Materials Chemistry and Physics 126 (2011) 54–57

Contents lists available at ScienceDirect

Materials Chemistry and Physics

journal homepage: www.elsevier.com/locate/matchemphys

Structural properties of P-doped ZnO

Ngo Thu Huong[a], Nguyen Viet Tuyen[a], Nguyen Hoa Hong[b,*]

[a] Faculty of Physics, Hanoi University of Science, 334 Nguyen Trai, Thanh Xuan, Hanoi, Viet Nam
[b] Department of Physics and Astronomy, Seoul National University, Seoul 151-747, South Korea

ARTICLE INFO

Article history:
Received 2 July 2010
Received in revised form 5 November 2010
Accepted 3 December 2010

Keywords:
Semiconductors
Nanomaterials
Structure
Doping

ABSTRACT

P was doped into ZnO in two forms: ceramics; and nano-wires fabricated by thermal evaporation technique. When P concentration is below 6%, the compounds could be *p*-type with the hole concentration is of about $10^{18}/\text{cm}^3$. However, this property could be lost after few weeks due to aging effect. When the P concentration is above 9%, peaks of P appear clearly in the X-ray spectra, and simultaneously, the compounds are found to be *n*-type. The size of grains in ceramic samples strongly depends on deposition conditions. As for wires, changing the substrate temperature and the pressure of gas flow could vary the size. The smallest size of P-doped ZnO wires that could be obtained is about 10 nm for the composition of doping with 3% of P.

1. Introduction

The II-VI semiconductor zinc oxide (ZnO) has great potential for applications in short-wavelength opto-electronics, light-emitting diodes, and lasers. It also has the potential to rival GaN, due to its promising properties such as a larger exciton binding energy (60 meV), lower cost, and higher chemical etching rate [1,2]. *p*-type doped ZnO compounds are also predicted to be ferromagnetic at room temperature so that they can be promising candidates for application in spintronics [3].

Although high quality *n*-type ZnO for device applications has been produced, it is well known that the growth of reproducible *p*-type ZnO remains as a big challenge due to the self-compensating effect from native defects (V_o and Zn_i) and/or H incorporation. Moreover, the low solubility and the deep acceptor levels of the dopants may yield low carrier concentration, making p–ZnO even harder to be fabricated [4].

Recently, many groups have tried to grow *p*-type ZnO [5]. Some group gave reported successfully fabricating *p*-type ZnO:N, which is reasonable because nitrogen has a similar ionic radius as oxygen and is easily substituted [6]. Unfortunately, obtaining stable *p*-type ZnO is still a remained issue. To seek better *p*-type dopants, a few groups have tried other elements such as phosphorous (P) [7,8], arsenic (As) [9], and antimony (Sb) [10], whose ionic radii are much larger than that of oxygen atom. Surprisingly, good *p*-type conductivities were observed from those films, indicating the feasibility of *p*-type doping with larger size-mismatched impurity.

However, the standing issue is that how to make those samples durable that can stand over time without being aged and degrading quality. Normally for example, N or P can be "doped" into the ZnO, but once they can get in then they also can evaporate to go "out" again [11]. Keeping those dopants incorporated in a appropriate way so that they could maintain inside the structure of ZnO should be a big problem to solve. However, in reality, so far, no one has achieved in doing so.

In this paper, we report on the fabrications and investigation of structural properties of P-doped ZnO ceramics s and wires made by evaporation effects. Even though the *p*-type compounds that we have obtained are still not durable with time, the fact that the samples could be made in a nanometer-size and it could be controlled by deposition conditions/technique gives some hope that stabilized *p*-type ZnO compounds could be well achieved in the future.

2. Experiment

Ceramic samples of $Zn_{1-x}P_xO$ (where $x = 0.03$; 0.06; 0.09 and 0.12) were prepared by a conventional solid-state reaction method. Appropriate temperatures for calcinations and annealing were chosen for each compound based on results of differential scanning calometry (DSC) and thermal-gravimetric analysis (TGA) measurements. Samples were pressed into pellets under a pressure of $5\ \text{T}\,\text{cm}^{-2}$, and then annealed at 750, 900, and 1100 °C for 10 h, and finally were slowly cooled down to room temperature.

As for wires of $Zn_{1-x}P_xO$ (where $x = 0.03$; 0.06; 0.09 and 0.12), the powders of ZnO, P_2O_5 and 1 wt% of C were well mixed then put into the middle of a tube furnace where the temperature, N_2 pressure, and annealing time could be well programmed. The furnace was at first heated up at 1100 °C for 30–60 min. Films with formed wires were evaporated onto (1 1 1) Si substrates in the range of temperature from 600 to 700 °C. During the whole process of evaporation, the N_2 gas was continuously flown in order to protect the films from any oxidation.

Compositions of samples were checked by energy dispensive spectrum technique (EDS). The structural properties were investigated by X-ray diffraction (XRD) measurements performed by Siemens D5005. Scanning electron microscopy (SEM)

---

* Corresponding author. Tel.: +82 2 880 66 06.
E-mail address: nguyenhong@snu.ac.kr (N.H. Hong).

0254-0584/$ – see front matter © 2010 Elsevier B.V. All rights reserved.
doi:10.1016/j.matchemphys.2010.12.012

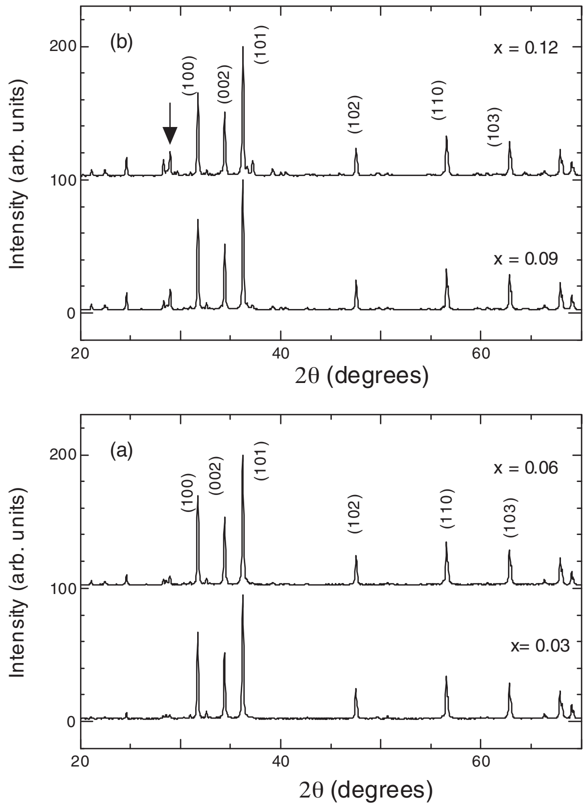

Fig. 1. XRD patterns for (a) $Zn_{0.97}P_{0.03}O$ and $Zn_{0.94}P_{0.06}O$ and (b) $Zn_{0.91}P_{0.09}O$ and $Zn_{0.88}P_{0.12}O$ ceramic samples.

method by JEOL-JSM5410LV. Hall effect measurements were carried out at room temperature by Hall apparatus 7604, while photoluminescence (PL) spectrum were detected by Fluorolog FL3-22 Jobin Yvon Spex USA.

3. Results and discussions

Hall effect measurements that were performed at room temperature have shown that the $Zn_{0.97}P_{0.03}O$ and $Zn_{0.94}P_{0.06}O$ ceramic samples are *p*-type semiconductors with the hole concentration is of $10^{18}\,cm^{-3}$, while the $Zn_{0.91}P_{0.09}O$ and $Zn_{0.88}P_{0.12}O$ ceramic samples are *n*-type. This seems to be understood from their XRD patterns that are shown in Fig. 1. As for the samples with P concentration up to 0.06, peaks of ZnO phase (with lattice parameters $a = b = 3.756$ Å, and $c = 5.028$ Å) are much more dominant than peaks of $Zn_3(PO_4)_3$ (small, seen in Fig. 1(a)), while as for samples with P concentration larger than 0.06, the intensity of peaks of the alien phase of P is very pronounced (see peaks below 30°, pointed by some arrow in Fig. 1(b)). It seems that a better incorporation of P into the ZnO lattice, as seen in $Zn_{0.97}P_{0.03}O$ sample, is the main reason to be able to obtain the *p*-type P-doped ZnO. EDS data in Fig. 2 shows that P has really got into ZnO (typical data for $Zn_{0.97}P_{0.03}O$). Data of samples with different concentrations of P dopant are presented in Table 1. In fact, when the concentration of dopant is little (such as 0.03), P can incorporate into the lattice much more easily (from the intensity of EDS spectrum for P, one can see clearly that when the P concentration is even larger, the amount of P that indeed got into ZnO host lattice is smaller).

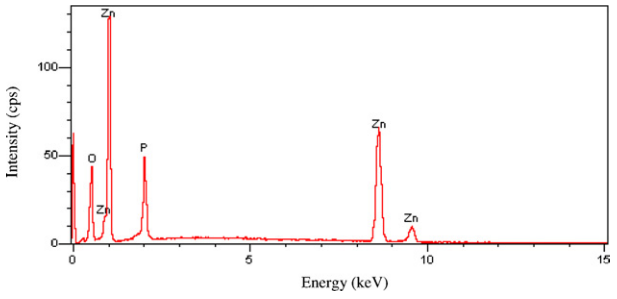

Fig. 2. EDS spectrum for a $Zn_{0.97}P_{0.03}O$ ceramic sample.

Table 1
Intensity of element's peaks from EDS.

P concentration	Intensity (cps)		
	Zn	O	P
0.03	210	45	55
0.06	225	35	10
0.09	180	30	3
0.12	225	55	35

However, note that after few weeks, the *p*-type characteristics of those samples is lost (most probably due to the instability of the incorporated P), since they have turned to be *n*-type with electron concentration of about $1.2 \times 10^{18}\,cm^{-3}$. This feature is the main issue in the field at the moment [5]. Changing conditions, creating some capping layer, or making samples with smaller size might help to solve that problem. However, it requires further work in the future.

The SEM pictures in Fig. 3 show that as for P concentration of 0.03 and 0.06, the ceramic samples that were heated at 750 °C could give a size of grains as of 200–500 nm. We note also that when we increase the heating temperature, the density of grains obviously increases.

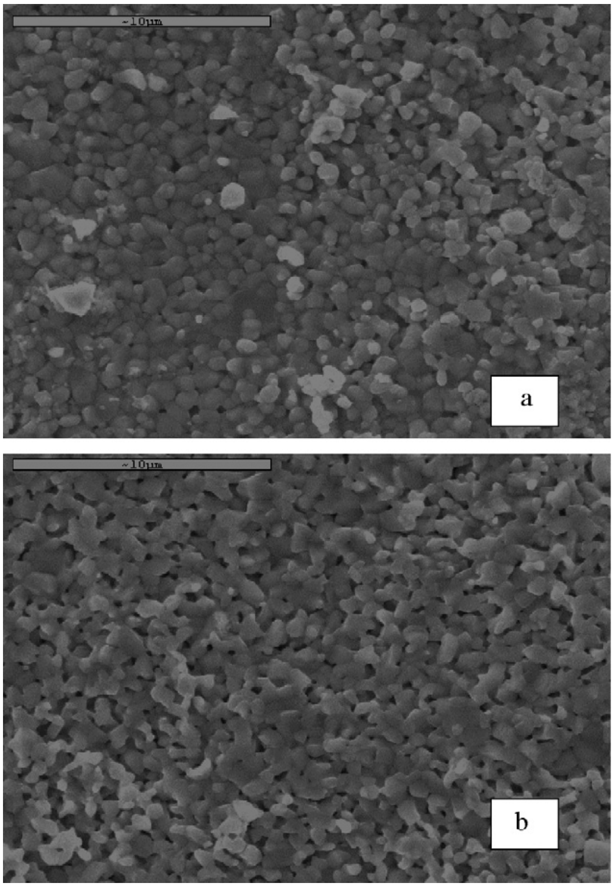

Fig. 3. SEM pictures for (a) $Zn_{0.97}P_{0.03}O$ and (b) $Zn_{0.94}P_{0.06}O$ ceramic samples.

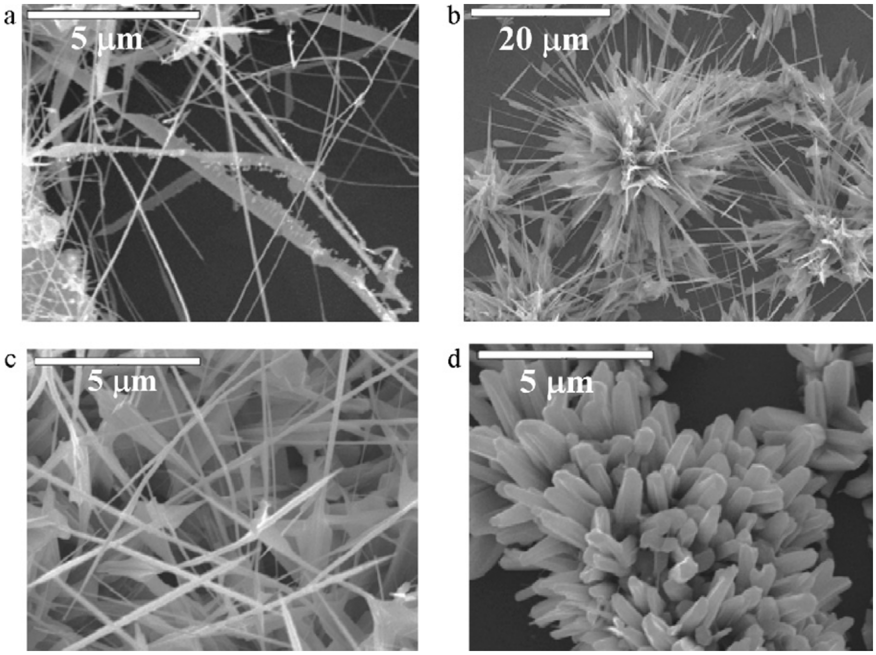

Fig. 4. SEM pictures for (a) $Zn_{0.97}P_{0.03}O$ wires grown on 600 °C-heated-substrate; (b) $Zn_{0.97}P_{0.03}O$ wires grown on 700°C-heated-substrate; (c) $Zn_{0.94}P_{0.06}O$ wires grown on 600 °C-heated-substrate; and (d) $Zn_{0.94}P_{0.06}O$ wires grown on 700 °C-heated–substrate.

Films sample were made in fact to verify if by changing the technique as well as deposition conditions, one could obviously change the structural properties of P-doped ZnO compounds. Fig. 4 shows SEM pictures for samples doped with 0.03 and 0.06 P, which were evaporated on substrates heated at 600 °C and 700 °C. As for the $Zn_{0.97}P_{0.03}O$ film, the smallest size of wires that were formed on the film is about 10 nm (with the average size for wires in the whole film is about 60 nm. See Fig. 4(b)) when the substrate temperature is 700 °C, and is about 20 nm (with the average size for wires in the whole film is 80 nm, see Fig. 4(a)), when the substrate temperature is 600 °C. As for the $Zn_{0.94}P_{0.06}O$ film, the size of wires are found to be larger, the smallest one is 100 nm for samples that were evaporated on 600 °C–heated-substrates (Fig. 4(c)), and 400 nm for samples that were evaporated on 700 °C–heated-substrates (Fig. 4(d)). This result suggests us to continue to investigate in this direction, i.e. optimizing preparation conditions, in order to obtain nanometer-sized *p*-type ZnO compounds.

In order to check initiatively if the P doping could change some optical properties of ZnO compound, the PL measurements were carried out. From Fig. 5, one can see 2 peaks: the first peak indicating an UV emission band at about 390 nm, and the second peak indicating a strong green band at about 509 nm). Different from the normal PL spectra of ZnO that one can expect to see the second peak below the wavelength of 500 nm, in the case of P doping that is shown here, those second peaks shift to above 500 nm. One also can notice that as for P concentration of 0.03 and 0.06, this second peak shifts more than the other two cases of larger P doping concentrations.

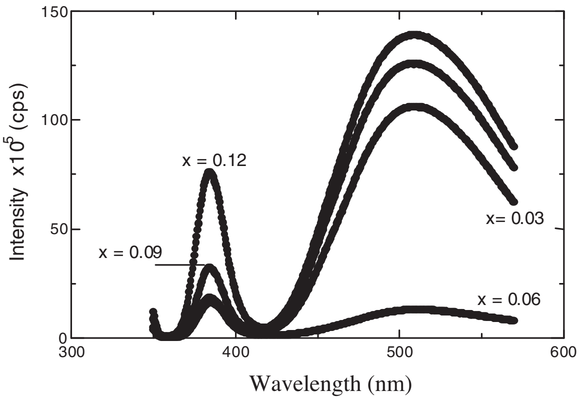

Fig. 5. PL spectrum taken at room temperature for $Zn_{1-x}P_xO$ wires.

4. Conclusions

Properties of P-doped ZnO bulks and thermal evaporated films made by different conditions were investigated. As the P concentration is equal or below 6%, the compounds could be *p*-type semiconductors with the hole concentration is of about 10^{18} cm^{-3}. However, after few weeks, the samples could turn to be *n*-type. When the P concentration surpasses 9%, an alien phase of P could be seen in the spectra, and it explains why the compounds are *n*-type. The size of grains in ceramic samples strongly depends on deposition conditions, while the size of wires that can be controlled by changing the substrate temperature. The smallest size of P-doped ZnO wires that could be obtained is about 10 nm for 3% of P doping. It gives some hope that by controlling the doping concentration below 6%, along with optimizing deposition conditions/technique, one can improve enormously structural and physical properties of P-doped ZnO to be a durable *p*-type compound.

Acknowledgements

The authors would like to thank the projects QT-08-11 and 103.02.73.09 (Vietnam) and the grant 0409-20100148 of SNU R&D Foundation (Korea) for financial supports.

References

[1] J.G. Lu, Y.Z. Zhang, Z.Z. Ye, L.P. Zhu, B.H. Zhao, Q.L. Liang, Appl. Phys. Lett. 88 (2006) 222114.
[2] V. Vaithianathan, B.T. Lee, C.H. Chang, K. Asokan, S.S. Kim, Appl. Phys. Lett. 88 (2006) 112103.
[3] T. Dietl, H. Ohno, F. Matsukura, J. Cibert, D. Ferrand, Science 287 (2000) 1019.
[4] S.B. Zhang, S.H. Wei, A. Zunger, Phys. Rev. B 63 (2001) 075205.

[5] L.J. Mandalapu, Z. Zhang, S. Chu, J.L. Liu, Appl. Phys. Lett. 92 (2008) 122101, and references therein.

[6] K. Tang, S. Gu, K. Wu, S. Zhu, J. Ye, R. Zhang, Y. Zheng, Appl. Phys. Lett. 96 (2010) 242101.

[7] K.K. Kim, H.S. Kim, D.K. Hwang, J.H. Lim, S.J. Park, Appl. Phys. Lett. 83 (2003) 63.

[8] F.X. Xiu, Z. Yang, L.J. Mandalapu, J.L. Liu, W.P. Beyermann, Appl. Phys. Lett. 88 (2006) 052106.

[9] V. Vaithianathan, B.T. Lee, S.S. Kim, Appl. Phys. Lett. 86 (2005) 062101.

[10] W. Guo, A. Allenic, Y.B. Chen, X.Q. Pan, Y. Che, Z.D. Hu, B. Liu, Appl. Phys. Lett. 90 (2007) 242108.

[11] Q. Wan, Appl. Phys. Lett 89 (2006) 082515.