

PREPARATION AND INVESTIGATION OF OPTICAL PROPERTIES OF ZnO: Co POWDERS

Nguyen Thi Thuc Hien, Le Thi Qui, Ngo Xuan Dai

Department of Physics, College of Science, VNU

Nguyen Hanh, Huynh Dang Chinh, Dao Viet Linh

Department of Organic Chemistry, Hanoi University of Technology

Abstract: ZnO: Co powders with Co concentrations ranging from 1at% to 15at% were prepared by sol-gel method. The powders show wurtzite crystal structure with the lattice constants changing with the cobalt content. The photoluminescence spectra (PL) consist of four bands : a exciton emission band of 380 nm, a band around 400-500 nm, and two bands at 588 nm and 690 nm. The existence and the intensity of the bands depend on the Co content, the optical excitation and the annealing condition. Origins of the emissions were proposed.

1. Introduction

Diluted magnetic semiconductors (DMSs) have attracted much attention because of the possibility of a spin source or spin injector in spintronic devices. Although ferromagnetism was observed in some of Co-doped ZnO, the origin of the ferromagnetism has not been clarified yet. Moreover, the growth condition also much influent on the physical properties especially on the optical properties [1].

In this study we investigate the optical properties of Co-doped ZnO powders prepared by sol-gel method, in which the cobalt contents were from 1 at % to 15 at %. We propose the formation of the phases at the different synthesis condition. We also study the influence of the annealing, the cobalt content on the PL spectra.

2. Experimental

Co-doped ZnO powders were prepared by sol-gel method. The main preparing procedure was described in [2]. The annealing temperatures were 350°C, 450°C, and 600°C. The crystal structure of the powder was characterized by X-ray diffraction (XRD) with a Bruker D5005 X-ray diffractometer. The Jobin-Yvon FL 3-22 spectrofluorometer was used for the optical characterization.

3. Results and discussion

The XRD patterns were exhibited in Fig.1. It is seen that for low cobalt concentrations (< 7 at %) a monophase of zinc oxide was formed and no extra peaks were found. For the cobalt concentrations higher than 7 at % the diffraction patterns

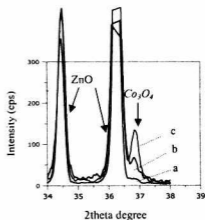


Fig.1. XRD patterns of (a) 7% at%, (b) 10 at%, (c) 15 at% Co-doped samples

correspond to zinc oxide and a new phase which may either have been Co_3O_4 or the zinc spinel ZnCo_2O_4 . It was not possible to identify which phase was present as the diffraction patterns for Co_3O_4 and ZnCo_2O_4 are very similar. The intensity of the peaks of the new phase increased as the percentage of cobalt increased. This suggested that this phase increased with increasing cobalt content.

Moreover, for the samples annealed in lower temperatures 350-450°C, the a-axis increased and the c-axis decreased when the cobalt contents increased. Besides, the peaks of Co-doped ZnO were broadened more than that of ZnO. This means the smaller sizes of ZnO:Co than ZnO itself. When the annealing temperature was 600°C, the a-axis and c-axis almost decreased with the increase of the Co contents. This indicates the content of Co^{3+} ions was higher in this case because the radius of Co^{3+} ions is smaller. If Co^{3+} ions coexist with Co^{2+} ion in $\text{Zn}_{1-x}\text{Co}_x\text{O}$ the alloy is expected to have lattice defects. When substitute Zn sites, such Co^{3+} ions are expected to act as donors as well as to distort the lattice structure for holding charge neutrality. It is also the reason for appearing new spinel phases.

The PL spectra measured at room temperature includes four bands: 380nm, 400-500nm, 580nm and 690nm. There are :

- *The UV emission near a band edge of 380nm:* exists only for the samples annealed at 350-450°C and disappeared when the annealing temperature was 600°C. For all samples the intensity of this peak decreased with increasing the cobalt contents. The PL spectra of UV emission for the samples annealed at 450°C for 1h are shown in Fig 2. The reduction of the excitonic strength with increasing cobalt doping can be explained in terms of the increased carrier scattering due to increased disorder in the crystal lattice with increasing cobalt doping. This also explain why the samples annealed at 600°C did not exhibit UV emission at room temperature.

- *The band around 400-500nm:* At annealing temperature of 450°C the example showed only one peak around 450nm and the intensity of the peak decreased with increasing of cobalt content (Fig.2).

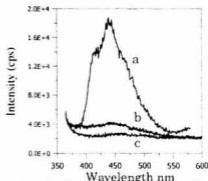


Fig.3. PL spectra of Co-doped ZnO (a) 1 at%, (b) 7 at%, (c) 15 at%

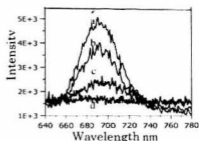


Fig.4. PL spectra of (a) 2 at% (b) 3 at% (c) 7 at% (d) 15 at% doped samples.

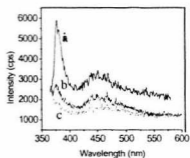


Fig.2. UV PL spectra of (a) 1 at%, (b) 4 at%, (c) 10 at% Co-doped ZnO.

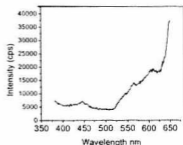


Fig.5. PLE spectrum of a 5 at% doped sample

However, at annealing temperature of 600°C this band separated into three peaks. There are 418, 440 and 467nm. Fig.3 shows the PL spectra of these bands. After Koild [5] the bands belong to the transitions ${}^4T_2 (F) \rightarrow {}^4A_2 (F)$ for Co^{2+} . However the behavior of these bands depends on the annealing regime, such as rapid or not. J.H.Kim [3] measured PL spectra for ZnO:Co. They found that the PL spectra consists of 415nm and 540nm peaks such that the intensity decreased monotonously with increasing cobalt content. Up to 25 at % Co, the band of 415nm disappeared and the band of 540nm shift to longer wavelength. In our case, when the annealing time and the cobalt content increased, the peak 418 nm disappeared while the peaks of 440 and 467 nm shifted to longer wavelength. The decrease of the intensity of 418 nm band with the increase of the cobalt content may be explain as the contribution of some absorption transition of the spinel oxides Co_3O_4 or $Zn_xCo_{3-x}O_4$ in this range of the wavelength. The higher cobalt concentration the higher possibility to form Co_3O_4 and $Zn_xCo_{3-x}O_4$ makes the decrease of the absorption transition in ZnO.

- **The band at 580 nm:** The spectrum around 580 nm existed also in ZnO itself. The peak is possibly formed by some impurity from the chemical precursor such as zinc acetate as the film ZnO:Co prepared from such zinc acetate also revealed this peak.

- **The band at 690 nm:** This band appeared when the sample was excited by 425 nm and 600 nm wavelength. The spectra of the peak were shown in fig. 4.

The intensity of the peak decrease with the increasing of cobalt content and the peak position shifted to longer wavelength. The photoluminescence excitation (PLE) spectrum of the 690 nm band was recorded. Fig. 5 is the PLE spectrum of the sample with 5 at% doping and annealed at 450°C. After Koild [4] the peak of 690 nm is attributed to the transition ${}^4T_1 \rightarrow {}^4A_2$ for Co^{2+} . From the PLE spectrum for this peak we can see the broad line spectrum. It is the feature of the absorption by the charge-transfer transition.

4. Conclusion

Co-doped ZnO powder have been synthesized by sol-gel method. The structure and photoluminescence of the samples were investigated. At higher cobalt-doping concentration there was the segregation of new cobalt oxide phase. The origin of the PL bands was proposed.

References

1. K. Ueda, H. Tabata and T. Kawai, *Appl. Phys. Lett.* **79**(2001), 988.
2. N.T.T Hien, N. Hanh, H.D. Chinh, L.T. Qui, L.V. Vu, and N.X. Dai, *The Ninth Asia Pacific Physics Conference*, Hanoi 2004 (in press).
3. M. Oku and Y. Sato, *Appl. Surf. Sci.* **55**(1992), 37.
4. Jae Hyun Kim, Jae Bong Lee, *IEEE Transactions on Magnetic*, **38**, (2002), 1.
5. P. Koidl, *Phys. Rev B* **15**(1997), 5.
6. K.J. Kim, Y. R. Dark, *Solid State Comm.*, **127**(2003), 25.