

Mechanochemical dry synthesis of nanocrystalline semiconductors

P. Baláž*, E. Godočiková*, K. Iždinský**, J. Kováč***, A. Šatka*** and M. Achimovičová*

* Institute of Geotechnics of Slovak Academy of Sciences, Watsonova 45, 043 53 Košice, Slovakia, balaz@saske.sk, godocik@saske.sk, achimovic@saske.sk

** Institute of Materials and Machine Mechanics, Račianska 75, 831 02, Bratislava 3, Slovakia, ummsizd@savba.sk

*** Department of Microelectronics, Slovak University of Technology and International Laser Centre, Ilkovičova 3, 812 19 Bratislava, Slovak Republic, jaroslav.kovac@stuba.sk, alexander.satka@stuba.sk

ABSTRACT

The composition and properties of zinc sulphide ZnS, cadmium sulphide CdS and lead sulphide PbS prepared by mechanochemical dry synthesis from metal acetates and sodium sulphide precursors have been studied. ZnS, CdS and PbS have been obtained with estimated sizes 5 nm, 5 nm and 8 nm, respectively. The overall solid state synthesis route is a very straightforward and permits the large quantities of semiconductors to be produced at an ambient temperature in a very reasonable time.

Keywords: ZnS, CdS, PbS, nanoparticle, mechanochemical synthesis

1 INTRODUCTION

Nanocrystalline semiconductors, also called quantum dots, appear to be interesting objects for studying basically novel properties of matter. In general, reducing the size of semiconductors down to the nanometer length scale is expected to increase the energy gap of the semiconductor structure and, consequently, to give rise to shorter wavelengths optical emission spectra relative to that of bulk semiconductors [1].

Nanosized solids have been synthesized by a number of techniques starting from vapor phase (e.g. inert gas condensation), liquid phase (e.g. rapid solidification) and solid phase (e.g. high-energy milling, mechanochemistry).

The mechanochemical synthesis has attracted considerable scientific and technical interest in recent years as a consequence of the unique nanostructures and properties developed by this process. The high-energy milling can be used to induce a wide variety of solid-solid and even solid-liquid reactions [2-15]. The chemical reaction occurs at the interfaces of the nanometer sized grains that are continually regenerated during milling. As a consequence, reactions, that would normally require high temperatures to occur, due to separation of the reacting phases by the product phases, can occur at low temperature in a ball mill. An important feature of the mechanochemical synthesis is the rapid refinement of the particle microstructure, i.e. grain size or crystallite size, during milling. While powder particle sizes generally decrease

only to the micrometer level, a nanometer grain size is developed within each particle.

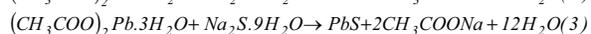
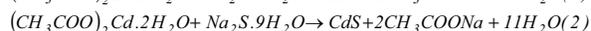
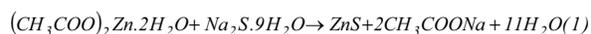
It is aim of this paper to study the mechanochemical synthesis of ZnS, CdS and PbS nanocrystalline semiconductors from organometallic and inorganic precursors in order to determine the overall feasibility of the process as well as to identify the reaction products.

2 EXPERIMENTAL SECTION

Mechanochemical synthesis of nanocrystalline ZnS, CdS and PbS was performed in a laboratory planetary mill Pulverisette 6 (Fritsch, Germany). Tungsten carbide (WC) grinding chamber of 250 ml volume and 50 WC balls of 10 mm diameter (total weight 360 g) were used. Weight of the total powder mixture for milling was 13.1 g, 10.5 g and 7.8 g for ZnS, CdS and PbS, respectively. The rotation speed of the planet carrier was 500 rev min⁻¹. Milling time was 10 min. The argon atmosphere inside the milling chamber was used.

Nanocrystalline PbS was also synthesized in an industrial vibratory mill ESM 654 (Siebtechnik, Germany) under the following conditions: milling time: 6 min for both, loading of the mill with steel balls of 30 mm diameter in total amount of 17 kg, weight charge in the mill 50 g, the rotation speed of milling chamber 960 rev min⁻¹.

ZnS, CdS and PbS nanocrystalline semiconductors were prepared from corresponding acetates and sodium sulphide according to the solid state equations



After the completion of reactions (1), (2) and (3) in the mill, the produced nanocrystalline semiconductors have been processed according to flowsheet given in Fig. 1.

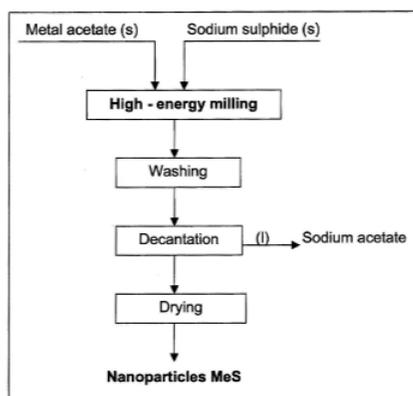


Figure 1: Flowsheet of mechanochemical synthesis and processing of nanocrystalline semiconductors

The X-ray diffraction measurements were carried out using a diffractometer DRON 2.0 (Russia) with goniometer GUR 5 and FeK_α radiation (Fig. 3 and 4) and using a PHILIPS X'Pert diffractometer, working in the 2θ geometry with CuK_α radiation (Fig. 7). The XRD lines were identified by comparing the measured patterns to the JCPDS data cards. The grain sizes of MeS nanoparticles were calculated from the Scherrer formula [16] as follows

$$D = \frac{K r \lambda}{b \cos \Theta} \quad (4)$$

where D – the average crystallite size, K – the shape factor, r – the radius of goniometer, λ – the X-ray wavelength, b – the angular line width of half – maximum intensity and Θ – the Bragg's angle.

Particles were dispersed in distilled water and captured on the surface of carbon foil supported by copper grid. The microstructure was analyzed by JEOL JEM 100C electron microscope operated at the accelerating voltage of 100 kV. The morphology of particles was observed by bright field image observations and the structure was determined by selected area electron diffraction.

The synthesized semiconductors were analyzed using FE-SEM LEO 1550 scanning microscope in order to investigate the surface morphology of the nanoparticles. The samples were left uncovered from any conductive material as to keep their original properties.

3 RESULTS AND DISCUSSION

3.1 Zinc sulphide ZnS

In Fig. 2 the X-ray diffraction pattern of ZnS nanocrystals synthesized according to reaction (1) and processed via the flowsheet presented in Fig. 1 is given. X-ray analysis confirmed the presence of α -ZnS (wurtzite-

JCPDS 5-0492) together with β -ZnS (sphalerite, JCPDS 5-0566) as the only reaction products. The value of grain size 5 nm was calculated by the Scherrer formula (4) for (111) plane of ZnS. The cubic sphalerite is more stable at low temperatures than hexagonal wurtzite [3]. The situation given in Fig. 2 indicates the occurrence of some type of “frozen” state, where both ZnS forms are presented. The influence of high-energy milling on ZnS phase transformations was carefully studied [17-20]. While the effect of mechanical stress on sphalerite results only in its amorphization, the same effect applied on wurtzite can bring about transformation into sphalerite [19]. Kosmac and Courtney [21] have observed at the mechanochemical synthesis of ZnS only formation of sphalerite. It can be presupposed that the mechanochemical synthesis of ZnS nanoparticles occurs through an intermediate stage where both forms are present. A more understanding about the mechanism of these transitions is presupposed by the study of the mechanochemical synthesis kinetics.

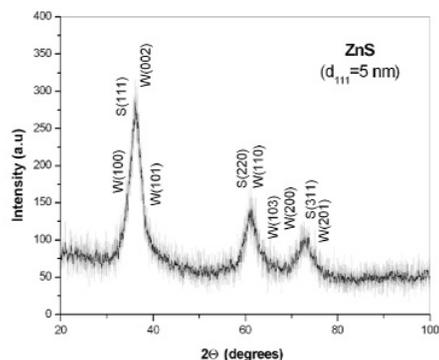


Figure 2: XRD pattern of the mechanochemically synthesized ZnS nanoparticles, W-wurtzite, α -ZnS, S-sphalerite, β -ZnS

3.2 Cadmium sulphide CdS

In Figure 3 the X-ray diffraction pattern of CdS synthesized according to reaction (2) and processed via flowsheet on Fig. 1 is given. Hexagonal α -CdS (greenockite, JCPDS 41-1049) together with cubic β -CdS (hawleyite, JCPDS 10-0454) are present among the products of mechanochemical solid-state synthesis. The value of grain size 5 nm was calculated by the Scherrer formula (4) for (111) plane of CdS.

The same situation as detected for ZnS nanoparticles was identified also for CdS nanoparticles. In literature the polymorphous transformation of CdS during high-energy milling were described [18-19, 22-23]. The milling of hexagonal CdS phase brings about its transformation into disordered cubic CdS phase. The rate of this transformation

is dependent on the method of CdS mechanochemical synthesis.

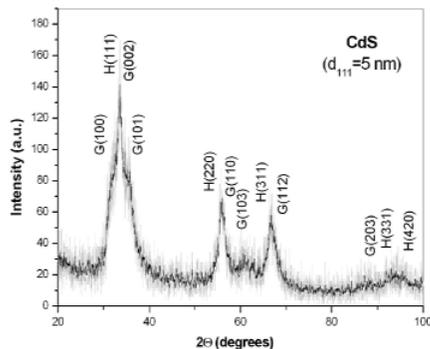


Figure 3: XRD pattern of the mechanochemically synthesized CdS nanoparticles, G-greenockite, α -CdS, H-hawleyite, β -CdS

3.3 Lead sulphide PbS

XRD pattern of PbS nanoparticles synthesized according to reaction (3) and processed via the flowsheet on Fig. 1 is given in Figure 4. We clearly see the diffraction peaks corresponding to (111), (200), (220), (311) and (222) planes of cubic PbS (galena, JCPDS 5-0592). No other products were confirmed in this well crystallized product with the grain size 8 nm calculated by the Scherrer formula (4). SEM surface morphology of the synthesized PbS nanoparticles with the size 20-100 nm is depicted as inset in Figure 4. Particles form strongly agglomerated entities.

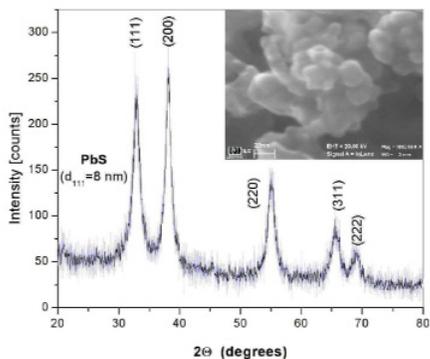


Figure 4: XRD pattern of the mechanochemically synthesized PbS nanoparticles in a laboratory mill

The TEM image in Figure 5a has evidenced nanoparticles aggregated in a complex network form. The particle size is very broad ranging to ten's nanometers. The

small particles have spherical morphology, the larger particles are rather in form of polyedric grains. Selected area electron diffraction pattern corresponding to random orientation of PbS particles shown in Figure 5b.

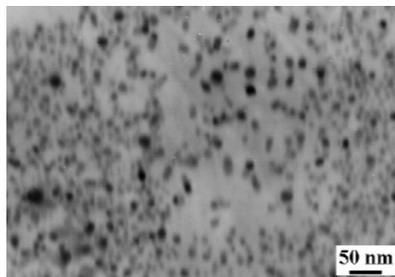


Figure 5a: TEM micrograph of the mechanochemically synthesized PbS nanoparticles (bright field image)

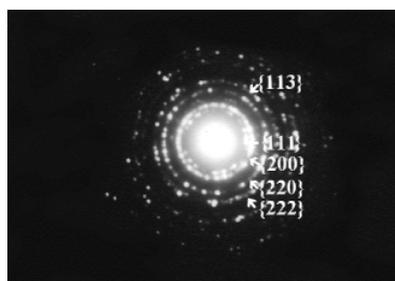


Figure 5b: Selected area electron diffraction of the mechanochemically synthesized PbS nanoparticles

UV-VIS optical absorption spectrum of the mechanochemically synthesized PbS nanoparticles is shown in Figure 6.

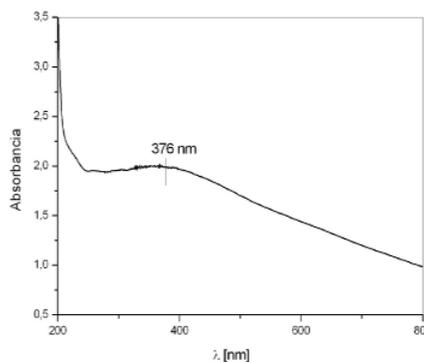


Figure 6: UV-VIS spectrum of the mechanochemically synthesized PbS nanoparticles

It can be seen that the UV-VIS absorption edge is about 376 nm which correspond to 3.28 eV and shows a blue shift from that the bulk PbS crystals where the direct band gap is

0.41 eV [24]. This is an indication of quantum confinement, because the average size of the PbS nanoparticles is smaller than the excitonic Bohr radius of the bulk PbS (ca 18 nm), [25].

The mechanochemical synthesis of lead sulphide PbS performed in a laboratory mill and documented by Figure 4 has been repeated in an industrial mill to verify the possibility to scale-up the whole process. The obtained PbS nanoparticles have been characterized by X-ray analysis (Fig. 7) and the value 13 nm for the grain size have been calculated. This result indicates the possibility to produce nanocrystalline semiconductors via high-energy milling in an industrial scale.

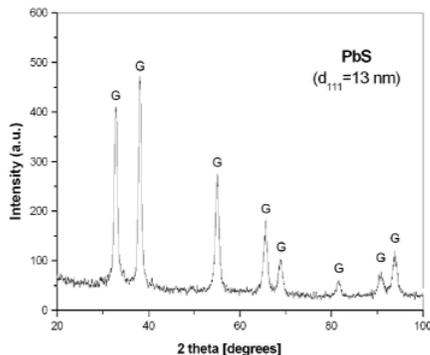


Figure 7: XRD pattern of the mechanochemically synthesized PbS nanoparticles in an industrial mill, G-galena

ACKNOWLEDGEMENT

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