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Synthesis and photoluminescence of zinc sulfide nanowires by simple thermal chemical vapor deposition

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Abstract

We present a synthetic method of zinc sulfide nanowires by a simple and safe reaction of zinc oxide and iron sulfide powders on a gold-coated silicon substrate through chemical vapor transport and condensation. High quality ZnS nanowires with single crystalline wurtzite structures are grown along [0 0 1] direction with diameters in the range of 10–30 nm and lengths up to tens of micrometers. Photoluminescence spectrum shows strong emission near 339 nm. These nanowires with cleaved ends could be a prominent candidate material for a nanoscale cavity as a ultra-violet nanolaser.

Keywords: A. Nanostructures; B. Vapor deposition; D. Luminescence

1. Introduction

Semiconductor nanowires have attracted much interest because of their potential use as nanoscale building blocks in nanoelectronic devices including field effect transistors (FET), logic gates, light emitting diodes (LED), nanoscale lasers, photodetectors and nanosensors [1].

Zinc sulfide (ZnS) is an II–VI semiconductor material and has been used in cathode-ray tubes (CRT) and field emission display (FED) phosphors for a long time [2]. It can also be used for electroluminescent devices [3] and photodiodes [4]. Various ZnS nanostructured materials have been reported: nanoparticles [5], nanowires [6–11], nanoribbons [12–15], and nanotubes [16]. Among them ZnS nanowires with high aspect ratio may become one of the prominent candidates in optoelectronic applications, ranging from telecommunication to medical therapeutics as a single-mode optical waveguide and ultra-violet (UV) nanoscale laser using the natural cavity [1,17]. A straight and smooth morphology is very important for the nanowires to be used in optoelectronic applications. Several synthesis methods of ZnS nanowires were reported such as the laser-assisted catalytic growth (LCG) method [1,11], the template method using gamma-irradiation [18], the solution method containing an anionic surfactant [7] and thermal evaporation [6,8–10]. In this letter, we show a simple and effective process by which very high quality single crystalline wurtzite ZnS nanowires are grown along [0 0 1] direction with strong ultra-violet (UV) emission near 339 nm.

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2. Experimental

This process is a facile and efficient route to mass production of single-crystalline ZnS nanowires by using commercially omnipresent zinc oxide (ZnO) and iron sulfide (FeS) powder without pre-treatments (pulverization, grinding, and so on):

$$\mathrm{ZnO\,(powder)} + \mathrm{FeS\,(powder)} \rightarrow \mathrm{ZnS\,(nanowires)} + \mathrm{Fe_3O_{4-x}\,(residues\ in\ the\ boat)}$$

ZnS is formed when ZnO reacts with FeS (1473–1653 K) [19]. In this reaction, ZnO is reacted as a possible desulfurisation reagent. Also, FeS powder becomes a safe and stable sulfur source instead of hydrogen sulfide (H_2S) or sulfur (S). In order to prevent oxidation of the produced ZnS nanowires at high temperatures, the iron (Fe) atoms decomposed from FeS react with oxygen atoms. As a result of the above reaction, paramagnetic Fe_3O_{4-x} clusters were produced in the alumina boat. Sulfur contained in FeS material enhances carbon nanotube (CNT) yield [20]. ZnS nanowires were grown on gold (Au) coated silicon substrates through a simple chemical vapor transport-condensation (CVTC) [1] based on the vapor–liquid–solid (VLS) mechanism. The Au film at high temperature breaks up and liquid Au nanodroplets were formed on the Si surface. These liquid Au droplets absorb ZnS vapor and Au–ZnS alloys were formed. When the concentration of ZnS in the alloy is over the saturation point, the ZnS alloy precipitates from the solid–liquid interface. ZnS nanowires originate from these precipitates [10,11]. Equal amounts of pure ZnO and FeS powders were mixed in an alumina boat, which was inserted to a quartz tube into a horizontal tube furnace. The temperature of the furnace was increased to 900–950 °C from room temperature in constant argon (Ar) flow. The silicon substrates were coated with a 50 nm gold film. It is well known that metal clusters such as Au have a catalytic effect on the nanowire growth in the VLS process [1]. After we cooled down the sample to room temperature, we found the substrate surface homogeneously covered by white ZnS nanowires. The crystal structure of products were characterized by X-ray diffraction (XRD, Rigaku D/max-rc) with a graphite monochromator and Cu Kα radiation (λ = 0.1541 nm) from a rotating anode X-ray generator operating at 40 kV and 100 mA. A scanning rate of 0.03/s was applied to record the patterns and data in a 2θ range of 20–70°. The morphology of the ZnS nanowires were characterized using scanning electron microscopy (SEM, Philips XL30S). Further structural analyses of a single nanowire were performed using selected area electron diffraction (SAED), transmission electron microscopy (TEM) and high resolution transmission electron microscopy (HRTEM, Philips F20 Techni and CM20FEG).

3. Results and discussion

Fig. 1 shows the morphology of ZnS nanowires investigated by SEM. This image shows uniform ZnS nanowires with diameters ranging from 10 to 30 nm and lengths up to several hundred micrometers. In addition, the ZnS nanowires were examined using energy dispersive X-ray spectroscopy (EDXS) in the SEM and TEM measurement.

The TEM image in Fig. 2 shows straight and uniform wurtzite ZnS nanowires with flat-ends. Such well-facetted nanowires can build a Fabry-Parot cavity that is necessary for realizing nanowire lasers [1,18]. The selected area

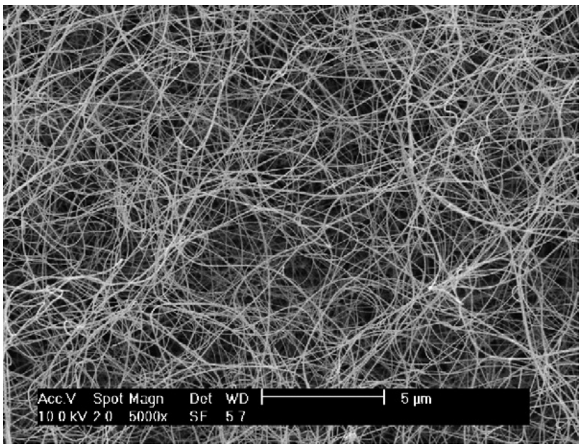

Fig. 1. SEM image of as-synthesized ZnS nanowires grown on an Au-coated Si substrate.