Electrical Properties of P-ZnO:(Al,N) Co-doped ZnO Films Fabricated by RF Magnetron Sputtering

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Abstract: Al-N co-doped ZnO films were fabricated on n-Si (100) and homo-buffer layers in the mixture of oxygen and nitrogen at 450^0C by magnetron sputtering. Target was ZnO ceramic mixed with 2wt%Al_2O_3. XRD spectra show that as-grown and 600^0C annealed films are prolonged along crystal c-axis. However they are not prolonged in (001) plane vertical to c-axix. The films annealed at 800^0C are not prolonged in any directions. Codoping makes ZnO films unidirectional variation. XPS show that Al content hardly varies and N escapes with increasing annealing temperature from 600^0C to 800^0C. The electric properties of as-grown films were tested by Hall Effect with Van der Pauw configuration show some of them to be p-type conduction.

Key words: ZnO:(Al, N) film, RF magnetron sputtering, co-doping method.

1. Introduction

ZnO is a material with wide energy bandgap (3.37eV) and large exciton binding energy (60meV) which can be used for optoelectronic devices such as UV or blue light emitting devices and photodetectors. Low solubility of p-type dopants and deep-level of p-type dopants are main problems to realize p-type ZnO [1]. To solve hard problems above, T. Yamamoto et al proposed a co-doping method with a ratio of2Ⅴ:Ⅲ elements [2]. It is known that ZnO films on buffer layers are usually better than those directly on substrates. But up to now, it is not very clear for the case of doped ZnO films, especially, for the case of co-doped ZnO films. In this study, we fabricated Al-N co-doped ZnO films by RF magnetron sputtering and did electric and chemical analysis.

2. Experimental process

ZnO films were prepared on n-(100) Si and homo-buffer layer templates by RF magnetron sputtering with post-annealing in the sputtering chamber. The homo-buffer layers were fabricated at 100^0C and 15mTorr of Ar mixed with O_2 by RF magnetron sputtering with ZnO ceramic as target and with subsequent in-situ annealing at 800^0C and 15mTorr of O_2. The (Al,N)-codoped ZnO films were fabricated in the mixture of N_2 and O_2 at 15mTorr and 450^0C by magnetron sputtering with ZnO ceramic mixed with 2wt% Al_2O_3 and with subsequent in situ annealed in O_2 at 600 and 800^0C of 10Torr respectively. The samples were tested by XRD, XPS and Hall Effect in Van der Pauw configuration.

3. Results and discussion

Fig.1 shows that the films grown on buffer layers have only (002) peak and 800^0C annealed film has corresponding peak at unstressed position. The films on Si show three peaks corresponding to (100), (002) and (101) planes, respectively. Fig.2. shows that all films grown in the ambient of N_2:O_2=3:2 exhibit only (002) peak, implying that high N_2 percentage in ambient of N_2 and O_2 avails the films to grow along c-axis. If N_2 percentage is too high, the crystallinity gets worse. Fig.3. shows that all films grown in N_2:O_2=1:0 have (100), (002) and (101) peaks.

All of three figures above have the same phenomena as following. The (002) peaks of as-grown

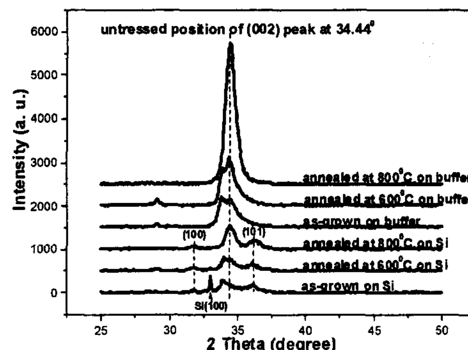

Fig.1 XRD spectra of films gown in N_2:O_2=1:4.

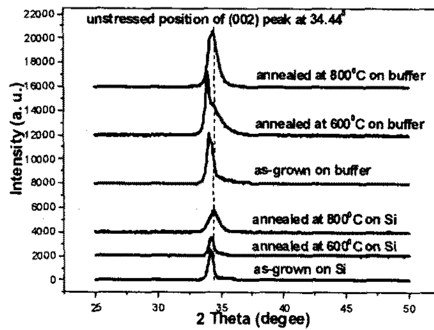

Fig.2 XRD spectra of films gown in N_2:O_2=3:2.

and 600^0C annealed films have lower angle position than unstressed position. As annealing temperature goes up to 800^0C, the (002) peak position goes to unstressed position. But (100) and (101) peak positions in Fig.1 and Fig. 3 do not vary or vary little with annealing temperature. Films on buffer layers have higher intensities and thus possess higher crystallinity than those on Si. It is implied from above that when Al and N are co-doped in ZnO, the lattice of films varies unidirectionally and the buffer layers are beneficial to Al-N codoped ZnO films grow along c-axis.

Fig.4 shows that O1s peak shifts from higher binding energy (532.5eV) to less binding energy (531.2eV) with increase of annealing temperature. In the film annealed at low temperature, the existence of N_2 makes oxygen deficient region near the O^{2-}[3] and with increasing annealing temperature to 800^0C, the N_2 splits and escapes, it make the film close to bulk ZnO crystal. In left inlet in Fig.4 shows that the film annealed at 800^0C has much less N compared to the film annealed at 600^0C, which means that most nitrogen near the surface escapes from film. In right

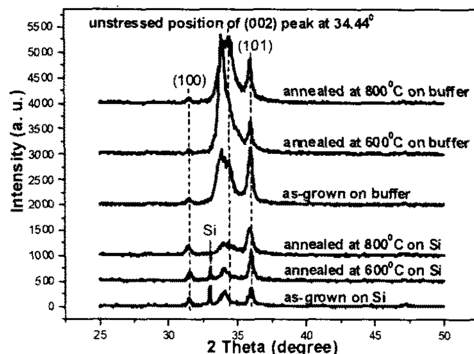

Fig.3 XRD spectra of films gown in N_2:O_2=5:0.

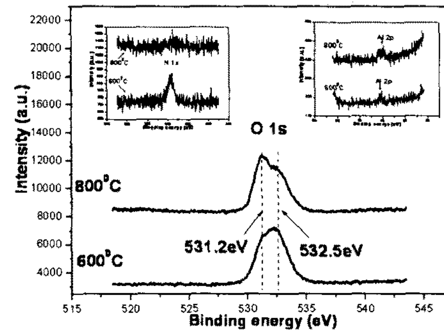

Fig.4 XPS spectra of films gown in N_2:O_2=3:2.

inlet in Fig.4 shows that the content of Al nearly doesn't vary with annealing temperature because Al prefers combining with O strongly rather than with N due to most N being in the molecular state N_2.

Most of Al-N co-doped ZnO show n-type. When Hall Effect measurements was conducted, some of films show p-type with unstable values of data initially and then convert to stable n-type. This is perhaps atomic N attracts each other to form N_2 when current flows.

4. Conclusion

N_2 in co-doped ZnO films makes the films prolonged along c-axis and hardly makes the films prolonged in (001) plane, which has unidirectional variation. At high temperature annealing of 800^0C, N_2 in the film splits and escapes from surface, which makes film relax to unstressed states. Films grown on homo-buffer layer have batter crystalinity and more preferred growth orientation along c-axis than those on Si.

5. Acknowledgement

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6. References

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