Realization of p-type ZnO Thin Films Using Codoping N and Al by RF Magnetron Sputtering

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Abstract: ZnO is a promising material for UV or blue LEDs. p-Type ZnO thin films which are imperative for the p-n junction of LEDs are difficult to achieve because of strong compensation of intrinsic defects such as zinc interstitial and oxygen vacancy. The method of codoping group three elements and group five elements is effective for the realization of p-type ZnO films. In this study, We codoped N and Al in ZnO thin films by RF magnetron sputtering and annealed the films in sputtering chamber. Some films showed p-type conductivity in Seeback effect measurement.

Key words: ZnO thin film, RF magnetron sputtering, homo-buffer layer, codoping

1. Introduce

ZnO is getting more attractive than any time before for its unique properties, such as large exciton binding energy of 60meV and wide energy bandgap of 3.37eV, which means that highly effective UV or blue LEDs based on ZnO can be realized. High quality ZnO bulks are available and n-type ZnO thin films with high electron concentration are easily achieved. Nevertheless, it is hard to fabricate p-type ZnO thin films needed for p-n junctions of LEDs. To get p-type ZnO thin films, many methods and dopant species have been used [1]. To solve the problem of bottleneck of p-type doping, co-doping of group three elements and group five elements in ZnO was proposed[2]. N-Al co-doped p-type ZnO films were achieved by DC reactive magnetron sputtering[3]. In this study, RF magnetron sputtering method was used to obtain co-doped p-type ZnO films.

2. Experiments

To compare ZnO film grown on (100)Si with ZnO film grown on homo-buffer layer, ZnO homo-buffer layers were achieved first. ZnO buffer layers were grown on (100)Si wafers in the mixture of gases of $Ar:O_2=4:1$ by RF magnetron sputtering at temperature 100^0C and pressure of 15mTorr with RF power supply of 120W in 30min. 5N ZnO ceramic disk was as sputtering target. After that, the buffer layers were in-situ annealed in 5N O_2 ambient for 20min at 15mTorr with annealing temperature of 800^0C. For codoped ZnO thin film growth, ZnO ceramic disk with $Al_2O_3$2% was selected as a target. (100)Si wafers and homo-buffer layer templates were used as substrates. The films were grown in the mixture of $N_2:O_2=1:4$ and 3:2 at total working pressure of 15mTorr and the annealing temperature of 450^0C in 240min with RF power of 210W. Then the films were annealed in the chamber for 5minutes by heating the substrates at 600^0C and 800^0C in O_2 at 10Torr. Afterwards, X-ray diffractions(XRD) were performed to evaluate the microstructure of films. Seeback effect was carried out with a simple electric multi-tester and a soldering iron to determine the conductivity type of the films.

3. Results and Discussion

Fig.1 shows that the all of the three ZnO films grown on (100)Si substrates have three peaks of (100), (002) and (101), but the films grown on templates with homo-buffer layer have only one peak of (002). It also can be seen that the intensities of annealed films get bigger and FWHMs get smaller with increasing annealing temperature, implying that annealing treatment improves the film crystallinity. The positions of (002) peak of as-grown and 600^0C annealed films shift lower than that of bulk ZnO which is about 34.44^0, but the (002) position of 800^0C annealed films get to that of bulk ZnO. The above phenomena occur on the films grown on different substrates and at different N_2 fraction in the mixture ambient (Fig. 2 shows that too), implying that N_2 is introduced in the films when the films

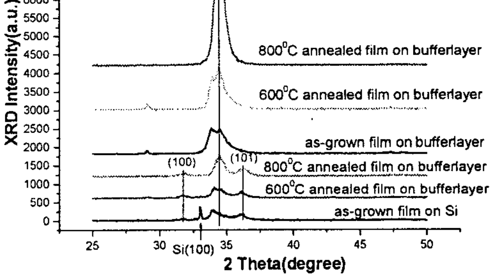

Fig. 1 XRD patterns of films grown in the mixture of $N_2:O_2=1:4$

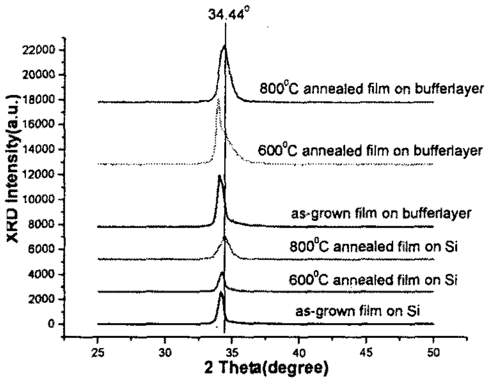

Fig. 2 XRD patterns of films grown in the mixture of N_2:O_2=3:2

grow and make the films inflate along c axis. 600°C is not enough to split N_2 to atomic N obviously because the bonding energy of N-N of N_2 is too large to be split at annealing temperature of 600°C in the films. But at the annealing temperature of 800°C, N_2 can be split to atomic N state sufficiently, which makes the films relax and the position of (002) peak of the films to that of bulk ZnO. Fig.2 shows that all of the samples grown in high fraction of N_2 in the mixture ambient have only one (002) peak. Each (002) peak intensity in Fig.2 is larger than the corresponding peak ones in Fig.1 and each FWHM of (002) peak in Fig.2 is smaller than that of corresponding peak in Fig.1, indicating that high N_2 density ambient helpful to crystal growth of the ZnO film in c axis direction with high quality.

In Seeback effect experiment with simple equipments, most of samples showed n-type conductivity or nothing. But the film grown in the ambient of N_2:O_2=1:4 at 600°C on buffer layer template showed explicit p-type property. The film grown in N_2:O_2=3:2 at 600°C on buffer layer template showed n-type first and then showed p-type at low heating state. But the other films grown on Si or homo-buffer layer show n-type conductivity or nothing, implying that homo-buffer layer is effective to fabricate p-type ZnO films.

The as-grown films and 800°C annealed films didn't show p-type. this can be explained as following. N_2 which was doped in the films when the films grew didn't split in as-grown films and at 600°C annealing temperature some of N_2 split in to atomic N state and was activated to make the films p-type conductivity. But too high temperature of 800°C made much oxygen vacancy in the films to compensate acceptor function of N and made the film go back to n-type conductivity state.

4. Conclusion

The ZnO films have preferential c-axis orientation for the growth in the mixture of N_2 and O_2. Homo-buffer layer and high annealing temperature have better crystallization effects for ZnO films. homo-buffer layer substrate is more effective to realize p-type ZnO films than silicon substrate. In future Hall effect should be performed on the films above to ascertain the resistivity, carrier concentration and mobility of the films to do further electric evaluation.

5. Acknowledgement

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6. References

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