Materials Science in Semiconductor Processing 16 (2013) 1566–1572

Contents lists available at ScienceDirect

Materials Science in Semiconductor Processing

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

Novel two-dimensional lead sulfide quadrangular pyramid-aggregated arrays with self-supporting structure prepared at room temperature

Hanmei Hu [a,b,*], Chonghai Deng [c], Kehua Zhang [a], Mei Sun [a], Han Xuan [a], Shangshang Kong [a]

[a] School of Materials and Chemical Engineering, Anhui University of Architecture, Hefei 230022, China
[b] Anhui Key Laboratory of Advanced Building Materials, Anhui University of Architecture, Hefei 230022, China
[c] Department of Chemical and Materials Engineering, Hefei University, Hefei 230022, China

ARTICLE INFO

Available online 5 July 2013

Keywords:
PbS
Self-supporting structure
Nanocrystalline materials
Optical property

ABSTRACT

Two dimensional (2D) self-supporting lead sulfide (PbS) arrays composed of ordered quadrangular nanopyramids were successfully fabricated through a convenient wet-chemical route at room temperature. The as-synthesized products were characterized by X-ray diffraction, field emission scanning electron microscopy, transmission electron microscopy, UV–vis–NIR absorption and photoluminescence spectroscopy. The as-prepared highly ordered self-supporting superstructures are stable under ultrasonic conditions. A "template-mediated *in situ* growth" mechanism is proposed for the formation of 2D PbS superstructures. With the prolongation of reaction time, the morphology evolution of PbS is clearly observed, which could be changed from nanopyramid-aggregated arrays into nanocube-aggregated arrays at original position. The optical properties of PbS self-supporting superstructures are investigated in detail.

1. Introduction

In recent years, direction fabrication of complex micro/nanostructures with desired morphologies remains an important goal in the field of material chemistry and nanotechnology due to their unique properties and potential applications [1–3]. As an important II–VI semiconductor, lead sulfide (PbS), with a cubic rock salt structure, has attracted considerable attention due to its small band gap energy (0.41 eV) and large exciton Bohr radius (18 nm) at room temperature, which enables the quantum size confinement effect to be clearly visible even for relatively large crystallites [4]. Due to its unique optical and electronic properties, lead sulfide has potential applications in light-emitting diodes, optical switches, IR detectors, solar absorbers, Pb^{2+} ion selective sensors, etc. [5–8].

The literature contains many reports of the preparation of PbS with novel morphologies by a variety of methods. PbS nanorods were synthesized by the surfactant-assisted hydrothermal route [9]. Multi-armed architectures were prepared by a hydrothermal process [10]. PbS nanowire pine trees were obtained by a chemical vapor deposition method [11]. Eight-horn-shaped PbS dendrites were fabricated through a complex solvothermal synthetic route [12]. Three dimensional (3D) PbS arrays of well-packed nanooctahedron with {111} exposed facets were synthesized through a surfactant-assisted solution route [13]. PbS nanocubes with {100} exposed facets were prepared in the presence of sulfonated polymer as both stabilizer and crystal growth modifier [14]. PbS hollow nanospheres were synthesized by a surfactant-assisted sonochemical

* Corresponding author at: School of Materials and Chemical Engineering, Anhui University of Architecture, Hefei 230022, China.
E-mail address: hmhu@ustc.edu (H. Hu).

1369-8001/$ - see front matter © 2013 Elsevier Ltd. All rights reserved.
http://dx.doi.org/10.1016/j.mssp.2013.06.003

technique [15]. A series of PbS polyhedral crystals were fabricated through hydrothermal decomposition of the lead diethyldithiocarbamate (Pb-DDTC) single-source precursor [16]. Star-shaped PbS dendrites, multipods, truncated nanocubes and nanocubes were synthesized by a surfactant-assisted route in the presence of cetyltriethylammnonium bromide (CTAB) under different conditions [17]. PbS hierarchical superstructures were prepared by employing a single-source precursor route [18]. PbS ultrathin sheets were recently obtained through a bottom-up approach [19]. Although much progress has been achieved, it is still a great challenge to tune the morphologies and microstructures through a green and low-energy consumption route. Herein, an effective room-temperature wet-chemical method is provided to controllably prepare 2D ordered PbS quadrangular pyramid-aggregated arrays. The growth process and formation mechanism of the PbS 2D arrays are well investigated. To the best of our knowledge, this kind of 2D PbS self-supporting architecture with well-ordered quadrangular nanopyramids arrays has not so far been reported.

2. Experimental details

In a typical experimental procedure, 1 mmol Pb $(CH_3COO)_2$ was dissolved in 30 mL deionized water in a 100 mL beaker to obtain solution A. Meanwhile, 2 mmol thiourea and 5 mmol NaOH were successively dissolved in 30 mL deionized water to obtain solution B. Then, solution B was added into solution A under stirring. The pH value of the reaction solution is about 12. After stirring for 20 min, the obtained reaction mixture has been standing for 2 h at room temperature, the obtained black precipitation was filtered out, washed several times with anhydrous ethanol and deionized water, and then dried in a vacuum at 60 °C for 6 h.

The crystal structure of the as-synthesized products was examined by X-ray diffraction (XRD) using a Bruker D8 Advance X-ray diffractometer (40 kV, 40 mA) equipped with graphite monochromatized Cu Kα radiation (λ= 0.15406 nm). The morphology of the products was determined on a field emission scanning electron microscope (JEOL JSM-6700F and Sirion 200) and a transmission electron microscope (H-7650). Optical absorption spectra of samples were measured by an UV–vis–NIR spectrophotometer (Shimadzu, DUV-3700). Photoluminescence (PL) spectra were recorded on a Laser MicroRaman Spectrometer (JY LABRAM-HR) using the 325 nm exciton of the He–Cd laser at room temperature.

3. Results and discussion

3.1. Analysis of phase and morphology

Fig. 1a presents the typical XRD pattern of the as-synthesized products. The seven diffraction peaks can be indexed to the (111), (200), (220), (311), (222), (400) and (331) crystal planes of face-centre-cubic rock salt structured PbS, which is very close to the literature datum (PDF no. 05-0592). The strong and sharp reflection peaks suggest that the products obtained at room temperature

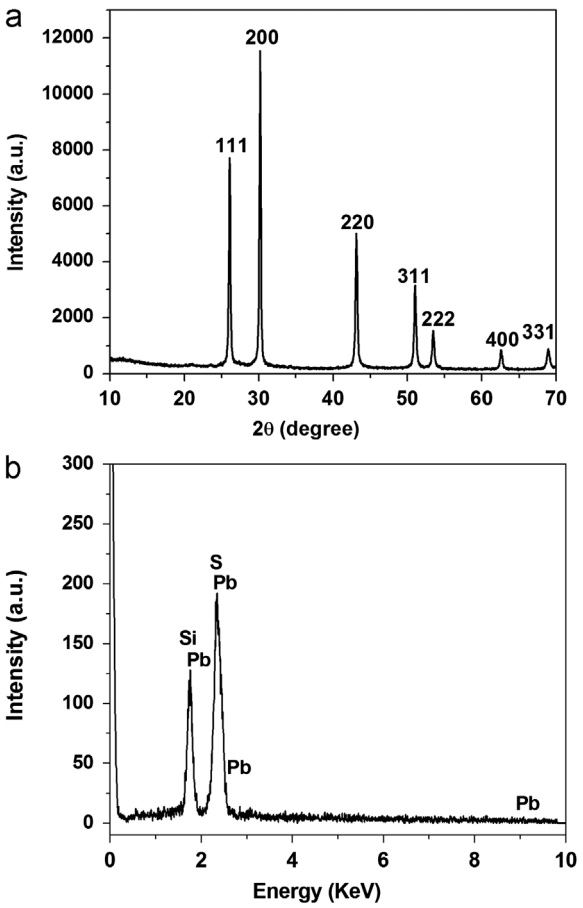

Fig. 1. XRD pattern (a) and EDX result (b) of the as-prepared sample.

are highly crystalline. The crystallite size is calculated to be about 150 nm from the half-width of the diffraction peaks by using the Debye–Scherrer formula [20,21]: $D_c = \alpha\lambda/\beta\cos\theta$, where D_c is the mean particle size, α is the shape factor (usually equal to 0.9), λ is the X-ray wavelength, β is the half-width of diffraction peak and θ is the angle of the diffraction peak. EDX spectrum of PbS products has been shown in Fig. 2b, which reveals that the products only contain elements of lead and sulfur (the peak of Si comes from the silicon substrate). The atomic percentage of Pb and S is 25.68% and 27.73%, and the mass percentage of them is 11.83% and 70.76%, respectively. The molar ratio of Pb to S obtained from the peak areas is 0.93:1.00, which is close to the stoichiometry of PbS.

The morphology of the products was determined by FESEM, as shown in Fig. 2. Fig. 2a demonstrates that as-prepared PbS sample is mainly consisted of a large number of 2D sheet-like arrays with the sizes of 3–15 μm. It is clear from the enlarged image of Fig. 2b that these 2D sheet-like arrays are actually assembled by quadrangular nanopyramids with an edge length of 100–200 nm, and the thicknesses are estimated to be 80–250 nm. Fig. 2c and d shows an individual 2D array. These nanopyramids interconnected with each other to form a well-organized sheet-like 2D array with irregular-shaped pore on its surface. The enlarged image in Fig. 2d indicates two quadrangular