Effect of annealing atmosphere on physical characteristics and photoluminescence properties of nitrogen-implanted ZnO thin films

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Abstract

ZnO films were pre-treated with nitrogen implantation in the range from 5×10^{12} to $5 \times 10^{15} \, cm^{-2}$. Effect of nitrogen concentration on structural crystallinity and photoluminescence properties of nitrogen-implanted ZnO films under different atmospheres and annealing treatments was investigated. It was found that there exists a solubility issue of nitrogen in ZnO films at $850 \,^\circ C$ via secondary ion mass spectrometry (SIMS). It was found that the peak intensity of near band-edge (NBE) emission remarkably decreases with the increase of concentration of implanted nitrogen if annealed in nitrogen atmosphere due to the increased oxygen vacancies. However, when the ZnO was implanted with $5 \times 10^{12} \, cm^{-2}$ and annealed in oxygen atmosphere, the optical properties are improved probably because the effective incorporation of O atom diminishes those donor levels (oxygen vacancies) and the crystallinity is also improved due to implanted nitrogen. However, excess nitrogen would reduce the crystallinity and promote the formation of the deep-level emission due to high amount of intrinsic and structure defects.
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1. Introduction

In wide band gap optoelectronics, zinc oxide (ZnO) is attracting more attention because of its potential applications in various fields, such as ultraviolet (UV) resistive coating, gas sensors, solar cells and optical devices [1,2]. One of these

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unique properties is that ZnO thin films present strong spontaneous and simulated emissions by excitons even at room temperature [3,4]. It has been recognized that to grow high quality both p and n types ZnO thin films are necessary for the development of ZnO-based optoelectronic devices. The n-type ZnO is easily available even without any doping because ZnO is a natural n-type semiconductor, while it has been recognized that p-type ZnO is very difficult to develop although high densities of holes could be achieved with nitrogen as the dopant. The presence of intrinsic defects such as interstitial zinc and oxygen vacancies has been considered to cause a deviation from stoichiometry [5]. Ogata et al. [6] reported that those intrinsic defects can be reduced by thermal annealing of ZnO layer in O_2 atmosphere but the electron carrier density was also decreased.

A number of groups have been trying to fabricate p-type ZnO films using N or As [7,8]. Nitrogen (N) doping has been considered as an effective method to realize p-type ZnO films because N has the smallest ionization energy in group V-dopants [9]. Recently, several investigations focused on nitrogen and donor co-implanted ZnO to study the solubility and diffusion behavior of nitrogen in ZnO crystal [10,11]. Georgobiani et al. [12] studied the electrical properties of ZnO films with ion implantation of nitrogen from 3×10^{14} to $3 \times 10^{15}\,cm^{-2}$ in oxygen atmosphere. It was shown that the nitrogen implantation could result in the formation of the hole type of conductivity but new peaks had appeared in the ultraviolet and visible ranges of photoluminescence spectra.

Even though it was reported that p-type ZnO may be developed by using nitrogen as an acceptor dopant, no detailed studies were made to investigate the effect of implanted-nitrogen concentration on the structural change and optical properties of sputtered ZnO films. The situation makes it difficult to study the optimal properties dependence of the doping parameters, which is essential for the full understanding of the physical and optoelectronic characterization. Furthermore, it is well known that both physical characterization and optoelectronic properties are strongly influenced by the defect concentration in ZnO films and this can be modified and controlled via nitrogen treatment under different atmosphere and annealing conditions. Therefore, in this work, ZnO films were pre-treated with nitrogen implantation in the range from 5×10^{12} to $5 \times 10^{15}\,cm^{-2}$. The photoluminescence behavior of the N-implanted ZnO films annealed in different atmospheres as a function of nitrogen concentration will be primarily focused. This study can provide more valuable optical information for the development of p-type ZnO doped with nitrogen in the applications of optoelectronic and other optical devices.

2. Experimental procedure

The ZnO thin films (~150 nm thick) were deposited on 4 in diameter Si substrates by RF magnetron sputtering, using 99.99% ZnO as the target. The growth chamber was evacuated by a turbo pump and mechanical pump. Before the deposition, a target was pre-sputtering by Ar ions for 10 min to remove contamination on the target. Argon and oxygen mixtures with oxygen molar ratio (OMR) of 5% were used as sputtering gases. Silicon substrates were cleaned by usual semiconductor technology methods before loading into the chamber. Sputtering conditions for ZnO films were performed at a substrate temperature of 50 °C, RF power of 50 W, sputtering pressure of 10 m Torr and sputtering time of 40 min. The as-grown ZnO film was subsequently subjected to N implantation at room temperature. The nitrogen ions with energy of 80 KeV were injected into the as-grown ZnO films. The fluences range studied was from 5×10^{12} to $5 \times 10^{15}\,cm^{-2}$. Based on Rutherford back scattering measurement followed by (the transport of ions in matter) TRIM simulations, the nitrogen ion distribution in ZnO films forms a nearly perfect Gaussian shape with the peak position at $(0.08 + 0.01)\,\mu m$ below the surface. After ion implantation, the specimens were annealed at 850 °C for 20 min under pure oxygen and nitrogen atmospheres. The thickness of ZnO films was measured using a surface profilometer (Tencor Alpha-Step 200) and the crystal structure was determined by X-ray diffractometer using CuKα

radiation. Photoluminescence measurement was performed by the excitation from 325 nm He–Cd laser at room temperature. The depth profile of the implanted ions was measured by secondary ion mass spectrometry (CAMECA IMS-SF). A 10 KeV Cs^+ primary beam was used to determine the atomic distribution of the implanted N.

3. Results and discussion

3.1. Physical characteristics

Fig. 1 shows the depth profile of nitrogen-implanted ZnO films with various fluences. As can be seen, a normal shape with almost Gaussian distribution was observed for the ZnO film after annealed at 850 °C in nitrogen atmosphere. An abrupt change as marked in Fig. 1 appears in the slope of the concentration profile. The concentration at this point corresponds to the solubility of N in ZnO film that is determined as 9.1×10^{17}, 4.2×10^{18}, and 6.3×10^{18} ions/cm^3 with the fluence of 5×10^{12}, 1×10^{14}, and 5×10^{15} ions/cm^2, respectively [13]. The value of solubility is equal to about 4–5 atom ppm and this implies that the N is a very insoluble element in ZnO.
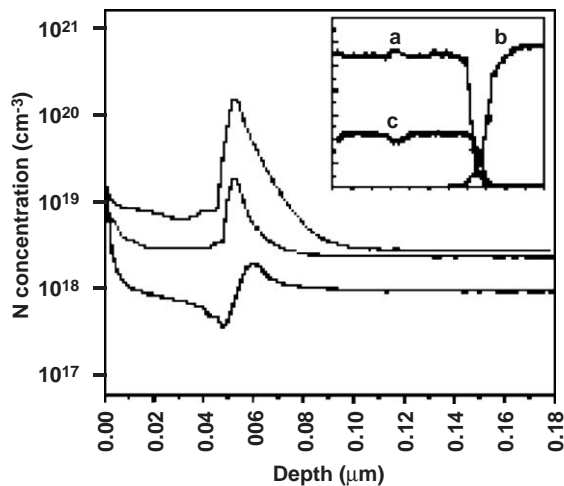
Fig. 2 shows the XRD patterns of the N-implanted (fluence of 5×10^{12}, 1×10^{14}, and 5×10^{15} cm^{-2}) and non-implanted ZnO thin films annealed at 850 °C in nitrogen atmosphere. A strong and sharp (0 0 2) peak is observed in non-implanted sample (Fig. 1a), which indicates that the ZnO film exhibits a preferred (0 0 2) orientation with *c*-axis perpendicular to the substrate. With an increase of nitrogen concentration, it was found that diffraction peak was shifted towards the smaller 2θ direction and the shift increases with an increase of fluence from 5×10^{12} to 1×10^{14} cm^{-2}. According to the Bragg Law, the shift implies that the lattice constant increases. This was considered due to the incorporation of the nitrogen at interstitial sites in ZnO, leading to an increase in the lattice constant. However, as the fluence exceeds 1×10^{14} cm^{-2}, the position of diffraction peak was almost unchanged, but a weak diffraction peak was observed at the fluence of 1×10^{14} cm^{-2} for the N-implanted ZnO films annealed at 850 °C in nitrogen atmosphere. It was believed that the phenomenon is strongly dependent on the solubility limit of N ion in the ZnO matrix. It could be postulated that part of nitrogen ions could have occupied the sites of O atom. Therefore, the (0 0 2) peak was shifted to lower diffraction angle side and the crystal structure was deteriorated.

Fig. 1. SIMS depth profile of various fluences of nitrogen implanted into ZnO films after annealing at 850 °C in nitrogen atmospheres.
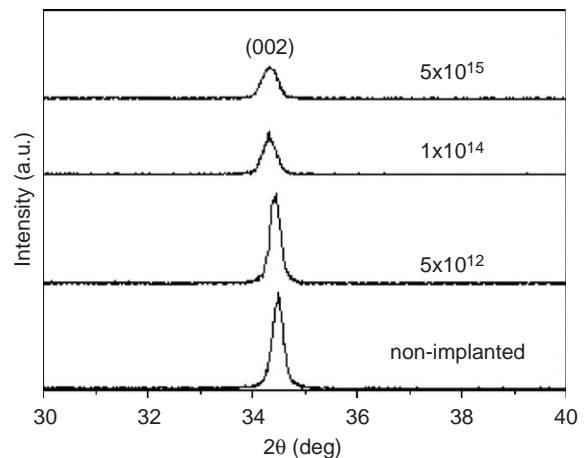

Fig. 2. XRD patterns of ZnO films with different fluences annealed in nitrogen atmospheres at 850 °C.
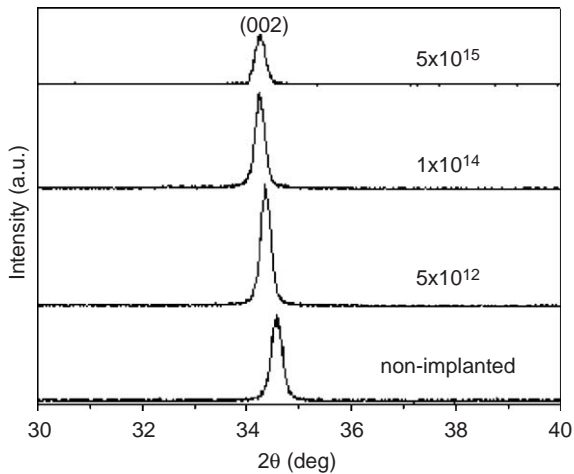
Fig. 3. XRD patterns of ZnO films with different fluences annealed in oxygen atmospheres at 850 °C.

On the other hand, as both N-implanted and non-implanted ZnO films were annealed in oxygen atmosphere at 850 °C, the XRD patterns in Fig. 3 illustrate that the diffraction peak (0 0 2) of N-implanted ZnO samples is also shifted with the implanted N concentration up to $1 \times 10^{14} \, \mathrm{cm}^{-2}$. Similar phenomenon is also observed in the samples annealed at nitrogen atmosphere and this indicates that there exists a solubility limit for N-implanted ZnO film annealed at 850 °C but seems independent of the annealing atmosphere. However, as comparing Fig. 2 with Fig. 3, it was found that the (0 0 2) peak is stronger for the samples annealed at O_2 than N_2 atmosphere. This may suggest that the nitrogen-implanted ZnO films present better crystallinity when annealed in oxygen atmosphere compared to that in nitrogen atmosphere.

3.2. Photoluminescence properties

In our previous studies, it was found that the predominant lattice defects in the as-grown ZnO films are the oxygen vacancies because the as-grown ZnO films were sputtered at the OMR 5%. As the samples were annealed below 500 °C, a very low intensity emission with the same feature as the as-grown films was observed. However, with the increase of annealing temperature, some lattice

and surface defects could be removed and the ZnO film would be re-structured into more perfect structure, indicating that the role of predominant defect may be different. At 850 °C, a strong NBE emission with a weak deep-level emission of 528 nm was obtained. However, when the films were annealed at a higher annealing temperature such as 1000 °C, a wide emission band appears around 560 nm and the deep-level emission peak shifts from 2.35 to 2.26 eV in comparison with that at 850 °C [14]. Therefore, 850 °C was used in this work to study the influence of implanted nitrogen concentration on the ZnO films in different atmospheres. As shown in Fig. 4(a), a very stronger NBE peak (378 nm) and a relatively low deep-level emission (528 nm) were obtained for the non-implanted sample. However, as the ZnO films were implanted with different fluences of nitrogen ion and annealed in this condition (N_2 atmosphere), the NBE peak becomes weaker and presents slightly red shift as compared to the non-implanted one. The decrease in the NBE emission must be related to the variation of the intrinsic defects such as zinc vacancy (V_{Zn}), oxygen vacancy (V_O) and interstitial zinc (Zn_i). As the samples were annealed at 850 °C in nitrogen atmosphere, either V_O or Zn_i should be apparently increased and this could promote the possibility of N_i to occupy the oxygen vacancies to form N_O defects. Therefore, both Zn_i and N_O will be increased with increasing implanted nitrogen concentration. Furthermore, it was found that with an increase of implanted nitrogen concentration, the NBE emission of ZnO film becomes weak. This PL result along with the XRD analysis implies that there exists a critical implanted nitrogen concentration corresponding to the defect transition that in turn influences the related PL properties. Generally, the defect reaction for non-implanted films can be expressed as follows:

$$Zn_{Zn} + O_O \Rightarrow Zn_i + V_O + \tfrac{1}{2}O_2. \qquad (1)$$
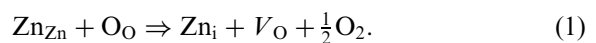
When the ZnO film was annealed at a higher temperature, both zinc interstitials and oxygen vacancies would be induced from the ZnO films as illustrated in Eq. (1). However, as the ZnO was implanted with nitrogen and then annealed at high temperature, the induced defect concentration and
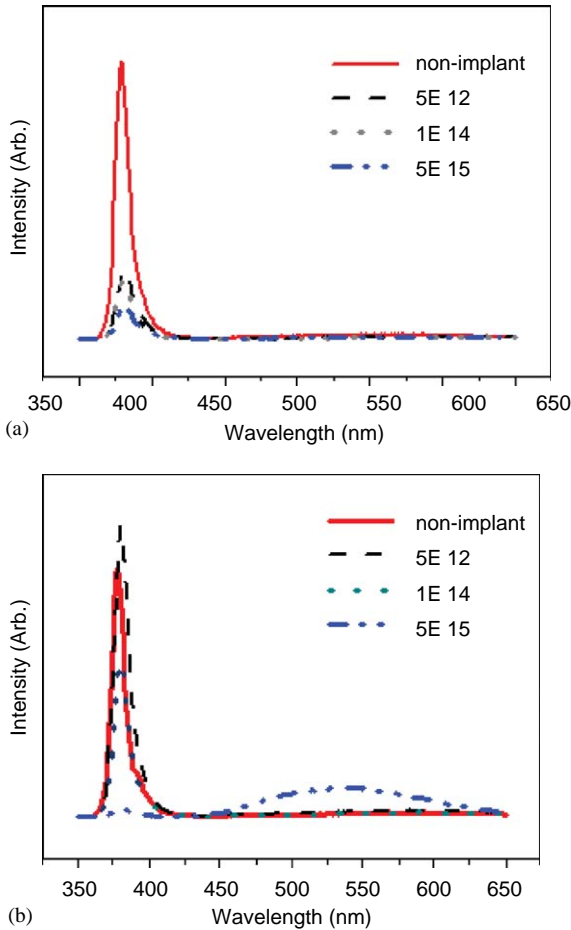
Fig. 4. Dependence of fluences conditions on the room temperature PL spectra of the annealed ZnO films treated at 850 °C in (a) N_2 and (b) O_2 atmospheres.

defect type would be changed with different fluences for the nitrogen-implanted ZnO films. In order to clarify the role of N-implanted concentration in the ZnO films, it can be further elucidated as follows. First, if the fluence was below $1 \times 10^{14} \, \text{cm}^{-2}$, the nitrogen ions may possibly substitute for the oxygen atoms in ZnO films depending on annealing conditions especially on atmosphere. Because the ZnO films in our experiment grew in lower oxygen partial pressure (OMR = 5%), V_O and Zn_i can be easily formed especially as the ZnO films were further annealed in nitrogen atmosphere at high temperature.

Therefore, the oxygen could be evaporated from the as-grown ZnO films and more oxygen vacancies will be produced in nitrogen atmosphere. Furthermore, it is possible for a certain amount of nitrogen ions to occupy oxygen sites in the N-implanted ZnO films after nitrogen annealing at high temperature. The defect chemistry (reaction) could be depicted as follows:

$$N_i + ZnO \xrightarrow{N_2} Zn_{Zn} + N_O + \tfrac{1}{2}O_2. \qquad (2)$$
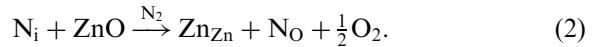
Therefore, the peak intensity of NBE emission decreases with the increase of implanted nitrogen concentration as illustrated in Fig. 4(a). Therefore, it is likely that high nitrogen concentration is responsible for producing high amount of structure defects (N_O) in ZnO films, which are the centers of non-radiative recombination.

In addition, according to XPS analysis for oxygen (O1s) peak in the ZnO films, the intensity of the peak (531 eV) shown in Fig. 5(a) for the non-implanted sample annealed at 850 °C in nitrogen atmosphere represents the measured amount of oxygen atoms in a fully oxidized stoichiometric surrounding. The binding energy side of the O1s spectrum at $531.25 \pm 0.20 \, \text{eV}$ is associated with O^{2-} ions in the oxygen-deficient regions within the matrix of ZnO [15]. Therefore, the change in this peak intensity (O1s at $531.25 \pm 0.20 \, \text{eV}$) may be partly correlated with the variation in the concentration of oxygen vacancies. Dependence of the relative intensity ratio of this component on O1s at $531.25 \pm 0.20 \, \text{eV}$ can be further depicted in Fig. 5(b). It was found that the concentration of oxygen vacancies decreases with an increase of the N-implanted fluence in ZnO film but this phenomenon is more obvious for the samples annealed in oxygen atmosphere. This indicates that part of nitrogen ions have occupied at the oxygen vacancies (sites). Based on above-mentioned results, it can be inferred that the amount of both zinc interstitials and concentration of antisite N_O would increase in proportion to the fluence of nitrogen ions for the N-implanted ZnO films annealed at 850 °C. The amount of both zinc interstitials and concentration of antisite N_O would increase in proportion to the fluence of nitrogen ions.
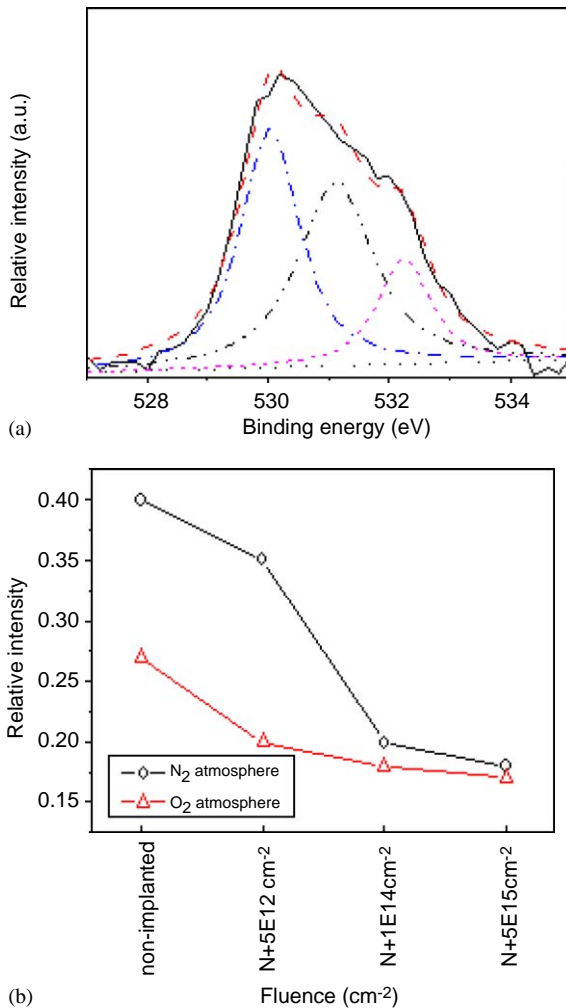
(a)

(b)

Fig. 5. (a) Displays the O1s fitted spectra of non-implanted sample. (b) Dependence of relative intensity of the fitted components centered at O1s 531.25 ± 0.2 eV, on N-implanted fluence in different atmospheres.

However, if the annealing atmosphere was exchanged and the oxygen atmosphere was used for annealing the N-implanted ZnO, the number of oxygen vacancies existing in the as-deposited ZnO film will be further decreases probably because the effective incorporation of O atom diminishes those donor levels. Therefore, higher (0 0 2) peak intensity and better crystallinity were obtained for the ZnO films annealed in oxygen

atmosphere compared to those annealed in nitrogen atmosphere (comparing Fig. 2 with Fig. 3). In this condition, part of the implanted nitrogen ions are probably located as the interstitial defects (N_i) in the ZnO films because of limited available oxygen vacancies. Therefore, when the N-implanted ZnO films were implanted with a lower dose of 5×10^{12} cm^{-2} nitrogen ions which is below the solubility limit, some of nitrogen ions could be incorporated into the oxygen sites to reduce the intrinsic defect and restore the radiation damage. Therefore, the peak intensity of NBE emission was slightly enhanced by the implantation of nitrogen ions. Furthermore, as comparing Fig. 4(a) with Fig. 4(b), it is clear that for the same lower N-implanted concentration, i.e. 5×10^{12} fluence, a stronger NBE peak intensity was detected in the N-implanted ZnO film annealed in oxygen atmosphere compared to that annealed in nitrogen atmosphere. However, with an increase of implanted nitrogen concentration, more implanted nitrogen ions were incorporated into the ZnO matrix and the structure defects were further increased. As the implanted fluence exceeds 1×10^{14} cm^{-2} i.e., 5×10^{15} cm^{-2}, a broader deep level peak around 532 nm due to high levels of nitrogen incorporation was observed in the sample annealed in oxygen atmosphere compared to that annealed in nitrogen atmosphere because a large amount of nitrogen ions could be dissolved in the ZnO films as the interstitial defects and the produced unstable defects would deteriorate the crystallinity and become some nonradiative center to absorb the light emission during photoluminescence process.

4. Conclusion

The ZnO films implanted with nitrogen ions from 5×10^{12} to 5×10^{15} cm^{-2} show high preferred orientation (c-axis) films with strong NBE emission property. It was found that there exists a solubility issue of nitrogen in ZnO films. Furthermore, the annealing atmosphere plays an important role in crystallinity and photoluminescence of nitrogen-implanted ZnO films. When annealed in nitrogen atmosphere, the peak intensity of near

band-edge (NBE) emission remarkably decreases with the increase of concentration of implanted nitrogen. However, when the ZnO films were implanted with $5 \times 10^{12} \, \mathrm{cm^{-2}}$ and annealed in oxygen atmosphere, the optical properties are improved probably because the effective incorporation of O atom diminishes those donor levels (oxygen vacancies) and the crystallinity is also improved due to implanted nitrogen. However, excess nitrogen would reduce the crystallinity and promote the formation of the deep-level emission due to high amount of intrinsic and structure defects. This study reveals that it is possible to control the crystallinity and the NBE emission of the ZnO films by using different annealing atmospheres and changing the nitrogen-implanted fluence.

Acknowledgments

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