Superlattices and Microstructures 46 (2009) 687–692

Contents lists available at ScienceDirect

Superlattices and Microstructures

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

Growth and characterization of large-scale uniform Zinc Sulfide nanowires by a simple chemical reaction technique

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ARTICLE INFO

Article history:
Received 16 April 2009
Received in revised form
14 August 2009
Accepted 18 August 2009
Available online 27 August 2009

Keywords:
Nanowires
Scanning electron microscopy
Chemical reaction technique
Micro-Raman
Semiconducting II–VI materials

ABSTRACT

Zinc Sulfide (ZnS) nanowires were grown in the pores of anodic alumina membrane. A simple chemical reaction technique was used where pores in the anodic alumina membrane act as reactors. Uniform morphology of nanowires was found using scanning electron microscopy (SEM). X-ray diffraction (XRD) and Micro-Raman spectroscopy revealed the wurtzite nature of ZnS nanowires. UV–visible spectroscopy of nanowires exhibited no blue shift. The room temperature photoluminescence measurement observed an emission peak around 390 nm.

1. Introduction

ZnS is a very significant direct wide-bandgap semiconductor material with the maximum bandgap of all II–VI group compounds [1]. It has been used as fluorescent material coatings in field emission display (FED) and cathode-ray tubes (CRT) for a long time [2], for the fabrication of photodiodes [3] and electroluminescent devices [4]. Various researchers have demonstrated the importance of fabrication techniques for ZnS based nanometric regime structures such as nanowires [5–8], nanotubes [9] and nanoparticles [10].

Among the diverse forms of ZnS nano-materials, nanowires with a high aspect ratio may become one of the outstanding candidates in optoelectronic applications [11,12]. For nanowires to be used in optoelectronics, one important requirement is that they should have straight and smooth morphology. Several techniques have been reported for the fabrication of ZnS nanowires such as thermal chemical vapor deposition [13], the laser-assisted catalytic growth [14], simple solution route [1], catalytic

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doi:10.1016/j.spmi.2009.08.008

growth [8], chemical bath deposition [15], template free microwave irradiation technique [16] etc. In this paper, we present a simple chemical technique (non-galvanic method) by which ZnS nanowires are grown in alumina template.

2. Experimental details

All the reagents used were RA grade. All solutions were prepared in de-ionized water. 60 μm thick sample of anodic alumina membrane having pore size 100 nm (commercially available Whatman) was used as template for the synthesis of ZnS nanowires.

As shown in Fig. 1, the alumina membrane was used as a dividing wall in a two compartment cell. In the first compartment, an aqueous zinc acetate solution (0.2 M with some drops of NH_4OH) was added and allowed to diffuse through the membrane during 30 s prior to the introduction of the second reagent sodium sulfide (0.1 M) in the second compartment. Both solutions diffuse toward each other through the pores of the membrane and react to yield the ZnS. The synthesis process was continued for 90 min at room temperature.

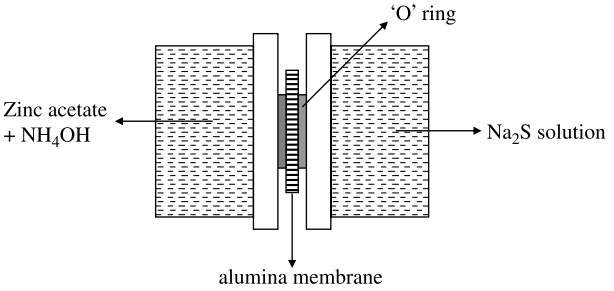

Fig. 1. Two compartment cell used for chemical reaction.

For the SEM characterization freshly prepared sample of ZnS nanowires embedded in the alumina membrane was put in the solution of NaOH to dissolve the alumina membrane. The concentration of NaOH solution was taken to be very small (0.5 M) so that it should not damage the ZnS nanowires. It took long time to completely remove the host membrane. After that nanowires were washed with distilled water and ethylene alcohol several times. Then a small drop of alcohol containing the nanowires was taken for the SEM characterization.

The cleaned and dried sample of ZnS nanowires were coated with gold–palladium alloy using Jeol JFC sputter coater and then examined under Jeol, JSM 6100 scanning electron microscope. The crystallographic studies of ZnS nanowires embedded in alumina template were carried out using Panalytical X'pert X-ray Diffractometer in 2θ range from 20° to 80° using Cu K_α radiation. The optical absorption spectra were recorded within the range 200–800 nm using Shimadzu 2500 UV–vis spectrophotometer. Photoluminescence (PL) measurements were recorded on a FluoroMax-3 (Jobin-Yvon, Edison, NJ, USA) equipped with photomultiplier tube and a xenon lamp.

The Raman spectroscopy is an important technique to investigate crystal structure of the nanomaterials. The frequency of an optical phonon which is Raman active is split into a longitudinal (LO) and a transverse (TO) component by the macroscopic electric field associated with the longitudinal phonon. This electric field serves to stiffen the force constant of the phonon and thereby raise the frequency of the LO over that of the TO. According to group theory prediction the variation types lattice phonon excited when light of fixed wavelength interact with the materials. WiTec CRM 2000 Raman spectrometer was used for structure analysis of ZnS nanowires, coupled with a high resolution Confocal optical microscope. With this combination it is not only possible to obtain a Raman spectrum of a sample but also to combine its chemical information with a lateral resolution in the sub-micrometer regime. Both the excitation and collection of the scattered light were done through the microscope objective. Excitation was provided by the 514 nm line of an argon ionized laser. The microscope objective used was Nikon 100X, with working distance 0.26. Thus, the laser beam diameter at the focus is approximately in sub-micron regime. All the measurements were made at room temperature, in order to avoid heating effects in the spectra. Therefore, the measurements

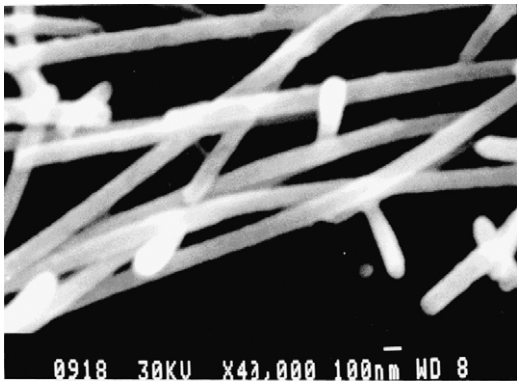

Fig. 2. SEM micrograph of ZnS nanowires.

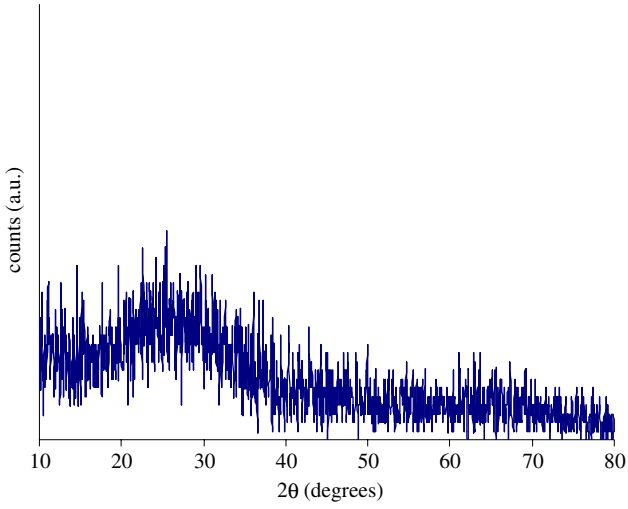

Fig. 3. X-ray diffraction of ZnS nanowires.

were performed at a laser power density below threshold to induce temperature enhancement. All the measured spectra were systematically compared to those obtained on cover slip under the same experimental conditions.

3. Results and discussion

The formation procedure of nano-ZnS may be as follows: When Zn^{+2} and S^{2-} ions met in the channels of porous alumina under hydrostatic pressure, ZnS was deposited virtually in the center of the channels. With increasing ZnS, the channels may be blocked. Further deposition will be carried out by diffusion of Zn^{+2} and S^{2-} ions in ZnS. Because Zn^{+2} is more easily diffused than S^{2-} from the side of $(CH_3COO)_2Zn$ to Na_2S, ZnS grows preferentially in the direction toward the Na_2S side. This is why the ZnS can be seen on the surface of the porous alumina membrane at the Na_2S side when the deposition period is long enough.

SEM micrograph [Fig. 2] presents the surface morphology of ZnS nanowires. It is clearly seen from micrograph that the diameter of the wires are similar to the pore size. One broadened peak is observed (from 20° to 35°) in X-ray diffractogram [Fig. 3]. This broadened peak may correspond to the wurtzite ZnS (broadening & overlapping of (100), (002), (101) peaks) [17].

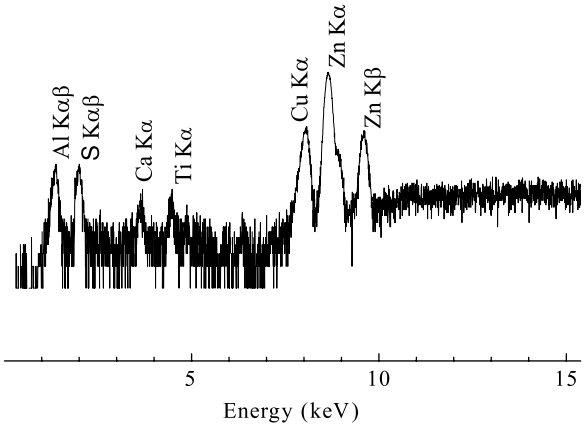

Fig. 4. EDXRF graph of ZnS nanowires.

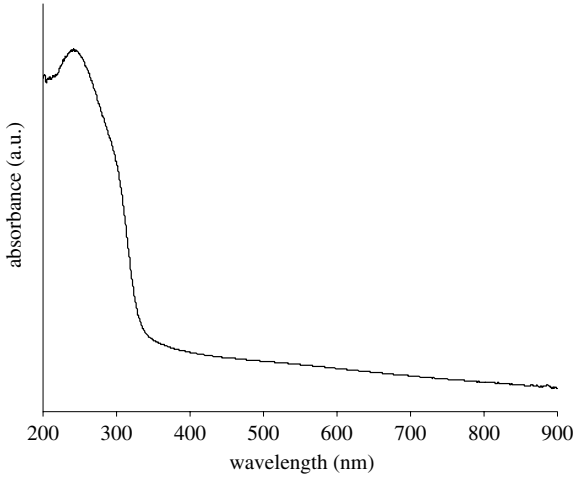

Fig. 5. UV–Visible absorption spectrum of ZnS nanowires.

Fig. 4 presents the Energy Dispersive X-Ray Fluorescence (EDXRF) graph of ZnS nanowires embedded in the anodic alumina membrane. EDXRF graph [Fig. 4] clearly confirms the purity of zinc and sulfur in the nanowires. EDXRF spectrum shows the presence of copper and aluminum peaks. These peaks are due to copper was used as target material and aluminum was as a host material for alumina membrane. The dealing of sample with naked hands during characterization may also be responsible for small amount of calcium (small peak ∼3.68 keV). There is one more small peak corresponds to titanium (small peak ∼4.5 keV) between the peaks due to calcium and copper. This may be due to some titanium residue as remains in the sample holder during previous measurements.

UV absorption spectrum of ZnS nanowires is shown in Fig. 5. The beginning of absorption is located at 340 nm. The value of the bandgap evaluated using UV absorption spectrum is 3.65 eV nearly same as that of bulk ZnS (3.6 eV). It is not feasible to observe any excitonic peak at the room temperature absorption spectrum. So no quantum size effects and blue shift is observed in 100 nm ZnS nanowires. This may be due to that the 100 nm diameter size is not coming in nanoscale. Fig. 6 presents the photoluminescence (PL) spectrum of ZnS nanowires observed at room temperature with 325 nm excitation wavelength. PL spectrum reveals one emission peak, located at around 390 nm. The PL peak at 390 nm is attributed to the sulfur vacancy and the interstitial sulfur lattice defect [18,19].

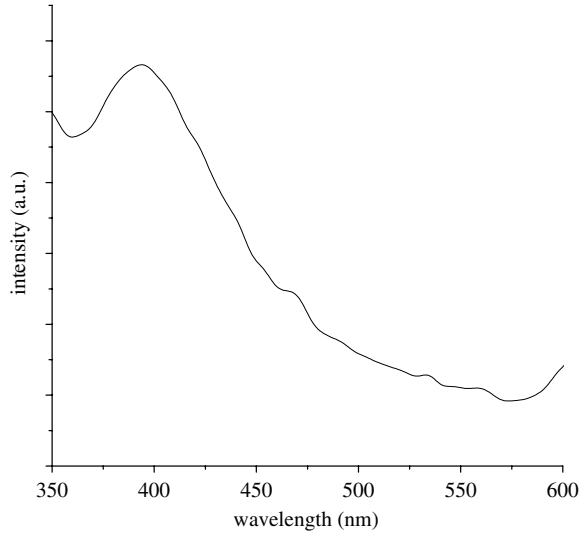

Fig. 6. Photoluminescence spectrum of ZnS nanowires.

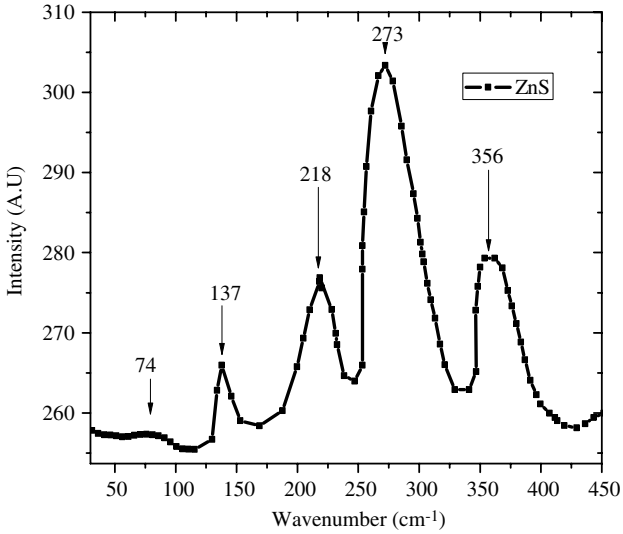

Fig. 7. Micro-Raman spectrum of ZnS nanowires at room temperature using 514 nm line of Ar^+ laser as the excitation source.

Fig. 7 shows the micro-Raman spectrum of ZnS nanowires. In case of ZnS nanowires, there are mainly two types of lattice phonons observed, an A_l branch in which the Raman-active phonon is polarized in the z direction and E_1 branch in which the phonon polarized in the xy plane and which is Raman active. In case of ZnS Raman spectrum, the E_2 modes were located at 74 cm^{-1} which satisfy its polarization characteristics of ZnS nanowires [20]. While this cannot unambiguously be assigned as an E_2 mode, its characteristics are strongly suggestive that this is in fact its origin. Other possibilities are that it is a second-order line from a zone point other than the edge or the center, or a local mode. These are unlikely, so we have assigned the band at 74 cm^{-1}. The TO mode of both A_l and E_1 symmetry was observed at 273 cm^{-1}, and the LO mode also of A_l and E_1 symmetry was located at 356 cm^{-1}. These vibration modes TO and LO have agreement with both prior Raman investigations of ZnS [21,22].

Because our sample is wire structured which is in accordance with the circular cylinder model very well and the result is in good agreement with the frequency of surface mode calculated, the line at 356 cm^{-1} can be assigned to surface phonon mode. The other bands at 137 cm^{-1} had been observed, which represent the wurtzite-2H type crystal. The E_2 modes 218 cm^{-1} showed the variance with previous assignments [23,24]. The two-phonon spectrum of hexagonal ZnS, indicate the second-order line resulting from the combination of two zone-edge longitudinal phonons. In which the line at 218 cm^{-1} does not have the proper temperature dependence to be a one-phonon line. The variation in intensity of scattering of a one-phonon line and a combination phonon should have a function of temperature [25]. These results indicate that ZnS nanowires grown from chemical reaction technique are Wurtzite-2H structure, which supports our previous results.

4. Conclusions

Simple chemical reaction technique is a useful technique for the preparation of semiconductor nanowires. For the generation of nanowires with required composition, reacting solutions should have proper concentrations of the reagents. For the observations of quantum size effects the diameter of nanowires should be very small (comparable to Bohr exciton radius). Nanowires having 100 nm diameter show the bulk ZnS behavior. Raman spectrum showed that ZnS nanowires had a Wurtzite-2H type structure, which is in agreement with the XRD also.

Acknowledgements

One of the authors (Sanjeev Kumar) is grateful to Dr. Sanjeev Aggarwal and Dr. Shyam Kumar, Physics Department, Kurukshetra University, Kurukshetra for providing the facilities of UV–visible and photoluminescence spectrophotometers. He is also grateful to Dr. D. Mehta, Physics Department, Panjab University, Chandigarh for providing the EDXRF facility. He also expresses his thanks to Mr. Jagtar Singh, CIL, Panjab University, Chandigarh for providing the XRD facility.

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