTorr, which makes films have high electron concentration about $10^{20}$ cm$^{-3}$ and makes deep depletion layers into p-type films. 200nm p-type thickness hardly cover depletion depth, making p-n junction have little turn-on voltage of 0.7 V (curve A). 400 nm p-type thickness cover more depletion depth, making p-n junction have larger turn-on voltage of 1.7 V (curve B). From slopes of Curve A and B, it is confirmed that curve A has larger series resistance than curve B, because for the case of A the growth time is shorter than for case of B, which makes

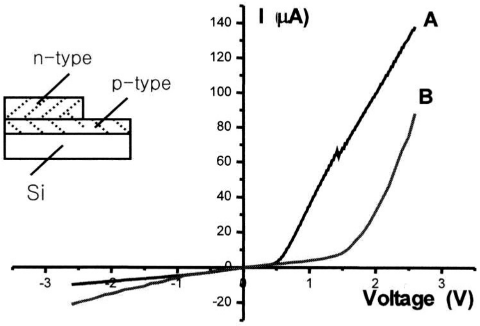

**Fig. 3.** V-I curves of p-ZnO:Al/n-ZnO:Al/Si with its structure in inset.

lower crystallinity for case A than for case B and makes lower mobility in case A. Curve B has more leakage current than curve A because for the case of B, shunt current which is induced by surface current increases. Surface current may be caused by low resistance at grain boundary. The V-I characteristics were measured directly by probe pins without paste electrode, which makes series resistance increase. In the case of GaN LEDs, hole mobility goes up abut 10~50 $cm^2V^{-1}s^{-1}$. But in our p-type case the hole mobility has lower values. This makes our p-n junctions have high series resistance. Because of high resistivity in p-type and n-type films, slopes of linear parts of I-V curves are not ideal.

## 4. CONCLUSION

In summary, Al-doped p-type ZnO films could be obtained in oxygen ambient by RF magnetron sputtering and high hole concentrations of $4.04x10^{18}$ $cm^{-2}$ is obtained. P-type ZnO:Al films have density of 5.40 $gcm^{-3}$. XPS spectra of O1s show the structure of O-O bonding and XPS spectra of Al2p show Al-O bonding. All Al is at Al-O state with electron binding energy of 74.4 eV shown in XPS without metal Al state at which electron binding energy should shows at 72.2 eV. V-I curves of Al-doped p-n homo-junctions have rectifying characteristic.

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