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# Defect Analysis via Photoluminescence of p-type ZnO:N Thin Film fabricated by RF Magnetron Sputtering

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**Abstract**

ZnO is a promising material to make high efficient ultraviolet(UV) or blue light emitting diodes (LEDs) because of its large binding energy and energy bandgap. In this study, we prepared ZnO thin films with p-type conductivity on silicon(100) substrates by RF magnetron sputtering in the mixture of $N_2$ and $O_2$. The process was accompanied by low pressure in-situ annealing in $O_2$ at 600 °C and 800 °C respectively. Hall effect in Van der Pauw configuration showed that the N-doped ZnO film annealed at 800 °C has p-type conductivity. Photoluminescence(PL) spectrum of the film annealed at 800 °C showed UV emission related to exciton and bound to donor-acceptor pair(DAP) as well as visible emission related to many intrinsic defects.

**Key Words** : RF magnetron sputtering, P-type conductivity, N-doped ZnO film, Photoluminescence analysis

## 1. INTRODUCTION

ZnO has attracted great attention because of its unique properties, such as large exciton binding energy of 60 meV and wide energy bandgap of 3.37 eV, which means that highly efficient UV or blue LEDs based on ZnO can be realized. High quality ZnO bulks which can be used as base materials to be doped are available and n-type ZnO thin films with high electron concentration are easily achieved experimentally which are essential for making p-n junctions of LEDs. Nevertheless, it is hard to fabricate p-type ZnO thin films which are also imperative for p-n junctions of LEDs. To get p-type ZnO thin films, many methods and dopant species have been used[1-6].

Theoretically, N is the shallowest acceptor dopant among group five elements for doping ZnO[7,8]. It is known that high quality ZnO thin films can be prepared by magnetron sputtering system. So, fabrication of p-type ZnO thin films by magnetron sputtering not only is a good idea but also has been achieved[2]. However, it is difficult to make stable N-doped p-type ZnO thin films by magnetron sputtering, especially, by using RF power. In reference, the N-doped p-type ZnO films showed gradual variation from p-type to n-type in dark[9].

In this study, we realized p-type ZnO thin film using n-type (100) Si substrate in the mixture of $N_2$ and $O_2$ by RF magnetron sputtering and did detail defect analysis on the p-type ZnO film via a PL spectrum and found out the cause of p-type conductivity, which is useful to promote the method of preparing p-type ZnO films.

## 2. EXPERIMENTS

In our experiments, the ZnO ceramic disk was used as target, $O_2$ gas and $N_2$ gas as growth

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**Table 1.** The conditions of ZnO thin film growth.

| Parameter | Process condition |
|---|---|
| Substrates | n-type Si(100) |
| Target | ZnO 5N |
| Base Pressure | Below $10^{-6}$ Torr |
| Work pressure | 15 mTorr |
| Ambient gas | $N_2$:$O_2$=3:2 |
| RF power | 210 W |
| Deposition time | 180 min |
| Substrate temperature | 450 °C |

**Table 2.** The conditions of annealing after the growth of ZnO thin films.

| Parameter | Process condition |
|---|---|
| Method | In-situ annealing |
| Base pressure | Below$10^{-6}$ Torr |
| Annealing ambient | $O_2$ |
| Annealing pressure | 10 Torr |
| Annealing temperature | 600 °C and 800 °C |
| Annealing time | 5 min |
| Cooling | Naturally in-situ at 10 Torr |

ambient. All were with purity of 5N. We fabricated N-doped ZnO thin films by RF magnetron sputtering using n-type (100) Si as substrates and $N_2$ gas as N dopant source. The detail conditions of film growth are listed in Table 1. After growth, two films were processed with in-situ annealing at temperatures of 600 °C and 800 °C, respectively. The conditions of annealing are listed in Table 2. X-ray diffr action(XRD), scanning electron microscope(SEM) and atomic force microscope(AFM) were performed to evaluate microstructure and surface morphology of the films. Seeback effect and Hall effect in Van der Pauw configuration were carried out for determination of conductivity types and other electric properties of the films. PL was performed on the film annealed at 800 °C to investigate the optical properties of the film and to find the cause of p-type conductivity.

## 3. RESULT AND DISCUSSION

From the XRD patterns in Fig. 1, (0002) peak is dominant for all three films, indicating that preferred growth orientation of ZnO films is along c-axis. From the FWHMs of (0002) peaks in Table 3, the film annealed at 800 °C has the narrowest (0002) peak of 0.280 °, while the two others have nearly the same larger values of about 0.372 °, which means that from 600 °C to 800 °C, the grains of the film get bigger due to recrystallization at high temperature. The (0002) peak positions of as-grown and 600 °C annealed films are nearly the same and a little lower than that of bulk ZnO which is about 34.4 °, while the (0002) peak position of the 800 °C annealed film is nearly the same as (but only slightly larger than) that of bulk ZnO. It can be implied that owing to interstitial N and existence of $N_2$ in the films, the as-grown and the 600 °C annealed films are under tensile stress which makes the films prolonged along c-axis orientation. However, as the temperature goes up to 800 °C, nearly all of $N_2$ splits into atomic N state, which makes the film relax sufficiently. Since Zn-N bond length is smaller than Zn-O one somewhat, the substitution of atomic N for O should result in decrease of the lattice constants and even make c-axis lattice constant smaller than that of bulk ZnO which is 0.5205 nm. However, radius of $N_2$ is much larger than that of atomic O or Zn, which makes lattice constants larger when $N_2$ substitutes for O site or Zn site in the as-grown and 600 °C annealed ZnO:N films. Besides, some $N_2$ should have penetrated interstitially and also made the lattice constants prolonged. Table 3 lists the c-axis lattice constants of (a)as grown, (b)600 °C annealed and (c)800 °C annealed ZnO films.

Figure 2 shows AFM images of (a)as-grown, (b)600 °C and (c)800 °C annealed films. AFM analysis offered us the roughness and the grain size for three kinds of samples. The RMS roughnesses of the as-grown, 600 ℃ annealed and 800 ℃ annealed films are 19.60, 19.58 and 16.71 nm respectively. The as-grown and 600 ℃

**Table 3.** XRD and AFM data of (a)as grown (b)600 °C annealed and (c)800 °C annealed ZnO films.

| | XRD | | | | AFM |
|---|---|---|---|---|---|
| Sample | Position[°] @(0002)peak | c-length [nm]lattice | FWHM[°] @(0002)peak | Grain size[nm] | RMS [nm] |
| (a) | 34.256 | 0.5232 | 0.372 | 22.3 | 19.60 |
| (b) | 34.176 | 0.5244 | 0.374 | 22.2 | 19.58 |
| (c) | 34.500 | 0.5197 | 0.280 | 29.3 | 16.71 |

annealed ZnO have nearly the same roughness value. 800 °C annealed film has a smaller roughness value, implying that 800 ℃ annealed film has smoother morphology than as-grown and 600 °C annealed films. But the variation is not large. The above phenomena can be explained as following. The annealing temperature of 600 °C and holding time of 5 minute are not high enough and long enough to make the surface morphology of film visibly vary by recrystallization; but the annealing temperature of 800 °C is high enough to make the surface morphology of film visibly vary, but 5 minute annealing holding time is not enough to make morphology sufficiently vary.

Seeback effect and Hall effect measurements were performed for the analysis of the electrical properties of ZnO thin films. Seeback effect exhibited that as-grown and 600 °C annealed films did not show any electrical conduction type and the film annealed at 800 °C showed p-type conducting property. Hall effect in Van der Pauw configuration[HL5500PC] was carried out on the film annealed at 800 °C and showed that the film annealed at 800 °C had p-type conductivity. Its hole concentration, hole mobility and resistivity were respectively $7.84\times10^{13}$ $cm^{-3}$, 1054 $cm^2V^{-1}S^{-1}$, and 75.3 Ohm.cm. The result of p-type conversion of the film annealed at 800 °C also indicates that when the annealing temperature goes up from room temperature to 800 °C, $N_2$ in the film undergoes dissociation and activation and it causes the film electric conversion

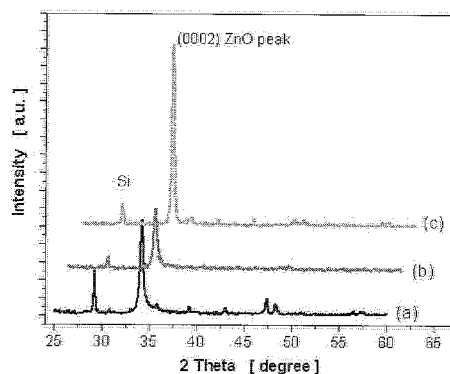
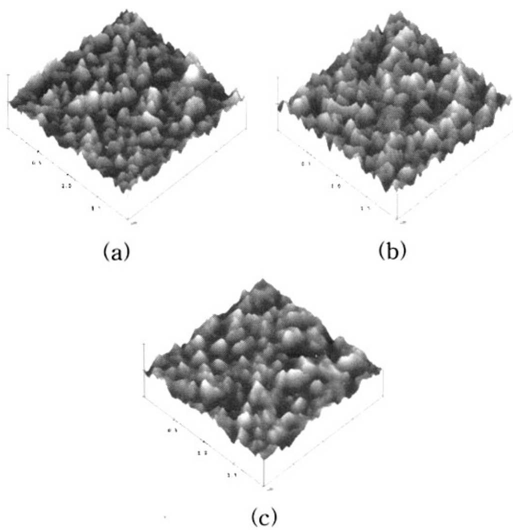



**Fig. 1.** XRD patterns of ZnO films for (a) as-grown, (b) annealed at 600 °C and (c) annealed at 800 °C.

into p-type. The PL spectra at 10 K of ZnO film annealed at 800 °C (PL intensity at region of high photon energy is enlarged by 5 times) in Fig. 3 shows two peaks and three shoulders in visible region and four explicit peaks in UV region. In UV region, the positions of peaks are at 3.3826, 3.3109, 3.2413, and 3.1658 eV, respectively. The peak of 3.3826 eV is ascribed to free exciton energy[10]. 3.3109 eV and 3.2413 eV are attributed to its first and second LO phonon replicas that by C. Klingshirn's theoretic calculation, the LO phonon replica energy is 72 meV[11].

The peak of 3.1658 eV is due to donor-acceptor pair transition(DAP). In visible region, two peaks are at 3.0516 and 1.9229 eV, and three shoulders are at about 2.36, 2.13 and 1.72 eV respectively. The peak of 3.0516 eV is assigned to zinc vacancy($V_{Zn}$)[12]. The peak of 1.9229 eV is due to atomic oxygen interstitial($O_i$). The value of 1.9229 eV is nearly the same as that in reference[13] which has 640 nm wavelength i.e. 1.937 eV photon energy. The shoulder at about 2.36 eV is attributed to oxygen vacancy($V_O$)[14-17]. There are the other two shoulders at about 2.13 and 1.72 eV which are not found in any references explicitly. The shoulder of 2.13 eV is attributed to oxygen antisite for zinc($O_{Zn}$). The shoulder of 1.72 eV can't be confirmed. Because of disequilibrium ZnO



(a) (b)

(c)

Fig. 2. AFM images of ZnO films for (a)as-grown, (b)annealed at 600 °C and (c)annealed at 800 °C.

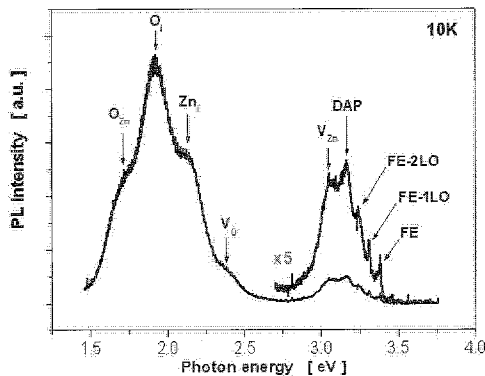



Fig. 3. PL spectra of ZnO film annealed at 800 °C.

film epitaxy in sputtering method, our film annealed at 800 °C shows many optical transitions related to defects which can be classified as n-type such as $V_O$ and p-type such as $O_i$, $V_{Zn}$ and $O_{Zn}$[18]. Interestingly, theoretical calculation shows that the emission from zinc interstitial($Zn_i$) which acts as a donor should have photon energy of 2.9 eV, but PL spectrum in this study doesn't show the corresponding peak, implying that defects of $Zn_i$ are not present or very few in the film annealed at 800 °C[12]. By comparison of PL intensities of emission resulting from p-type defects with that resulting from n-type defects, sum of the intensity from p-type defects is superior to that from n-type defects. We can infer that the p-type defects dominate the n-type defects. Therefore the film shows p-type conductivity.

## 4. CONCLUSION

From the experimental results, it can be concluded that the film annealed at temperature from 600 °C to 800 °C undergoes carrier type conversion from semi-insulated ZnO to p-type and at the same period of temperature $N_2$ in the ZnO films undergoes splitting variation which makes the film relaxed. Although the film annealed at 800 °C contains n-type defects and p-type defects, the amount of p-type defects is superior to that of n-type defects and it makes the film p-type conductivity. Short in-situ annealing time of 5 min at 800 °C and low $O_2$ ambient pressure of 10 Torr after RF magnetron sputtering growth makes ZnO thin film have high p-type carrier mobility.

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