Materials Science in Semiconductor Processing 16 (2013) 410–417

Contents lists available at SciVerse ScienceDirect

Materials Science in Semiconductor Processing

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

Synthesis, characterization and optical properties of mercury sulfides and zinc sulfides using single-source precursor

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ARTICLE INFO

Available online 13 October 2012

Keywords:
Nanoparticles
Nanodendrites
HgS
ZnS
Optical properties
Single-source precursor

ABSTRACT

HgS and ZnS nanostructures were prepared by using two different methods. HgS nanodendrites and ZnS nanospheres were synthesized via hydrothermal decomposition of $[M(TSC)_2]Cl_2$ complex (M=Hg, Zn and TSC=thiosemicarbazide), without any surfactant. And using oleylamine ($C_{18}H_{37}N$) and TPP ($C_{18}H_{15}P$) as surfactant, HgS nanoparticles with an average diameter of approximately 20–40 nm were synthesized by thermal decomposition of the $[Hg(TSC)_2]Cl_2$, whereas the coalesced particles and bulk structures were formed by thermal decomposition of $[Zn(TSC)_2]Cl_2$. To study the crystalline structure, size, morphology and composition of the products, characterization techniques including X-ray powder diffraction (XRD), scanning electron microscopy (SEM), transmission electron microscopy (TEM) and Fourier transform infrared (FT-IR) spectroscopy were employed. Ultraviolet visible (UV–vis) absorption and photoluminescence (PL) spectroscopy exhibited optical properties of nanostructures.

1. Introduction

Recently nanostructure materials, such as metals, metal oxides and chalcogenides are known to have many fascinating physical properties, and are of great importance in both basic scientific research and potential technological applications [1,2]. Transition metal chalcogenides, as important semiconductor materials, have attracted widely attentions because of their wonderful physical and chemical properties, quantum size effect, luminescence properties and non-linear optical properties. These chalcogenides have a wide range of applications in solar cells, photodetectors, light-emitting diodes, laser communications and so on [3–5]. Among the semiconductor sulfides, zinc sulfides and mercury sulfides have attracted considerable attention because of its relatively easy synthesis and distinct particle size dependent on optical properties.

ZnS is a direct wide band gap (E_g=3.65 eV) material with a large exciton binding energy (40 meV) and a small Bohr radius (2.5 nm) [6,7]. It shows various luminescence properties such as photoluminescence, electroluminescence, mechanoluminescence, acousticluminescence, thermal luminescence, and triboluminescence [8,9]. ZnS is an excellent candidate in exploring the intrinsic recombination processes in dense excitonic system [10,11]. It has received great attention for its potential optoelectronic applications [12–14] and has been widely used in the fields of ultraviolet light-emitting diodes, injection lasers, flat-panel displays, cathodes-ray tube luminescence, thin film electroluminescent devices, infrared (IR) windows, sensors, solar cells, and so forth [9,10].

HgS belongs to group II–VI compounds material with an optical band gap varied between 1.9 and 2.6 eV, depending upon the composition. HgS usually crystallizes in two forms, one is hexagonal α-HgS (cinnabar) with space group P3121 and band gap of 2.1 eV and the other is

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http://dx.doi.org/10.1016/j.mssp.2012.09.002

cubic β-HgS (metacinnabar) with space group F43m and band gap of −0.15 eV [15]. Mercury is ubiquitous in the global environment and mainly appears as cinnabar, but metacinnabar and metallic Hg are occasionally present. HgS can be widely used in ultrasonic transducers, electrostatic image materials, photoelectric conversion devices, light emitting diodes and electrochemical cells [16].

Much effort has been devoted to the synthesis of metal chalcogenides with various techniques and methods. The microwave-assisted synthesis [17], sonochemical method [18,19], biomimetic method [20], hydrothermal treatment [21], wet chemical route [15] and other methods [22,23] have been reported to prepare nano HgS. To synthesize ZnS nanostructures, various methods have been employed, including solvothermal and hydrothermal [24–26], microwave [27], single-source molecular precursor [28], chemical vapor deposition (CVD) [29], liquid-crystal template [30], γ-irradiation [31] and so on.

The problems of aggregation mainly can be circumvented by the use of two different strategies, applying various protecting agents and appropriate precursors [32,33]. The protecting agents have a dual role to control the growth of the particles. The precursors also play an important role in control of particle size. At the moment a major interest is in the development of organometallic or inorganic precursors. Herein we report for the first time an efficient and simple approach to the synthesis of ZnS and HgS nanostructures via thermal decomposition of single precursors in oleylamine, and also via a surfactant-free hydrothermal route. For these approaches $[M(TSC)_2]Cl_2$ was selected as new precursor. Transition metal complexes containing sulfur–nitrogen chelating agents derived from TSC and their Schiff bases have been extensively studied due to their interesting coordination chemistry [34–36]. The use of TSC complexes of different structures allows controlling the structure of obtained semiconductor materials.

2. Experimental

2.1. Chemicals

All the chemical reagents such as oleylamine, toluene, hexane, and ethanol used in our experiments were of analytical grade, were purchased from Aldrich and used as received without further purification. Precursor complex, $[M(TSC)_2]Cl_2$, was synthesized according to this procedure: metal (II) chloride, 2 mmol, was dissolved in 20 ml distilled water. A solution of TSC, 4 mmol, dissolved in 50 ml of distilled water containing 37% hydrochloric acid was dropwise added into the above solution under magnetic stirring. After addition of all the reagents, the mixture was refluxed for about 6 h. with evaporation of the solution, a crystalline solid was recovered. It was filtered, washed with distilled water and ethanol and dried. We suppose that TSC is coordinated to zinc and mercury ions as bidentate cyclic ligand through the S atom and the terminal N atom of the hydrazine fragment. Since zinc (II) and mercury (II) being d^{10} ions usually adopt a coordination number four with tetrahedral stereochemistry, it may be presumed that the ligand in these metal complexes has been arranged in a tetrahedral manner.

2.2. Equipment

XRD patterns of products were recorded by a Rigaku D-max C III XRD using Ni-filtered Cu Kα radiation. SEM images were obtained on Philips XL-30ESEM equipped with an energy dispersive X-ray spectroscopy. TEM images were obtained on a Philips CM10 transmission electron microscope with an accelerating voltage of 100 kV. FT-IR spectra were recorded on Shimadzu Varian 4300 spectrophotometer in KBr pellets. Room temperature PL was studied on a Perkin Elmer (LS 55) fluorescence spectrophotometer. The electronic spectra of the samples were taken on a Scinco UV–vis scanning spectrometer (Model S-4100).

2.3. Preparation of ZnS nanospheres and HgS nanodendrites

ZnS nanospheres and HgS nanodendrites were prepared by a hydrothermal route from $[M(TSC)_2]Cl_2$ as precursor. 0.8 g $[M(TSC)_2]Cl_2$ was dissolved in 50 ml of distilled water, was transferred into a 100 ml Teflon-lined stainless steel autoclave and heated to 150 °C for 12 h, then allowed to cool to room temperature naturally. The as-formed precipitates were collected via centrifugation after 15 min of stirring and washed repeatedly with distilled water and ethanol to remove impurities. The products were dried in vacuum at 50 °C for 5 h. The overall synthetic procedure is shown in Scheme 1. The synthesized samples were characterized by SEM, XRD, TEM, FT-IR, PL and UV–vis techniques.

2.4. Preparation of ZnS coalesced particles and HgS nanoparticles

The main synthetic procedure in order to approach to final products is a modified version of the method developed by Hyeon and others for the synthesis of metals and metal oxides that employs the thermal decomposition of transition metal complexes [37,38]. In this synthesis, ZnS coalesced particles and HgS nanoparticles were prepared by the thermal decomposition of $[M(TSC)_2]Cl_2$ complex. The $[M(TSC)_2]$–oleylamine complex prepared by reaction of $[M(TSC)_2]Cl_2$ with oleylamine was placed in a 25 ml flask and heated up to 150 °C for 120 min. At this moment, the temperature was increased to 210 °C. The solution was aged at 210 °C for 90 min, and was then cooled to room temperature. The precipitates were centrifuged and washed with ethanol several times to remove impurities, if any, and dried at 50 °C. The synthesized products were characterized by XRD, SEM, TEM, FT-IR, PL and UV–vis techniques. Table 1 lists the reaction conditions for the synthesis of nano-sized ZnS and HgS.

3. Results and discussion

The XRD pattern of as-prepared HgS (sample no. 3) by hydrothermal method is shown in Fig. 1a. The diffraction peaks at 26.54, 30.71, 43.88, 51.92, 54.41, 63.72, 70.14 and 72.20 degree, which correspond to the (111), (200),