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Effect of hydrogen gas on the growth process of PbS nanorods grown by a CVD method

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ABSTRACT

PbS nanostructures were grown by sulfuration of two lead sheets in a tube furnace under nitrogen (N_2) and argon/hydrogen (Ar/H_2) conditions. All conditions, such as the sheet temperature, sulfur powder temperature, and the carrier gas rate, were the same for two samples. Field emission scanning electron microscope (FESEM) images showed that the nanostructures with rod morphology were formed on the sheets. However, the nanorods that were grown under N_2 gas, were denser, more compact, and a different shape and size in comparison to another sample. In addition, the nanorods grown under N_2 gas exhibited a rectangular shape, while another sample showed nanorods that were tapered. X-ray diffraction (XRD) patterns indicated that these nanorods were PbS with a cubic phase. Furthermore, Raman measurements confirmed the XRD results, and indicated three Raman active modes of PbS phase. The optical characterization results showed a band gap for the PbS nanorods in the infrared region.

1. Introduction

Metal chalcogenide semiconductors have considerable attracted much attention because of their potential for various applications. In fact, semiconducting metal chalcogenide nanocrystals (II–VI and IV–VI) are a class of materials that exhibit band-gap energies, spanning from the mid-to-near infrared (PbS, PbSe, PbTe) to the visible (CdS, CdSe, CdTe), and into the ultraviolet (ZnS, ZnSe) region.

Lead sulfide (PbS) is one of these semiconductors with a direct and narrow band gap of 0.41 eV at room temperature and a large exciton Bohr radius of 18 nm, which permits size-quantum confinement effects to be clearly visible, even for larger particles [1]. Therefore, it has important optical applications, such as solar cells and infrared detectors [2], solar control coatings [3], optical fibers, and broadband optical amplifiers [4]. In addition, from a technological perspective, PbS is an extremely promising material for a large number of applications in the mid- and near-infrared emission and detection range, biological applications, and optoelectronic devices, owing to its wide range of size-dependent properties [5]. So far, various forms of PbS nanostructures, such as nanowires [6], nanorods [7–9] and nanoclusters [10], have been reported, which were grown by various methods such as chemical bath deposition (CBD) [11], electrochemical deposition [6], hydrothermal [12,13], and vacuum evaporation [14]. Most of these techniques are usually complex, expensive, and time-consuming.

Based on these reasons, in this work we present a simple and cost-effective method to grow PbS nanorods on a large scale. A simple sulfuration of the lead sheets was used to grow PbS nanorods in a chemical vapor deposition (CVD) set-up. In addition, we report and discuss the effect of hydrogen gas on morphology, structure, and optical properties of the PbS nanorods.

2. Experimental sections

The PbS nanostructures were grown using the following procedure. Firstly, six high purity Pb sheets (99.99%), with dimensions of 2×1 cm and a thickness of 0.5 mm were used as substrates. The sheets were cleaned ultrasonically with acetone and methanol, for 10 min in each solvent. Then the sheets were put into a horizontal tube furnace

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(CVD set-up) at 280, 330, and 400 °C. Stoichiometric sulfur powder (Merck, sulfur (S_8) (99.999%)) was used as the source material to create the sulfur ambiance in the tube furnace, in an alumina boat at the right side of the furnace (at 185 °C) (Fig. 1(a)). A high purity carrier gas was fed into the furnace at about 120 sccm at one end, while the other end was connected to a rotary pump. The growth process was allowed to proceed for 1 h. A vacuum of 50 Torr was maintained inside the tube furnace during sulfuration of the Pb sheets. After deposition, a black thin film appeared on the sheets (Fig. 1(b)). In this manner, two sets of PbS nanostructures were made, one using N_2 gas and another using Ar (90%)/H_2 (10%) gas as carrier gases.

The morphology and crystal structure of the products were investigated using a field emission scanning electron microscope (FESEM; Hitachi S4160), and an X-ray diffractometer (XRD; Siefert ID 3003). The elemental contents of the products were measured using energy dispersive x-ray (EDX; Quanta 200 F). Room temperature photoluminescence (Jobin Yvon Horiba HR 800 UV), UV–vis (Lambda 25-Perkin–Elmer), and Raman (Bruker-Senterra Raman Spectrometer) spectrometers were employed, to study the optical properties and crystallinity of the PbS nanostructures. An Nd:YLF laser, with a wavelength of 785 nm and a He–Cd laser with a wavelength of 325 nm, were used for Raman measurements and PL spectrometer, respectively.

3. Results and discussion

Fig. 2(a)–(f) shows the Pb sheets that were placed in the high, mid, and low temperature zones. It can be seen that the shapes of the products vary with the distance from the source material to the substrates. In addition, it can be observed that PbS nanostructures were formed in the mid temperature zone at 330 °C for both conditions (Fig. 2(c) and (d)). Higher magnification FESEM images of these samples show that, the morphology of the nanostructures is nanorods for both samples (Fig. 3(a) and (b)). However, the nanorods, which were grown under N_2 gas, show a rectangular shape with an average diameter of 95 nm and an average length of 400 nm (Fig. 3(a)), while the other sample shows nanorods that are tapered, with tip diameters of 20 ± 5 nm and base diameters of 100 ± 5 nm (Fig. 3(b)). In addition, the sample that was grown under N_2 gas indicates denser and more compact nanorods than the other sample that was grown under Ar/H_2 gas. Fig. 3(c) and (d) shows the EDX spectra of the samples. Strong signals from Pb and S elements are detected by the EDX spectra for all samples. However, the EDX spectrum of the sample grown under N_2 gas indicates more sulfur content than the other sample. In addition, a weak oxygen signal is also detected by the EDX spectra. The appearance of the oxygen signal could be due to diffusion of oxygen into the tube furnace during the growth process or could be due to the inevitable reaction of the samples with atmosphere when the samples were taken out from the set-up.

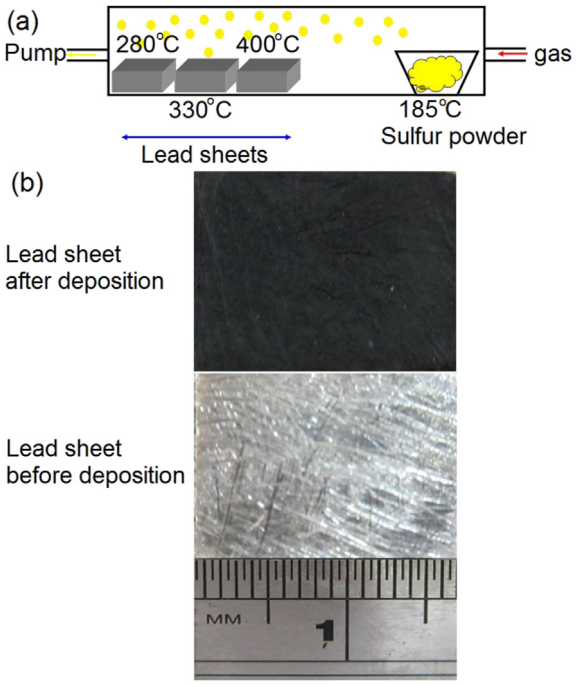

Fig. 1. (a) Schematic of the set-up that was used to grow PbS nanorods; (b) a photograph of the lead sheet before and after sulfuration.

Fig. 4 shows the XRD patterns of the samples. The XRD patterns in Fig. 4 agree with the standard card of bulk PbS with an fcc cubic phase (JCPDS Card No. 05-0592), with calculated lattice constant of 5.972 Å. This lattice constant corresponds well to those of the bulk material, 5.940 Å. The addition of the PbS peaks, the lead peaks from the sheets are also detected. However, these lead peaks are stronger for the sample that was grown by Ar/H_2 in comparison to the sample that was grown by N_2 gas.

The further evidence for the formation of PbS in the present simples system comes from XPS analysis of the product. Fig. 5 is the high-resolution XPS spectra of the nanorods, which were grown by N_2 gas. The binding energies of Pb and S are 139.08, 143.68 eV and 161.44 eV, respectively, which are very close to the values reported in literature. No clear sulfur peak was detected for the sample that was grown by Ar/H_2 gas. Therefore, the XPS spectra of this sample are not shown here.

Based on these results, the plausible growth mechanism of the PbS nanorods can be explained by the following CVD reactions:

$$\mathrm{S\ (s) \rightarrow S\ (g)}, \tag{1}$$

$$\mathrm{Pb\ (s) + S\ (g) \rightarrow PbS\ (nanorods)} \quad \text{(grown under } N_2 \text{ gas)}, \tag{2}$$

$$\mathrm{Pb\ (s) + S\ (g) + H_2\ (g) \rightarrow PbS_x\ (nanorods)} + \mathrm{H_2S_{1-x}} \quad \text{(grown under Ar/}H_2\text{ gas)}. \tag{3}$$

In fact, two factors are important to obtain PbS nanorods: one is the supersaturation of sulfur gas at 330 °C; and the other is the creation of the Pb cluster on the Pb sheets at this temperature. Actually, the lead sheets start to change to Pb clusters on the surface, and these clusters could be the best nucleation sites to grow PbS nanorods. It can be seen such clusters in Fig. 2(a) and (b) that were obtained under lower temperature. In addition, for proof of this claim, the nanorods were examined at an earlier stage of growth (15 min rather than 60 min) under the same temperature. It was seen that only scattered clusters of Pb with several very small PbS nanorods were appeared on the substrate. However, hydrogen as a reaction gas with sulfur can reduce the concentration of the sulfur gas in the set-up. Therefore, the formation rate of the nanorods was reduced for the samples that were grown under Ar/H_2 gas. In fact, sporadic growth of nanorods, which were grown under Ar/H_2 gas, could be a result of this phenomenon. Usually, anion concentration is the most important factor to obtain different morphology in metal-chalcogenide nanostructures [15,16]. Therefore, according to H_2 gas role as a reduction of sulfur concentration in the set-up, obtaining different morphology in two these methods could be due to different sulfur concentration.

Raman spectroscopy is an effective technique for estimating the crystallinity of materials. According to the group theory, single crystalline PbS belongs to the Fm_3m space group. Fig. 6 shows the Raman spectra of the PbS nanorods. The spectra contain bands at