

Ag-doped ZnO Nanorod Structures Grown by Hydrothermal-based Process

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Abstract

This work reports on the synthesis of Ag-doped ZnO p-type nanorods films grown on glass substrates by hydrothermal process. The ZnO nanorods were synthesized via aqueous solution process with zinc nitrate hexahydrate, hexamethylenetetramine and dopant precursor including AgNO₃ on ZnO seed layers. The ZnO seed layers were deposited by sol-gel spin coating method starting by zinc acetate dihydrate as a precursor dissolved in absolute ethanol. The precursor was coated 8 times then annealed in air at 500°C for 2 h. The dopant concentration was varied from 0-10 mol% by adding a cathodic dopant, into an aqueous solution for hydrothermal process. The influence of dopant concentration on structural, morphological and optical properties is investigated by X-ray diffraction spectroscopy (XRD), field emission scanning electron microscope (FESEM) and ultraviolet-visible (UV-Vis) spectrophotometer. These results exhibit ZnO hexagonal wurtzite with no impurity phase on undoped ZnO nanorods. The deterioration in phase of Ag-doped ZnO indicates that Ag ion may substitute on zinc site that is in agreeable with the morphological result. The optical properties exhibit low transparency at visible region implying that as-grown ZnO nanostructure may act as light absorber or scattering species.

Keywords: Ag-doped ZnO, Nanostructure, Hydrothermal

1. Introduction

Zinc oxide is typically an intrinsic n-type semiconductor material, with a wide direct band gap of 3.37 eV coupled with a large exciton binding energy of about 60 meV at room temperature. ZnO-based materials have been extensively applied to many fields of applications such as random laser diode^[1], gas sensors^[2], field emission material^[3] and UV photo sensors^[4]. Many fascinating morphologies of ZnO were synthesized such as nanoparticles^[5], nanowires^[6] and nanorods^[7] that would be applicable for specific applications. Various techniques have been recently applied to prepare low-dimension ZnO films such as vapor-liquid-solid (VLS)^[8], chemical vapor deposition (CVD)^[9], and hydrothermal processes^[10]. hydrothermal process is one of the most widely used technique for preparing ZnO low-dimensional structures regarding to ease of apparatus set up, mild process and adjustability of composition and dopant. Meanwhile, doping is one of effective techniques to improve designated properties and performance of ZnO. An obstacle in the development of P-N junction ZnO device is quality of p-type ZnO because of native defect

in ZnO showing strong n-type conductivity ^[11]. Up to now, many researchers have utilized group-IA and IB elements such as Li, Na, Ag ^[12-14] for substituting into the Zn-site, and group-VA such as P and Sb ^[15, 16] on the O-site to achieve p-type ZnO. However, Ag as a group IB element is considered to be one of good candidate acceptors for ZnO.

In this work, we report a one-step hydrothermal process for the synthesis of Ag-doped ZnO nanorod structure on glass substrate. The influence of Ag concentration on physical and optical properties of ZnO nanorods is investigated.

2. Experimental

Ag-doped ZnO nanorods were grown by hydrothermal process on undoped ZnO thin film seed layer deposited on glass substrate. These undoped ZnO thin films were grown using sol-gel spin coating technique. First, the sol-gel for ZnO layer was prepared starting from zinc acetate as precursor dissolved in absolute ethanol and 1 ml of diethanolamine. The mixture was heated at 75°C for 2 h and aged for 24 h. The glass substrates were washed consecutively by DI water, acetone, methanol and isopropanol for 10 min with ultrasonic cleaner. The sol-gel ZnO were dropped on glass substrate and spun at 2000 rpm for 30 s. The ZnO seed layer thin films were baked at 100°C between spinning process then the coating was repeated 8 times. After that the ZnO thin films were annealed in air at 500°C for 2 h. The hydrothermal solution was prepared by zinc nitrate, hexamethylenetetramine and dopant dissolved in DI water. The doping concentration was varied from 0 to 10 mol percentage. The ZnO Thin films were placed up-side down in the Teflon autoclave then heated at 90°C for 4 h. After the hydrothermal process, the ZnO nanorod films were washed by DI water followed by ethanol and were dried at 100°C for 15 minutes.

The structural properties of the ZnO nanorod films were characterized by Rigaku SmartLab X-ray diffractometer (XRD). Hitachi S4700 field emission scanning electron microscope (FESEM) were performed to find surface morphology and length of nanorod by cross section. The PerkinElmer LAMBDA 950 UV-Vis spectrophotometer was performed to find the optical properties of the ZnO nanorod films. For the reflection mode. The data were collected at normal incident angle.

3. Results and discussion

Fig. 1. (a) shows X-ray diffraction patterns of ZnO thin films and ZnO nanorods films with various Ag doping concentration. The diffraction patterns of ZnO thin films and undoped ZnO nanorods films are nicely matched with hexagonal wurtzite phase of ZnO (ICSD no. 157724) and no impurity phase is detected. It shows the dominant (002) peak for undoped ZnO nanorods sample. The result confirms the growth orientation along the c-axis. Moreover, after silver dopant was added the results show that diffraction peaks at 38.1°, 44.3°, 64.5° and 77.4° are well-matched with (110), (200), (220) and (311) (ICSD no. 53761), respectively. When silver concentration was increased, the crystallinity of (002) plane decreased indicating that the growth of ZnO nanorods was deterred by silver dopant. Decreasing ZnO peak when a doping element with larger ionic radius than Zn²⁺ was replaced as substitution on the zinc site ^[17]. Fig. 1. (b) shows the crystalline size of samples calculated by Scherrer's equation. The average crystallite size of ZnO of the undoped and Ag-doped ZnO films are 55, 79, 84, 83, 88 and 82 nm for undoped and 3 to 10% Ag-doped ZnO, respectively. The average crystalline size of Ag of the Ag-doped ZnO films are 82, 67, 68 and 102 nm for 3 to 10% Ag-doped ZnO, respectively.

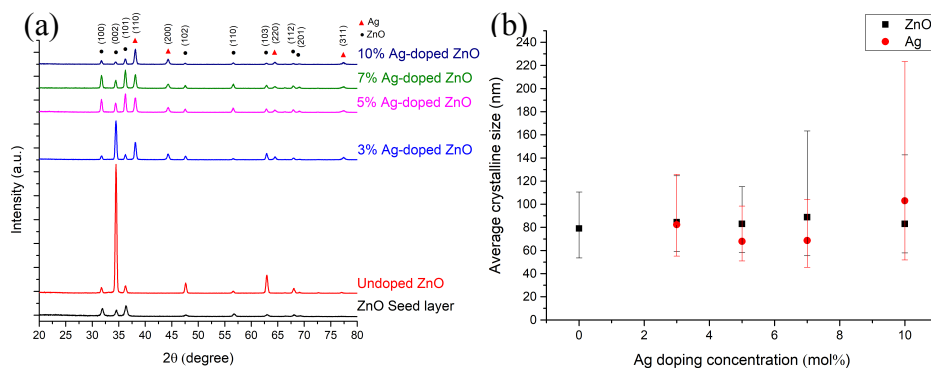


Fig. 1. XRD pattern of hydrothermally grown ZnO nanorods with various silver doping concentrations (a) and the average crystalline size of undoped and Ag-doped ZnO films (b).

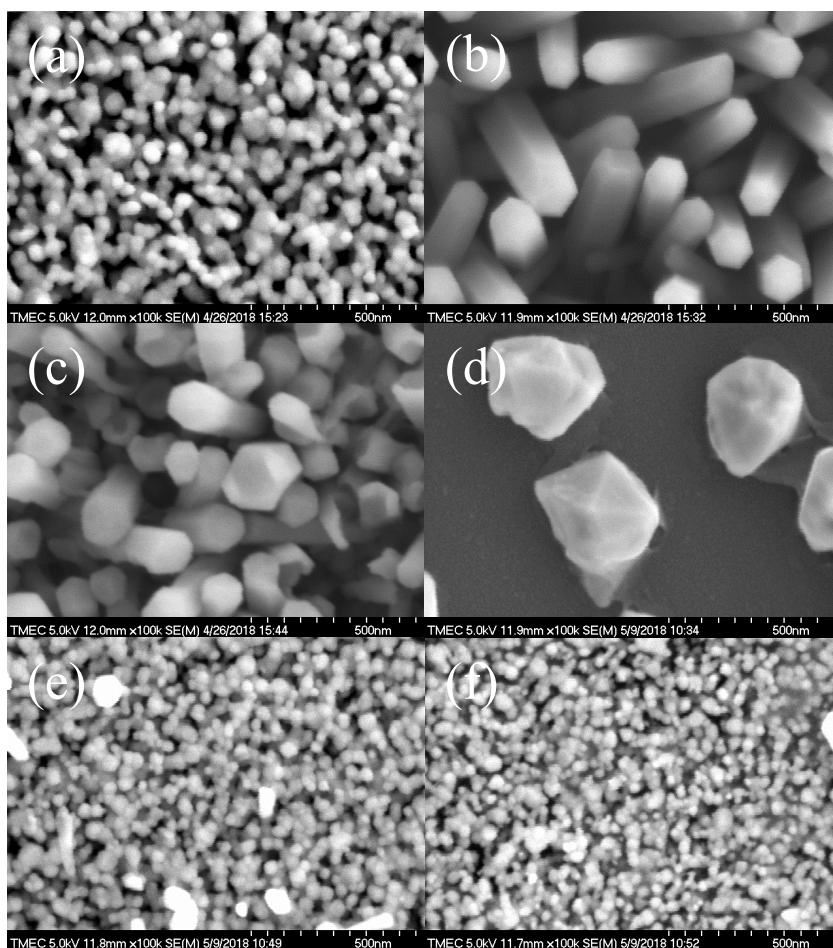


Fig. 2. Surface morphology of (a) ZnO seed layer, (b) undoped ZnO nanorods, (c)-(f) 3-10% Ag-doped ZnO.

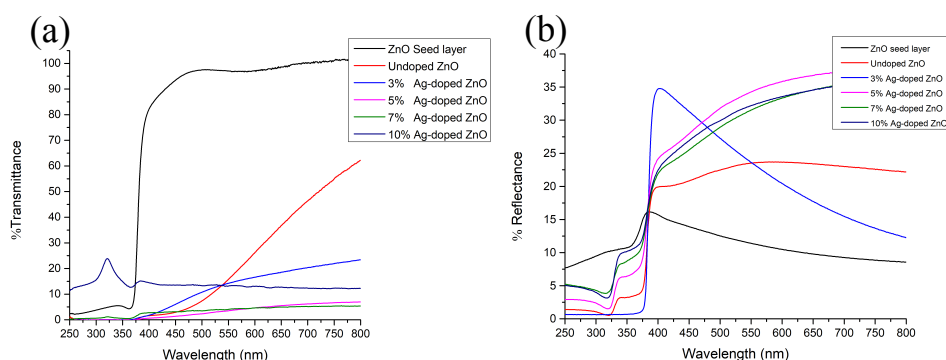


Fig. 3. Optical properties of ZnO seed layer, undoped and Ag-doped ZnO films (a) Transmittance spectra and (b) reflectance.

Fig. 2. shows the surface morphologies of all samples showing the ZnO nanoparticle with average size diameter 42 nm. After the hydrothermal process as shown in Fig. 2. (b) the ZnO nanorods were randomly grown in c-axis with size diameter approximately 120 nm. For the Ag-doped ZnO (Fig. 2. (c)-(f)) these results exhibited the deterioration of ZnO nanorod as Ag doping concentration was increased that is in accordance with the XRD results. The deterioration of ZnO nanorod may be due to the agglomeration of Ag particles acting as nanorod growth inhibitor.

The transmittance spectra of the samples are illustrated in Fig. 3. (a). This result exhibits high transparency (>90%) in visible region for ZnO seed layer. After hydrothermal process the undoped and 3 to 7% Ag-doped ZnO exhibit inferior transparency (<10%) in visible region. For 10% Ag-doped ZnO film, the result shows transparency peak at 325 nm. The reflectance technique was used instead of transmission measurement due to low transparency of film. The corresponding results indicate that the reflectance of undoped ZnO nanorod increases to 25% after hydrothermal process. As Ag-doping concentration was increased to 10mol%, the result showed highest reflectance of about 35% at 400 nm. The inferiority in transparency and reflectance may possible due to the structure of ZnO nanostructure grow on ZnO seeding layer that can obstruct the transmission of light and/or act as light scattering layer.

4. Conclusion

In summary, this work reports on the synthesis of Ag-doped ZnO films via hydrothermal process with bare ZnO thin film seeding layer prepared by sol-gel spin coating method. The physical structure exhibits the deterioration of ZnO nanorods after doped with silver. The XRD results show significant decrease in ZnO diffraction peak and increase in Ag diffraction peak indicating that the ZnO growth together with silver particle as composite material corresponding with morphology by FESEM. The optical properties show low transparency after hydrothermal process suggesting that ZnO nanostructure could act as light scattering and/or absorbing layer.

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References

- [1] S.B. Bashar, M. Suja, M. Morshed, F. Gao and J. Liu, An Sb-doped p-type ZnO nanowire based random laser diode, *Nanotechnology* 27 (2016) 065204-065210.
- [2] L. Zhu and W. Zeng, Room-temperature gas sensing of ZnO-based gas sensor: A review, *Sensor. Actuat. A-Phys.* 267 (2017) 242-261.
- [3] J. He, X. Zheng, X. Hong, W. Wang, Y. Cao, T. Chen, L. Kong, Y. Wu, Z. Wu and J. Kang, Enhanced field emission of ZnO nanowire arrays by the control of their structures, *Mater. Lett.* 216 (2018) 182-184.
- [4] Y.K. Kim, S.H. Hwang, S. Kim, H. Park and S.K. Lim, ZnO nanostructure electrodeposited on flexible conductive fabric: A flexible photo-sensor, *Sensor. Actuat. B-Chem.* 240 (2017) 1106-1113.
- [5] S. Rajaboopathi and S. Thambidurai, Green synthesis of seaweed surfactant based CdO-ZnO nanoparticles for better thermal and photocatalytic activity, *Curr. Appl. Phys.* 17 (2017) 1622-1638.
- [6] A. Vazinishayan, S. Yang, D.R. Lambada and Y. Wang, Mechanical behavior enhancement of ZnO nanowire by embedding different nanowires, *Results. Phys.* 9 (2018) 218-224.
- [7] Z.N. Urgessa, J.R. Botha, S.R. Tankio Djiokap, C. Coleman and S.Bhattacharyya, Patterned growth of ZnO nanorods by chemical bath deposition, *Physica B.* 535 (2018) 79-83.
- [8] N.H. Alvi, Wasied ul Hassan, B. Farooq, O. Nur and M. Willander, Influence of different growth environments on the luminescence properties of ZnO nanorods grown by the vapor-liquid-solid (VLS) method, *Mater. Lett.* 106 (2013) 158-163.
- [9] S. Kumar, P.D. Sahare and S. Kumar, Optimization of the CVD parameters for ZnO nanorods growth: Its photoluminescence and field emission properties, *Mater. Res. Bull.* 105 (2018) 237-245.
- [10] N. Kumaresan, K. Ramamurthi, R. Ramesh Babu, K. Sethuraman and S. Moorthy Babu, Hydrothermally grown ZnO nanoparticles for effective photocatalytic activity, *Appl. Surf. Sci.* 418 (2017) 138-146.
- [11] F.C. Liu, J.Y. Li, T.H. Chen, C.H. Chang, C.T. Lee, W.H. Hsiao, D.S. Liu, Effect of Silver Dopants on the ZnO Thin Films Prepared by a Radio Frequency Magnetron Co-Sputtering System, *Materials.* 10 (2017) 797.
- [12] Q. Hou, X. Jia, Z. Xu, C. Zhao and L. Qu, Effects of Li doping and point defect on the magnetism of ZnO, *Ceram. Int.* 44 (2018) 1376-1383.
- [13] D. Akcan, A. Gungor anv L. Arda, Structural and optical properties of Na-doped ZnO films, *J. Mol. Struct.* 1161 (2018) 299-305.
- [14] F. Xian, K. Miao, X. Bai, Y. Ji, F. Chen and X. Li, Characteraction of Ag-doped ZnO thin film synthesized by sol-gel method and its using in thin film solar cells, *Optik* 124 (2013) 4876-4879.
- [15] P. Murkute, S. Vatsa, H. Ghadi, S. Saha and S. Chakrabarti, Role of Pzn-2Vzn centre on the luminescence properties of phosphorus doped ZnO thin films by varying doping concentration, *J. Lumin.* 200 (2018) 120-125.

- [16] R. Nasser and H. Elhouichet, Production of acceptor complexes in sol-gel ZnO thin films by Sb doping, *J. Lumin.* 196 (2018) 11-19.
- [17] S. Khosravi-Gandomani, R. Yousefi, F. Jamali-Sheini and N.M. Huang, Optical and electrical properties of p-type Ag-doped ZnO nanostructures, *Ceram. Int.* 40 (2014) 7957–7963.