



Letter

Concentration-dependent behavior of hydrogen in Al-doped ZnO thin films

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ABSTRACT

The Al-doped ZnO thin films were synthesized by aerosol-assisted chemical vapor deposition. The concentration-dependent behavior of hydrogen in the films was discussed, finding that as hydrogen is introduced at a relatively low level, it tends to take the oxygen vacancy site and form a hydrogen-oxygen vacancy complex which behaves as a shallow donor, on the other hand it reduces the solubility of the substitutional Al; then higher hydrogen concentration results in the formation of H₂ neutral molecular complex.

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1. Introduction

The wide-band-gap II–VI compound semiconductor zinc oxide (ZnO) always exhibits *n*-type conduction. It is one of the promising film materials for novel optoelectronic devices [1,2]. Recently, research on doping with donor impurities such as Al, Ga and In to improve the *n*-type conduction of ZnO thin films has attracted great attention. It is known that hydrogen may be unintentionally incorporated into the films as long as H⁺ and/or H₂O is involved during the synthesization, such as chemical vapor deposition (CVD), spray pyrolysis and sol–gel processes. The influences of existing hydrogen in the films cannot be neglected.

However, there has been no consensus on the role of H in ZnO as well as in other semiconductor materials, because it is difficult to confirm its locations in the lattices and the complexes that H forms with native defects and dopants [3,4]. Conventional point of view regarded that H acts only as a compensating center and always counteracts the prevailing conductivity [5]. However, recent research experimentally and theoretically revealed that H can be incorporated and behaves as a shallow donor [6,7].

2. Experimental details

Al-doped ZnO (AZO) thin films were deposited on glass substrates by aerosol-assisted chemical vapor deposition (AACVD) process at 400 °C, with the constant carrier gas (N₂) rate of 30 L/h. In the precursor solution (0.1 mol/L), zinc acetate [Zn(CH₃COO)₂·2H₂O], aluminum nitrate [Al(NO₃)₃·9H₂O] and carbinol (CH₃OH)

were used as starting material, doping source and solvent, respectively, with constant Al:Zn atomic ratio of 4:100. Different H concentration was controlled by varying the quantities of acetic acid (CH₃COOH) that was added into the precursor solutions. The pH value of the obtained precursor solutions were 5.85, 5.75, 5.65 and 5.55, respectively. The glass substrates were first cleaned by detergent, then by methanol and acetone, and finally rinsed by deionized water.

The samples were characterized by X-ray diffractometer (Rigaku D-max-2500/PC, with Cu Kα radiation), and by photoluminescence (PL) spectrometer (Jobin Yvon FL3-11, with excitation at 325 nm). The ultraviolet–visible (UV–vis) absorption and transmitted spectra were operated on a UV–vis spectrophotometer (Shimadzu UV-2550).

3. Results and discussion

3.1. Crystal structure analysis

Fig. 1 shows the XRD patterns of the AZO thin films, which reveals the existence of ZnO single phase with the hexagonal wurtzite structure. No peak of either Al metal or any of its oxide is observed. The three intense peaks are identified as the (1 0 0), (1 0 1) and (1 1 0).

The XRD patterns of ZnO thin films by AACVD process are different from those of films synthesized by other techniques. Owing to that the (0 0 2) plane has the lowest surface energy, those patterns usually exhibit the intense (0 0 2) orientation, indicating high texture with the *c*-axis perpendicular to the substrate surface [8]. However, the (0 0 2) peaks in Fig. 1 are weak, which can be attributed to that the dynamics of gas flow rather than thermodynamics took prevailing influence on particle deposition. By AACVD process, atoms deposited on the substrate at a high rate, which made them do not have enough time to diffuse to positions of the

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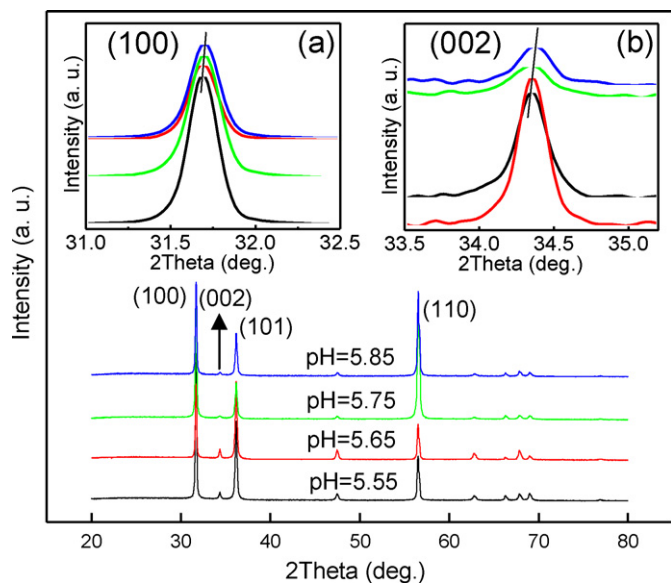


Fig. 1. XRD patterns of AZO thin films deposited from precursor solutions with different H content. (a) magnified peak (100) and (b) magnified peak (002).

lowest energy. Similar observations in XRD patterns were reported by other research [9].

The peaks (100) and (002) were magnified and re-plotted in the inserts (a) and (b) of Fig. 1, respectively. Clearly, the two peaks exhibit lower-angle shifts as the pH value decreasing from 5.85 to 5.55 in the precursor solutions. According to Bragg's law:

$$n\lambda = 2d \sin \theta$$

the shifts indicate the increase in interplanar distance as H concentration increasing.

The lattice dilatation can be explained in terms of the gradual decrease in the concentration of substitutional Al for Zn sites (the radius of Al^{3+} is smaller than that of Zn^{2+}) and the increasingly incorporation of H atoms that located at the oxygen vacancy (V_{O}) sites, maybe also at interstitial sites, as H atoms introduced from the precursor solutions with pH varying from 5.85 to 5.75 [6,10]. Then further increase in H^+ concentration in the precursor solutions resulted in the formation of H_2 molecules at the interstitial channels. The H_2 molecules were centered on the $\text{AB}_{\text{Zn}\perp}$ sites (anti-bonding sites that were parallel to the c -axis) and oriented roughly along the c -axis, as shown in Fig. 2. The H_2 complexes also caused the lattice dilatation and some influence on the orientation along the c -axis. For the two samples deposited from the precursor solutions with pH 5.65 and 5.55, the slight intensity increase in peak (002) may result from the formation of H_2 complexes, as shown in Fig. 1 and its insert (b).

It should be also noticed that the V_{O} is a low-energy native defect that may form in large concentration in ZnO and H is usually an inevitable impurity which may be unintentionally doped into films during the deposition. A V_{O} which is occupied by an H atom can be regarded as a point defect with +1 valence [5–7].

3.2. Optical analysis

Fig. 3 shows the room-temperature photoluminescence (PL) spectra (left side) and corresponding absorption spectra (right side) of the samples. Additionally, to clarify the influence caused by impurities, the band gap energy was also calculated by extrapolat-

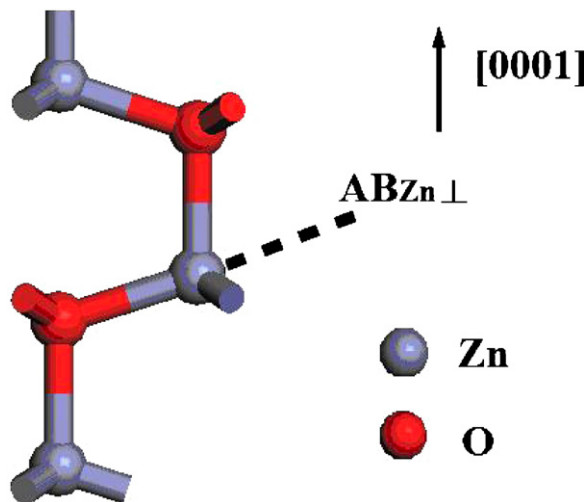


Fig. 2. Schematic representation of ZnO wurtzite structure, and location of H_2 complex.

ing the linear portion of $(\alpha h\nu)^2$ against photon energy $h\nu$, according to the formula: [11]

$$(\alpha h\nu)^2 \propto h\nu - E_g$$

where α is the optical absorption coefficient [calculated by $\alpha = (1/d)\ln(1/T)$, d is the film thickness and T is the optical transmittance], $h\nu$ is the photon energy and E_g is the optical band gap [11]. As shown in Fig. 4, all samples exhibit almost the same band gap energy of about 3.28 eV.

As the PL spectra indicate, each sample exhibits a visible emission and an ultraviolet emission caused by near-band-edge (NBE) transition. An evident red shift of the NBE emission can be observed with H^+ increasing in the precursor solutions, as shown in the inset of Fig. 3. The red shift can be attributed to the decrease in carrier concentration. However, the corresponding absorption spectra exhibit nearly no shift. These can be explained in terms of the increase in Stokes shift. The Stokes shift is defined as the energy difference between absorptive optical transition and emissive transition. As is generally acknowledged that in n -type ZnO an absorptive transition occurs from the valence band to conduction band, or to Fermi level for the heavily doped samples, while an

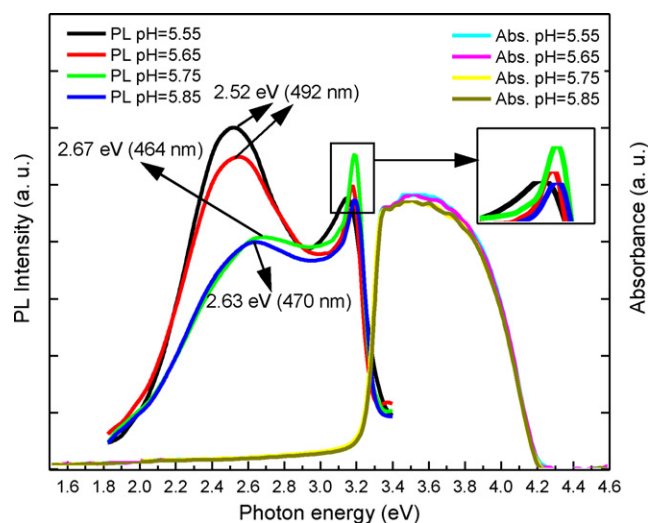


Fig. 3. Room-temperature PL spectra (left side) of AZO thin films deposited from precursor solutions with different H content, and corresponding absorption spectra (right side).

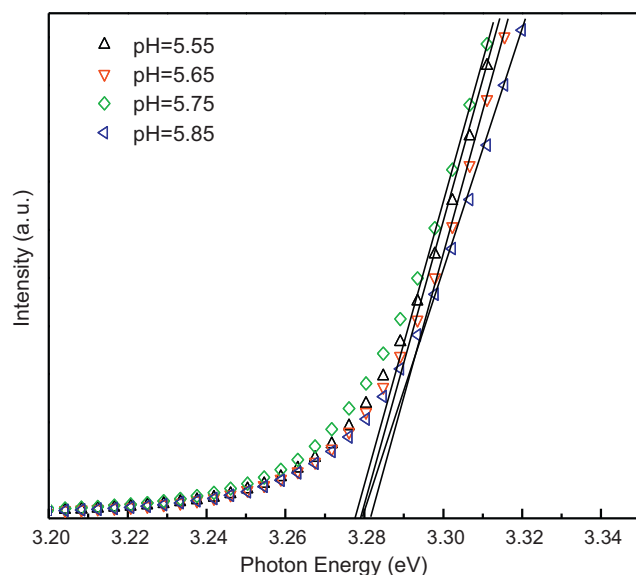


Fig. 4. $(\alpha hv)^2$ vs $h\nu$ of AZO thin films deposited from precursor solutions with different H content.

emissive transition occurs from the donor impurity band to acceptor level or to valence band. As ZnO is continually doped with n -type impurities such as Al, states below ξ_n of the conduction band will be gradually filled up [12,13]. Further more, the Fermi level will even be inside of the conduction band if the sample is heavily doped, resulting in the blue shift of optical band gap and NBE emission (called Burstein-Moss shift), consequently [11].

In Fig. 3, the Stokes shift increases and no change of band gap energy can be observed in Fig. 4, indicating the gradual decrease in carrier concentration as the continually introducing of H. A reasonable explanation for this is that the introducing of H reduced the solubility of the substitutional Al, even though all the films were deposited from the precursor solutions with constant Al:Zn atomic ratio of up to 4:100 [14,15]. Therefore, the influence of introduced H on Al concentration should be directly responsible for the decrease in carrier concentration.

Additionally, the intensity variation of NBE emission can also be observed, as shown in the inset of Fig. 3. The most intense peak of NBE emission can be observed for the sample deposited from the precursor solution with pH 5.75. As we know, the NBE emission results from the recombination of excitons. In ZnO, the V_O is an electrically inactive point defect. It can be considered as a deep level donor [6]. The introduced H atom was located very close to the center of the V_O (to within 0.05 Å). This configuration could thus be considered as a H- V_O complex. The addition of a substitutional H atom activated the V_O into a shallow donor. The activation was beneficial for electrons to be captured by V_O and to be turned into excitons. Therefore, the intensity of NBE emission increased as pH varying from 5.85 to 5.75 in the precursor solutions. Evidence is also provided by the PL spectra in visible range. As shown in Fig. 3, for the two samples deposited from the precursor solutions with pH 5.85 and 5.75, the broad peaks of blue emission can be observed. The two peaks located at 470 nm (2.63 eV) and 464 nm (2.67 eV) correspond to transition from Zn interstitial (Zn_i) to Zn vacancy (V_{Zn}) and transition from V_O shallow level to V_{Zn} , respectively, according to the defects energy level calculated by full-potential linear muffin-tin orbital (FP-LMTO) method [16]. Transitions in visible range of these samples and corresponding data are shown in Fig. 5. The shift in visible emission indicates the increase in activated V_O shallow donor as well as the decrease in Zn_i concentration. The Al^{3+} substitute is an acceptor. Therefore, Zn_i might decrease with the decrease

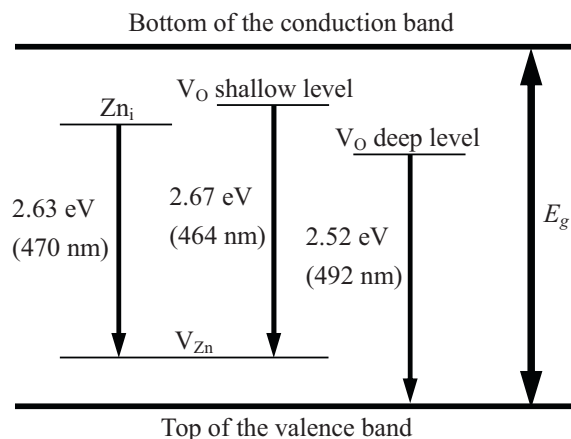


Fig. 5. Schematic representation of transitions in visible range of ZnO thin films.

in Al^{3+} substitute, because ZnO is a self-assembled oxide compound [14,15]. Thus, this observation also confirms our speculation that the introducing of H reduced the solubility of substitutional Al.

The NBE emission continually weakens as H^+ concentration further increasing in the precursor solutions (pH value decreasing from 5.75 to 5.65 and finally to 5.55), as shown in the inset of Fig. 3. This can be attributed to that the further incorporation of H resulted in the formation of H_2 molecules at the AB_{Zn} sites [6]. The H atoms formed the neutral complexes rather than took V_O sites. Thus the V_O shallow donors turned into inactive deep level defects, and then led to the decrease in exciton density. Therefore, the NBE emission weakens.

This conclusion is also supported by the shift in visible range of PL spectra. The blue emission located at 464 nm red shifts to 492 nm and then remains as pH value decreasing from 5.75 to 5.65 and to 5.55 finally. The blue-green emission at 492 nm consists well with the transition from V_O deep level to valence band [16]. The shift also suggests that H was off the V_O site, and then the V_O shallow donor (with +1 valence) turned into deep level V_O .

4. Conclusions

The concentration-dependent behavior of H in AZO thin films deposited by AACVD was discussed. The analysis revealed that H exhibits double character in the films. It tends to take a site that is very close to the center of the V_O and acts as a substitutional impurity when it is introduced at a relatively low level. The formation of the H- V_O complex activates the deep level V_O into a shallow donor, which is good for n -type doping. On the other hand, introducing of H reduces the solubility of the substitutional Al. Thus H can also be regarded as a disadvantage factor for n -type doping. Then, further increase in H concentration results in the formation of H_2 molecules, the neutral complexes at the interstitial sites.

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References

- [1] L.Y. Chen, W.H. Chen, J.J. Wang, F.C.N. Hong, Y.K. Su, Appl. Phys. Lett. 85 (2004) 5628.
- [2] Y.B. Zhang, G.K.L. Goh, K.F. Ooi, S. Tripathy, J. Appl. Phys. 108 (2010) 083716.
- [3] E. Mollwo, Z. Phys. 138 (1954) 478.
- [4] D.G. Thomas, J.J. Lander, J. Chem. Phys. 25 (1956) 1136.
- [5] X. Li, B. Keyes, S. Asher, S.B. Zhang, S.H. Wei, T.J. Coutts, S. Limpijumnong, C.G. Van de Walle, Appl. Phys. Lett. 86 (2005) 122107.
- [6] C.G. Van de Walle, Phys. Rev. Lett. 85 (2000) 1012.

- [7] E.V. Monakhov, J.S. Christensen, K. Maknys, B.G. Svensson, A.Yu. Kuznetsov, *Appl. Phys. Lett.* 87 (2005) 191910.
- [8] P.M. Ratheesh Kumar, C. Sudha Kartha, K.P. Vijayakumar, *J. Appl. Phys.* 98 (2005) 023509.
- [9] G. Walters, I.P. Parkin, *Appl. Surf. Sci.* 255 (2009) 6555.
- [10] H.C. Park, D. Byun, B. Angadi, D. Hee Park, W.K. Choi, J.W. Choi, Y.S. Jung, *J. Appl. Phys.* 102 (2007) 073114.
- [11] F.K. Shan, B.I. Kim, G.X. Liu, Z.F. Liu, J.Y. Sohn, W.J. Lee, B.C. Shin, Y.S. Yu, *J. Appl. Phys.* 95 (2004) 4772.
- [12] E. Burstein, *Phys. Rev.* 93 (1954) 632.
- [13] T. Makino, Y. Segawa, S. Yoshida, A. Tsukazaki, A. Ohtomo, M. Kawasaki, *Appl. Phys. Lett.* 85 (2004) 759.
- [14] H.X. Chen, J.J. Ding, X.G. Zhao, S.Y. Ma, *Physica B* 405 (2010) 5.
- [15] J.J. Ding, S.Y. Ma, H.X. Chen, X.F. Shi, T.T. Zhou, L.M. Mao, *Physica B* 404 (2009) 16.
- [16] P.S. Xu, Y.M. Sun, C.S. Shi, F.Q. Xu, H.B. Pan, *Nucl. Instrum. Methods Phys. Res. B* 199 (2003) 286.