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Activation of Nitrogen-acceptors in Al-N Codoped Zinc Oxide Films Prepared by Radio Frequency Magnetron Cosputtering Technology

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Abstract—Al-N codoped zinc oxide films were prepared by rf magnetron cosputtering system using AlN and ZnO targets. With a post-annealing treatment, p-ZnO behavior was achieved with the hole concentration of 4.84×10^{17} – 3.91×10^{18} cm^{-3} as a consequence of the doping nitrogen acceptors effectively activated. PL spectrum of the annealed codoped films performed an acceptor-bound exciton peak at 3.333 eV and a free electron to the acceptor transition at 3.280 eV. In addition, a broad emission peak at about 3.02 eV observed from the p-ZnO film was suggested to be contributed from the activated nitrogen-acceptor related transitions. From XPS spectra, the evolutions of Zn 2p3/2 and N 1s core level of the p-type ZnO film also provided evidences of the contribution from the activated nitrogen-related acceptors.

1. Introduction

Zinc oxide (ZnO) material with wide and direct bandgap of 3.37 eV is a promising next generation semiconductor for its larger exciton binding energy of 60 meV at room temperature. Unfortunately, p-type ZnO films are very hard to achieve for the self-compensation effect as well as the lower solubility and inactivation of the acceptors in ZnO films. Recently, several researchers have put their efforts on the exploration of p-ZnO film by doping elements [1]. Nitrogen with shallow acceptor level is a promising candidate to substitute for oxygen as N_O due to their similar ionic radius. However, the reliability and reproducibility in obtaining p-type ZnO:N is still under controversial because of the doping concentration must be high enough to avoid the apparent compensation effect in ZnO. To solve the above-mentioned problems, the codoping method using acceptors and reactive donors simultaneously is proposed to decrease the Madelung energy originated from the formation of an N-III-N complex in ZnO that increase the solubility of N in ZnO [2-3]. In our previous research, Al-N codoped ZnO films had been prepared by cosputtering [4]. The nitrogen-related acceptors were inactive in the as-deposited cosputtered films and performed n-type conduction behavior.

In this study, in an effort to activate the nitrogen-related acceptors, post-annealing treatments were carried out. The activation of these acceptors after thermal annealing was recognized from the electrical property evolutions. The related optical and material behavior was conducted from the low-temperature Photoluminescence (PL) spectra and X-ray photoelectron spectroscopy (XPS) measurements.

2. Experimental procedure

Al-N codoped ZnO films were deposited on n-type Si (100) substrates at room temperature by rf magnetron cosputtering system using ZnO and AlN targets. A dual rf power supply synchronized phase was employed to control the rf power supplied to AlN and ZnO targets simultaneously. To achieve the optimal composition of Al and N contents in the ZnO film for the consideration of the formation of N-Al-N complex, the rf powers supplied on AlN and ZnO target were 85 and 270 W, respectively. In addition, the undoped ZnO films deposited at an rf power of 270 W on the ZnO target were also prepared for comparison. Detail description for this cosputtering technology was discussed elsewhere [4]. Post-annealing treatments in the range of 300-800°C for 30 min in nitrogen ambient were carried out to activate these doping impurities. Hall effect measurements were conduct in the Van der Pauw configuration at room temperature. Low-temperature (12K) PL measurements were performed using He-Cd laser (λ =325 nm). XPS measurements were used to investigate the existence of Zn-N related chemical bonds in the films.

3. Experimental results

Carrier concentration and hall mobility of the Al-N codoped ZnO film as a function of annealing temperature are illustrated in Fig. 1. The as-deposited Al-N codoped ZnO films performed n-type conduction with the carrier concentration of 3.29×10^{19} cm^{-3}, whereas that of the undoped-ZnO film showed an insulated property with the electron carriers ~ 10^{12} cm^{-3}. This revealed that the introduced nitrogen-related acceptors were inactive and the donor impurities of Al^{3+} and N_O-double-donor complexes such as N_O-V_O, N_O-Zn_i, and N_O-Zn_O were predominated in the as-deposited cosputtered films. By processing with a post-annealing treatment in nitrogen ambient, the conduction type of the Al-N codoped ZnO films could be

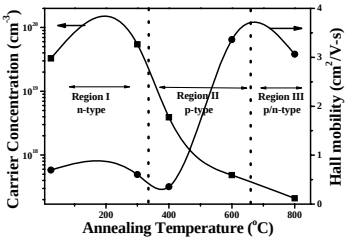

Fig. 1 Carrier concentration and hall mobility of the Al-N codoped ZnO film as a function of annealing temperature.

divided into three regions. As the annealing temperature reached 400°C, the conduction type transformed from n-type (region I) to p-type (region II) behavior with a high carrier concentration of 3.91×10^{18} cm^{-3}. This indicated that the nitrogen-related acceptors had been effectively activated. However, the carrier concentration was found to be decreased with increasing annealing temperature. At an annealing temperature of 800°C (region III), the conduction type showed delicate behavior between p and n type. The outdiffusion of the nitrogen contents in the codoped films was suggested to be responsible for the gradually decreased in the hole carrier concentration even led to the reconversion of n-type ZnO behavior. Low-temperature PL spectra of the undoped ZnO annealed at 400°C and codoped ZnO films annealed at 300 and 400°C (indicated as curve A and B in Fig.2 (b)) under nitrogen ambient are shown in Fig. 2(a) and (b). The emission peaks appeared in the annealed undoped-ZnO films were identified as donor-bound-exciton (D^oX), donor acceptor pair (DAP), and LO-phonon replicas. The PL spectrum of the annealed codoped ZnO film was much different from that of the annealed undoped ZnO film. The emission peaks at 3.333, 3.280, and 3.240 eV were identified as the acceptor-bound-exciton (A^oX), free electron to acceptor (FX), and DAP transitions, respectively [5]. Compared with curve A and B shown in Fig.2 (b) and related electrical properties, p-type ZnO conduction seem to be connected with the appearance of the broad emission peak at 3.02 eV. As a result, this emission band was concluded to be emerged from the thermally activated nitrogen-acceptor related transition. The XPS spectra of Zn

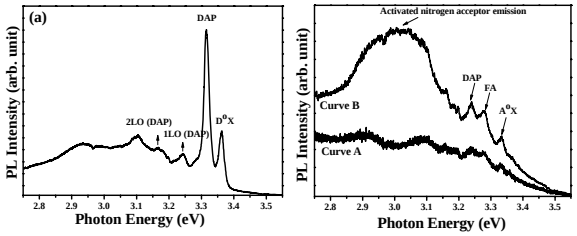

Fig. 2 Low-temperature PL spectra of (a) undoped ZnO and (b) Al-N codoped ZnO films annealed at 300 (curve A) and 400°C (curve b).

$2p_{3/2}$ core level for the undoped and codoped ZnO films annealed at 400°C are shown in Fig. 3. The Zn $2p_{3/2}$ peak of the annealed codoped ZnO shifted toward higher binding energy, indicating large amounts of Zn-N chemical bonds (the symmetry of the crystal lattice was degraded due to nitrogen doping) were formed by thermal annealing, whereas the Zn $2p_{3/2}$ peak of the annealed undoped ZnO film mainly composed of Zn-O chemical bonds [5]. The related N 1s core level XPS spectra are shown in Fig. 4(a) and (b). As can be seen in Fig. 4(b), no obvious peak is observed for the annealed undoped ZnO film, whereas the annealed codoped ZnO film performed two peaks at about 395.7 and 399.8 eV. The core level at high binding energy was consisted with the chemical state of N-N observed in ZnO:N samples [6]. The other core level was mainly composed of the Zn-N chemical bond contributed by the activation of nitrogen acceptors of the Al-N codoped ZnO film by thermal annealing.

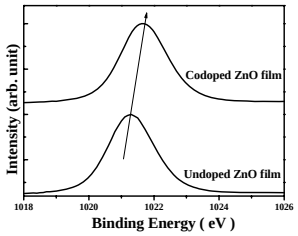

Fig. 3 Typical XPS spectra of Zn $2p_{3/2}$ core level for the undoped and codoped ZnO films annealed at 400°C.

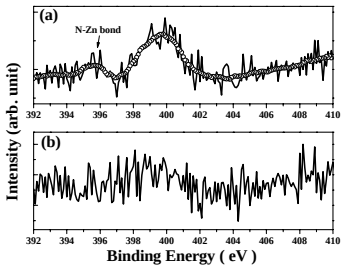

Fig. 3 Typical XPS spectra of N 1s core level for (a) codoped and (b) undoped ZnO films annealed at 400°C.

4. Conclusions

P-type ZnO films with a hole concentration of $4.84 \times 10^{17} - 3.91 \times 10^{18}$ cm^{-3} were achieved from the cosputtered Al-N codoped ZnO films annealed at 400 to 600°C in nitrogen ambient. From the PL spectra, the appearance of the broad emission peak at about 3.02 eV that corresponded to the level of N_O acceptors in ZnO bandgap was responsible for the activation of the nitrogen acceptors by thermal annealing. In addition, the binding energy of the Zn $2p_{3/2}$ and N 1s core levels composed of notable Zn-N chemical bonds in the related XPS spectra also provided evidence for the activation of the nitrogen acceptors and resulted in the p-type conductive behavior.

Acknowledgments

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