A simple route to ZnS hollow micro-spheres

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Novel ZnS hollow micro-spheres are synthesized via a simple vapor-phase transport route. XRD pattern indicates as-prepared sample is hexagonal phase. SEM observed the hollow micro-spheres have the diameters ranging from 5 to 10 μm with a shell thickness of about 60 nm. UV–vis and PL spectra recorded the high quality optical properties of the sample. The formation and growth mechanism of ZnS hollow micro-spheres, as well as the optical properties,were also analyzed in details.The present method may be applicable to some other compound semiconductors and may open a practical route to yield hollow micro-spheres.

(Received February 23, 2011; accepted March 16, 2011)

Keywords: ZnS;chemical vapor deposition(CVD);Crystal growth; micro-spheres; microstructure

1. Introduction

ZnS is one of the most attractive semiconductors that has been used as base material for cathode-ray tube luminescent materials[1], as efficient phosphors in flat-panel displays, in thin-film electroluminescent devices, infrared windows and the new mechano-optic applications.It has a wide band gap of 3.5–3.7 and 3.7–3.8 eV for zinc blende and wurtzite ZnS respectively. It can crystallize in two allotropic forms: a cubic form (c-ZnS) with sphalerite structure and a hexagonal form (h-ZnS) with wurtzite structure. Also, the exciton-binding energy (38 meV) is higher than the room-temperature thermal energy (25 meV), which can provide excitonic emission at room temperature. These features have led us to explore this material for many device applications[2-4]. It has been well accepted that a good knowledge of surface morphology and structural details of thematerials is essential for their application. Recently, low dimensional ZnS hollow nanostructures are receiving increasing attention owing to their novel electronic and optical properties resulting from high porosity and large surface area[5-7].

Conventionally, inorganic hollow spheres are prepared by two-step templating routes using suitable sacrificial templates[8-9].However, in most cases, the pure product was obtained only after the complete removal of the templates, which makes the experiment more complicated with some awful effects on the morphology and properties of the final product[4]. So, it remains a challenge to develop simple methods for the fabrication of uniform hollow nano- and microspheres of chalcogenide semiconductors with tunable size and shell thickness.

In the present study, using Zn droplets as self-sacrificed templates,we succeeded in yielding the ZnS hollow micro-spheres by a vapor-phase transport route. and the shell thickness of the hollow nanostructures obtained was relatively homogeneous. To the knowledge of the authors, there is no report of ZnS hollow nanostructures via a vapor-phase transport route by employing the liquid droplet as the initial materials, The hollow structures obtained may have important applications in optoelectronic nanodevices.

2. Experimental

ZnS hollow micro-spheres has been achieved by a simple chemical vapor deposition (CVD) process using S powers onto Si (100) substrates, under controlled conditions. a horizontal high-temperature tube furnace was used as evaporation apparatus, and the powders was placed at the furnace center of the alumina tube. Several silicon plates were first etched by hydrofluoric acid (0.2M) for 10 min, A thin Zn layer with thickness of about 5nm was sputtered onto the silicon plates surface and then followed by a annealing at 200℃ for 45min. These silicon plates were used as substrates and placed at downstream positions of the source materials. The following parameters were adopted in our experiment: weight of the S powders, 2g; evaporation temperature, 700℃; and argon flow rate, 100 standard cubic centimeters per minute (sccm). After the tube was evacuated to 2×10^{-2}Toor,the synthesis was conducted at 700℃ for 30 min with vacuum pressure 200 Toor.In the synthesizing process, the substrate temperature was typically in the range of 700-750℃. After the furnace had slowly cooled to room temperature, the substrates were removed from the tube and the products was rinsed several times with distilled water and absolute alcohol. The product was dried at 50°C for 10h.

The X-ray diffractometry (XRD) for the crystal structure of the products was carried out in a Bruker D8 advance diffractometer equipped with Ni-filtered Cu Kα radiation (λ=1.5418Å). The morphology of samples was observed using a Hitachi S-3400N scanning electron microscope (SEM) .The composition of Zn and S in complexes was detected on an Atom scan Advantage inductively coupled plasma atomic emission spectrometer (ICP-AES), UV-vis absorption spectrum was measured on a 760CRT double beam UV-vis spectrophotometer. Photoluminescence (PL) spectrum was recorded on an Edinburgh FLS920 luminescence spectrophotometer. The Raman spectra were obtained on an inVia Reflex laser Raman spectrometer using excitement wavelength of 532 nm.

3. Results and discussion

The XRD pattern of the products shown in Fig. 1 reveals that all the diffraction peaks can be readily indexed as wurtzite ZnS in good agreement with the literature (JCPDS card no. 36-1450, a =3.820Å, c=6.257Å). The sharp highest (002) peak indicates that the ZnS hollow micro-spheres with a wurtzite structure grow priority along the [002] direction. No diffraction peaks from other crystalline forms are detected, which indicates a high purity and well crystallinity of these hollow micro-spheres.

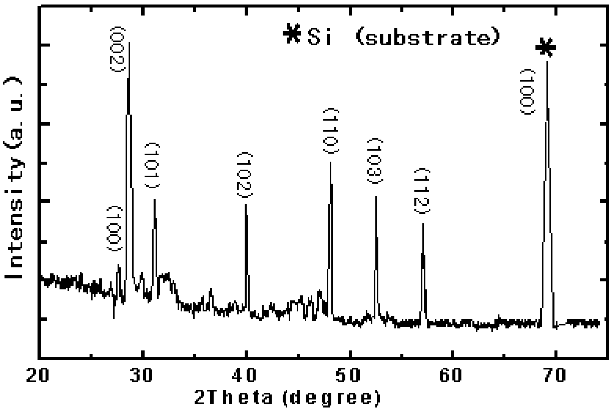

Fig. 1. XRD spectra of ZnS hollow micro-spheres

Fig. 2(a) presents the SEM images of the as-synthesized product. It is obvious that ZnS hollow micro-spheres show the regular hemisphere with diameters of about 1~!10μm . Figure 2(b) shows the bottom part of the micro-spheres after the samples removed, we can see that no products can be formed in the region without etch pits, demonstrating that etch pits is necessary to synthesize the products in our experiments. The broken hollow micro-spheres shown in Figure 2 (c) confirmed the hollow structures. It is interesting to note that the shell thickness of the hollow micro-sphere yielded is relatively homogeneous. From the figure 2 (d), it may be well observed that the surfaces of hollow micro-spheres are smooth.

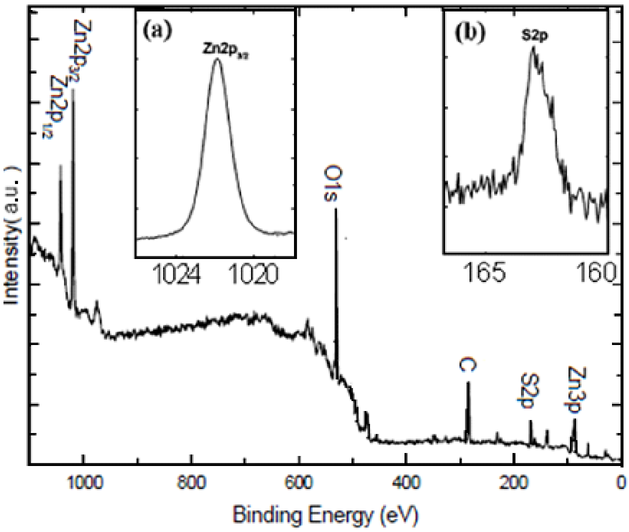

Fig. 2. (a) SEM images of the hollow micro-sphere, (b) SEM image after the removal of samples,(c) a broken micro-sphere show obvious hollow structures, (d) the surfaces of the ZnS hollow micro-spheres.

XPS is also used to determine the composition of the ZnS hollow micro-spheres. Figure 3 shows the whole scanning spectrum. The peaks located at 1025 and 162.5 eV correspond to the electronic states of Zn2p3/2, and S2p, respectively [10]. The fine XPS spectra of Zn 2p3/2 and S2p are also displayed in insert Figure (a) and Figure (b) of Fig. 3, respectively. The atom ratio quantified from the peak areas of Zn/S is 28:25, which is close to the expected values.

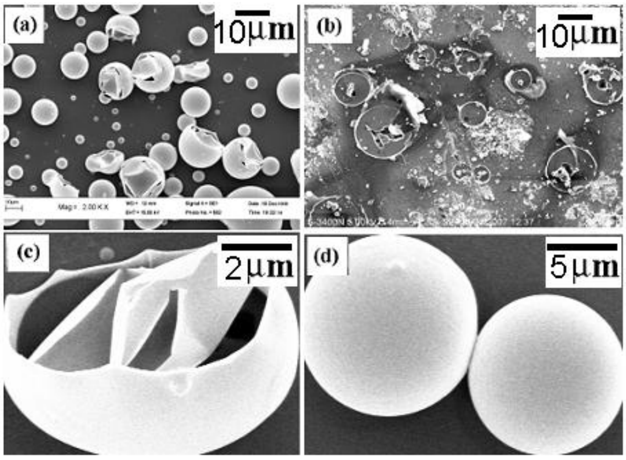

Fig. 3. XPS spectra of ZnS hollow micro-spheres

The optical properties of the ZnS hollow micro-spheres have been studied by UV-vis and PL to further assess their quality. It is worth mentioning that the ZnS microspheres exhibit high quality optical properties. The room temperature UV–vis absorption of the hollow micro-spheres shows a strong absorption peak about 335 nm, corresponding to a band gap of 3.7 eV, (see Fig. 4), indicating a bulk like nature of the hollow micro-spheres[11]. This is in good agreement with the results obtained from the XRD and SEM.

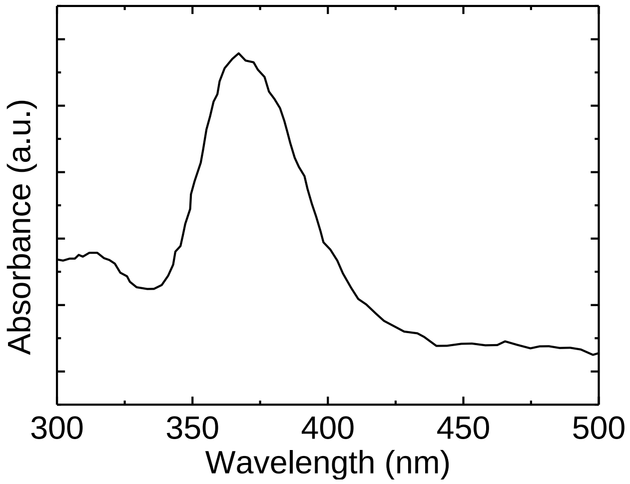

Fig. 4. UV-vis absorption spectrum of ZnS hollow micro-spheres.

The room-temperature PL spectrum of the ZnS nanowires was obtained with 300 nm excitation. The spectrum in Fig. 5 shows two strong emission peaks at 395 nm, the other at 455 nm. According to Hu et al.'s report [12] the blue emission from the ZnS nanobelts at around 400 nm is due to point defects such as the sulfur interstitials or zinc vacancies in the nanobelts, while the emission band at 455 nm may be originated from surface states.

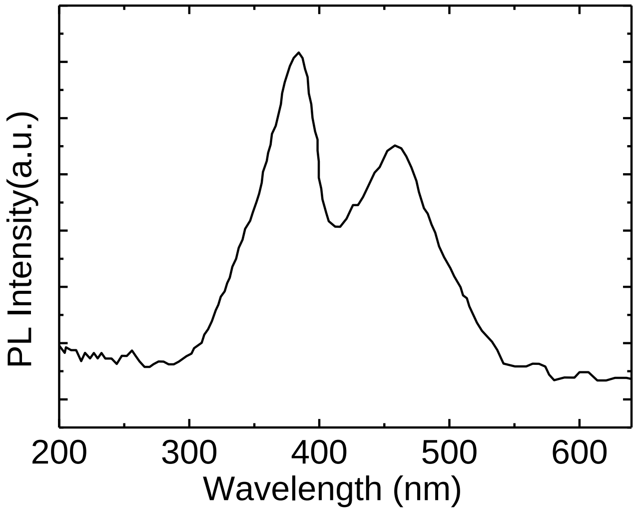

Fig. 5. Photoluminescence emission spectrum of ZnS hollow micro-spheres

Fig. 6 shows the Raman spectrum of the ZnS hollow micro-spheres using excitation wavelength of 532 nm. Two strong peaks, locating at 252 cm−1 and 350 cm−1, can be visible in the spectrum. According to the related data [13], the former peak can be assigned to mode and the latter peak can be assigned to LO mode of ZnS. It is similar to the results of ZnS quantum crystallites [14].

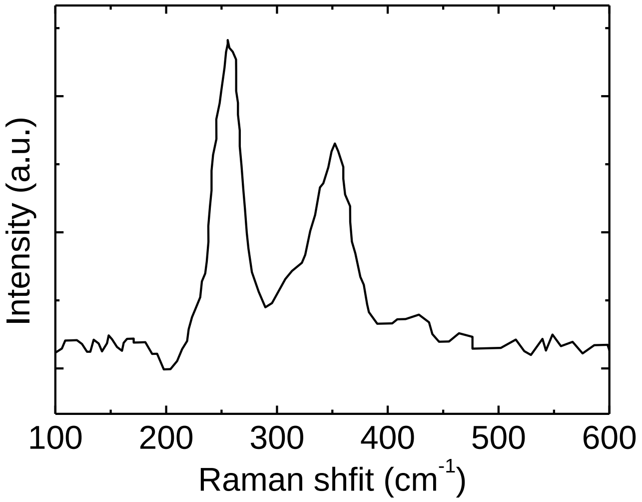

Fig. 6. Raman spectrum of the ZnS hollow micro-spheres.

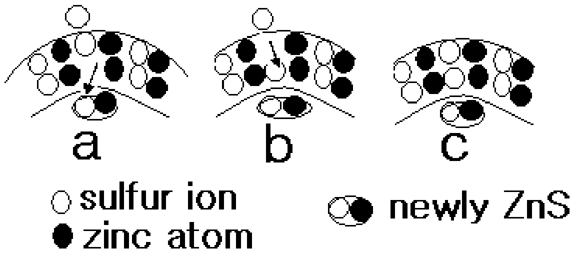

Fig. 7.Schematic illustration of the the formation processes of ZnS hollow micro-spheres.

Based on the morphologies of ZnS microspheres, it is supposed that the ZnS hollow micro-spheres can be produced by employing the zn doplets as self-sacrificed templates.Vapor-phase S reacts with zinc continuously under suitable conditions.Consequently, the ZnS shells form on the surface of Zn droplets. Once the ZnS shell forms, it is favorable for the yielding hollow structure in the Zn/S system. On the interface of the liquid–solid (zn doplets-ZnS shell), a sulfur vacancy is formed in the inner layer of ZnS film After a zinc atom reacts with a sulfur ion which dissolve from the ZnS shells(Fig. 7(a)), and the vacancy will be filled by neighboring sulfide ion soon(Fig. 7(b)), which means that sulfide vacancies diffuse outward the ZnS film,and S ions diffuse inward the film.This mutual diffusion process facilitates the formation of newly ZnS shell at the interface of the Zn core and the ZnS shell (Fig. 7(c)).

4. Conclusions

Using Zn droplets as sacrificing templates, we succeeded in yielding the ZnS hollow micro-spheres, which have homogeneous thickness, by a vapor-phase transport route .The obtained hollow structures may have important applications in novel optoelectronic devices. Moreover, the approach presented here can be extended to the synthesis of hollow structures of other binary or tertiary compounds, and thus should be of wide interest.

Acknowledgements

The work is supported by Shandong Provincial Foundation of National Science (No. 2005ZRB01602) and Shandong Provincial Supported Foundation of Excellent Young Scientist (No. 2006BSB01302).

References

[1] P. Jiang, J. F. Bertone, V. L. Colvin, Science **291**, 453 (2001).

[2] R. Rengarajan, P. Jiang, V. Colvin, D. Mittleman, Appl. Phys. Lett. **77**, 3517 (2000).

[3] C. Leiggener, G. Calzaferri, Chem. Eur. J. **11**, 7191 (2005).

[4] K. Ueda, S. Hirose, H. Kawazoe, H. Hosono, Chem. Mater. **13**, 1880 (2001).

[5] X. Fan, X. M. Meng, X. H. Zhang, W. S. Shi, W. J. Zhang, J. A. Zapien, C.S.Lee, S. T. Lee, Angew. Chem. Int. Ed. **45**, 2568 (2006).

[6] J. S. Hu, L. L. Ren, Y. G. Guo, H. P. Liang, A. M. Cao, L. J. Wan, C.L. Bai, Angew. Chem. Int. Ed. **44**, 1269 (2005).

[7] H.M. Yang, C. H. Huang, X. H. Su, A. D. Tang, J. Alloys Compd. **402**, 274 (2005).

[8] H.S. Zhang,Y. Zhang, S. Pan, G.P. Li, J.G. Hou, Nanotechnology **15**, 945 (2004).

[9] Z.W. Wang, L. L. Daemen, Y. S. Zhao, C.S. Zha, R.T. Downs, X.D. Wang, Z.L. Wang, R. J. Hemiey, Nat. Mater. **4**, 922 (2005).

[10] Y. C. Zhu, Y.S. Bando, D.F. Xue, D. Golberg, Adv. Mater. **16**, 831 (2004).

[11] S. W. Kim, M. Kim,W.Y. Lee, T. Hyeon, J. Am. Chem. Soc. **124**, 7642 (2002).

[12] P. Hu,.Y. Liu,. Fu, L.; Cao, L.; Zhu, D. J Phys. Chem. B,**108**, 936 (2004).

[13] O. Brafman, S. S.Mitra, Physical Review, **171**, 931 (1968).

[14] M. Abdulkhadar, B.Thomas, Nanostruct. Mater. **5**, 289 (1995).

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