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ZINC SULPHIDE (ZnS) NANPARTICLES FOR ADVANCED APPLICATION

NANOCZĄSTKI SIARCZKU CYNKU (ZnS) DO ZAAWANSOWAYCH APLIKACJI

A b s t r a c t

Zinc sulphide (ZnS) is one of the first discovered semiconducting materials, which due to their unique properties can be applied in optoelectronic devices, such as ultraviolet-light-emitting diodes, flat-panel displays, electroluminescent and sensors. As we present in this short review, the properties of ZnS are highly dependent on their size, structural form and morphology. Nowadays, one-dimensional (1D) structures of ZnS have been of great interest, mainly due to their luminescent and electrical properties.

Keywords: zinc sulphide, nanoparticles, optoelectronic devices

S t r e s z c z e n i e

Siarczek cynku (ZnS) jest jednym z pierwszych poznanych półprzewodnikowych materiałów, który dzięki swoim unikalnym właściwościom znalazł zastosowanie w optoelektronice m.in. do budowy diod świecących w zakresie ultrafioletu, płaskich monitorów, diod elektroluminescencyjnych i czujników. Jak zostanie to pokazane w tym krótkim artykule przeglądowym, właściwości ZnS silnie zależą od rozmiaru, morfologii i struktury krystalicznej. Obecnie szczególnym zainteresowaniem cieszą się jednowymiarowe kryształy (1D) ze względu na swoje właściwości luminescencyjne i elektryczne.

Słowa kluczowe: siarczek cynku, nanocząstki, urządzenia optoelektroniczne

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1. Introduction

The properties and applications of zinc sulphide (ZnS) nanoparticles (NPs) and related materials have been the fields of research over the last decade [1]. The nanostructures of ZnS, according to Siegel's classification, can be divided into zero-dimensional (0D), one-dimensional (1D) and two-dimensional (2D) structures [2, 3]. Different forms of one-dimensional ZnS nanostructures have been fabricated, for example: nanowires, nanotowers and nanotubes [1]. ZnS nanocrystals can be synthesised via several types of methods, including the microwave-assisted reaction, the micro-emulsion processes, the vapour-liquid-solid growth method, electrospinning and solvothermal methods [4]. Zinc sulphide is a semiconductor with very unique properties, which can be found in one of the two structural forms –- cubic sphalerite or hexagonal wurtzite. This nontoxic material, which is chemically more stable than other semiconductors, is characterised with a wide band-gap energy of ~3.7 eV [5]. Because of these properties, ZnS nanoparticles can be used in both biomedical and optoelectronic applications, such as biosensors, biocomposites [6] light-emitting diode (LED), screens, sensors or lasers [5] or nanocomposites [7].

This short review is concentrated especially on the optoelectronic applications of materials based on 1D ZnS nanocrystals. The selected methods of synthesis, as well properties and applications of these materials, will be presented.

2. One-dimensional nanostructures

Nanomaterials are a group of materials, which have at least one size between 1 to 100 nm. Siegel classified nanostructured materials into four categories according to their dimensionality: zero dimensional, one dimensional, two dimensional and three dimensional [3]. In the first category, the atomic clusters, filaments and cluster assemblies are classified. The multilayers are classified as one dimensional nanomaterial. The third category contains ultrafine-grained over-layers or buried layers. The nano-phase materials consisting of equiaxed nanometre-sized grains are classified as three dimensional. According to the above information, 1D nanostructures possessed two dimensions on the nanoscale range, i.e. the diameter of the tube is below 100 nm and its length could be much greater. It is believed that 1D nanostructures are the best systems for exploring a large number of novel phenomena at the nanoscale, and investigating the size and dimensionality dependence of functional properties. 1D crystals also play an important role as interconnects or the key units in the fabricating electronic, optoelectronic, electrochemical and electromechanical devices [1, 3, 7].

One-dimensional nanostructures are characterised with two nanoscale dimensions, so the movement of electrons is limited in these dimension. The free flow of electrons is possible only in one direction – along the nanoparticles. For a nanostructure with a square cross-section, the total energy can be described by the below equation (1):

$$E_{n,m,k_x} = \frac{h^2 n^2}{8m^* L_z^2} + \frac{h^2 m^2}{8m^* L_y^2} + \frac{h^2 k_x^2}{8m^*} \tag{1}$$

where:

E_{n,m,k_x} – total energy,
h – Planck constant

m^* – mass of the electron,
L_z, L_y – nanoscale dimensions in 1D structure,
n,m, = 1, 2, 3.

Total energy depends on two quantum numbers and the wave vector for electron's movement along the k_x dimension. The real nanostructures have more complicated shapes than the above example. In order to compute the total energy, numerical solving of an appropriate Schrödinger equation is necessary [8].

One-dimensional nanocrystals can form a variety of shapes (Fig. 1). In the recent years, the preparation of such morphologies of 1D nanocrystals as nanotubes, nanobelts, nanocombs, nanoawls, nanotowers, and the most important nanorods and nanowires, have been reported. The classification of morphologies of 1D nanostructures is not entirely clear. It is believed that nanowires are long, flexible and have a circular cross-section in contrast to nanorods, which are shorter, stiffer and have a hexagonal cross-section [1]. All of the various morphologies of one-dimensional nanostructures are presented in Fig. 1.

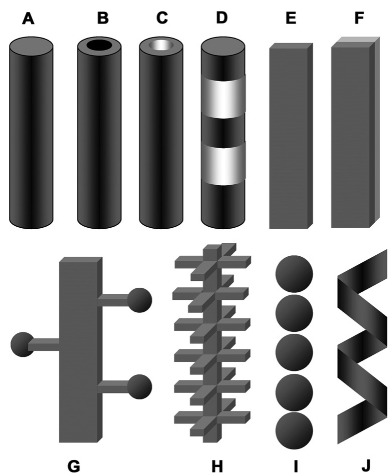

Fig. 1. Different morphologies of 1D nanostructures: nanowire (A), core-shell structure (B), nanotube (C), heterostructure (D), nanobelt (E), nanotape (F), dendrite (G), hierarchical nanostructure (H), nanosphere assembly (I) and nanosprings (J) [9]

There are several methods by which one-dimensional nanosturctures can be obtained: spontaneous growth from the liquid or the vapour phase; synthesis based on templates; solvothermal methods with the electrospinning method and with lithography [1, 4].

3. Zinc sulphide – crystallographic forms

ZnS has two available allotropic forms. One is with the hexagonal crystallographic form and it is named wurtzite. The second, more common and stable form has a cubic crystallographic structure and it is named zinc blende. The wurtzite and the zinc blende forms have band gaps of about 3.77 and 3.72 eV, respectively. The zinc blende transforms into wurtzite at temperatures over 1052°C [1, 10]. The crystal structures of zinc sulphide are presented in Fig. 2. The nanoparticles of ZnS can change their crystallographic form easier than particles in the macroscale. The zinc sulphide nanocrystals can transform from zinc the blende to wurtzite at about 400°C [1].

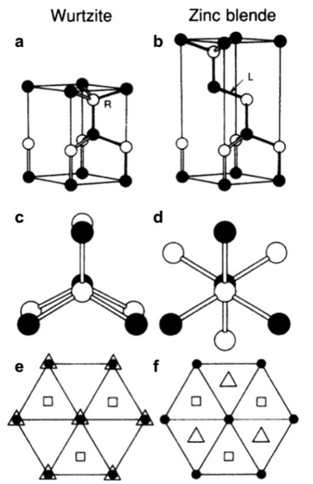

Fig. 2. Crystal forms of zinc sulphide. Difference in the hardness of the fourth interatomic bond along the right (R) for wurtzite and along the left (L) for zinc blende (a, b). The respective eclipsed and staggered dihedral conformations (c, d). Atomic arrangement along the close packing axis (e, f) [1]

The crystal structure has an impact on the bonds energy. Between the cubic and the hexagonal form, the difference in the bond energy is about 5.6 meV/atom. For one-dimensional nanoparticles, the diameter has an influence on the bond's energy. The energy bond decreases with the increase of the nanoparticle's diameter. This phenomenon is observed only for the material that is in the nanoscale. For the bulk material, the diameter has no impact to the value of the bond's energy [11]. In Fig. 3, the influence of diameter on the bond's energy is depicted. For the bulk material, the bonds energy is stable for different diameters in contrast to ZnS nanowires. For the lower values of crystal diameters, the bond's energy is higher. The difference in the bond energy between cubic and hexagonal forms is also depicted.

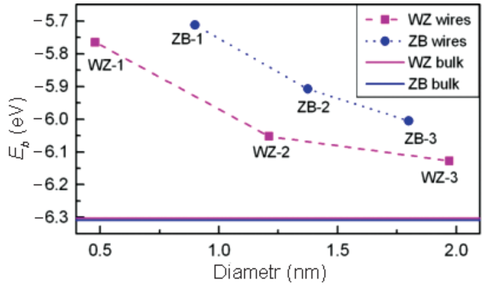

Fig. 3. The influence of diameters ZnS nanowires on bonds energy [11]

4. Photo- and electroluminescence of ZnS

ZnS is well known for its photoluminescence (PL) and electroluminescence (EL). ZnS-based phosphors exhibit excellent conversion efficiencies for fast electrons into electron-hole pairs [12]. The PL properties of ZnS (1D) nanocrystals in most cases depend on their shape or size, but for example for nanowires and nanoribbons, they are very similar. The PL measurement of both structures of ZnS at room temperature shows strong and broad emission spectra with the maximum centred at 398 nm [13]. Generally, the 1D ZnS nanoparticles have a strong green emission band, centred at about 530–540 nm, and a weaker blue emission band, centred at about 440 nm [1].

The electroluminescence process is defined as non-thermal generation of light through the application of an electric field to the sample. Zinc sulphide is one of the best semiconducting functional materials for EL devices [14]. The temperature has a strong influence on the electroluminescence in ZnS. With an increase in the temperature, the EL brightness increases. The nanoparticles of ZnS also have a promising electroluminescence properties. They are used in semiconductor-based light emitting diodes (LEDs), which are described in section 6. The highly saturated colour emission could be obtained in such devices based on ZnS nanoparticles [1]. The ZnS nanoparticles are often dotted with another metal in order to improve their EL properties. Dotted ZnS nanocrystals have a high quantum efficiency with narrow emission and broad excitation spectra [15].

5. Solvothermal synthesis of ZnS nanoparticles

The pioneers of the synthesis of ZnS nanocrystals were Brus and co-workers. They successfully synthesised it first time via a colloidal reaction of ZnS colloidal nanoparticles in the 1980's. Sodium sulphide and zinc perchlorate in the methanol and water were used as the sources of sulphide and zinc [1]. Nowadays 1D ZnS nanocrystals can be fabricated by many different methods. The synthesis can be carry in gas or liquid phase. The following belong to the most common methods of receiving ZnS nanoparticles: synthesis with microwave irradiation [16]; micro-emulsion techniques [17]; the vapour-liquid-solid growth method [18]; the solution-liquid-solid growth [2]; synthesis with template; electrospinning [19]; and the most common solvothermal methods [2, 5].

Originally, the solvothermal synthesis was called hydrothermal because of the use of water as a solvent. The reactions were kept in a sealed reaction container with a temperature of above 100 ^{o}C. The pressure in the container was determined by the temperature and the volume of the solvent in the vessel. Usually, the hydrothermal reactions were kept at a temperature of about 300 ^{o}C. At that temperature, the water is in the supercritical regime. Nowadays, the water is replaced with nonaqueous solvents, such as alcohols, benzene, polyamines or hydrazine. The reaction temperature is kept above the boiling point of the solvent. The most popular container is a Teflon vessel, so that the reaction can be kept at about 270°C under a pressure nearing to 150 bar [2].

Solvothermal synthesis has a few advantages over the other methods of synthesis of nanoparticles. With the solvothermal methods, it is possible to remove diffusion control by the use of a suitable solvent under mild condition. Due to the use of various precursors and reaction environments, it is possible to control the physicochemical and morphological properties of the obtained product, and the time of synthesis is usually shorter than that of other methods. The influence of parameters on the reaction is not exactly known, due to the possible synergistic effects. It is known that the temperature, pressure, percentage fill of the vessel or used reagents have an influence on the final product [2], 20]. At lower temperatures, the substrates could not react fully, but the higher temperature could cause the formation of bigger nanoparticles. The longer time of reaction mostly caused an increase of the average diameter of nanocrystals [20]. The percentage fill of the vessel has an influence on the reaction pressure. An increase of pressure could lead to the formation of smaller nanoparticles [21]. For the ZnS 1D nanoparticles, various temperatures (130–200°C) and reaction times (for few minutes to 20 hours) are used [10, 22, 23].

6. Applications of ZnS nanocrystals – optoelectronic devices

ZnS nanocrystal semiconductors are one of the most interesting and important groups of compounds used in electronic and optoelectronic devices. The development of these materials is one of the most important trends in this field [24].

1D nanocrystals can be used in Field-Effect Transistors (FETs). He et al. fabricated FET based on ZnS/SiO_2 core/shell nanocables. For the fabrication of FETs, the synthesised ZnS/silica nanocables were transferred from the Si substrate to Au/Ti electrodes. In order to firmly contact the Au/Ti metal electrodes and ZnS core of the nanocable, focused ion beam microscopy was used to cut the nanocable at the two ends of exposed ZnS core. Then, a Pt mixture was deposited at the ends in order to make contacts between the ZnS core and Au/Ti electrodes [25]. The typical FET is a three terminal device. The names of terminals refer to their function and they are called: gate, drain and source. The gate terminal controls the opening and closing of the physical gate with permits or blocks of electron flow by creating or eliminating conductive the channel between drain and source [24]. An example of FET is presented in figure 4. The grey balls in Figure 4 illustrate the crystals of the semiconductor.

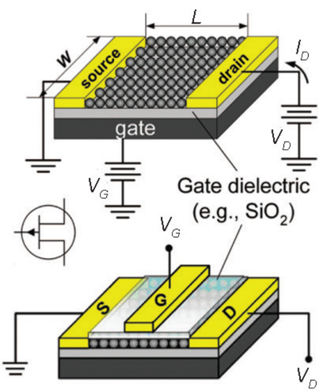

Fig. 4. Typical bottom-gated (a) and top-gated (b) of Field-Effect Transistors [24]

The connecting source with a drain is called the semiconductor channel. For the isolator, the most commonly used materials are silicon or aluminium oxides in the polymer matrix [24].

The other devices, where the one-dimensional ZnS nanocrystals are very useful, are Light-Emitting Diodes. In a typical LED, a thin layer of light emitting nanocrystals is placed between the hole and the electron transporting layers. The recombination of the electron-hole pairs in the nanocrystals generates photons with energy corresponding to the gap between the highest occupied (1Sh) and the lowest unoccupied (1Se) states in the nanocrystal [24]. A typical thin film LED with semiconductor nanocrystals is presented in Fig. 5.

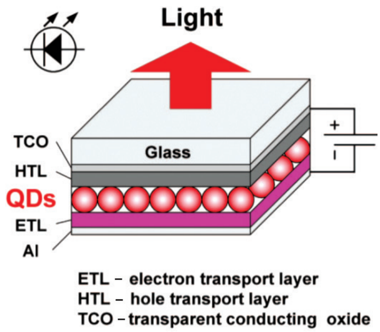

Fig. 5. Schematic picture of a thin film LED with semiconductor nanocrystals [24]

The LEDs are characterised by External Quantum Efficiency, which is the ratio of the number of photons emitted into free space to the number of injected carriers. ηext can be defined as (2):

$$\eta_{ext} = \frac{\text{(number of emitted photons per second)}}{\text{(number of electrons injected into LED per second)}} = \frac{P/h\nu}{I/e}$$

where:

- h – Planck constant,
- e – electron charge,
- P – optical power emitted into free space,
- I – injection current,
- v – frequency.

The most important properties of LEDs are:

- the high purity of the emitted light,
- the light emission proportional to the current,
- unordered spontaneous emission,
- fairly broad continuous spectrum of emission,
- low power emission signal – below 100 mW,
- much lower cost in comparison with the semiconductor laser [12, 24].

Lu et al. fabricated Organic LED (OLED) with a ZnS nanocolumn. The ZnS nanocolumn was grown on the indium tin oxide (ITO) substrates by the glancing angle deposition technology. The inorganic ZnS material was evaporated onto ITO by the electron beam deposition method. The electroluminescence of OLED with ZnS 1D nanocrystals was about 1.2 times bigger than that of devices with a continuous layer or without a layer of ZnS [26].

The last important devices based on one-dimensional nanocrystals are photodetectors and solar cells. There is a large variety of sensitive photon detection devices operating in the visible spectral range, but in the infrared, the available detection systems are insensitive or very expensive. The last studies focus on the photodetectors with semiconductor nanocrystals or the blend of the nanocrystals connecting with the semiconducting organic materials [24]. The typical photodetector based on the nanocrystals is presented in Fig. 6.

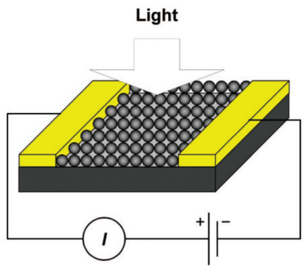

Fig. 6. Schematic picture of a typical NCs-based photodetector [24]

The progress in NC-based photoconductors allow to produce the near-IR detectors with device characteristics comparable to commercial devices [24].

The demand for renewable sources of energy implies the development of efficient and inexpensive photovoltaic materials. Due to the optical and electronic properties of semiconductor nanocrystals, these materials are promising candidates for producing new and inexpensive photovoltaic devices. Photovoltaic cells based on materials that absorb light and separate photogenerated electrons and holes, and replace the light energy with the electrical energy [24]. The schematic solar cell with n- and p- conductivity is presented in Fig. 7.

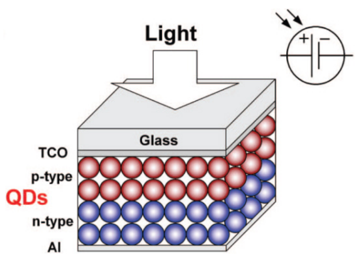

Fig. 7. The schematic solar cell with n- and p- conductivity [24]

The current polymer solar cell with single nanocrystals can achieve a power conversion efficiency of about 5%. For the tandem solar cell with different band gaps, it is possible to achieve about 7%. The outdoor lifetime of such materials is more than 1 year [24]. Huang et al. improved the efficiency of Si-based solar cell with ZnS nanoparticles. The obtained efficiency increased from 6.57 to 7.20% [27].

7. Conclusion

The one-dimensional nanocrystals of zinc sulphide have very interesting electrical and optoelectrical properties. There are a several methods to obtain this material. The most popular are the solvothermal methods. The optoelectronic industries focus on producing new devices, which are based on the semiconductor nanoparticles. The one-dimensional nanocrystals of ZnS are a promising material for electric and optoelectric devices due to their low production cost and good optical and electrical properties.

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