

## Research Article

# Zinc Sulfide Tubes Reinforced with Carbon Nanofibers

N. N. Kolesnikov, D. N. Borisenko, E. B. Borisenko, A. V. Timonina, and V. V. Kveder

*Institute of Solid State Physics, Russian Academy of Sciences, Laboratory of Physical-Chemical Basis of Crystallization, Chernogolovka, 142432 Moscow, Russia*

Correspondence should be addressed to E. B. Borisenko, borisenk@issp.ac.ru

Received 10 October 2008; Revised 16 January 2009; Accepted 27 January 2009

Recommended by Burtrand Lee

Zinc sulfide submicron and nanotubes with outer diameters in the range from 100 to 1000 nm were produced through chemical deposition from vapor under argon pressure. The novel process provides formation of ZnS tubes reinforced with carbon nanofibers. This is the first time that the ZnS tubes are grown with fibers during deposition.

Copyright © 2009 N. N. Kolesnikov et al. This is an open access article distributed under the Creative Commons Attribution License, which permits unrestricted use, distribution, and reproduction in any medium, provided the original work is properly cited.

## 1. Introduction

Interest in nanocomposites increases due to their special properties and potential applications. Semiconductor II-VI composites are interesting because of their size-dependent optical properties, size-dependent band gap energies [1–3]. Core/shell products, for example, ZnS/HgS, CdSe/ZnS fabricated by electro-deposition, or chemical solution transport [1, 2] are of special interest due to varying electronic properties dependent on core/shell weight ratio. In [3] ZnS/Si core/shell tubes were fabricated by epitaxial growth. ZnS was a substrate used to produce Si tubes for semiconductor industry. ZnS templates were afterwards chemically removed. The core/shell structures are similar to the structures we obtain, but not the same.

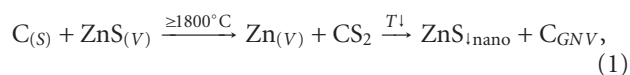
We have developed a method of fabrication of ZnS/C nanocomposite tubes by direct ZnS evaporation in a graphite crucible. This technique is a kind of CVD method: carbon from graphite crucible reacts with ZnS. Then at lower temperature carbon deposits along with ZnS according to (1), so that the ZnS forms tubes and the tubes' walls are reinforced with the graphite nanofibers. This material is new and may be interesting as a reinforced semiconductor nanomaterial.

## 2. Experimental

Zinc sulfide tubes of the outer diameter 100–500 nm were grown in a graphite crucible of 40 mm in diameter and

100 mm in height. The crucible was loaded with 100 g of zinc sulfide. The crucible was placed into the autoclave which had a graphite resistance heater. The setup is shown in Figure 1.

First, the pressure in the autoclave reached  $1.3 \cdot 10^{-2}$  mbar, then the chamber was filled with argon. The ZnS powder was preliminary annealed for 1 h at the temperature 600°C in argon atmosphere under pressure 52 atm. After cooling to room temperature, the furnace was three times cleaned with high-purity argon and then heated to 1800°C. The synthesis was performed for 1.5 h by the first reaction in (1) in the temperature range 1800–1850°C under 58 atm argon pressure, then the furnace was cooled and ZnS submicro and nanotubes deposited simultaneously with graphite nanofibers by the second reaction in (1):



where  $C_{(s)}$  is graphite,  $ZnS_{(v)}$  is gaseous ZnS,  $C_{GNV}$  is graphite nanofibers.

The ZnS submicro and nanotubes with carbon fibers were deposited on cool parts of the furnace (no. 7 in Figure 1). Macroscopically, the product of the reaction looked like gray soot. The deposited tubes were studied by transmission electron microscopy (TEM) on a JEM 100 CX TEM microscope. X-ray diffraction (XRD) patterns were taken on a Siemens 500D X-ray diffractometer, whereas electron probe microanalysis (EPMA) was performed on a VegaTescan setup.

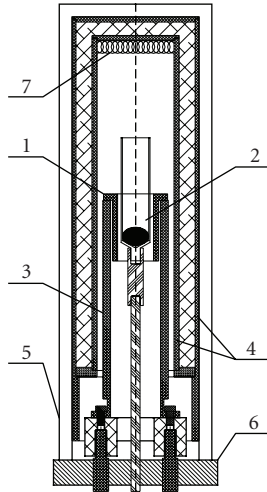


FIGURE 1: Scheme of the setup for growth of ZnS + C nanocomposite: (1) heater, (2) graphite crucible with ZnS in the working position, (3) current leads, (4) heat screen, (5) case of high-pressure vessel (with water cooling jacket), (6) flange, and (7) soot with ZnS and graphite nanocomposite.

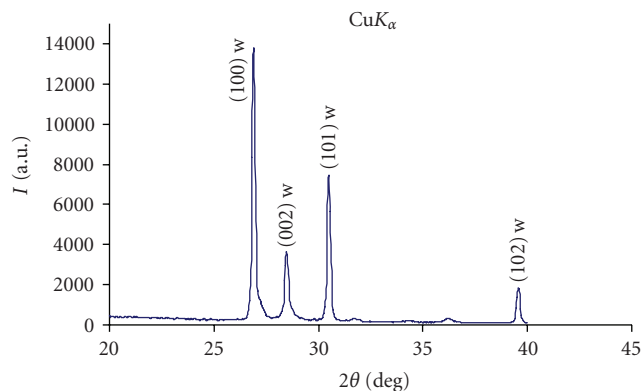


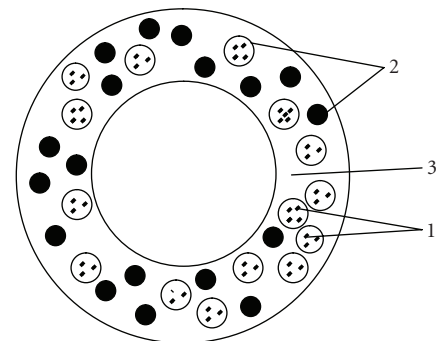
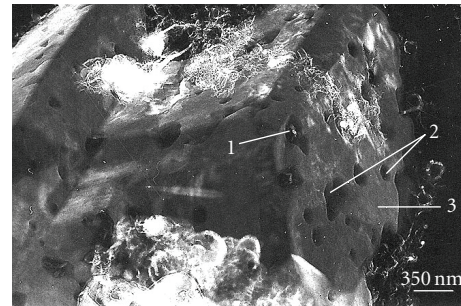
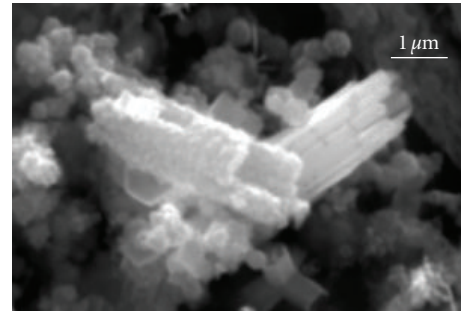
FIGURE 2: X-ray diffraction pattern of the deposited ZnS tubes.

The tubes were then etched in hot HCl and rinsed in distilled water. Some of these samples were annealed after etching at 870–890°C during 7 days, then cooled to room temperature. Microstructure, phase content and composition of the etched, and annealed samples were also studied by the abovementioned TEM, XRD, and EPMA techniques.

### 3. Results and Discussion

The X-ray diffraction pattern of the product of the reaction is shown in Figure 2. The product consists mostly of wurtzite ZnS. Some carbon is sometimes present in the diffractograms.

Figure 3 shows (a) ZnS tubes, (b) the tube wall (3) containing channels (2) filled with graphite fibers (1), (c) the schematic view of a ZnS tube (3) containing channels (2)



1- C nanotubes  
2- Channels  
3- ZnS tube

FIGURE 3: ZnS tubes deposited from vapor: (a) ZnS tubes; (b) ZnS tube walls with channels containing graphite nanofibers; (c) schematic diagram of ZnS tubes reinforced with C nanofibers: (1) graphite fibers, (2) channels, (3) ZnS tubes.

filled with graphite fibers (1). TEM image and the electron diffraction pattern of the grown ZnS crystals (2) containing C fibers (1) are shown in Figure 4 on the left. The electron diffraction pattern in the inset contains reflections from ZnS crystal and rings from carbon. The electron diffraction patterns were taken so that the incident beam was normal to the amorphous substrate. The ZnS tubes are randomly oriented on the surface. However, one zone (0001) can be distinguished.

In the stable state ZnS has a cubic lattice with sphalerite structure. However, it undergoes a polymorphic transition at 1020°C when sphalerite transforms in wurtzite. In our case ZnS is quenched from the high-temperature state (see the reaction) and exists in hexagonal phase at room temperature.

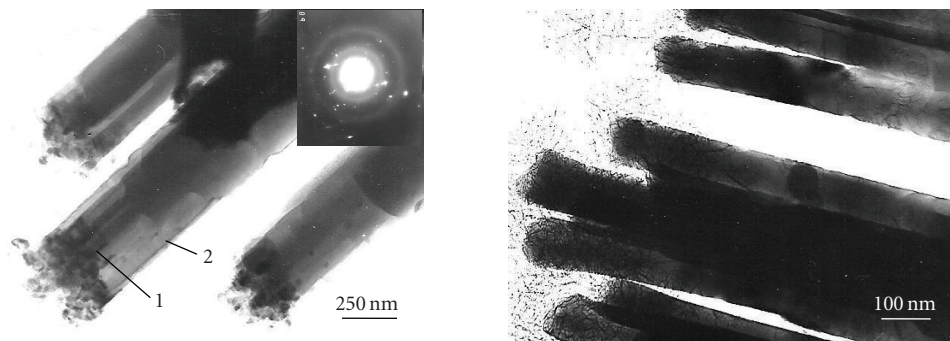


FIGURE 4: (1) ZnS tubes; on the right: graphite nanofibers, (2) ZnS tube; on the left: after etching in HCl a network of C fibers is revealed.

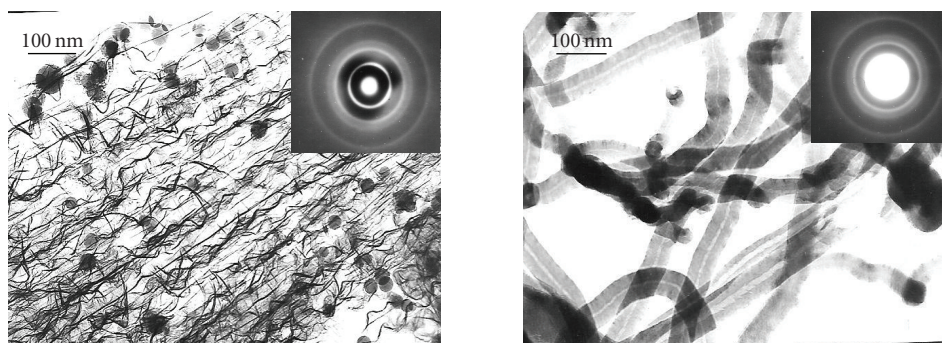


FIGURE 5: Graphite fibers from ZnS tubes remained after etching and annealing (on the left), annealing (on the right).

Intensities of the diffraction lines in the XRD patterns (Figure 2) differ from the ratio of intensities of a standard sample (JCPDS card 36-1450). These TEM diffraction and XRD data confirm that some grown directions prevail in the tubes, in particular,  $c$  direction of the wurtzite structure.

The image in Figure 4 on the right is taken from the samples etched in hydrochloric acid. It is seen that etching in HCl causes dissolution of zinc sulfide and reveals network of carbon fibers.

The following annealing ZnS removes completely and only carbon fibers remain. This is seen from Figure 5 which shows the TEM images of the etched and annealed samples (left) and the annealed sample (right). In the insets on the left and on the right, electron diffraction patterns show rings from carbon.

It should be noted that the effect of annealing can be detected visually: the initially gray powder of ZnS and carbon mixture becomes absolutely black after annealing, which confirms indirectly that only carbon remains after quite long heating. White pure ZnS crystallites deposit on the cold end of the sealed tube. Semiquantitative EPMA microanalysis performed by energy-dispersion (ED) detection system confirms that only about 4% of ZnS remain after annealing, while 2% remain after combination of etching in hot HCl and the following annealing.

The experimental data show that during growth of ZnS submicro and nanotubes in graphite crucible the nanocomposite forms ZnS tubes reinforced with graphite nanofibers deposit as the furnace temperature is decreased.

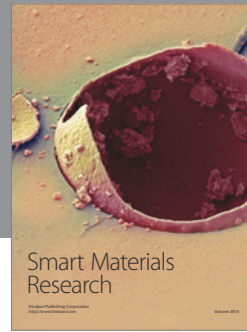
The annealing or etching of the tubes removes ZnS, so that only graphite nanofibers from the tube walls remain.

Thus, we have developed a chemical vapor deposition technique to produce ZnS submicro and nanotubes reinforced with graphite nanofibers.

## References

- [1] M. Kawa, H. Morii, A. Ioku, S. Saita, and K. Okuyama, "Large-scale production of CdSe nanocrystal by a continuous flow reactor," *Journal of Nanoparticle Research*, vol. 5, no. 1-2, pp. 81–85, 2003.
- [2] I. Chakraborty, D. Mitra, and S. P. Moulik, "Spectroscopic studies on nanodispersions of CdS, HgS, their core-shells and composites prepared in micellar medium," *Journal of Nanoparticle Research*, vol. 7, no. 2-3, pp. 227–236, 2005.
- [3] J. Hu, Y. Bando, Z. Liu, J. Zhan, D. Goldberg, and T. Sekiguchi, "Synthesis of crystalline silicon tubular nanostructures with ZnS nanowires as removable templates," *Angewandte Chemie International Edition*, vol. 43, no. 1, pp. 63–66, 2003.





**Hindawi**

Submit your manuscripts at  
<http://www.hindawi.com>

