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Electrical and structural properties of p-type ZnO:N thin films prepared by plasma enhanced chemical vapour deposition

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Abstract

Thin films of p-type ZnO:N have been obtained by thermally oxidizing zinc oxynitride films prepared by plasma enhanced chemical vapour deposition (PECVD). The p-type ZnO:N thin film with a hole concentration of 2.7 × 10^{16} cm^{-3} was obtained after an annealing process was conducted at 600 °C. A conductivity transition from n-type to p-type was observed, which was systematically researched via structural and compositional analyses. In terms of these analyses, it helped to better understand the properties and behaviour of nitrogen in ZnO. First, nitrogen was incorporated into ZnO films during the growth process to occupy oxygen positions, and also partly compensated some donors induced from non-stoichiometric (ZnO_{1-x}) composition. Second, the amount of activated nitrogen gradually increased in an oxidizing atmosphere and exceeded those donor states to realize an effective compensation, yielding p-type conductivity during the course of thermal oxidation.

1. Introduction

At present, zinc oxide is receiving considerable attention because of its potential application as an ultraviolet light emitter [1–3]. To realize such an optoelectronic device, control of electronic properties, such as the nature of conduction and carrier density, is required. Undoped zinc oxide film generally exhibits natural n-type conduction due to the presence of intrinsic donor-type defects induced by deviation from stoichiometry [4, 5]. Therefore, one of the major obstacles in the development of ZnO material is the difficulty encountered in finding an efficient p-type dopant.

Theoretical calculation predicts that nitrogen is an outstanding candidate in current research for p-type doping of ZnO [6]. Since nitrogen radical doping has been successful in fabricating p-type ZnSe [7], a number of groups have been trying to realize p-type ZnO employing nitrogen as a dopant source by various methods such as molecular beam epitaxy, magnetron sputtering, ion-implantation and so on [8–14]. To the best of our knowledge, there are still few reports on nitrogen-doped p-type ZnO films by plasma enhanced chemical vapour deposition (PECVD). In previous work, we have reported optical properties and electrical characterization of p-type ZnO thin films prepared by PECVD [12]. In the present study, we particularly emphasize the transforming process from n-type to p-type conductivity, which was researched by the structural and compositional analyses. With these results, we can

Table 1. Electrical properties of samples annealed at different temperatures in oxygen ambient.

Annealing temperature	Conductivity type	Carrier density (cm^{-3})	Resistivity (ohm cm)	Mobility ($cm^2\ V^{-1}\ s^{-1}$)
As-grown	*n*	4.8×10^{15}	2.6×10^3	0.6
500 °C	*p*	3.5×10^{13}	7.9×10^5	0.8
600 °C	*p*	2.7×10^{16}	1.6×10^3	0.3
700 °C	*n*	9.4×10^{12}	3.4×10^5	2.7

better understand the properties and behaviour of nitrogen in ZnO.

2. Experiments

As-grown ZnO thin film (sample A) with a thickness of 500 nm was deposited on the fused silica substrate at a low temperature of 100 °C by employing the PECVD system, which was introduced previously [12, 15]. Diethylzinc (DEZn) was used as the Zn source, which was kept at 10 °C by a home-built fine-controlled semiconductor temperature device, and high-purity Ar was the carrier gas. High-purity NH_3 and CO_2 served as the nitrogen source and the oxygen source, respectively. The flux ratio of NH_3 to CO_2 is 4. A large amount of NH_3 is to assure more nitrogen be kept in the growth process. The pressure of the growth chamber was maintained at 250 Pa. After deposition, the samples were transferred into a tube furnace and annealed at 500 °C, 600 °C and 700 °C in an ultrapure oxygen ambient for 1 h, labelled as samples B, C and D, respectively.

Film thickness was measured to be in the range of 400–500 nm by means of field-emission SEM. The resistivity of all the samples was measured using van der Pauw sample configuration. The type of conductivity, carrier concentration and mobility were measured by Hall effect measurements with Lakeshore's 7707 Hall measurement system at room temperature. The Ohmic contacts were made by an indium electrode, which was operated at a pressure of 10^{-3} Pa for 20 min at near 300 °C. All the measurements were conducted after the samples were kept in the dark for more than 15 h to avoid the effect of persistent photoconductivity (PPC) [16]. X-ray diffraction measurement was performed using a D/max-rA x-ray diffractometer (Rigaku) with the Cu$K\alpha$ line of 1.54 Å to determine the crystal structure. The chemical nature of surfaces was analysed by x-ray photoelectron spectroscopy (VGESCALAB MK II XPS, VG Co., East Grinstead, UK). The binding energies were calibrated by centring the aliphatic carbon peak at 284.6 eV. To investigate the local vibration modes affected by nitrogen incorporated into ZnO films, Raman scattering spectra were obtained using the 488 nm line of an Ar^+ laser and signals were collected with a microprobe system made by Jobin–Yvon Company in France.

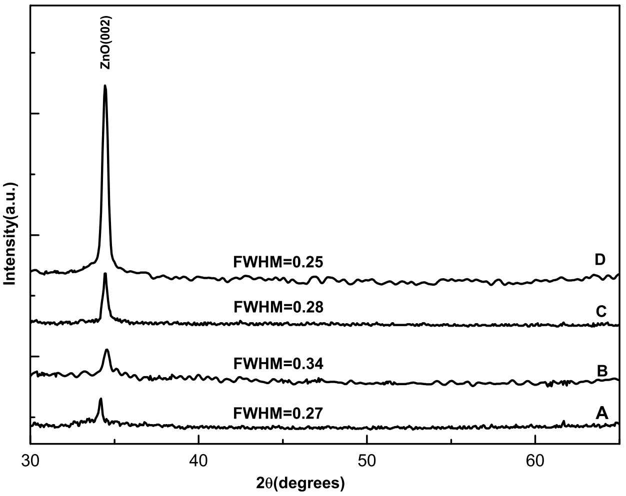

Figure 1. XRD spectra of films: (*a*) as-deposited and (*b*)–(*d*) annealed at 500, 600 and 700 °C, respectively.

3. Results and discussions

The conductivity of samples is summarized in table 1 on the basis of Hall effect measurements. It can be seen that the n-type conductivity of the as-grown film is about two orders of magnitude lower than the undoped ZnO film with typical electron concentration of $\sim 10^{17}$ cm^{-3} [17, 18], close to intrinsic ZnO, which gives evidence that nitrogen is incorporated into ZnO films during the growing process to occupy oxygen positions, partly compensating some donors induced from non-stoichiometric composition. However, p-type conversion was not obtained for the as-grown sample, due to both the limited electrical activity of nitrogen and a high concentration of donor defects at very low growth temperature (100 °C). For the films annealed at 500 and 600 °C, the Hall coefficient is inverted to positive from negative, indicating a hole-dominant transport effect. The hole concentrations increase by three orders of magnitude, from 3.5×10^{13} cm^{-3} to 2.7×10^{16} cm^{-3} and the resistivity drops more than two orders of magnitude. In the present paper, the nitrogen source was NH_3, and a part of N binds strongly with H to form NH pairs because the formation energy of this defect is lower than 'pure' N_O (N-on-O substitution) defects. In this case, the N_O acceptor defects are electrically inactive because of a so-called hydrogen passivation [19]. It has been reported that N_O acceptor defects can be reactivated via the removal of H by thermal annealing [20]. However, the growth temperature is too low for the N_O acceptor defects to be activated. Thus, the electrical property of the as-grown film is n-type conductivity. With the increase of annealing temperature, more N_O acceptor defects in ZnO will be activated to compensate donor-like defects. So the concentration of electrons will decrease with increasing annealing temperature. Finally, the amount of activated nitrogen exceeded those donor states to realize an effective compensation, yielding p-type conductivity. As the annealing temperature further increased (700 °C), the oxidation process is prominent and the residual nitrogen atoms will be almost replaced by the oxygen atoms, leading to reconversion of p-type ZnO back to weak n-type with high resistivity. This conductivity transformation can be confirmed by the structural and compositional analyses.

XRD θ–2θ scan spectra of samples A, B, C and D are shown in figure 1. For sample A, the XRD spectrum shows only one diffraction peak located at 34.19°. This position is between the (0 0 2) peak of ZnO (34.42°) and the (2 2 2) peak of Zn_3N_2 (31.70°), which suggests the formation of zinc oxynitride films. When samples were annealed above 500 °C,

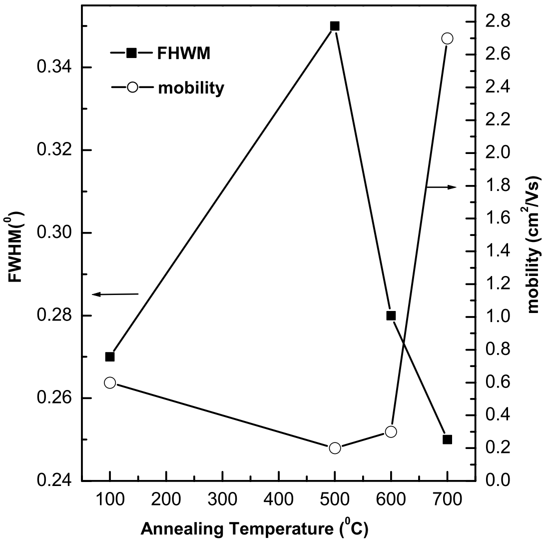

Figure 2. The full width at half maximum and the mobility as function of annealing temperature.

the diffraction peaks moved to 34.48°, which coincides with the diffraction peak of the (0 0 2) ZnO. This result indicates that the zinc oxynitride film was entirely transformed to be a preferred *c*-oriented ZnO film with a hexagonal wurtzite structure after thermal oxidation. The oxygen atoms adsorb and diffuse into the zinc oxynitride film, then bond to Zn due to its larger electronegativity (3.50) compared to a nitrogen atom (3.04) [21]. As a result, nitrogen atoms were partially replaced by oxygen atoms, resulting in the formation of nitrogen-doped ZnO films. For the sample annealed at 500 °C, the temperature is low to provide enough energy to diffused O atoms substituted for the N atoms to form a high-quality nitrogen-doped ZnO film, leading to the increase of the FWHM (0.35°) with respect to the as-grown sample (0.27°). When the annealing temperature continues to increase, the intensity of the (0 0 2) peak increases, and its FWHM narrows, which indicates the improvement of crystalline quality. It is well known that the mobility is closely related to the crystal quality, that is, the better the crystal quality, the higher the mobility is. Figure 2 illustrates the FWHM of the (0 0 2) peak and the mobility as functions of annealing temperature. As seen in figure 2, these curves show that the XRD results are consistent with the results of Hall effect measurements.

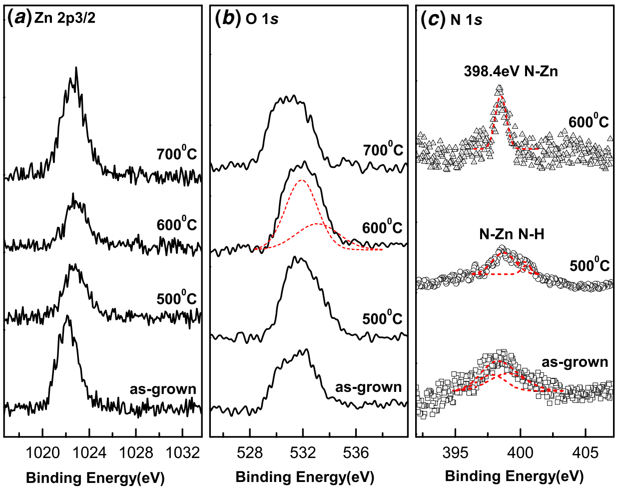

Figure 3. (*a*) Zn $2p_{3/2}$, (*b*) O 1s and (*c*) N 1s XPS spectra at different annealing temperatures.

Figure 3 shows Zn $2p_{3/2}$, O 1s and N 1s spectra for the samples annealed at different temperatures. The binding energy of the Zn $2p_{3/2}$ peak for the as-grown sample (1022.1 eV) is lower than the samples suffering from the annealing process, as illustrated in figure 3(*a*). The decrease in binding energy is related to the decrease in ionicity [22]. According to Pauling theory [23], the negativity difference of a Zn–N bond should be smaller than that of a Zn–O bond. Therefore, the ionicity of a Zn–N bond is weaker than that of a Zn–O bond. The lower binding energy indicates that there are a few Zn–N bonds in sample A, which confirms that the nitrogen was incorporated into ZnO films during the growth process to occupy oxygen positions. The blue-shift of the binding energy indicates that Zn–N bonds were replaced by Zn–O bonds during the oxidation process, which implied that the structure phase transforms from zinc oxynitride film to ZnO film. This result is in good agreement with the XRD diffraction analysis. However, the binding energy of the Zn $2p_{3/2}$ peak for samples B and C (1022.9 eV) is slightly larger than in previous reports (1022.4 eV) [21, 22]. The absolute position of the Zn $2p_{3/2}$ core level generally reflects the charge and the chemical environments around the Zn atom. For samples B and C, the symmetry of the crystal lattice was degraded because of nitrogen doping. The electrical cloud around the Zn atom becomes asymmetric, resulting in the increase of the binding energy of the Zn $2p_{3/2}$ peak for samples B and C. This result also indirectly illuminated that N was incorporated into ZnO. When the annealing temperature is up to 700 °C, the centre of the Zn $2p_{3/2}$ peak is slightly red-shifted compared with samples B and C, in good agreement with other reports [21, 22], implying the symmetry of the film has been renewed because the N atoms have been almost replaced by the oxygen atoms, leading to the formation of ZnO films during further oxidization. Consequently the conductivity type changes from p- to n-type at 700 °C.

Figure 3(*b*) comprises spectra of the O 1s region for all samples. They were consistently fitted by two nearly Gaussian curves. The high binding energy component located at 532.8 eV is usually attributed to the presence of loosely bound oxygen on the surface of the films, belonging to a specific species, e.g., $–CO_3$, adsorbed O–H or adsorbed O_2 [24]. The component on the low binding energy side of the O 1s spectrum at around 531.3 eV is attributed to O^{2-} ions on wurtzite structure of hexagonal Zn^{2+} ion array [24]. In other words, the intensity of this component is a measure of the amount of oxygen atoms in a fully oxidized stoichiometric surrounding. As illustrated in figure 3(*b*), the quantity of oxygen atoms is gradually increased as the annealing temperature increased. In addition, the bonding energy of the O 1s peak for the film annealed at 700 °C shows lower energy than others. A possible reason for this is that the N atoms were entirely replaced by oxygen atoms when the annealing temperature was up to 700 °C and the excess oxygen would give rise to surface states such as free O^{2-} ions and interstitial oxygen. In this case, the bonding energy would be red-shifted compared with other samples.

XPS revealed two distinct forms of nitrogen in figure 3(*c*). The binding energy located at 398.4 eV is typical of

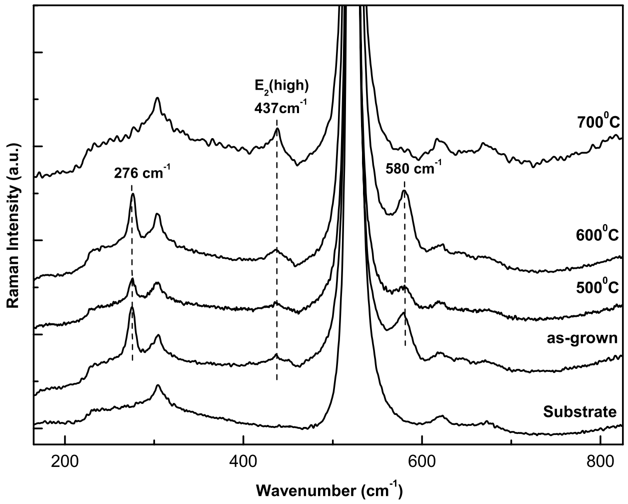

Figure 4. Room temperature Raman scattering spectra for N-doped ZnO samples, silicon (1 0 0) substrate spectra for comparison.

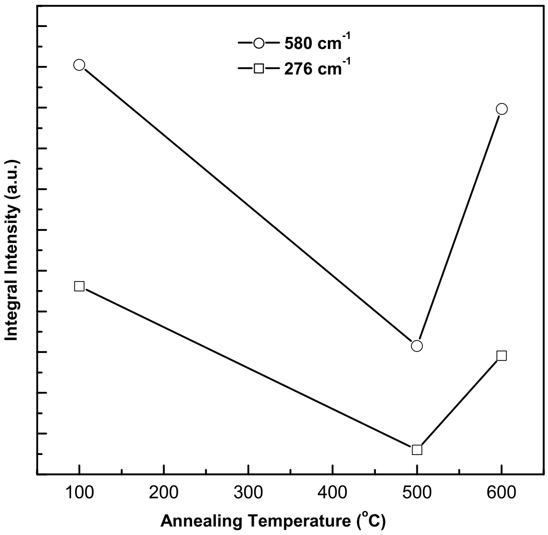

Figure 5. Variation of the integral intensities of Raman peaks at 580 cm^{-1} (○) and 276 cm^{-1} (□) depending on annealing temperature.

N–Zn bonds [21, 25], and the peak at 400 eV could be attributed to N–H bonds. As demonstrated in figure 3(*c*), the relative abundances of the N–H chemical states in sample A indicated that parts of N_O acceptors were passivated by N–H so that the effective acceptors are not enough to compensate donors, accordingly yielding n-type conductivity. Whereas XPS results on sample B show an increased concentration of the N–Zn bonds relative to the N–H pairs. This implies that H atoms are removed during the annealing process, leading to a number of effective N_O acceptors which slightly exceeds that of donor-like defects. Consequently sample B offered weak p-type behaviour [26]. When the annealing temperature is up to 600 °C, the chemical state of N–H has been seldom observed and a prominent N–Zn bond peak appeared. It implied that more nitrogen is activated to form effective N_O acceptors, which accomplished a sufficient compensation. Therefore, the hole density increases for sample C compared with sample B. But with increasing annealing temperature up to 700 °C, N 1s signals were near the noise level. This indicated that nitrogen almost disappeared because of a process of further oxidation, which accorded with the n-type conductivity for sample D.

Local vibration modes of nitrogen in ZnO are also observed via Raman spectra, as shown in figure 4 with the spectrum of the substrate for comparison. For all samples, the peak at 437 cm^{-1} is assigned to the vibration modes of E_2 (high). In addition, two peaks can also be observed at 276 and 580 cm^{-1}. Kaschner *et al* have reported that the peak shift frequency at 276 cm^{-1} is attributed to nitrogen-related local vibration modes [27]. In general, the peak around 580 cm^{-1} is attributed to A_1 (LO) or E_1 (LO) modes for ZnO film. However, we interpret these two bands as nitrogen-related local vibration modes. The reason is that these two peaks show a similar change of trend in the intensities with increasing annealing temperature, as illustrated in figure 5, although their absolute intensities are not the same. The N concentration in sample A is the highest, estimated by XPS [12]. Hence, the maximal integral intensities of the N-related Raman peaks at 276 cm^{-1} and 580 cm^{-1} are observed. As the temperature is increased to 500 °C in oxygen ambient, oxidation reaction, film recrystallization and growth become the major processes. As a result, the Zn–N bonds are gradually replaced by Zn–O bonds, which leads to the decrease of the band intensities of 276 and 580 cm^{-1}. The annealing temperature up to 600 °C is high enough to activate more nitrogen becoming an effective acceptor, accompanied by an increase in the intensities of 276 and 580 cm^{-1}. These two Raman peaks seldom appear when the annealing temperature reaches 700 °C indicating that the films have been almost oxidized at this temperature. As illustrated by the results of XPS, there is a small amount of nitrogen for the sample annealed at 700 °C so that one can hardly find these two N-related peaks in sample D. The result of the Raman spectrum is in good agreement with that of XPS.

4. Conclusion

We have fabricated nitrogen-doped p-type ZnO thin films by thermal treatment of ‘zinc oxynitride’ films prepared by PECVD at low temperature. Electrical and structural properties of ZnO:N thin films were researched. XRD measurements demonstrate a transformation process from zinc oxynitride film to ZnO with an increase in annealing temperature. The Raman spectra of N-doped ZnO films show two spectral features at 276 cm^{-1} and 580 cm^{-1} that can be assigned to N-related vibration modes. XPS results indicate the formation and reactivity of effective acceptors in N-doped ZnO films during the annealing process. All results have elucidated the process of nitrogen being incorporated into films to compensate donors and being activated during the course of annealing, leading to the conduction converting from n-type to p-type. The clarification of this transfer will be instructive to realize p-type doping and to improve the properties of the p-type ZnO films.

Acknowledgments

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