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Low temperature synthesis, characterization and photoluminescence study of plate-like ZnS

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ABSTRACT

The plate-like ZnS microstucture has been prepared at low temperature in high yield *via* catalyst-free chemical precipitation method without using any surfactant, organic solvent or capping agent. The method is a highly reproducible route which could be applicable for preparation of other semiconductors. The as-synthesized ZnS belongs to cubic structure. The formation of plate-like microstructure, with the grain size of about 80–200 nm (from SEM), is possibly due to assembling of many crytallites (crystallite size of 2.7–3.4 nm, from XRD). FT-IR spectrum indicates stability of ZnS without oxidizing to ZnO during the preparation process. The blue emission in photoluminescence (PL) spectrum is quite broad over the range of 420–500 nm. This may originate from the radiative combination due to surface defect states in the ZnS microstructure.

1. Introduction

Zinc sulfide (ZnS), one of the important II–VI semiconductors with large direct band gap of 3.66 eV, has been widely studied due to its potential applications in optoelectronic and luminescent devices [1–2]. The structure, size, size distribution, and morphology influence the properties of ZnS. These parameters strongly depend on preparation method and also experimental conditions. To synthesize ZnS semiconductor, various methods have been used, including the solvothermal and hydrothermal routes [1,3–6], the solid-state method [7], chemical vapor deposition (CVD) method [8], the liquid crystal-template [9], ultrasonication method [10], simple thermal evaporation method [11], and the high temperature thermolysis of organic precursor route [12]. Moreover, in some cases the capping agents such as thioglycolic acid (TGA), mercaptoethanol, L-cysteine, polyethylene glycol (PEG), and polyvinylpyrrolidone (PVP) have also been used [1–3,5,7,13]. Among these methods, chemical precipitation method has been received much considerable attention due to the advantages of low cost, good yield, and high potential for a large scale production [2,13–16].

In this paper, we report the low temperature synthesis of plate-like ZnS microstucture *via* chemical precipitation method without using any surfactant or organic solvent. By controlling pH and molar ratio of Zn^{2+}/S^{2-} during preparation process, the uniform morphology of ZnS could be obtained. The process can be applied for preparation of other II–VI group semiconductors. In addition, thermal and optical properties of the ZnS semiconductor have been investigated. The semiconductor remains stable during the preparation process and shows blue emission in photoluminescence (PL) spectrum over the range of 420–500 nm due to surface defect states in the microstructure. Considering the simplicity of the procedure and the promising properties of the ZnS, the method is likely to be of interest to fabricate semiconductor with high potential applications in optoelectronic and luminescent devices.

2. Experimental sections

All analytical (AR) grade chemicals were used in this work without further purification. The de-ionized water was used throughout the experiment. In a typical synthesis, 0.01 M zinc nitrate hexahydrate [$Zn(NO_3)_2 \cdot 6H_2O$] aqueous solution was prepared first, followed by addition of sodium hydroxide solution to adjust the pH of the solution to about 10. Then, an aqueous solution of 0.01 M sodium sulfide (Na_2S) was slowly dropped into the above solution under continuous stirring. The mixture turned milky and was further stirred at room temperature for a few hrs. The white precipitate was collected by centrifugation. The sample was washed with ethanol and water alternately for 3–4 times, then dried at 80 °C for 6 h and, finally ground into powder for further analysis.

The powder X-ray diffraction (XRD) pattern was recorded on a Bruker D8 ADVANCE diffractomer using monochromatic CuKα

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radiation. Scanning Electron Microscopy (SEM) was carried out using LEO 1450VP, UK. The Fourier transform infrared (FT-IR) spectrum was monitored on a Perkin Elmer Spectrum One FT-IR spectrophotometer using a KBr pellet. The UV–vis diffused reflectance spectrum was investigated on a Shimazu UV-vis-NIR-3101PC scanning spectrophotometer. Themal analysis was carried out by recording the thermogravimetric (TG) curve using a Perkin Elmer Pyris Dimond TG-DTA instrument. The photoluminescence (PL) spectrum was determined using a Shimadzu RF-5301PC spectrofluorometer.

3. Results and discussion

The powder XRD pattern (Fig. 1(a) of the as-prepared ZnS was well matched with the cubic zinc blend structure (JCPD No. 77-2100). The diffraction peaks were at 2θ=28.6°, 48.0°, and 56.9° corresponding to the reflection from (111), (220), and (311) planes, respectively. No impurity peak was observed. In addition, the peak broadening may indicate either the amorphous nature of the compound or the nanocrystalline behavior of the sample. The crystallite size (D) of ZnS was calculated from the width of the first peak (the most intense peak) using Debye-Sherrer equation:

$$D = K\lambda/\beta \cos\theta \quad (1)$$

where k is a constant (k=0.9), λ is the wavelength of X-ray

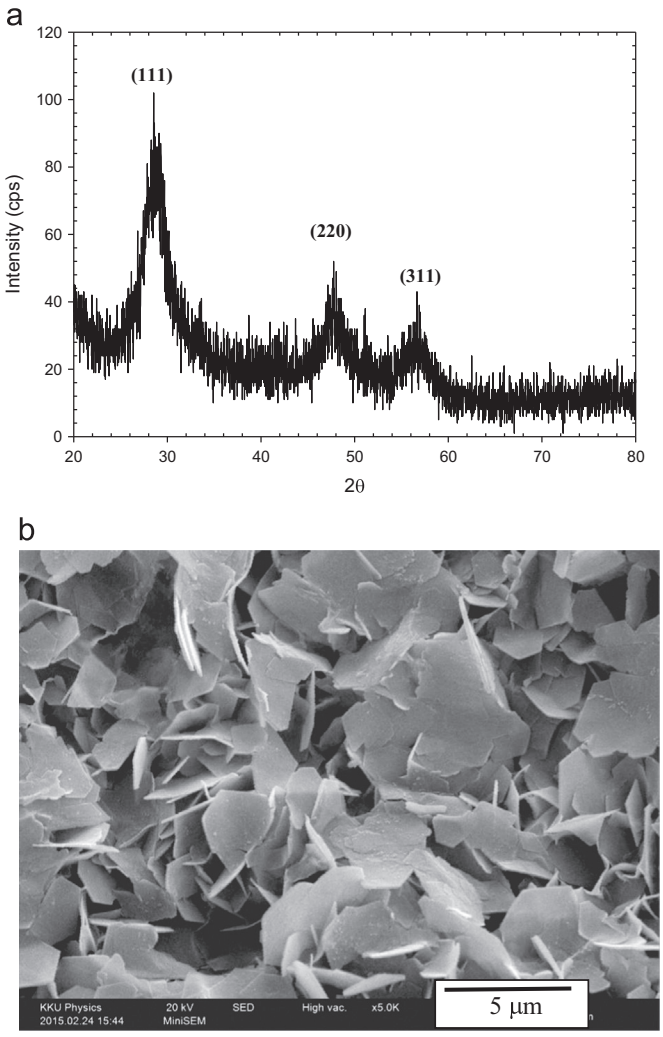

Fig. 1. XRD pattern (a) and SEM micrograph (b) of the as-synthesized ZnS.

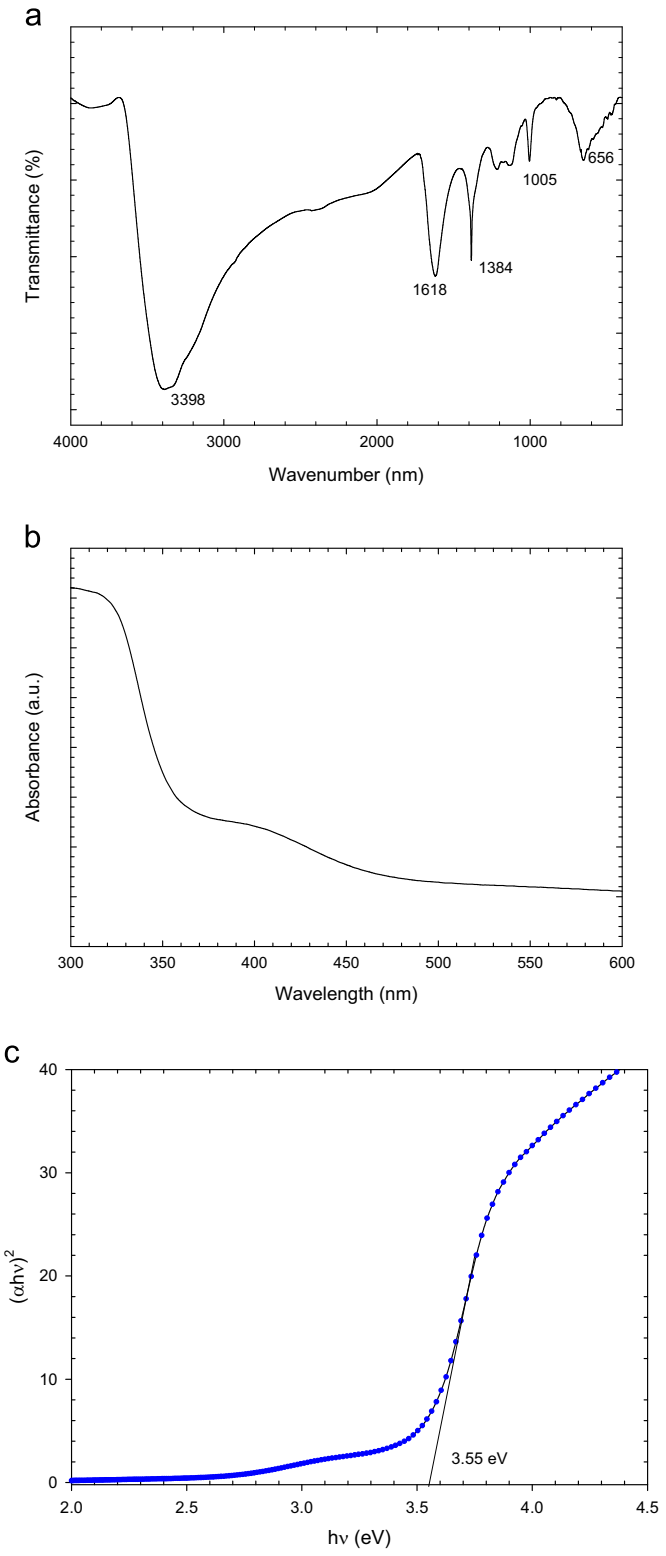

Fig. 2. FT-IR spectrum (a), diffused reflectance spectrum (b) and Tauc plot for determination of band gap of ZnS (c).

(0.15418 nm), β is the full-width at half maximum (FWHM), and θ is the diffraction angle. The calculated crytallite sizes were in the range of 2.7–3.4 nm.

The thin plate-like microstructure of ZnS with the grain size of about 80–200 nm was observed from SEM micrograph shown in Fig. 1(b). These values are much higher than the crystallite size