

---

## Investigation on the origin of green light emission in ZnO bulk materials

---

Jinghai Yang\* and Lili Yang

The Institute of Condensed State Physics,  
Jilin Normal University, Siping 136000, PR China

Key Laboratory of Excited State Processes,  
Changchun Institute of Optics,  
Fine Mechanics and Physics,  
Chinese Academy of Sciences,  
Changchun 130033, PR China  
E-mail: jhyang@jlnu.edu.cn  
E-mail: yanglili1998@126.com

\*Corresponding author

Yongjun Zhang, Dandan Wang and Jihui Lang

The Institute of Condensed State Physics,  
Jilin Normal University,  
Siping, 136000, PR China  
E-mail: zhangyongjunwxy@126.com  
E-mail: ddwang@ntu.edu.sg  
E-mail: langjihui80@126.com

Qingxiang Zhao

Physical Electronics and Photonics,  
Department of Science and Technology (ITN),  
Linköping University,  
SE-60174 Norrköping, Sweden  
E-mail: Qingxiang.Zhao@itn.liu.se

**Abstract:** ZnO bulk materials were implanted by O and Zn with different concentration and their photoluminescence (PL) properties were investigated in detail. The results clearly show that O and Zn implantation indeed have great influence on the green light emission. By comparing the PL spectra for the samples with different implantations, O<sub>i</sub>, Zn<sub>i</sub> and Cu-related defects have been excluded from the possibility of the origin of green light emission step by step. Finally, it can be concluded that V<sub>Zn</sub> is responsible to the observed green light emission, which has good agreement with the theoretical results from first principle calculation.

**Keywords:** bulk ZnO; implantation; PL; photoluminescence; green light emission.

**Reference** to this paper should be made as follows: Yang, J., Yang, L., Zhang, Y., Wang, D., Lang, J. and Zhao, Q. (2009) 'Investigation on the origin of green light emission in ZnO bulk materials', *Int. J. Materials and Product Technology*, Vol. 34, No. 3, pp.360–368.

**Biographical notes:** Jinghai Yang is a Professor at the Institute of Condensed State Physics of JiLin Normal University. He is also employed to be a Doctorial Mentor in Changchun Institute of Optics, Fine Mechanics and Physics, Chinese Academy of Sciences. He received his MS Degree in Condensed Matter Physics and PhD in Material Science at JiLin University. He also acted as a visitor in Bowling Green University and Michigan University in USA for about two years. His interests include synthesis, characterisation and nature of semiconductor and rare earth ion luminescence materials.

Lili Yang is now working as a visiting researcher in Linköping University in Sweden. She got her PhD in 2008 at the Key Laboratory of Excited State Processes, Changchun Institute of Optics, Fine Mechanics and Physics, Chinese Academy of Sciences. She is engaging in the preparation and characterisation of ZnO nanostructures and rare earth ion luminescence materials.

Yongjun Zhang is an Associate Professor of JiLin Normal University now. He graduated from JiLin Normal University, he got MS Degree in YanBian University and received his PhD in the Institute of Condensed State Physics of NanJing University. His interests mainly focus on magnetic recording materials.

Dandan Wang is a PhD student majored in Condensed Matter Physics at Key Laboratory of Excited State Processes, Changchun Institute of Optics, Fine Mechanics and Physics, Chinese Academy of Sciences. Her research is on the synthesis and characterisation of rare-earth-doped ZnO nanostructures.

Jihui Lang is an editor of the Journal of Jilin University, and also a PhD student in JiangSu University. Her research is on the synthesis and characterisation of rare-earth-doped ZnO nanostructures.

Qingxiang Zhao is an Associate Professor in Linköping University now. He got his PhD Degree in Department of Physics in Linköping University in 1988. From 1988 to 1996, he ever worked as visiting scientist or postdoctoral researcher in France, Germany and Norway. His interests include synthesis, characterisation and nature of semiconductor, especially the defects behaviour in low dimensional structures, such as InGaAs quantum well, InAs quantum dots, ZnO nanostructures and so on.

---

## 1 Introduction

Zinc oxide (ZnO) as one of the most important semiconductor has attracted significant attention in recent years. Compared to other wide band-gap materials, such as ZnSe (2.2 eV) and GaN (3.4 eV), ZnO is a direct bandgap wurtzite-type semiconductor with bandgap energy of 3.37 eV at room temperature. Due to the extreme large exciton binding energy (about 60 meV), the excitons in ZnO are thermally stable at room temperature, and thus ZnO has significant advantages in optoelectronic applications such

as in the Ultraviolet (UV) lasing media laser diodes, varistors, sensors, transducers and photovoltaic devices (Huang et al., 2001; Wang, 2004; Look, 2001; Pearton et al., 2004; Minami, 2000; Wager, 2003). So far, lots of works have been done on the optical properties and its mechanism. It is well known that the Photoluminescence (PL) spectra of ZnO comprise near band edge ultraviolet luminescence located at 380nm and White Light Emission Band (WLEB) in the wavelength range between 400 nm and 700 nm. The UV emission band could be related to a near band-edge transition of ZnO, namely, the recombination of free excitons through an exciton–exciton collision process (Kong et al., 2001). WLEB could be related to the deep-level defect in ZnO. Theoretical and experimental studies have shown that the defect states in the ZnO can be of several types: neutral, singly or doubly charged O-vacancies ( $V_O$ ) (Kasai, 1963; Reihl and Ortman, 1956; Kröger and Vink, 1954; Vanheusden et al., 1996; Kang et al., 2003; Yamauchi et al., 2004), singly charged or neutral Zn- interstitial ( $Zn_i$ ), O-interstitial ( $O_i$ ) (Liu et al., 1992; Hahn and Nink, 1965), neutral, singly or doubly charged Zn-vacancies ( $V_{Zn}$ ) (Bylander, 1978; Yang et al., 2003; Zhong et al., 1993; Johnston et al., 2004), a complex of  $V_O$  with  $Zn_i$  ( $V_OZn_i$ ), a complex of  $V_{Zn}$  with  $Zn_i$  ( $V_{Zn}Zn_i$ ), substitution of O on a Zn site ( $O_{Zn}$ ) (Vanheusden et al., 1996; Djuricic and Leung, 2006; Zhang et al., 2001; Lin et al., 2001; Xu et al., 2003) and extrinsic impurities such as substitutional Cu (Dingle, 1969). The centre of WLEB is usually 520 nm, which corresponds to green light emission. Several mechanisms were proposed in order to explain green emission from these defects in ZnO. Xu et al. (2003) and Dingle (1969) discussed three probable mechanisms for green light emission from ZnO:

- transitions from conduction band to deep acceptor levels ( $O_i$  or  $Zn_i$ )
- transitions from deep donor levels ( $V_OZn_i$  complex) to shallow acceptor levels of ( $V_{Zn}$  and  $O_i$ )
- shallow donor levels ( $Zn_i$ ) to shallow acceptor levels ( $V_{Zn}O_i$  complex).

The intrinsic defects of ZnO have also been modelled using a full-potential linear muffin-tin orbital method, and Lin et al. (Xu et al., 2003) proposed that transitions between the conduction band and either  $O_{Zn}$  (2.38 eV) or  $O_i$  (2.28 eV) could result in green luminescence. However, the probability of the second transition was small, because formation of  $O_i$  in ZnO is less probable due to the large diameter of oxygen. Based on experimental data, Vanheusden et al. (1996) and Lin et al. (2001) suggested that the green luminescence originated from the transition from a singly charged oxygen vacancies  $V_{O+}$  to the valance band. According to van Dijken et al. (2001), a doubly charged oxygen vacancy,  $V_{O2+}$ , was formed first by tunneling of a trapped hole in a surface state to  $V_{O+}$  located in the interior of ZnO nanostructures. Finally a recombination between the  $V_{O2+}$  and a shallow trapped electron produced green light. However, the exact mechanism for green light emission is still controversial. Therefore, more research still should be done to get further information on the origin of the green light emission.

In this report, ZnO bulk materials implanted with O and Zn at various densities were investigated by photoluminescence. The samples were thermally treated in an oxygen gas environment after the implantation. The results clearly show the influence of O and Zn implantation on the deep level emission. By comparing the photoluminescence spectra for the samples with different implantations, the origin of the green light emission can be obtained.

## 2 Experiments details

ZnO bulk materials used in this investigation were bought from Universitywafer, grown by hydrothermal method. The O and Zn were respectively implanted into a same sample but at different position with implantation concentrations of  $1 \times 10^{17}/\text{cm}^3$  and  $5 \times 10^{17}/\text{cm}^3$ . These implantation concentrations were estimated from the dose and mean depth of ion implantation, which was estimated from the used ion energy. The ion backscattering and sputtering effects are not taken into account, but may influence the aimed implantation concentration. The energy of Zn- and O-implantation is 220 eV and 55 eV, respectively. The implanted samples were annealed in oxygen pressure for 10 min at 500°C and then following 10 min at 700°C. A piece of the as-grown ZnO sample was also annealed in Ar-air mixing gas with ratio 2 : 1 under the same conditions. Since the samples were polished in both sides, the backsides of implanted samples can be used as reference samples.

Photoluminescence (PL) measurements were carried out at room temperature. A double grating monochromator and a photomultiplier detector were used to disperse and detect the ZnO emission. The laser lines with a wavelength of 350 nm from an Ar<sup>+</sup> laser were used as the excitation sources. The excitation power was 20 mW. We estimate that the laser penetration depth is less 200 nm, which is slightly deeper than the implantation depth (100 nm).

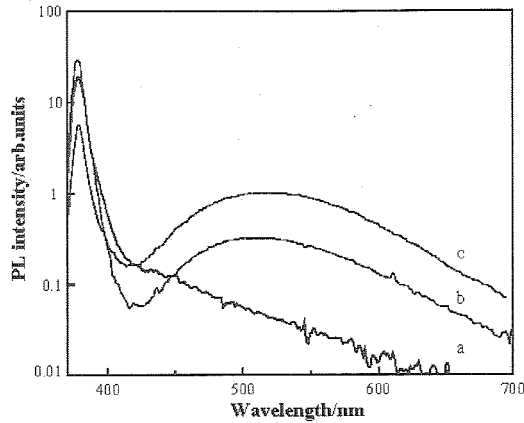
## 3 Results and discussion

The effect of complex defects as mentioned in the part of introduction is ignored in order to simplify the analysis process. That is to say, only O-vacancy ( $V_{\text{O}}$ ), Zn-vacancy ( $V_{\text{Zn}}$ ), Zn-interstitial ( $\text{Zn}_i$ ), O-interstitial ( $\text{O}_i$ ) and extrinsic impurities such as substitutional Cu probably induces green light emission. In order to determine which kind of defects in ZnO ultimately induces the green light emission, three series of samples were prepared in this study. The first series consist of as-grown sample, the samples annealed in O gas and the samples annealed in Ar-air mixing gas. The second series consist of as-grown samples and Zn-implanted samples with implantation concentrations of  $1 \times 10^{17}/\text{cm}^3$  and  $5 \times 10^{17}/\text{cm}^3$ . The third series consist of as-grown samples and O-implanted samples with implantation concentrations of  $1 \times 10^{17}/\text{cm}^3$ ,  $5 \times 10^{17}/\text{cm}^3$ ,  $1 \times 10^{19}/\text{cm}^3$  and  $5 \times 10^{19}/\text{cm}^3$ .

Figure 1 shows the PL spectra of the first series of samples. From Figure 1, it can be seen that there was almost no emission between 400 nm and 700 nm in the PL spectrum from the as-grown sample. However, after annealing in O and Ar-air mixing gas respectively, a broad emission peak appears in this range. The centre is located at 520 nm, which corresponds to green light emission. In order to obviously see the change of green light emission intensity, logarithmic coordinates was used at here. From this phenomenon, it can be believed that the samples annealed in O or Ar-air mixing gas have enough deep level defects so that the emission can be obviously seen in the PL spectra. Moreover, when the sample was annealed in O gas, it is expected that the rich O environment can make O interstitial concentration increase and the PL intensity of green light emission will be much higher than that of samples annealed in Ar-air mixing gas. However, from Figure 1, it can be seen that the PL intensity of green light emission from the sample annealed in Ar-air mixing gas was significantly higher than from the sample

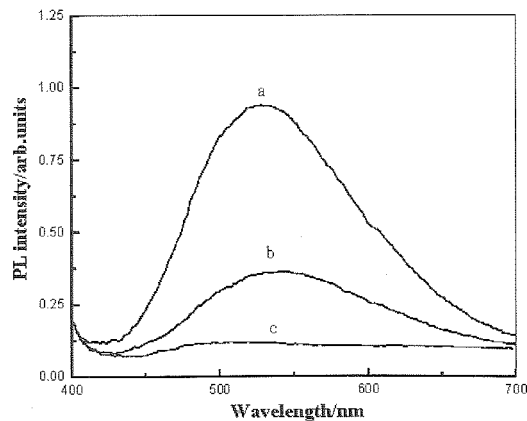
annealed in O gas. According to these results, we can believe that the  $O_i$  is not involved in this emission. This will be further confirmed by the results as the follows.

**Figure 1** PL spectra of the first series samples measured at room temperature: (a) as-grown; (b) annealed in O-gas and (c) annealed in Ar-air mixing-gas



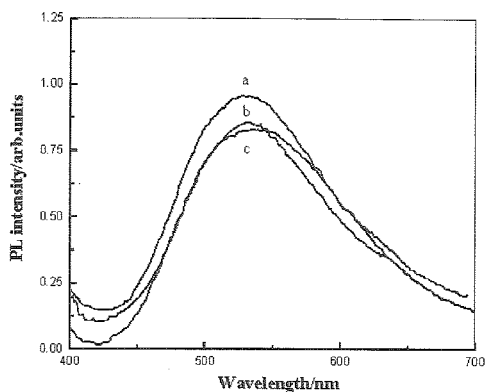
In order to testify the effect of  $Zn_i$  on the green light emission, the second series of samples with Zn-implantation were prepared. Figure 2 shows the PL spectra of the Zn-implanted ZnO samples after thermal annealing in oxygen gas. It should be paid great attention that the PL intensity is normalised to the free exciton emission in order to eliminate the possible effects caused by implantation damage. Since only the emission of free exciton and green light emission appear in the PL spectrum, the relative intensity of the green light emission in the normalised PL spectra provides a relative indication of the defect concentration involved in it. In Zn-implanted samples with increasing Zn-implantation concentration, it is expected that  $Zn_i$  concentration increases. However, from Figure 2, it can be seen that the intensity of the green light emission was significantly suppressed after Zn-implantation. Therefore, the experimental results as shown in Figure 2 testified that  $Zn_i$  was independent of the green light emission.

**Figure 2** PL spectra of the Zn-implanted ZnO samples after thermal annealing in oxygen gas measured at room temperature: (a) 0; (b)  $1 \times 10^{17}/\text{cm}^3$  and (c)  $5 \times 10^{17}/\text{cm}^3$

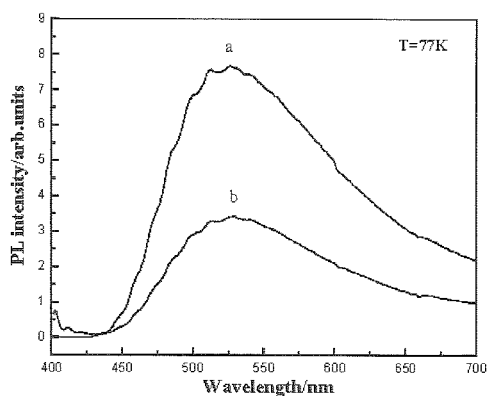


In order to further testify the effect of  $O_i$  on the green light emission, the third series of samples with O-implantation were prepared. Figure 3 shows the PL spectra from the O-implanted samples after thermal annealing in oxygen gas. In O-implanted samples with increasing the concentration of O-implantation, it is expected that  $O_i$  concentration increases. However, from Figure 3, it can be seen that the intensity of the green light emission was a little suppressed after O-implantation. The samples with much higher O-implanted concentration were even measured at low temperature. The PL spectra were shown in Figure 4. It still has same tendency. Moreover, according to the comparison between Figures 2 and 3, it was obviously seen that the intensity of green light emission was less decreasing with the increase of O-implantation concentration. So the O implantations have much less of an effect on the green light emission, which further confirmed that  $O_i$  was not involved in the green light emission.

**Figure 3** PL spectra of the O-implanted ZnO samples after thermal annealing in oxygen gas measured at room temperature (a) 0; (b)  $1 \times 10^{17}/\text{cm}^3$  and (c)  $5 \times 10^{17}/\text{cm}^3$



**Figure 4** PL spectra of the O-implanted ZnO samples after thermal annealing in oxygen gas measured at 77 K: (a)  $1 \times 10^{19}/\text{cm}^3$  and (b)  $5 \times 10^{19}/\text{cm}^3$

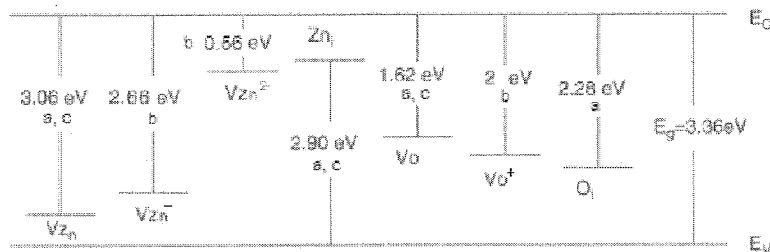


As the discussion in the introduction, the different origins involved in the green light emission have been proposed such as  $Zn_i$ ,  $O_i$ ,  $V_O$ ,  $V_{Zn}$  and Cu-related defects. Since all thermal treatments and the original ZnO samples used for implantations are exactly same except the O- and Zn-implantation concentrations, the difference of the green light

emission PL intensity observed in the different implanted samples can not be explained by Cu-related defects. Since  $O_i$ ,  $Zn_i$  and Cu-related defects have been excluded,  $V_O$  and  $V_{Zn}$  are the only two possible defects that are involved in the green light emission. From Figures 2 and 3, it can be seen that the Zn-implantations have more effect on the green light emission than the O implantation. This indicates that the creation of the defects that are involved in the green light emission was more effectively suppressed by the existing additional Zn atoms in comparison with the existing additional O atoms during the process of annealing. This is consistent if  $V_{Zn}$  is involved in the green light emission. Because the Zn atoms implanted into the bulk ZnO materials will fill into the Zn vacancy place during the annealing process, which will strongly decrease the concentration of  $V_{Zn}$ . As a result, the PL intensity of green light emission will be suppressed a lot. Therefore, it can be concluded that  $V_{Zn}$  is probably involved in the green light emission. Kohan et al. (2000) from Cambridge applied a first principles pseudo-potential approach to determine the electronic structure, atomic geometry, and formation energy of native point defects in ZnO. They pointed that the green luminescence observed in ZnO may originate from transitions between electrons in the conduction band and  $V_{Zn}$  levels, which has a good agreement with our results.

As the same situation in Figures 3 and 4, we also can assume that there is  $V_O$  in the samples. But the effect of O-implantation on the green light emission is not as obvious as that of Zn-implantation. Figure 5 showed the illustration of the calculated defect energy levels in ZnO from different literature sources. The data marked with the subscript a, b and c respectively originates from Lin et al. (2001), Lima et al. (2000) and Xu et al. (2003).  $V_{Zn}$ ,  $V_{Zn}^-$  and  $V_{Zn}^{2-}$  denote neutral, singly charged, and doubly charged zinc vacancies, respectively.  $V_O^+$  denotes a singly charged oxygen vacancy. From Figure 5, it also can be seen that the energy between  $V_O$  (or  $V_O^+$ ) and conduction band is much smaller than green light energy (2.38 eV). Therefore, it can not conclude that  $V_O$  is responsible to the green light emission. The exact reason for the slight intensity decrease with the O-implantation still need further research.

**Figure 5** Illustration of the calculated defect energy levels in ZnO from different literature sources



#### 4 Conclusions

In this paper, O and Zn at various densities were implanted into bulk ZnO and their photoluminescence were investigated in detail. By comparing the intensity of green light emission for the samples with different concentration of Zn and O implantations,  $O_i$ ,  $Zn_i$  and Cu-related defects have been excluded from the possibility of the origin of green light emission step by step. It can be finally concluded that  $V_{Zn}$  is probably responsible to

the green light emission. On the basis of this result, ZnO samples can be prepared under rich Zn environment in order to reduce the concentration of  $V_{Zn}$  in them, which will be a very effective method to suppress the green light emission and enhance the UV emission efficiency.

## Acknowledgement

This work is supported by the National Natural Science Foundation of China (NNSFC, Nos. 60778040 and 60878039), the Key Project for Science and Technology of Chinese Ministry of Education (Item No. 207025), the Program for the Development of Science and Technology of Jilin province (Item No. 20070707), the program for importing foreign technology and management talents into China (Item No. S20072200001), and the 11th Five-Year Program for Science and Technology of Education Department of Jilin Province (Item Nos. 20080154, 20080156, 20070149 and 20070162).

## References

- Bylander, E.G. (1978) 'Surface effects on the low-energy cathodoluminescence of zinc oxide', *J. Appl. Phys.*, Vol. 49, pp.1188–1195.
- Dingle, R. (1969) 'Luminescent transitions associated with divalent copper impurities and the green emission from semiconducting zinc oxide', *Phys. Rev. Lett.*, Vol. 23, pp.579–581.
- Djurisic, A.B. and Leung, Y.H. (2006) 'Hierarchically structured ceramics by high-precision nanoparticle casting of wood', *Small*, Vol. 2, pp.994–998.
- Hahn, D. and Nink, R. (1965) *Phys. Cond. Mater.*, Vol. 3, p.311.
- Huang, M.H., Mao, S., Feick, H., Yan, H., Wu, Y., Kind, H., Weber, E., Russo, R. and Yang, P. (2001) 'Room-temperature ultraviolet nanowire nanolasers', *Science*, Vol. 292, pp.1897–1899.
- Johnston, K., Henry, M.O., Cabe, D.M., Agne, T. and Wichert, T. (2004) *Proceedings of the Second Workshop on 'SOXESS European Network on ZnO'*, 27–30 October, Caernarfon, Wales, UK.
- Kang, H.S., Kang, J.S., Pang, S.S., Shim, E.S. and Lee, S.Y. (2003) 'Variation of light emitting properties of ZnO thin films depending on post-annealing temperature', *Mater. Sci. Eng., B*, Vol. 102, pp.313–316.
- Kasai, P.H. (1963) 'Electron spin resonance studies of donors and acceptors in ZnO', *Phys. Rev.*, Vol. 130, pp.989–995.
- Kohan, A.F., Ceder, G., Morgen, D. and Van de Walle, C.G. (2000) 'First-principles study of native point defects in ZnO', *Phys. Rev., B*, Vol. 61, pp.15019–15027.
- Kong, Y.C., Yu, D.P., Zhang, B., Fang, W. and Feng, S.Q. (2001) 'Ultraviolet-emitting ZnO nanowires synthesized by a physical vapor deposition approach', *Appl. Phys. Lett.*, Vol. 78, pp.407–409.
- Kröger, F.A. and Vink, H.J. (1954) 'The origin of the fluorescence in self-activated ZnS, CdS, and ZnO', *J. Chem. Phys.*, Vol. 22, pp.250–252.
- Lima, S.A.M., Sigoli, F.A., Jafellicci Jr., M. and Davolos, M.R. (2000) 'Luminescent properties and lattice defects correlation on zinc oxide', *Internet Symp. Food Allergens Intern. J. Inorg. Mat.*, Vol. 3, pp.749–754.
- Lin, B.X., Fu, Z.X. and Jia, Y.B. (2001) 'Green luminescent center in undoped zinc oxide films deposited on silicon substrates', *Appl. Phys. Lett.*, Vol. 79, pp.943–945.
- Liu, M., Kitai, A.H. and Mascher, P. (1992) 'Point defects and luminescence centres in zinc oxide and zinc oxide doped with manganese', *J. Lumin.*, Vol. 54, pp.35–42.



- Look, D.C. (2001) 'Recent advances in ZnO materials and devices', *Mater. Sci. Eng., B*, Vol. 80, pp.383–387.
- Minami, T. (2000) 'Image-processing techniques applied to the study of the musculoskeletal system and its interactions with biomaterials', *MRS Bull.*, Vol. 25, pp.38–41.
- Pearnton, S.J., Norton, D.P., Ip, K., Yeo Heo, Y.W. and Steiner, T. (2004) 'Recent advances in processing of ZnO', *J. Vac. Sci. Technol., B*, Vol. 22, pp.932–948.
- Reihl, N. and Ortman, Z.H. (1956) 'Injection of activators into ZnS phosphors by diffusion', *Elektrochem.*, Vol. 60, p.149.
- van Dijken, A., Makkinje, J. and Meijerink, A. (2001) 'The influence of particle size on the luminescence quantum efficiency of nanocrystalline ZnO particles', *Journal of Luminescence*, Vol. 92, pp.323–328.
- Vanheusden, K., Warren, W.L., Seager, C.H., Tallant, D.R., Voigt, J.A. and Gnade, B.E. (1996) 'Mechanisms behind green photoluminescence in ZnO phosphor powders', *J. Appl. Phys.*, Vol. 79, pp.7983–7990.
- Wager, J.F. (2003) 'Applied physics: transparent electronics', *Science*, Vol. 300, pp.1245–1246.
- Wang, Z.L. (2004) 'Zinc oxide nanostructures: growth, properties and applications', *J. Phys., Condens. Matter*, Vol. 16, pp.R829.
- Xu, P.S., Sun, Y.M., Shi, C.S., Xu, F.Q. and Pan, H.B. (2003) 'The electronic structure and spectral properties of ZnO and its defects', *Nucl. Instrum. Methods Phys. Res., B*, Vol. 199, pp.286–290.
- Yamauchi, S., Goto, Y. and Hariu, T. (2004) 'Photoluminescence studies of undoped and nitrogen-doped ZnO layers grown by plasma-assisted epitaxy', *J. Cryst. Growth*, Vol. 260, pp.1–6.
- Yang, X., Du, G., Wang, X., Wang, J., Liu, B., Zhang, Y., Liu, D., Liu, D., Ong, H.C. and Yang, S. (2003) 'Effect of post-thermal annealing on properties of ZnO thin film grown on c-Al<sub>2</sub>O<sub>3</sub> by metal-organic chemical vapor deposition', *J. Cryst. Growth*, Vol. 252, pp.275–278.
- Zhang, S.B., Wei, S.H. and Zunger, A. (2001) 'Intrinsic n-type versus p-type doping asymmetry and the defect physics of ZnO', *Phys. Rev., B*, Vol. 63, p.075205.
- Zhong, J., Kitai, A.H., Mascher, P. and Puff, W. (1993) 'The influence of processing conditions on point defects and luminescence centers in ZnO', *J. Electrochem. Soc.*, Vol. 140, pp.3644–3649.