VNU Journal of Science: Mathematics – Physics, Vol. 33, No. 4 (2017) 67-72

Morphology, Phase and Photoluminescence of ZnS Microstructures Grown by Thermal Deposition at Different Temperature of Substrates

Nguyen Van Nghia[1,2,*], Nguyen Duy Hung[1]

[1]Advanced Institute of Science and Technology (AIST), Hanoi University of Science and Technology (HUST), 01 Dai Co Viet, Hanoi, Vietnam

[2]Thuy Loi University, 175 Tay Son, Dong Da, Hanoi, Vietnam

Received 19 July 2017
Revised 23 September 2017; Accepted 27 September 2017

Abstract: ZnS microstructures were prepared by thermal evaporating ZnS powder in Ar gas ambient at atmospheric pressure. The influent of temperature at the possitions puted the silica substrates on morphology, phase and photoluminescence of ZnS was investigated. It is clearly seen from the X-ray diffraction pattern that there is only ZnS phase with hexagonal structures at high temperature. Whereas, both ZnS and ZnO appear at lower temperature areas. The morphology of the microstructures change depending on substrate temperatures. The photoluminescence spectrum (PL) at room temperature shows that there is the shift from ultraviolet (UV) emission at high substrate temperature to strong blue emission at lower substrate temperature. The origin of these bands will be discussed in detail.

Keywords: ZnS, microstructures, photoluminescence.

1. Introduction

ZnS is considered as a versatile semiconductor material with exceptional physical and chemical properties. It has been extensively investigated due to its potential applications in optics, photoelectronics, sensors, catalysts and so on [1–3]. Recently, numerous efforts have been employed to control the fabrication of micro and nanostructured materials with various morphologies, since the novel properties and potential applications of nanomaterials depend sensitively on their shapes and sizes [4]. Due to the wide band gap (3.68 eV for cubic phase and 3.70 eV for hexagonal-wurtzite phase at room temperature, ZnS owns the largest band gap among A^{II}–B^{VI} semiconductors) and relatively large exciton binding energy (40 meV), ZnS is recognized as one of the most promising materials for a number of optoelectronic applications. Much effort has been devoted towards developing synthesis and characterization of one-dimensional ZnS nanostructures, such as nanowires,

---

[*] Corresponding author. Tel.: 84-984915472.
Email: nghiaaist@gmail.com

https//doi.org/ 10.25073/2588-1124/vnumap.4211

nanobelts, nanocables and nanotubes. Many techniques are used to synthesize ZnS such as thermal evaporation, hydrogen-assisted thermal evaporation, thermal chemical vapor deposition, hydrothermal synthesis route, solvothermal route, chemical vapor transport and condensation, electrodeposition-template, pulsed laser vaporization method [1, 5–10]. For thermal evaporation method, there are many parameters that affect the morphology as soon as physical properties of ZnS structures such as deposition temperature, deposition time, kind of carried gas, kind of substrate, catalysis and so on [11]. However, very few works concern to influent of substrate temperature on morphology, phase and photoluminescence property of ZnS structures [12]. In this work, we report the studied resutls on this topic.

2. Experimental

First, a pure silicon (100) wafer was subjected to ultrasonic cleaning in ethanol for 10 min. Then, the wafer was treated with dilute HF (1 wt %) for 20 s and with deionized water and subsequently blow dried with nitrogen. After that, the wafer is oxidized then covered with a layer of gold with 10 nm thickness. High-purity ZnS (0.5 g, Aldrich, 99.99%) powders, which acted as the precursor materials, were placed into an alumina boat and positioned at the constant temperature zone of the horizontal tube furnace. The silica substrates with size of 0.5 x 0.5 cm were placed in the low temperature zone. The first substrate was placed at about 10 cm downstream from the aluminum boat. The other substrates were placed after the first substrate, and the substrates were spaced about 3 cm apart. One haft of the quartz tube of aluminum boat, silicon substrates was setup outside the tube furnace until the furnace was heated to deposition temperature. After the quartz tube was pumped down to pressure of 1×10^{-3} Torr and heated to 600 ^{o}C, then the high-purity argon was discharged into and the mechanical rotary pump was turn off. The flow rates of Ar were controlled by a mass flow meter at 160 sccm. The temperature of the furnace was raised continually to growth temperature at a ramping rate of 10 ^{o}C/min. To control ZnS nanostructures, the substrate temperature is set up at 1100 ^{o}C. During synthesis the furnace temperature was maintained at growth temperature for 45 min, after that the furnace was allowed to cool naturally to room temperature. The morphology was examined by a field emission scanning electron microscopy (FESEM, JSM-7600F, Jeol). The phase structure, crystallinity and preferred orientation of as-synthesized ZnS were characterized by an X-ray diffraction (XRD) (X-ray Siemens D5000) using Cu Kα radiation (λ=1.5406 Å) operated at 40 mA tube current. The XRD patterns were collected in the range of $20° \le 2\theta \le 70°$ with a step of 0.03 ° and collection time for each data point was set at 4 seconds. The emission spectra were recorded on a spectrophotometer (FHR1000, Horiba Jobin Yvon).

3. Results and discussion

In order to study the morphology of the as-grown structures, FESEM were employed. Figure 1(a) shows a series FESEM images of the microstructures grown on Au thin film deposited silica substrates. Figure 1(b) describes the distribution of temperature in the horizontal furnace by the distance from the center of the furnace. S1, S2, S2 and S4 are samples which were placed at a distance of 10, 13, 16 and 19 cm from the center of the furnace corresponding to a temperature range of around 1060, 1040, 1010 and 980 ^{o}C, respectively. It is clear from the Fig. 1(a) that the blade with a length of about more than ten microns and a width of a few micrometers appeared at the highest temperature area in the experiment (S1 sample). Meanwhile, at lower temperature range, next to the S1 area (S2 sample), the structures turned into microbelts with a width of from one to several micrometers and several tens of micrometers in length. At the further erea (S3 sample), there were microbelts and microwires at the same time. The microbelts are less than two micrometres wide and the microwires are several hundred nanometers in diameter. At the lowest temperature area (S4), the materials were made clusters and there were some microwires quite straight with low density. Therefore, the structures have different morphology depending on the temperature of the substrate. There are two reasons for these. The first reason is that ZnS crystal grew along the two optimized directions at higher temperature. At the start of condensation the lower energy side surfaces are formed. At high temperatures, the mobility of ZnS vapour increases and the side surface area expands. At slightly lower temperature, ZnS crystal structures generally grow along single direction to have the lowest energy states. Secondly, thickness of catalyst can determine the size of the structures. The used silica substrates were Au-coated. Hence, the mismatch between the lattice constants of Au and Si can cause the formation of nanometer scale Au islands with temperature. At high temperatures, the sizes of islands can be larger than those of that formed at lower temperatures due to the increase in the kinetic energy of Au atoms and these small islands can coalesce with each other. This is reason why ribbon-like structures form. At the lower temperatures, structures generally grow along single direction to have the lowest energy states [12].

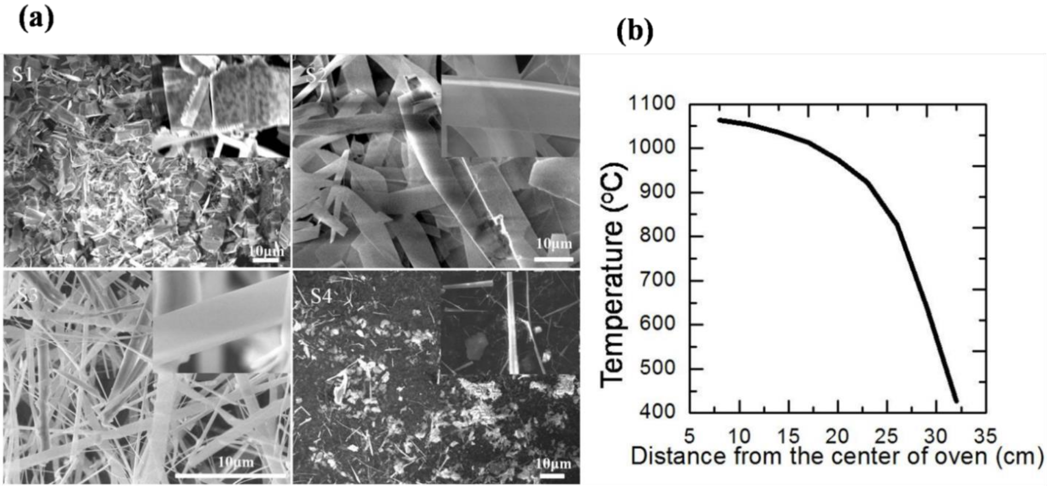

Figure 1. FESEM images of the samples at different possitions (a)
and distribution of temperature in the furnace (b).

Phase of the microstructures is studied through X-ray diffraction pattern. Figure 2 shows XRD patterns of all the samples. It is clear from the figure that all of the samples have the peaks representing the wurtzite phase of ZnS, which matches well in the JCPDS of No: 36-1450 with a good crystalline quality. In detail, at the regions having higher temperature (S1 and S2 samples), there is only phase of ZnS with the highest intensity peak corresponding to (100) plane. However, at the lower temperature region (S3 sample), some peaks representing the phase of ZnO appear with low intensity beside the peaks corresponding to ZnS phase. At the lowest temperature region (S4 sample), the peaks corresponding to ZnO phase are dominant, and the peak corresponding to (002) plane of ZnO phase has the highest intensity. From the analysis of XRD pattern, it can be seen that the higher substrate temperature, the more dominant ZnS phase. In other word, the lower substrate temperature, the more dominant ZnO phase. At output of the quartz tube, there are still oxygen in the air because it is pulled away from the vacuum pump before inserting in the water. Oxygen maybe interacted with ZnS vapor to form ZnO phase at low temperature region. In constract, at high temperature region, the Ar gas follow maybe prevented the combination between oxygen and ZnS vapor.

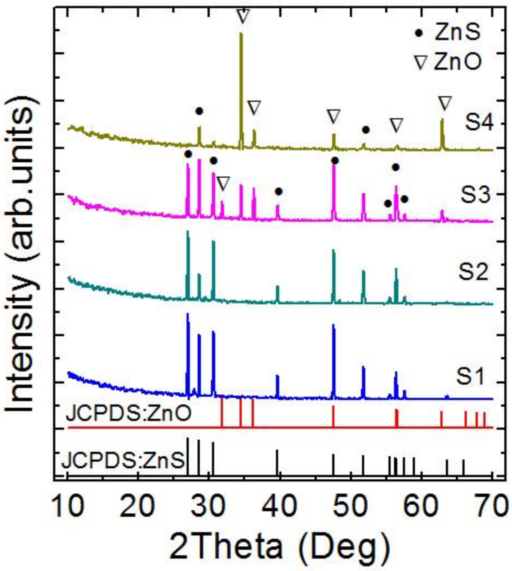

Figure 2. X RD pattern of the samples.

In order to study optical property of the structures, the photoluminescence emission was performed at room temperature with excited wavelength of 347 nm. This excitation wavelength has been chosen by taking into account the excitation spectra, which are shown in Figure 4. Figure 3 shows the PL spectra of all the samples. From the figure, it can be seen that there are two emission bands, one at utraviolet (UV) and the other at visible region. For S1 sample, both of the bands exist with low intensity, and the intensity of the UV band is higher than that at visible band. Whereas there is only the UV band in the emission spectrum of S2 sample. However, at lower temperature region (S3), the visible band at around 492 nm appears and dominates in comparision with UV band. Furthermore, the blue band at about 490 nm is very strong and dominates totally at the lowest substrate temperature region in the experiment. The UV band with the center at around 356 nm is due to band to band transition of ZnS, ZnO or ZnOS [13, 14], and this band only appears when the crystal has perfect quality [11, 15]. The visible blue band peaking at around 490 nm and 492 nm may come from radiative centers of ZnS and ZnO such as S vacancies or isolated Zn vacancies [1, 16, 17]. Therefore, it could be received from our experiment that at the substrate temperature of around 1040 ^{o}C (S2 sample), we can gain the best quality of the ZnS crystal.

To confirm again about the origin of the UV emission band, PL excitation spectra of the samples were recorded by monitoring at the emission wavelength of 490 nm and shown Figure 4. For all of the samples, the spectra show that the microstructures are absorbed strongly at around 347 nm to 375 nm which are corresponded with the band to band transitions of ZnS, ZnO or ZnOS [18]. In detail, PL and PLE spectra of S4 sample at room temperature were depicted at the same time in photon energy unit (eV) (Figure 5). The PLE spectrum measured at room temperature exhibits a broad peak from 3.31 eV to 3.57 eV. Comparing the PLE spectra with the PL spectra measured at the same temperatures (Figure 5), the peak at 3.72 eV in the PL spectrum may be originated from free exciton emission [18]. The peaks at 3.46 eV, 3.29 eV and 3.13 eV in the PL spectrum may be related to lattice defects [18].

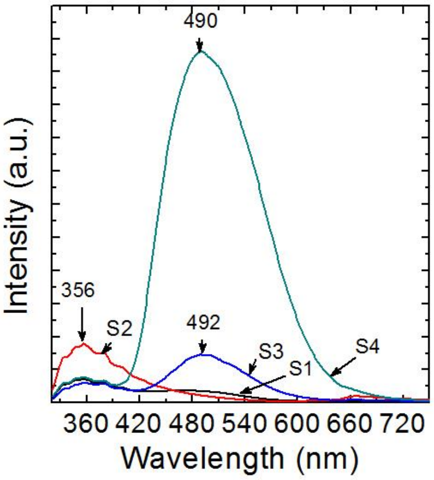

Figure 3. PL spectra of the samples.

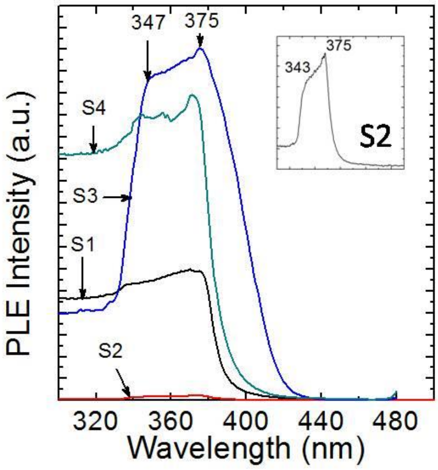

Figure 4. PLE spectra of the samples.

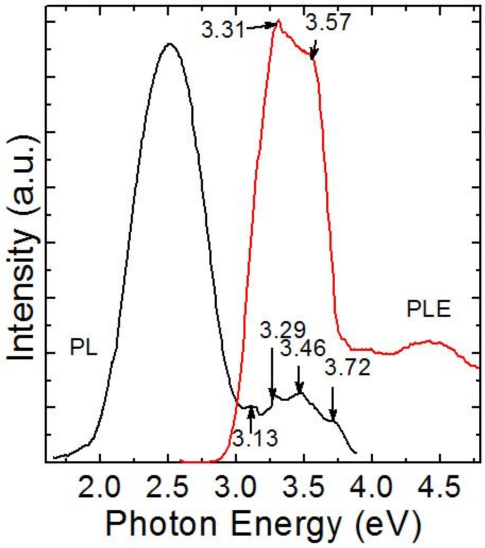

Figure 5. PL and PLE spectra of S4 sample at room temperature.

4. Conclusion

In conclusion, we have synthesized the microstructures from ZnS powder by the thermal evaporation method and studied the influent of substrates on morphology, phase and photoluminescence of the structures. FESEM showed that it can be received different structures at the different substrate temperatures. XRD illustrated that the ZnS nanostructures have a wurtzite structure and there was ZnO phase beside ZnS phase at the low temperature areas. The UV and blue emissions in the PL spectra of the structures were changed depending on the structure of ZnS crystal, it means they depend on substrate temperatures.

References

[1] G. H. Yue, P. X. Yan, D. Yan, X. Y. Fan, M. X. Wang, D. M. Qu, and J. Z. Liu, Hydrothermal synthesis of single-crystal ZnS nanowires, Appl. Phys. A Mater. Sci. Process., vol. 84, no. 4, (2006) 409.

[2] W. W. G. Becker and A. A. J. Bard, Photoluminescence and photoinduced oxygen adsorption of colloidal zinc sulfide dispersions, J. Phys. Chem., vol. 78712, no. 24, (1983) 4888.

[3] Alireza Goudarzi, Ghaffar Motedayen Aval, Sung Soo Park, Myeon-Cheon Choi, Reza Sahraei, M. Habib Ullah, Armen Avane, and Chang-Sik Ha, Low-Temperature Growth of Nanocrystalline Mn-Doped ZnS Thin Films Prepared by Chemical Bath Deposition and Optical Properties, Chem. Mater., vol. 21, no. 12, (2009) 2375.

[4] Tran Thi Quynh Hoa, Ngo Duc The, Stephen McVitie, Nguyen Hoang Nam, Le Van Vu, Ta Dinh Canh, and Nguyen Ngoc Long, Optical properties of Mn-doped ZnS semiconductor nanoclusters synthesized by a hydrothermal process, Opt. Mater. (Amst)., vol. 33, no. 3, (2011) pp. 308.

[5] Y. Jiang, X. M. Meng, J. Liu, Z. Y. Xie, C. S. Lee, and S. T. Lee, Hydrogen-assisted thermal evaporation synthesis of ZnS nanoribbons on a large scale, Adv. Mater., vol. 15, no. 4, (2003) 323.

[6] Q. Li and C. Wang, Fabrication of Zn/ZnS nanocable heterostructures by thermal reduction/ sulfidation, Appl. Phys. Lett., vol. 82, no. 9, (3003) 1398.

[7] J. S. McCloy and B. G. Potter, Photoluminescence in Chemical Vapor Deposited ZnS: Insight into electronic defects, Opt. Mater. Express, vol. 3, no. 9, (2013) 1273.

[8] L. Chai, J. Du, S. Xiong, H. Li, Y. Zhu, and Y. Qian, Synthesis of wurtzite ZnS nanowire bundles using a solvothermal technique, J. Phys. Chem. C, vol. 111, no. 34, (2007) 12658.

[9] H. Y. Sun, X. H. Li, W. Li, F. Li, B. T. Liu, and X. Y. Zhang, Low-temperature synthesis of wurtzite ZnS single-crystal nanowire arrays, Nanotechnology, vol. 18, no. 11, (2007) 115604.

[10] Qihua Xiong, G. Chen, J. D. Acord, X. Liu, J. J. Zengel, H. R. Gutierrez, J. M. Redwing, L. C. Lew Yan Voon, B. Lassen, and P. C. Eklund, Optical properties of rectangular cross-sectional ZnS nanowires, Nano Lett., vol. 4, no. 9, (2004) 1663.

[11] Xiaosheng Fang, Tianyou Zhai, Ujjal K. Gautamb, Liang Li, Limin Wu a, Yoshio Bando, and Dmitri Golberg, ZnS nanostructures: From synthesis to applications, Prog. Mater. Sci., vol. 56, no. 2, (2011) 175.

[12] NESLIHAN ÜZAR and M ÇETIN ARIKAN, Synthesis and investigation of optical properties of ZnS nanostructures, Bull. Mater. Sci., Vol. 34, No. 2, (2011) 287.

[13] D. Q. Trung, N. Tu, N. D. Hung, and P. T. Huy, Probing the origin of green emission in 1D ZnS nanostructures, J. Lumin., vol. 169, (2016) 165.

[14] N. Kumbhojkar, V. V. Nikesh, A. Kshirsagar, and S. Mahamuni, Photophysical properties of ZnS nanoclusters, J. Appl. Phys., vol. 88, no. 11, (2000) 6260.

[15] Yongqin Changa, Mingwei Wangb, Xihong Chenc, Saili Ni, Weijing Qianga, Field emission and photoluminescence characteristics of ZnS nanowires via vapor phase growth, Solid State Communications 142 (2007) 295

[16] H. Tang, B. J. Kwon, J. Kim, and J. Y. Park, Growth modes of ZnS nanostructures on the different substrates, J. Phys. Chem. C, vol. 114, no. 49, (2010) 21366.

[17] T. Mitsui, N. Yamamoto, T. Tadokoro, and S. Ohta, Cathodoluminescence image of defects and luminescence centers in ZnS/GaAs (100), J. Appl. Phys., vol. 80, no. 12, (1996) 6972.

[18] Ngo Xuan Dai, Do Thanh Long, Nguyen Ngoc Long, and Nguyen Thi Thuc Hien, Fabrication and Photoluminescence Properties of ZnS Nanoribbons and Nanowires, Journal of the Korean Physical Society, vol. 52, no. 5, (2008) 1530–1533.