Materials Science in Semiconductor Processing 16 (2013) 1779–1783

Contents lists available at SciVerse ScienceDirect

Materials Science in Semiconductor Processing

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

Facile synthesis and photocatalytic activity of hollow micro-spherical zinc sulfide caps

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ARTICLE INFO

Available online 24 July 2013

Keywords:
ZnS
Physical vapor deposition
Crystal growth
Photocatalytic activity

ABSTRACT

Novel zinc sulfide (ZnS) hollow micro-spherical caps were produced via a facile thermal evaporation of ZnS and Zn powders without any types of templates. The samples are characterized by X-ray diffraction, scanning electron microscopy, Raman spectra and fluorescence spectra. The results demonstrate that the synthesized ZnS nanoparticles are hollow micro-spherical caps with the diameters ranging from 4 to 8 μm and a relatively homogeneous shell thickness of about 40 nm. Furthermore, the formation mechanism of ZnS hollow micro-spherical caps was also suggested. Moreover, the photocatalysis test shows that the ZnS hollow micro-spherical caps exhibit a high photocatalytic activity, thereby implying that the surface of ZnS can promote the separation of photogenerated electron–hole pairs and enhance the photocatalytic activity.

1. Introduction

Zinc sulfide (ZnS) is an important II–VI semiconductor with wide band gap energy of 3.7 eV at 300 K; it has a wide range of applications due to its interesting electronic and optical properties such as in the fields of flat-panel display, luminescent devices, infrared windows, light emitting diodes, solar cells, ion-selective sensors, mode-locking in lasers, secondary batteries, and catalysis [1–4]. However, to bring its new types of applications and enhance the performance of currently existing photoelectric devices, research on modulating its existing optical properties is necessary.

It has been well accepted that size and morphology of nanomaterials are crucial issues for their application and great efforts have been devoted to achieve size and morphology controllable syntheses of semiconductor nanocrystals [5]. Among various specific shapes, hollow micro-structure is a representative and has wide potential application in many fields, such as photonic crystals, fillers, catalysts and delivery vehicle systems [6]. So, the facile synthesis of hollow micro-structures has attracted considerable attention. Up to now, several methods, including the aqueous solution growth method [7], metal-organic chemical vapor deposition [8,9], thermal evaporation [10], the hydrothermal method [11,12] etc., have been employed to synthesize ZnS hollow structures. However, it can be seen that such methods usually require strict conditions or somewhat complicated manipulation, meaning that the shape-controlled synthesis of hollow-structured semiconductors needs to be further studied.

In this paper, we have successfully synthesized ZnS hollow micro-spherical caps via a simple physical vapor deposition method. Furthermore, the information of the samples was investigated using X-ray diffraction (XRD), scanning electron microscopy (SEM), and photoluminescence spectroscopy, which were carried out in an attempt to understand well the synthesized sample. It is interesting to find that ZnS hollow micro-structure shows the regular

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http://dx.doi.org/10.1016/j.mssp.2013.07.003

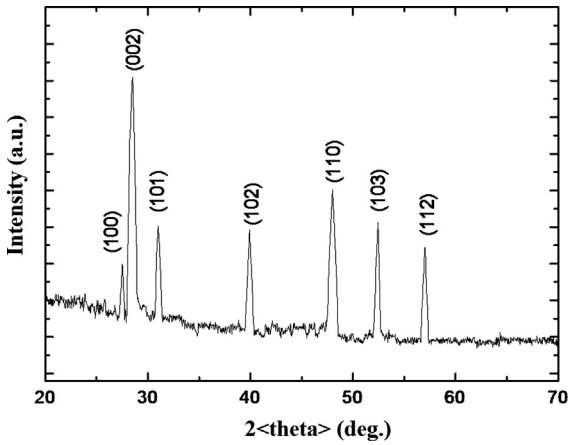

Fig. 1. XRD pattern of ZnS hollow micro-spherical caps.

micro-spherical caps and relatively homogeneous shell thickness. Moreover, the photocatalytic activity of ZnS hollow micro-spherical caps was also displayed. To our knowledge, such a micro-structure of ZnS has not been reported before.

2. Experimental sections

2.1. Materials

Zinc sulfide (ZnS) was obtained from Shanghai Chem. Co. Zinc (Zn) and P-type (100) silicon (Si) wafer were obtained from Aldrich. Ultra-pure water ($>17\ M\Omega\ cm^{-1}$) from Milli-Q water system was used throughout the experiment. All the chemicals were of analytical grade and used as received without further purification.

2.2. Synthesis of ZnS hollow micro-spherical caps

ZnS and Zn powders (molar ratio of 3:1) were placed on a quartz boat that was inserted in the center of a horizontal furnace. P-type (100) silicon (Si) wafer was etched using hydrofluoric acid and cleaned using ultra-pure water and ethanol. The cleaned Si wafer was placed on a quartz boat adjacent to ZnS source at a distance of about 5–10 mm. The following parameters were adopted in our experiment: weight of the ZnS and Zn powders, 4 g; evaporation temperature, 800 °C; the rate of temperature rise, 15 °C min^{-1} and argon flow rate, 100 standard cubic centimeters per minute (sccm). Before the evaporation occurred, the reaction chamber was cleaned three times using argon gas flow, to eliminate any remaining oxygen. After the tube was evacuated to 2×10^{-2} Torr, the synthesis was conducted at 800 °C for 30 min with vacuum pressure 200 Torr. Followed by the reaction, the quartz tube was naturally cooled to room temperature maintaining the gas flow. Many white colored products appeared on the Si substrate as well as on the inner wall of the quartz tube.

2.3. Characterization

The crystal structure of the products was identified by X-ray diffraction (XRD, Bruker D8 advance) with Cu Kα radiation. Scanning electron microscopy (SEM) images of the products were obtained using a scanning electron microscope (SEM, Hitachi S-3400N). 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. For photocatalytic measurement, 10 mg of each catalyst was suspended in 200 mL of methyl orange aqueous solution (20 ppm), and then the mixture was put into quartz tubes and agitated for about 3 h in the absence of light to attain equilibrium adsorption on the catalyst surface. Ultraviolet (UV) irradiation was carried out by using a 500 W fluorescent Hg-lamp which has maximum emission at 350 nm. The distance between the light and the reaction tube was 5 cm. After a given irradiation time, about 3.5 mL of the mixture was withdrawn and the catalysts were separated through centrifugation. The photocatalytic degradation process was monitored by a UV–vis spectrophotometer (UV-1201) to measure the absorption of methyl orange at the wavelength of 463 nm.

3. Results and discussion

3.1. The XRD patterns

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 reported literature (JCPDS Card no. 36-1450, $a=3.820$ Å, $c=6.257$ Å) [13]. The sharp highest (002) peak indicates that the ZnS hollow micro-spherical caps with a wurtzite structure grow priorly along the [002] direction. No diffraction peaks from other crystalline forms are detected, which indicates a high purity and well crystallinity of these ZnS hollow micro-spherical caps.

3.2. The morphology of the ZnS hollow micro-spherical caps

The detail morphology of the ZnS hollow micro-spherical caps is shown in Fig. 2. From Fig. 2(a), it can be seen that ZnS nanoparticles with hollow micro-structure show the regular micro-spherical caps with diameters of about 4–8 μm. Fig. 2(b) shows the bottom part of the micro-structures after the samples are removed; we can see that no products can be formed in the region without etch pits; this means that etch pits are necessary to synthesize the products in our experiments. The broken hollow micro-structure shown in Fig. 2(c) further confirmed the hollow structures. It is interesting to note that various micro-spherical caps show a good uniformity, and the shell thickness of the micro-spherical caps yielded is relatively homogeneous although the starting ZnS shells have a variable thickness, which should be because the vapor pressure has the same effects on all direction of the ZnS shells. From Fig. 2(d), it may be well observed that ZnS hollow micro-spherical caps have a smooth surface morphology.