Photoluminescence properties of ZnO films grown on InP by thermally oxidizing metallic Zn films

2003 J. Phys.: Condens. Matter 15 1975

(http://iopscience.iop.org/0953-8984/15/12/314)

INSTITUTE OF PHYSICS PUBLISHING JOURNAL OF PHYSICS: CONDENSED MATTER

J. Phys.: Condens. Matter **15** (2003) 1975–1981 PII: S0953-8984(03)58787-2

Photoluminescence properties of ZnO films grown on InP by thermally oxidizing metallic Zn films

S J Chen[1], Y C Liu[1,2,3], J Y Zhang[2], Y M Lu[2], D Z Shen[2] and X W Fan[2]

[1] Advanced Centre for Optoelectronic Functional Material Research, Northeast Normal University, Changchun 130024, People's Republic of China
[2] Key Laboratory of Excited State Process, Changchun Institute of Optics, Fine Mechanics and Physics, Chinese Academy of Sciences, 16 East South Lake Road, Changchun 130021, People's Republic of China

E-mail: ycliu@nenu.edu.cn

Received 24 January 2003
Published 17 March 2003
Online at stacks.iop.org/JPhysCM/15/1975

Abstract

Photoluminescence (PL) properties of ZnO films grown on (001) InP substrates by thermal oxidization of metallic Zn films, in which oxygen vacancies and interstitial Zn ions are compensated by P ions diffusing from (001) InP substrates, are investigated. X-ray diffraction spectra indicate that P ions have diffused into the Zn films and chemically combined with Zn ions to form Zn_3P_2. Intense free exciton emission dominates the PL spectra of ZnO films with very weak deep-level emission. Low-temperature PL spectra at 79 K are dominated by neutral-donor bound exciton emission at 3.299 eV (I_4) with a linewidth of 17.3 meV and neutral-acceptor bound exciton emission at 3.264 eV. The free exciton emission increases with increasing temperature and eventually dominates the emission spectrum for temperature higher than 170 K. Furthermore, the visible emission around 2.3 eV correlated with oxygen deficiencies and interstitial Zn defects was quenched to a remarkable degree by P diffusing from InP substrates.

1. Introduction

ZnO has a direct band gap of 3.37 eV with a large exciton binding energy of 60 meV. Owing to the strong exciton binding energy, ZnO is recognized as a promising photonic material for the UV region. Recently, many different techniques, such as sputtering [1], reactive thermal evaporation [2], spray pyrolysis [3], pulsed laser deposition [4], metal–organic chemical vapour deposition (MOCVD) [5], and molecular beam epitaxy (MBE) [6], have been used to prepare ZnO thin films. They showed promising optical properties based on excitonic mechanisms which included optically pumped excitonic lasing at room temperature [7, 8]

[3] Author to whom any correspondence should be addressed.

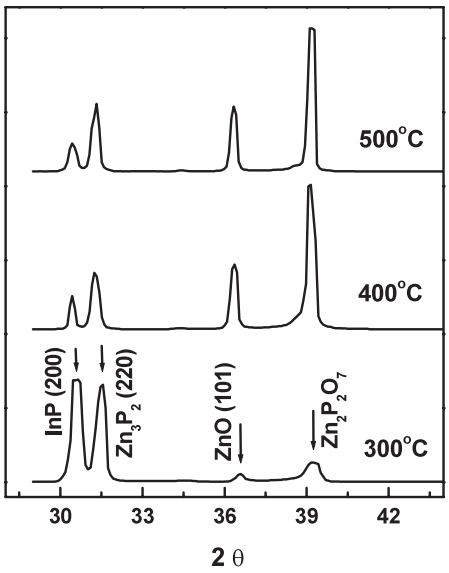

Figure 1. XRD spectra of ZnO thin films grown on InP with different annealing temperatures.

and high-temperature stimulated emission due to exciton–exciton scattering [7, 9]. However, reported photoluminescence (PL) spectra of polycrystalline thin films have shown very strong deep-level (DL) emissions; in general, the DL emissions are associated with oxygen vacancies and interstitial Zn ions in the ZnO lattice [8, 10–12].

In this paper, we report a simple method for preparing high-quality ZnO thin films on InP substrates by using a resistive thermal evaporation technique followed by a post-annealing process. The advantage of this process is that we can obtain more pure ZnO crystallites, because a highly pure Zn source is used and no impurities are introduced during the process. X-ray diffraction (XRD) spectra indicate that P ions diffused into the Zn films and chemically combined with Zn ions forming Zn_3P_2 when the films were annealed in oxygen ambient. In the room temperature PL spectra, strong and sharp near-edge emissions with very weak DL emission are obtained, which indicates that the contents of oxygen vacancies and interstitial Zn ions in the ZnO lattices are decreased to a remarkable extent by introducing P ions into ZnO films.

2. Experiment

The Zn films were deposited onto (001) InP substrates at 200 °C by resistive thermal evaporation of metallic Zn. The substrates were pre-cleaned by the normal method before deposition. The pressure of the growth chamber was of the order of 10^{-4} Pa. After deposition, the films were oxidized in a thermal oxidation furnace. Thermal oxidation was carried out in oxygen ambient at temperatures from 300 to 500 °C for 1 h. To characterize the film structure, the XRD was measured using a D/max-rA XRD spectrometer (Rigaku) with a Cu Kα line of 1.54 Å. To study the luminescence properties, the PL spectra from 330 to 600 nm were measured for temperature varying from 79 to 300 K. The 325 nm line of a He–Cd laser with a power of 50 mW was used as the excitation light.

3. Results and discussion

The crystal structure and orientation of the films annealed at different temperatures were investigated by making θ–2θ scans of XRD, as shown in figure 1. Four main peaks appear at $2\theta = 30.61°$, 31.57°, 36.34°, and 39.14°, which are the (200) InP substrate peak, the (220) Zn_3P_2 peak, the (101) ZnO peak, and the peak of $Zn_2P_2O_7$, respectively. The XRD spectra indicate that P ions have diffused into the Zn films and chemically combined with Zn ions to form Zn_3P_2; at the same time the Zn and some of the Zn_3P_2 were oxidized into ZnO and $Zn_2P_2O_7$, respectively, when the Zn films were annealed in O_2 ambient at 300 °C for 1 h. As the annealing temperature increases from 300 to 500 °C, the (101) ZnO peak and $Zn_2P_2O_7$ peak increase markedly in intensity, and the (200) InP peak and (220) Zn_3P_2 peak decrease in intensity, which indicates that the content of ZnO and $Zn_2P_2O_7$ in the films increases with increasing annealing temperature.

Figure 2 shows the room temperature normalized PL spectra for ZnO thin films deposited on InP substrate annealed at different temperatures from 300 to 500 °C. A distinct feature can be seen: the intense free exciton emission dominates the PL spectra with a negligibly small DL emission band from 450 to 600 nm. Most of the bulk ZnO crystals [13] and epitaxial ZnO layers [14] exhibit dominant DL emission commonly observed at around 2.3 eV, ascribed to radiative emission at oxygen vacancy-related defects [15]. The negligibly weak DL emission and dominant exciton emission suggest a low density of defects in the ZnO films grown on InP substrates by thermal oxidation of metallic Zn films. It is generally accepted that the DL emission is associated with oxygen vacancies and interstitial Zn ions in the ZnO lattices [8, 10–12]. The negligibly weak DL emission in our samples suggests that P ions diffuse into Zn films and chemically combine with Zn ions to form Zn_3P_2, resulting in an obvious decrease in the number of oxygen vacancies and interstitial Zn ions in the ZnO lattices. As the annealing temperature increases, there is no difference in the PL spectra for all samples, except that the dominant exciton emission peak has a slight shift to shorter wavelengths and becomes sharper. The full widths at half-maximum (FWHM) of the PL peak are shown in the inset of figure 2. As the annealing temperature is raised, the FWHM decreases from 128 meV for the sample annealed at 300 °C and to 90 meV for the sample annealed at 500 °C, which indicates that a higher annealing temperature can improve the quality of the ZnO films.

We have compared the PL spectra between ZnO films grown on InP substrates and ones grown on Si substrates by thermally oxidizing Zn films at 500 °C for 1 h. It was found that those grown on Si substrates exhibit dominant excitonic emission with appreciable DL emission at around 2.3 eV. The typical intensity ratio of the exciton emission to the deep emission is about 10 for ZnO thin films grown on Si substrates, while it is 560 for those grown on InP substrates. This suggests that the contents of oxygen vacancies and interstitial Zn ions in the ZnO lattice are decreased to a remarkable extent by introducing P ions into ZnO films prepared by thermal oxidization of Zn films grown on InP.

Figure 3 shows a typical excitonic emission spectrum at 79 K. The emission line located at 3.299 eV is the strongest in the spectrum with a FWHM of 17.3 meV. In view of its energy position, this line can be assigned to the bound excitonic emission at neutral donors (I_4) [16]. Another near-band-edge emission line is observed at 3.264 eV accompanied by three phonon replicas observed at 3.199, 3.133, 3.066 eV. This emission can be attributed to emission from excitons bound to neutral acceptors (hereafter we call this emission I_a) [18]. A shoulder on the higher-energy side of I_4 is observed at around 3.321 eV, accompanied by phonon replicas observed at 3.24 eV, which should be assigned to free exciton emission.

As temperature increases, I_4 and I_a decrease in intensity, thermally releasing excitons from the donor and acceptor impurities. Then, the free exciton emission shows up and eventually

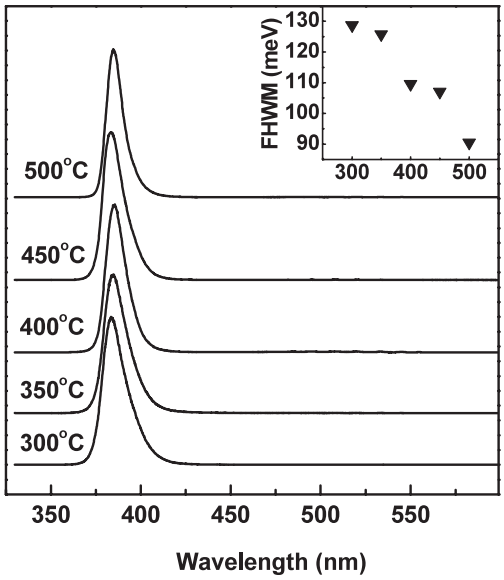

Figure 2. Room temperature PL spectra of polycrystalline ZnO thin films grown on InP annealed at different temperatures. The inset shows the FWHM for the samples against annealing temperature.

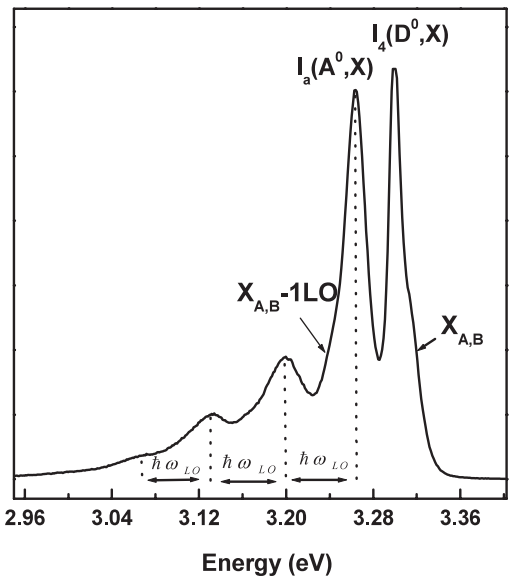

Figure 3. The detail of the near-band-edge region of the PL spectrum at 77 K for ZnO film grown on an InP substrate annealed at 500 °C.

comes to dominate the PL spectra at higher temperature. This transition from the bound exciton emission dominating to the free exciton emission dominating the spectrum is shown in figure 4.

If the film quality was poor, the exciton lifetime would be very short due to additional scattering by impurities and defects. Since such exciton scattering becomes more frequent as

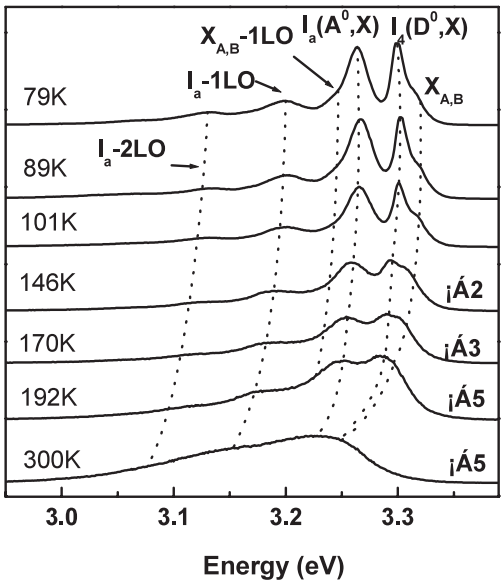

Figure 4. PL spectra of the sample annealed at 500 °C measured with varied temperature.

the temperature increases, the PL spectrum would be dominated by DL emission, in most cases located at around 2.3 eV [14]. However, it was noted that the free exciton emission is still dominant with very weak DL emission, even in the room temperature PL spectrum for the ZnO films grown on InP. Also the FWHM at room temperature is about 90 meV, which should be compared with those of ZnO films grown on CaF_2 (98 meV) [17], on sapphire (117 meV) [18], on GaN/SiC (129 meV) [19], and on bulk ZnO (115 meV) [20]. The observed slightly narrower free exciton emission from ZnO films grown on InP may result from effective compensation of oxygen vacancies and interstitial Zn ions in the ZnO lattice by introducing P ions into ZnO films.

The peak positions of the observed excitonic emission lines are plotted against temperature in figure 5. Assuming that the peak positions of the free exciton emission (◄), the donor bound exciton emission (I_4; •), and the acceptor bound exciton emission (I_a; ■) vary with temperature as the energy band gap, it is possible to fit the following semiempirical formula to the observed temperature dependence:

$$E_x(T) = E_x(0) - \alpha T^2/(T + \beta) \tag{1}$$

where α, β, and $E_x(0)$ are fitting parameters [21]. The α- and β-values obtained are $-2 \times 10^{-4}(\pm 0.5 \times 10^{-4})$ eV K^{-1} and $-500(\pm 0)$ K for the three emissions; $E_x(0)$ is 3.32 eV for free exciton emission, 3.30 eV for donor bound exciton emission, and 3.27 eV for acceptor bound exciton emission. The calculated temperature dependence is shown by solid curves and fits well to the experimental values.

4. Conclusions

Optical properties of ZnO thin films grown on InP(001) substrates by thermal oxidization of metallic Zn films were investigated. InP(001) substrate was used to compensate for oxygen vacancies and interstitial Zn ions in the ZnO lattice by introducing P ions into ZnO films through annealing in oxygen ambient. The XRD spectra indicate that P ions have diffused

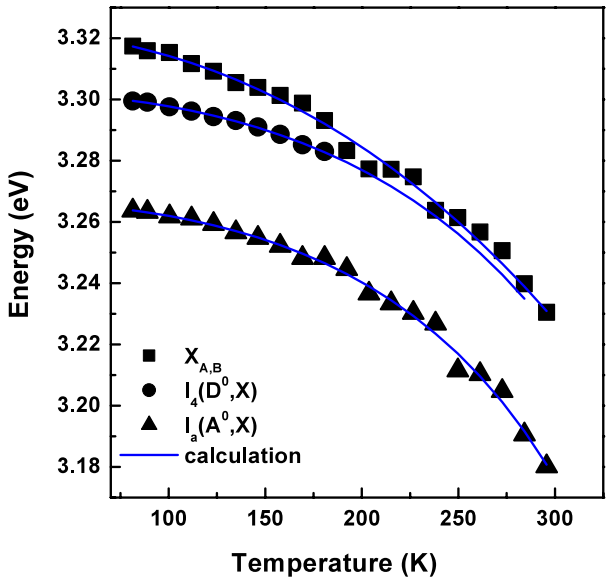

Figure 5. The temperature dependence of the emission energies of a ZnO film for free exciton (◀), for neutral-donor bound exciton (●), and for neutral-acceptor bound exciton emission (■). The solid curves denote the calculation using the Varshni formula.

(This figure is in colour only in the electronic version)

into the Zn films and chemically combined with Zn ions to form Zn_3P_2; at the same time Zn and some of Zn_3P_2 were oxidized into ZnO and $Zn_2P_2O_7$, respectively, when the Zn films were annealed in O_2 ambient. The negligibly small DL emission intensity and the intense exciton emission that dominates the PL spectra suggest that the contents of oxygen vacancies and interstitial Zn ions in the ZnO lattice are decreased to a remarkable extent by introducing P ions into ZnO films.

Acknowledgments

This work was supported by the 'Hundred Talents' Programme of the CAS, the National Natural Science Foundation of China, No 60176003, the 'Innovation' Foundation of CIOFP, the 'Excellent Young Teacher' Foundation of the Ministry of Education of China, and the 'Excellent Researchers to go Beyond the Century' Foundation of the Ministry of Education of China.

References

[1] Cho Sungale, Ma Jing and Kim Yunki 1999 *Appl. Phys. Lett.* **75** 2761
[2] Brus L E 1984 *J. Chem. Phys.* **80** 4403
[3] Nanto H, Minami T and Takata S 1981 *Phys. Status Solidi* a **65** K131
[4] Morgan H and Brodie D E 1982 *Can. J. Phys.* **60** 1387
[5] Aronovich J, Ortiz A and Bube R H 1979 *J. Vac. Sci. Technol.* **16** 994
[6] Vispute R D, Talyansky V, Choopun S, Sharma R P, Venkatesan T, He M, Tang X, Halpern J B, Spencer M G, Li Y X, Salamanca-Riba L G, Iliados A A and Jones K A 1998 *Appl. Phys. Lett.* **73** 348
[7] Bagnall D M, Chen Y F, Zhu Z, Yao T, Shen M Y and Goto T 1997 *Nonlinear Opt.* **18** 243
[8] Bagnall D M, Chen Y F, Zhu Z, Shen M Y, Goto T and Yao T 1998 *J. Cryst. Growth* **184/185** 605

[9] Bagnall D M, Chen Y F, Zhu Z, Yao T, Shen M Y and Goto T 1998 *Appl. Phys. Lett.* **73** 1038
[10] Spanhel L and Anderson M A 1991 *J. Am. Chem. Soc.* **113** 2826
[11] Studenikin S A, Golego N and Cocivera M 1997 *J. Appl. Phys.* **84** 2287
[12] Vanheusden K, Warren W L, Seager C H, Tallant D R, Voigt J A and Gnade B E 1996 *J. Appl. Phys.* **79** 7983
[13] Reynolds D C, Look D C, Jogai B and Morkoc H 1997 *Solid State Commun.* **101** 643
[14] Bethke S, Pan H and Wessels B W 1998 *Appl. Phys. Lett.* **52** 138
[15] Kroger F A and Vink H J 1954 *J. Chem. Phys.* **22** 250
[16] Heitz R, Fricke C, Hoffmann A and Broser I 1992 *Mater. Sci. Forum* **83–87** 1241
[17] Ko H J, Chen Y F, Zhu Z and Yao T 2000 *Appl. Phys. Lett.* **76** 1905
[18] Chen Y F, Bagnall K M, Ko H J, Park K T, Zhu Z and Yao T 1998 *J. Appl. Phys.* **84** 3912
[19] Johnson M A L, Fujita S, Rowland W H Jr, Hughes W C, Cook J W and Schetzina J F 1996 *J. Electron. Mater.* **25** 855
[20] Suscavage M, Harris M, Bliss D, Yip P, Wang S Q, Schwall D, Bouthillette L, Bailey J, Callahan M, Look D C, Reynolds D C, Jones R L and Litton C W 1999 *MRS Internet J. Nitride Semicond. Res.* **40**
[21] Varshni Y P 1967 *Physica* **34** 149