Optical Analysis of p-Type ZnO:Al Thin Films

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Abstract : We have prepared p-type ZnO:Al films in pure oxygen ambient on n-type Si (100) and homo buffer layers by RF magnetron sputtering system. Hall effect measurement shows that the film annealed at 600°C possesses p-type conductivity and the film annealed 800°C does not. PL spectra show different properties of p- and n-type ZnO film. The corresponding peaks of PL spectra of p- and n-type show at about same positions. The intensities of high photon energy of n-type film on buffer shows decreasing tendency.

Key words : RF magnetron sputtering, Homo-buffer layer, P-type AZO films

1. Introduce

ZnO is a wide bandgap material with large exciton binding energy of 60 meV, together with other unique properties, makes this material have advantages over GaN in photoelectronic devices. Although ZnO has these merits, it has not been employed in commercial photoelectronic device production because effective p-n junctions, especially high-quality p-type ZnO films, is hard to be prepared. Column five elements usually are chosen to dope ZnO p-type. Theoretically, N is the best choice to ZnO p-type because it has the nearly same radius as that of O and is the shallowest acceptor in ZnO [1], but it is difficult to dope ZnO p-type with it. S. Limpijumnong and his co-workers proposed a new route to dope ZnO p-type with large-size-mismatched impurities such as As and Sb. They proposed new complex mechanism model of X_{Zn}-$2V_{Zn}$ (X=As, Sb) as an acceptor in p-type ZnO doping [2], indicating that X supplies a donor on Zn site and induces two acceptors of Zn vacancy. These theoretic interpretation and practices present a new clue if other elements can take the role of being a donor and inducing 2 acceptors of Zn vacancy which is the same as As or Sb. In this study we tried to dope ZnO p-type with Al as a role of the element in this mechanism. General speaking, Al is a donor in ZnO. Up to our knowledge, Al-doped ZnO films are not found to have p-type conductivity in any references. In present study we have achieved Al-doped p-type ZnO film with 2wt% Al_2O_3 in ZnO ceramic as RF magnetron sputtering target.

2. Experiments

We prepared Al-doped ZnO films in pure oxygen ambient by RF magnetron sputtering system. n-Si (100) and homo-buffer layer on n-Si(100) were selected as substrates. Buffer layers on n-Si (100) were fabricated in 20% O_2 in Ar ambient at temperature of 100°C by RF magnetron sputtering with 5N ZnO ceramic as target and RF power was set at 150W for 25min to get about 70nm ZnO layers. Subsequently the films were annealed in-situ at 800°C and 15mTorr in O_2 for 20min to get buffer layers needed. For fabrication of p-type ZnO:Al films, ZnO ceramic (5N) mixed with 2wt% Al_2O_3(5N) was selected as RF magnetron sputtering target, and pure O_2 (5N) of 15mTorr pressures,210W, 450°C and 180min were selected as ambient gas, RF power growth temperature and growth time respectively. Also in-situ annealing processes were carried out at 600°C and 800°C at pure O_2 of 10Torr to compare the variation of properties for 5min. XRD spectra, Hall effect measurements with Van der Pauw method and PL spectra were carried out to determine the properties of the films.

3. Results and Discussion

XRD spectra of buffer layer and the ZnO:Al films grown at 450°C and 15mTorr are shown in Fig.1. All films

Table 1 Hall effect measurement

sample	type	con. ($10^{18}cm^{-3}$)	μ ($cm^2V^{-1}s^{-1}$)	ρ (Ωcm)
S1	p	0.0966	2.03	18.4
S2	n	8.99	0.161	4.32
S3	n	2.45	1.98	1.29
B1	-	-	-	-
B2	p	4.04	0.194	7.97
B3	n	4.0	1.15	1.35

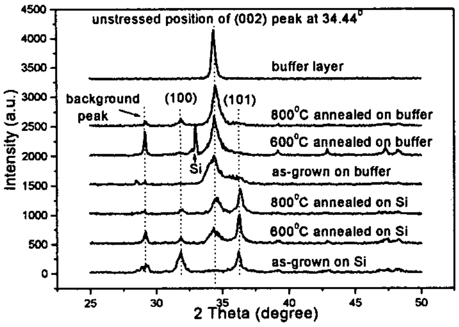

Fig.1. XRD spectra of buffer layer, as-grown and annealed films fabricated on Si and buffer layers in pure O_2 gas

exhibit (002) peak of two theta diffraction angle at about 34.44^0 which is the (002) peak value of bulk ZnO, implying that all films have not obvious internal stress. The ZnO:Al films also show (100) and (101) peaks. From the intensities of (100) and (101) peaks we can conclude that buffer layers and high annealing temperatures are beneficial to ZnO film growth along c-axis. In Table 1, samples S1-S3 are the films on Si of as-grown, annealed at 600^0C and 800^0C, and B1-B3 are the films on buffer layers of as-grown, annealed at 600^0C and 800^0C, respectively. As-grown sample on Si has p-type conductivity, but annealed ones have n-type conduction. As annealing temperature goes higher, electron mobility gets large and resistivity lower, but electron concentration gets lower. As-grown sample on buffer layer has high resistivity so that Hall effect measurement can't be test. The film annealed at 600^0C shows p-type conductivity with high hole concentration of $4.04 \times 10^{18} cm^{-3}$. The mobility is low and resistivity is a little large. Fig.2 shows PL of p- and n-type films. The p-type film on buffer 600^0C (B2) shows its PL spectrum peaks and shoulders at about 1.87, 2.15, 2.48, 2.74, 2.97, 3.17, 3.31 and 3.82 eV respectively. The n-type film on buffer layer annealed at 800^0C (B3) shows its PL spectrum peaks and shoulders at about 1.87, 2.18, 2.76, 2.99, 3.20 and 3.82 , respectively. The peaks have

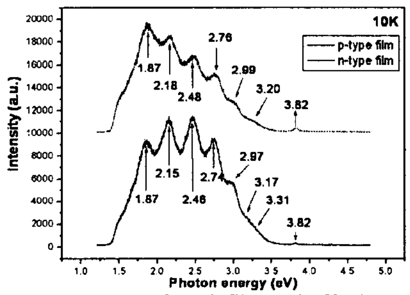

Fig.2 PL spectrum of ZnO film on buffer layer.

corresponding relation although there is a little difference The higher peaks of n-type shows obviously decrease of intensities. So the higher photon energy peaks, such as at about 2.74 and 2.97 eV, are ascribed to p-type defects. As the annealing temperature goes to higher values the p-type defects decrease and peak intensities decrease. The shoulders at about 3.31 and 3.17 eV are attributed to free electron-acceptor (FA) and donor-acceptor (DAP) transitions respectively. The corresponding peaks decrease obviously in n-type film because of lack of acceptors. Interestingly there is a peak at 3.82 eV in the two spectra which has not reported in any references before. Previous study by other AZO shows n-type conductivity with high electron concentration in a Zn-rich condition [3]. But in our high O-rich condition the AZO can convert to p-type conductivity. Al acts as a donor in Zn site and induces two Zn vacancy in O-rich condition, which constructs an acceptor complex of Al_{Zn}-$2V_{Zn}$. This should be confirmed further.

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. The higher peaks in PL spectrum of n-type AZO film decreases obviously compared with those of p-type films.

5. Acknowledgement

This research was supported by the Program for the Training of Graduate Students in Regional Innovation which was conducted by the Ministry of Commerce Industry and Energy of the Korean Government.

6. References

[1] H. Park, S. B. Zhang, and S. H. Wei, Physical Review B, Vol. 66, p. 073202, 2002.

[2] Limpijumnong, S. B. Zhang, S.H. Wei, and C.H. Park, Physical Review Letters, Vol. 92, p. 155504, 2004.

[3] Y. Igasaki and H. Saito, Journal of Applied Physics Vol. 70, No. 7, p. 3613, 1991.