The Electrical and Microstructural Properties of ZnO:N Thin Films Grown in The Mixture of N_2 and O_2 by RF Magnetron Sputtering

Hu-Jie Jin, Eun-Cheal Lee*, Soon-Jin So* and Choon-Bae Park
Wonkwang Univ. School of Electrical Electronic and Information Engineering, Knowledge*On semiconductor Inc.*

Abstract: ZnO is a promising material to make high efficiency violet or blue light emitting diodes (LEDs) for its large binding energy (60meV) and big bandgap. But the high quality p-type conduction of ZnO is a dilemma to achieve LEDs with it. In present study, we presented a reliable method to prepare ZnO thin films on (100)silicon substrates by RF magnetron sputtering in the mixture ambient of N_2 and O_2, accompanying with low pressure annealing in the sputtering chamber in O_2 at 600^0C and 800^0C respectively. X-ray diffraction and Hall effect with Van der Paul method were performed to test ZnO films. Seeback effect was also carried out to identify carrier types in ZnO films and showed the N-doped ZnO film annealed at 800^0C had achieved p-type conduction.

Key words: RF magnetron sputtering, p-type conduction, N-doped ZnO film.

1. Introduction

ZnO is getting more attractive than any time before for its charming properties of 60meV exciton binding energy and 3.37eV bandgap for the potential highly effective white light emitting diode which can be used as non-polluting economical light source. High quality ZnO bulks which can be used as base materials to be doped have been realized and ZnO thin films with n-type conduction have been easily achieved experimentally which are essential for making p-n junctions of white LEDs. Nevertheless, it is hard to fabricate high quality p-type ZnO thin films which are also imperative for p-n junction of effective white LEDs are. To get p-type ZnO thin films, many methods and dopant species[1-5] have been used. However, in contrast to the case of GaN, ideal manner of making p-type ZnO thin films hasn't been found. The difficulty of fabrication of p-type ZnO thin films whose quality is satisfied to make a p-n junction possessing high internal quantum efficiency has been the bottleneck to realize highly effective white LEDs based on ZnO material. Preparing high quality ZnO thin films by magnetron sputtering system is convenient, applicable and effective. But it is difficult to make p-type ZnO thin films with high hole concentration, carrier mobility and low resistivity by magnetron sputtering, especially, by using RF power though it can supply more stable power than DC power. In the previous papers[6,7] which reported to succeed in obtaining p-type ZnO films by RF magnentron sputtering, the p-type conduction has low hole concentration or unstable. In present study, we used Si (100) wafers as substrates to realize p-type ZnO thin films in the mixture of N_2 and O_2 by RF magnetron sputtering.

2. Experimental process

In our experiments, all of ZnO target, O_2 gas and N_2 gas were with purity of 5N. We fabricated a N-doped ZnO thin film by RF magnetron sputtering using Si (100) wafers as a substrates. Silicon wafer was mounted on the heating hold in sputtering chamber and then the chamber was pumped to the bases pressure of up 10^{-6} Torr. The N_2 gas of 60% in total mixture of N_2 and O_2 was introduced into the chamber to 15mTorr and the substrate was heated to the temperature of 450^0C. The RF power was set at 210W and growth period was 180minutes. After that, the film was annealed by holder heater in the sputtering chamber with O_2 ambient of 10 Torr for 5 minutes at 600^0C and 800^0C respectively, The times of temperature ascent from room temperature to 600^0C and to 800^0C were 5 minutes and 10 minutes respectively and the descent of temperature was carried out naturally in chamber for both. To evaluate the samples, X-ray diffraction (XRD), scanning electron spectra (SEM) and Hall effect with four point probe Van der Paul method were performed. For determination of carrier type, Seeback effect was also carried out.

3. Results and discussion

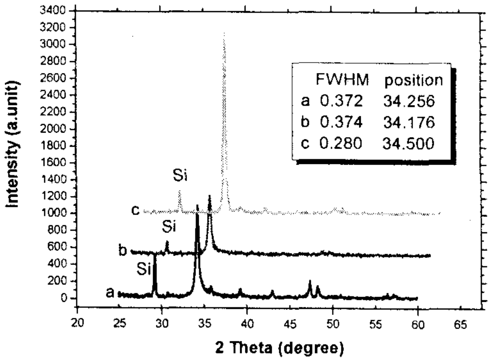

Fig. 1. XRDs of ZnO films for (a) as-grown, (b) annealed at 600^0C and (c) annealed at 800^0C

From the XRD patterns shown as Fig.1, (002) peaks are dominant for all three cases, indicating that preferred growth orientation of ZnO films is c-axis. From the FWHMs of inlet in Fig.1, the film annealed at 800^0C has narrowest (002) peak, while the other of two have nearly the same larger values of about 0.372, which means that from 600^0C to 800^0C, the grains of film get bigger for reconstruction at high temperature. The values of (002) peak positions of as-grown film and the film annealed at 600^0C have much smaller than that of bulk ZnO which is with about 34.4^0, while the value of (002) peak of the film annealed at 800^0C has nearly the same as that of bulk ZnO, which means that because of interstitial N_2 and substitutional N_2 for O positions, the as-grown film and the film annealed at 600^0C are under internal tensile stress, however, as the temperature goes up to 800^0C, nearly all of N_2 was split and this made the crystal of film relaxed sufficiently. Since Zn-N bond length is somewhat smaller than Zn-O one, the substitution of atomic N for O position should result in decrease of the lattice constants. However, radius of N_2 is much larger than that of atomic O, therefore, the increase of lattice constants induced by N doping should be attributed to substitution of N_2 for O in the as-grown and low temperature annealed ZnO:N. Beside that, some N_2 should have penetrated interstitially and also made the lattice constants prolonged. Fig.2 shows that the film annealed at 800^0C has good evenness and hasn't been damaged at high temperature. The film's growth rate is 6.5nm per minute which shows higher growth rate. For as-grown and 600^0C annealed film, Seeback effects couldn't determine the carriers' types in the films. this is perhaps because of high resistivity in the films. But for the case of the film annealed at 800^0C, Seeback effect showed p-type conduction in the film. This is because sufficient splitting of molecular N_2 and activation occurred, making the conversion of the film happen.

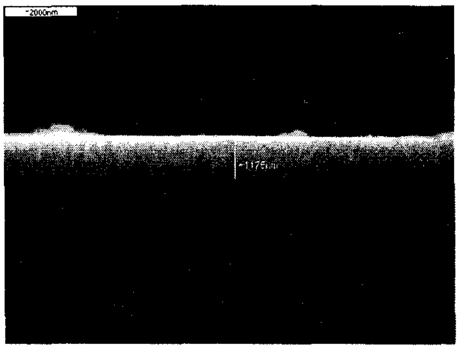

Fig. 2. cross sectional image of film annealed at 800^0C

4. conclusion

From the experiment and results, it can be concluded that the film annealed at temperature from 600^0C to 800^0C undergoes carrier type conversion from n-type to p-type and at same period of temperature N_2 gas undergoes splitting variation.

5. Acknowledgement

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6. References

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