Realization and Analysis of p-Type ZnO:Al Thin Film by RF Magnetron Sputtering

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Al-doped p-type ZnO thin films were fabricated by RF magnetron sputtering on n-Si (100) and homo-buffer layers in pure oxygen ambient. ZnO ceramic mixed with 2 wt% Al_2O_3 was selected as a sputtering target. XRD spectra show that the Al-doped ZnO thin films have ZnO crystal structure. Hall Effect experiments with Van der Pauw configuration show that p-type carrier concentrations are arranged from 1.66×10^{16} to 4.04×10^{18} cm^{-2}, mobilities from 0.194 to 198 $cm^2V^{-1}s^{-1}$ and resistivities from 0.0963 to 18.4 Ωcm. FESEM cross section images of different parts of a p-type ZnO:Al thin film annealed at 800 ^0C show a compact structure. Measurement for same sample shows that density is 5.40 cm^{-3} which is smaller than theoretically calculated value of 5.67 cm^{-3}. Photoluminescence (PL) spectra at 10 K show a shoulder peak of p-type ZnO film at about 3.117 eV which is ascribed to electron transition from donor level to acceptor level (DAP).

Keywords : Al-doped p-type ZnO, RF magnetron sputtering, Oxygen ambient

1. INTRODUCTION

ZnO, a material with wide energy bandgap of 3.37 eV at room temperature and large exciton binding energy of 60 meV, is a promising candidate for photoelectronic devices. Recent investigations on this material have gotten important progress and even light emitting diodes (LEDs) have been made[1-4]. Although great progress of study on this material has been taken place, a tough bottleneck of getting high-quality p-type ZnO hinders the development of LEDs based on this material. Group Ⅰ elements are used as acceptors to dope p-type in ZnO [5,6]. Group Ⅴ elements are more extensively used to dope p-type in ZnO[7-11] and nitrogen seems to be the best acceptor of group Ⅴ elements since nitrogen has nearly the same radius as oxygen and is the shallowest acceptor in ZnO[12]. But nitrogen is hard to dope ZnO p-type. To solve hard p-type doping with single elements of goup Ⅴ, Yamamoto proposed a new approach to dope ZnO p-type: codoping. Codoping group Ⅴ and Ⅲ elements with ratio of 2:1 is another method to realize p-type ZnO because, compared with monodoping, codoping can make deep acceptor levels shallower and make acceptors more soluble in ZnO[13]. Though the methods mentioned above can dope p-type in ZnO, practically, it is hard to get agreeable results of high quality p-type. The large radius elements in group Ⅴ, such as As and Sb, show unexpectedly fairish effects of p-type dopants in ZnO[14,15], which is theoretically explained as a complex acceptor model of X_{Zn}-$2V_{Zn}$ (X=As,Sb)[16] or a cluster model of X_{Zn}-$4V_{Zn}$[17]. A hint could be gotten that it is a salutary attempt to find other appropriate elements that act as complex acceptors like as the models above and even group Ⅲ elements should not be excluded. It is easy to dope n-type in ZnO with aluminum under the condition of oxygen-deficient growth. Heavily Al-doped ZnO films (AZO) usually show high electron concentration with low resistivity [18] and are employed as a transparent conduction oxide electrode (TCO). Aluminum can be bound tightly with oxygen. When heavily Al-doped ZnO is grown under oxygen-rich condition, many zinc vacancies (V_{Zn}) should be produced due to the strong bonding of Al-O. In this study heavily Al-doped ZnO thin films were grown under the condition of pure oxygen ambient to grow Al-doped p-type ZnO films.

2. EXPERIMENT

We prepared Al-doped ZnO films in pure oxygen gas (5N) by RF magnetron sputtering. Homo-buffer layers and n-(100) Si (1 ~ 30 Ωcm) were selected as substrates. The buffer layers were fabricated on n-(100) Si in the mixture of O_2 and Ar with ratio of 1:4 at temperature of 100 ^{0}C and pressure of 15 mTorr by RF magnetron sputtering. ZnO ceramic (5N) was selected as target and RF power was set at 150 W for 25 min to get about 70 nm ZnO layers. Subsequently the buffer layers were annealed in-situ at 800 ^{0}C and 15 mTorr in O_2 for 20 min. The Al-doped ZnO thin films were realized in O_2 by RF magnetron sputtering. ZnO ceramic (5N) mixed with 2 wt% Al_2O_3 (5N) was selected as sputtering target and RF power was set at 180 ~ 210 W for 180 min to get Al-doped ZnO thin films with about 400 ~ 900 nm thickness. Some films were annealed in situ at 10 Torr in O_2 for 5 min. We denoted samples as Wxyz. W=B or S means that the substrate is a buffer layer template or a silicon wafer, x=1 or 2 means that the growth temperature is 100 ^{0}C or 450 ^{0}C; y=1 or 2 means that the ambient pressure is 6 or 15 mTorr and z=0, 1 or 2 means that the film is as-grown (i.e. unannealed), 600 ^{0}C or 800 ^{0}C annealed one. Microstructure of the films was characterized by X-ray diffraction (XRD) and field-emission scanning electron microscope (FESEM). Electrical, chemical and optical properties of the films were evaluated by Hall effect measurements with Van der Pauw configuration, X-ray photoeletron spectroscope (XPS) and photoluminescence (PL) respectively.

3. RESULTS AND DISCUSSION

Figure 1 shows the XRD spectra of the buffer layer and the ZnO:Al thin films grown at 450 ^{0}C and 15 mTorr. All films exhibit (002) peak of two theta diffraction angle at about 34.44 ^{0} which is the value of corresponding peak of bulk ZnO, implying that all films have not obvious internal stress. The films also show (100) and (101) peaks. From the comparison of the intensities of (100), (101) and (002) peaks, it can be concluded that buffer layers and high annealing temperatures are beneficial to ZnO:Al film growth along crystal c-axis.

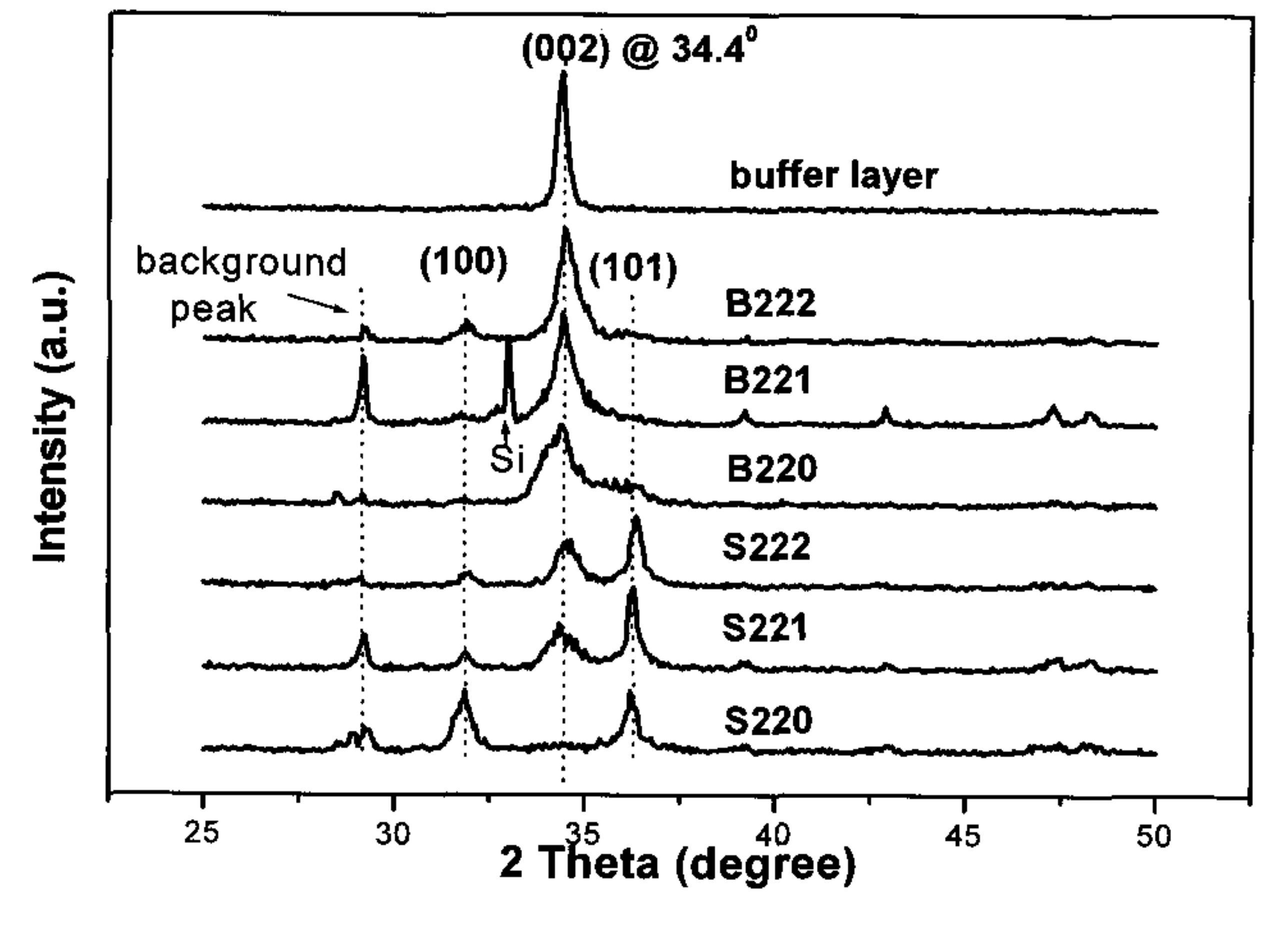

Fig. 1. XRD patterns of homo-buffer layer and ZnO films grown at 450 ^{0}C in oxygen ambient on buffer layers.

Figure 2 shows cross-section FESEM images of the different parts of sample S212* which was annealed for 120 min. Fig. 2 shows compact microstructures. It is found by weighting measurement that the density of sample S212* is 5.40 g/cm^{-3} which is much less than theoretically calculated value of 5.67 g/cm^{-3} for bulk ZnO which has the crystal constants of a=0.325 and c=0.5207 nm and practically measured value of 5.72 g/cm^{-3} for n-type ZnO:Al (AZO) grown in Zn-rich condition[18]. It can be inferred indirectly from the density value of S212* that many Zn vacancies were formed because Zn atomic mass is much heavier than O atomic mass and low density of the film is attributed to Zn scarcity.

Table 1 shows results of Hall effect measurement with Van der Pauw configuration. S220, S221, S222, B220, B221 and B222 are the films grown on Si or buffer layers at temperature of 450 ^{0}C and pressure of 15 mTorr. The as-grown film (S220) on Si shows p-type conduction with low carrier concentration of 0.0166x10^{18} cm^{-3}. From conduction types of S221 and S222 shown in the table, as annealing process is implemented at 600 ^{0}C and 800 ^{0}C, the conduction type converts to n-type with reduction of resistivity from 18.4 to 4.32 then to 1.29 Ωcm. The as-grown film (B220) on buffer layer has high resistivity so that its electric properties can't be measured. But the film annealed at 600 ^{0}C (B221) shows p-type conduction and high carrier concentration of 4.04x10^{18} cm^{-3} with resistivity of 7.97 Ωcm. As annealing temperature goes up to 800 ^{0}C the conduction type of the film (B222) converts back to n-type with reduction of resistivity to 1.35 Ωcm. B210, B211 and B212 are the films grown at 450 ^{0}C and 6 mTorr. The as-grown film (B210) shows p-type conduction and moderate carrier concentration of 0.327x10^{18} cm^{-3}. The film annealed at 600 ^{0}C (B211) converts of conduction type to n-type. Interestingly and delusively, as annealing temperature goes to 800 ^{0}C the

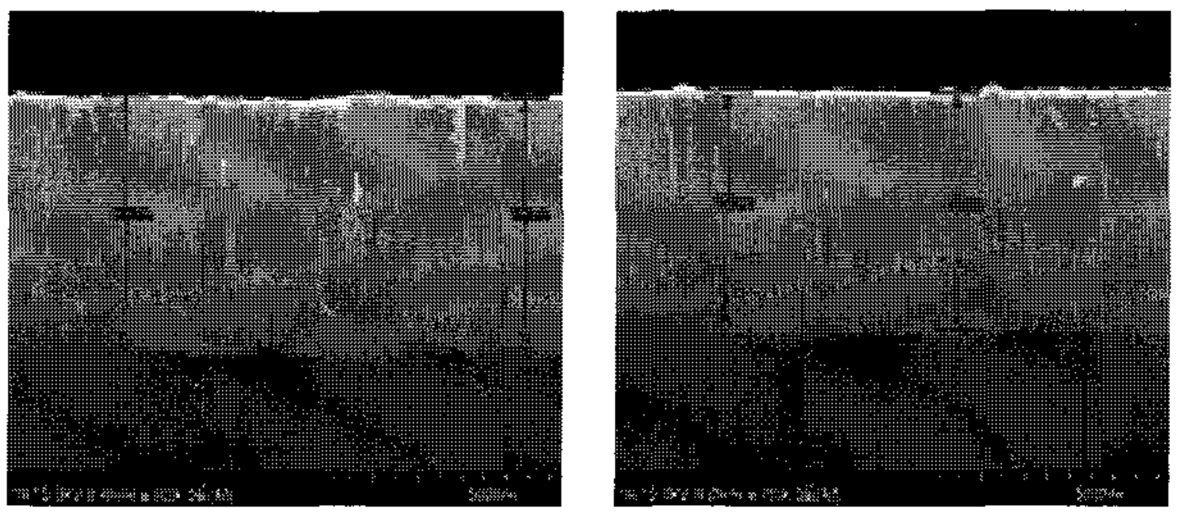

Fig. 2. FE-SEM images of different parts of sample S212* annealed at 800 ^{0}C for 120 min.

Table 1. Results of hall effects in Van der Pauw configuration.

Sample	Type	Concent. (10^{18}cm^{-3})	Mobil. (cm^{2}V^{-1}s^{-1})	Resist. (Ωcm)
S220	p	0.0166	2.03	18.4
S221	n	8.990	0.161	4.32
S222	n	2.45	1.98	1.29
B220	--	--	--	--
B221	p	4.04	0.194	7.97
B222	n	4.00	1.15	1.35
B210	p	0.327	198	0.096
B211	n	0.994	3.01	2.09
B212	p	0.31	5.1	3.95
B121	n	0.208	1.58	19
B112	n	3.45	1.21	1.49
S212*	p	0.564	11.1	0.999

film (B212) shows conduction type back to p-type again. This is hard to understand and needs to investigate further. B121 and B112 are the films grown at 100 ^{0}C and both of them show n-type with respective resistivities of 19 and 1.49 Ωcm. Other films grown at 100 ^{0}C, not only as-grown ones but also annealed ones, have too high resistivities to perform electrical measurement (not shown here). It is inferred that at low growth temperature ZnO:Al films can not be doped p-type. It is also seen in Table1 that the n-type films have moderate resistivities from 1.49 to 19 Ωcm and moderate carrier concentrations from 0.994x10^{18} to 8.99x10^{18} cm^{-3}. The resistivities and carrier concentrations of n-type ZnO:Al films in this paper are much higher and much lower, respectively, than the highly Al-doped n-type ZnO films usually grown in Zn-rich condition[18]. The table also shows that the carrier concentrations of p-type films are ranged from 0.0166x10^{18} to 4.04x10^{18} cm^{-3}, their mobilities are ranged from 0.194 to198 cmV^{-1}s^{-1} and their resistivities are ranged from 0.0963 to 18.4 Ωcm, indicating that the electrical properties of p-type films are not too poor to meet the demand of p-n junctions of LEDs.

Figure 3 shows XPS spectra of O1s and surveys after plasma etching for 30s. From the spectra of O1s (a) (b) it can seen that peaks appear at about 530.7 eV which are attributed to O^{2-} ion on Wurtzite structure of ZnO, surrounded by Zn atoms, and shoulders appears at about 532.4 eV which are attributed to O^{2-} ion of loosely bound oxygen on the surface of ZnO[19] and inner O^{2-} which also can be assigned to Zn-deficient state around O, indicating presence of Zn vacancies. By Gaussian fitting, it can be demonstrated that the area ratio of shoulder and peak of the p-type film is a little larger than that of n-type film, indicating that the p-type films have more Zn vacancies than the n-type films. FWHM of the peak of 800 ^{0}C annealed film is narrower than that of 600 ^{0}C annealed one, implying that the 800 ^{0}C annealed film

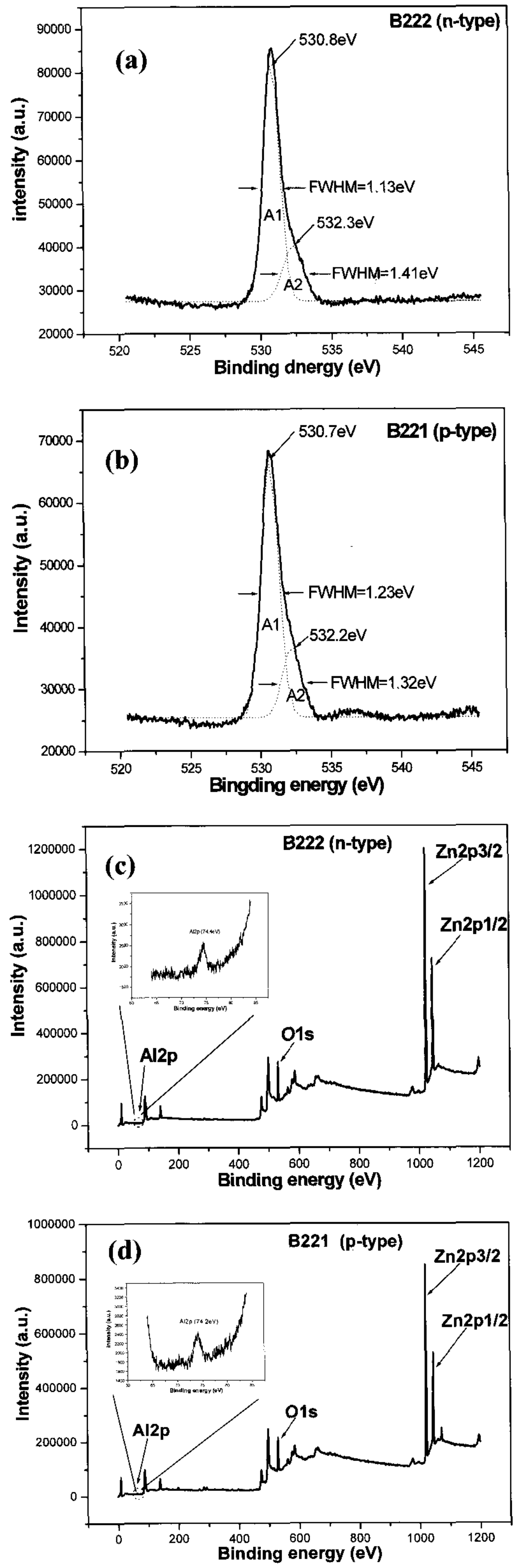

Fig. 3. XPS spectra of (a), (b) O1s and (c), (d) surveys with Al2p in insets inserts for B222 and B221.

shows better crystallinity than the 600 ^{0}C annealed one. (c) and (d) show that the spectra of surveys have common features of ZnO XPS spectra. Al2p spectrum in inlets shows its peak at 74.4 eV which is different to the value of 72.4 eV of Al2p for metal Al and is attributed to Al-O bonding. Normalized element contents by XPS show that Al:O:Zn is 0.025:1:0.987 and 0.028:0.873:1 for 600 ^{0}C annealed film (B221) and 800 ^{0}C annealed film (B222) respectively, indicating that the film annealed at 600 ^{0}C has more O content than 800 ^{0}C annealed one. Higher annealing temperature makes atomic O escape from films, which annihilates Zn vacancies.

Figure 4 shows PL spectra at 10 K for 600 ^{0}C and 800 ^{0}C annealed films grown on buffer layers at 450 ^{0}C and 15 mTorr (B221 and B222). Seven-curve Gaussian fittings show much different photonic transition characteristics related to defects of Al-doped ZnO films than those of ZnO films[19,20]. The PL spectra of films show very broad ranges with many peaks and shoulders. The 600 ^{0}C annealed film (B221) has Gaussian fitting peaks at 3.117, 2.979, 2.754, 2.466, 2.154, 1.852 and 1.570 eV respectively. The 800 ^{0}C annealed film (B222) has Gaussian fitting peaks at 3.078, 2.998, 2.772, 2.492, 2.167, 1.860 and 1.584 eV respectively. As annealing temperature goes up to 800 ^{0}C from 600 ^{0}C the intensities of high photon energy peaks reduce and the intensities of low photon energy peaks hardly change, which means that defects corresponding to high photon energy are related to p-type contribution. The peak of 3.117 eV of 600 ^{0}C annealed film (B221) should be related to electron transition from donor level to acceptor level (DAP) and disappears at 800 ^{0}C annealing temperature. 3.078 eV level of 800 ^{0}C annealed film can not be confirmed.

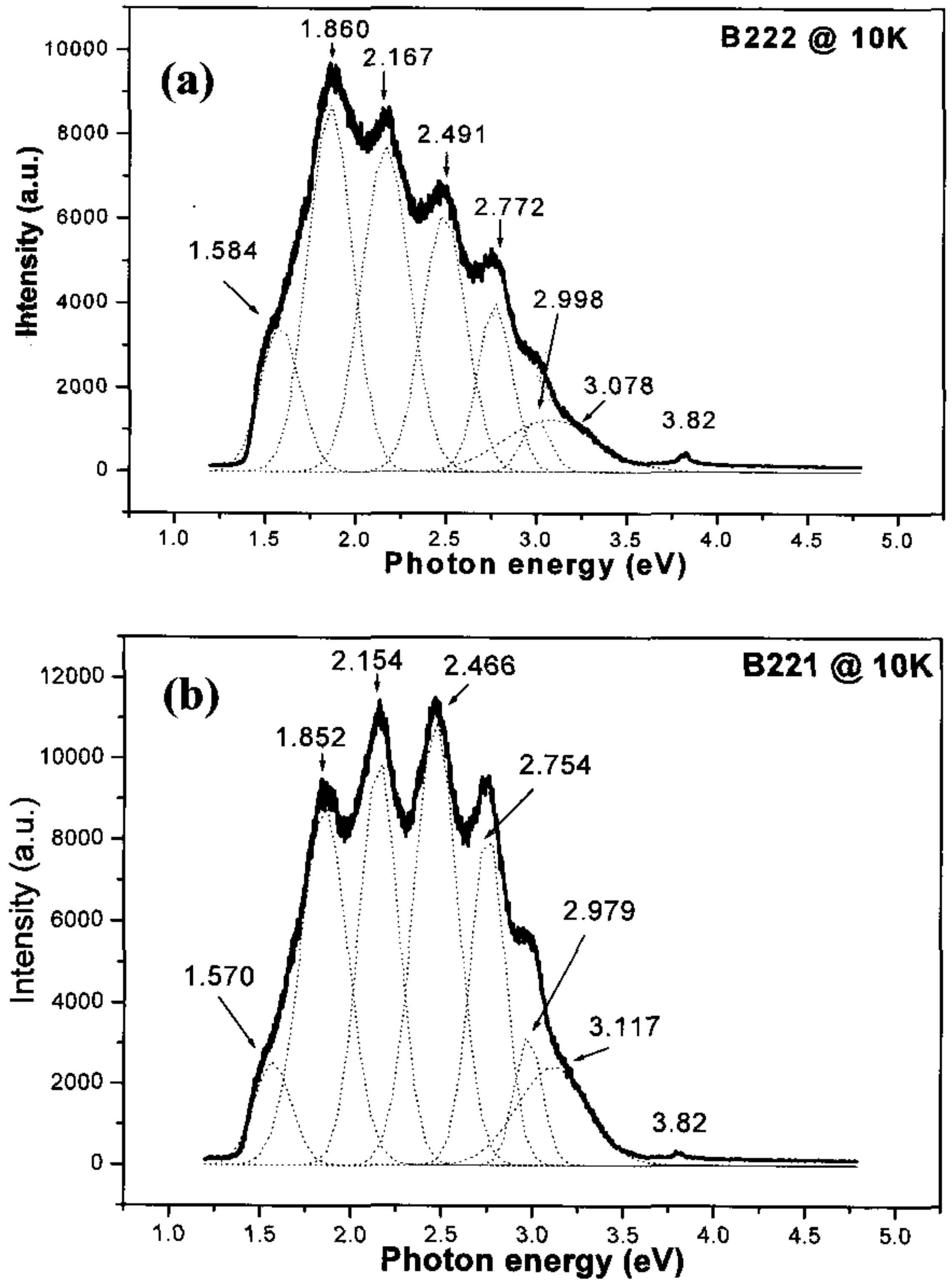

Fig. 4. PL spectra of (a) B222 and (b) B221.

From the density of 5.40 gcm^{-3} for the p-type ZnO:Al film of S212*, it can be inferred that the other p-type films should have nearly the same density as S212*. The density value of highly Al-doped p-type ZnO is much lower than theoretical value of 5.67 g/cm^{-3} for intrinsic ZnO which can be calculated by the parameters of c=0.5207 nm and a=0.325 nm for bulk ZnO[21] and practically measured value of 5.72 gcm^{-3} for highly Al-doped n-type ZnO grown at Zn-rich condition[17]. And XPS spectra show obvious binding energy of 532.4 eV of O^{2-} due to Zn deficiency or Zn vacancies. From above phenomena of Zn vacancy and theoretical mechanism of complex acceptor model X$_{Zn}$-2V$_{Zn}$ (X=As,Sb) which is confirmed experimentally by Kang et al[22], the acceptor mechanism for highly Al-doped p-type ZnO should be Al$_{Zn}$-2V$_{Zn}$. An Al atom substituted for Zn site offers one electron and induces two Zn vacancies which supply two holes. The complex of Al$_{Zn}$-2V$_{Zn}$ acts as one acceptor.

Tables and illustrations should be originals or sharp prints. They should be arranged throughout the text preferably being included on the same page as they are first discussed. They should have a self-contained caption and be positioned in center margin within the column. If they do not fit into one column they may be placed across both columns in which case place them at the top or at the bottom of a page.

4. CONCLUSION

In summary, all Al-doped films have ZnO crystal structure and the films grown on buffer layers have more preference of growth along c-axis than those on Si substrates. Al-doped p-type ZnO films could be obtained in pure oxygen ambient gas by RF magnetron sputtering and p-type carrier concentrations are arranged from 1.66x10^{16} to 4.04x10^{18} cm^{-2}, mobility from 0.194 to 198 cm^{2}V^{-1}s^{-1} and resistivity from 0.0963 to 18.4 Ωcm. A p-type ZnO:Al film (S212*) shows low density of 5.40 gcm^{-3} which is lower than theoretical calculation value

(5.67 gcm^{-3}) and n-type Al-doped films (5.72 gcm^{-3}). XPS spectra show the p-type film (B221) has more O-O structure characteristic (about 532.4 eV) than the n-type film (B222). PL spectra show defect feature with broad spectra range and also show that p-type film has DAP transition.

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