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Modulated interference effect by ZnS nanoparticles / 3-Mercaptopropyltrimethoxysilane quasi core-shell structure: Far-infrared spectroscopy

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The ZnS nanoparticles, as starting materials in the present study, were synthesized mechanochemically. Surface modification of the obtained nanoparticles was performed by 3-Mercaptopropyltrimethoxysilane. SEM analysis indicates that modification of ZnS nanoparticles with 3-Mercaptopropyltrimethoxysilane causes the appearance of the quasi core-shell structure. The FIR spectrum analysis was performed by fitting procedure, taking into account the appearance of quasi core-shell structure. Optical and structural characteristics of both ZnS and 3-Mercaptopropyltrimethoxysilanes are revealed on the spectrum. An interference effect modulated by the ZnS phonon properties was also detected. Obtained results indicate that the quasi core-shell structures could be successfully applied in the interferometry.

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1. Introduction

Nanostructures in which the properties of organic molecules are combined with the optoelectronic properties of semiconductors are the best example of theoretical and experimental research that found its place in the industry. At the present, this primarily refers to the colour control of these structures, as a direct consequence of quantum confinement of electronic states [1]. This effect found its application in optoelectronic systems such as light-emitting diodes [2, 3] and photovoltaic cells [4], or as components of future nanoelectronic devices. The search for new nanodimensional systems and effects that can lead to their new applications is ongoing and represents a significant challenge.

It is well known that the characteristics of nanomaterials are essentially different from the characteristics of bulk materials [5]. Nanomaterials, due to their specific structure and small size, cannot be used on a large scale, especially when engineering applications are concerned [6].

The core-shell semiconductor nanostructures consist of the quantum semiconductor dots in the core and some other semiconductor material in the shell that surrounds the core. Due to their modularity, these structures are easily designed and engineered with the aim to obtain new characteristics. It is interesting to note that these new properties are somewhere between those registered in the balk materials and those created as a result of the material dimensions reduction [7]. On the other hand, the colloidal semiconductor nanocrystals [8, 9] consist of semiconductor nanoparticles with diameters in the range of 1–10 nm surrounded by organic material. This structure allows the simultaneous manifestation of the physical and chemical properties of organic molecules and the optoelectronic properties of semiconductors.

For the surface modification of inorganic particles, most often the silane-based products with bifunctional molecules are used, *i.e.* the hydrolysable group that bonds with the surface of inorganic particles and the non-hydrolyzed group as R group, which reacts with the polymer matrix [10]. When the ZnS surface modification is concerned, 3-Mercaptopropyltrimethoxysilane is considered due to the thiol functional group presence. The bonding with ZnS can be established through hydrogen bonding between the S-H group and dipole-dipole bonding. This modification enables better ZnS dispersion in polymer nanocomposite and in that way provides very favourable optical properties of the obtained nanocomposite [10, 11].

In our earlier reports [12, 13] far-infrared and Raman spectroscopy were utilized to study the structural and optical characteristics of ZnS obtained by mechanochemical synthesis. The relation between the synthesis parameters and the effects related to the nanoparticles dimensions was investigated. Previously published results indicated that the ZnS nanopowders obtained during milling for 10 min are characterized with the best properties.

In the present work, the ZnS nanoparticles with the surface-modified by 3-Mercaptopropyltrimethoxysilane were synthesized and analyzed with the scope to obtain a quasi core-shell structure with a pronounced interference effect modulated by the ZnS phonon properties.

2. Methods and materials

The samples morphology was analyzed using the high-resolution MIRA3 TESCAN scanning electron microscope (SEM) operated at the accelerating voltage of 5, 12, and 20 kV. Far-infrared reflection spectra were recorded in the wave number range up to 600 cm^{-1} utilizing an A BOMEM DA - 8 FTIR spectrometer with a deuterated triglycine sulphate (DTGS) pyroelectric detector.

The ZnS nanoparticles were synthesized by mechanochemical treatment, detailly described in the literature [12-14]. The milling time was 10 min and the crystallite size of the obtained ZnS nanoparticles was estimated to be 2.3 nm. After milling, the powder mixtures were cold isostatic pressed into tablets with a diameter of 8 mm and thickness of 3 mm by applying a pressure of 3 t cm^{-2}.

The ZnS surface modification was achieved by using a 3-Mercaptopropyltrimethoxysilane (MPTMS), Dynasylane, Evonik Industries, and toluene-hexane, Sigma Aldrich, as a solvent. Synthesized ZnS nanoparticles were mixed with 150 ml of toluene and put into the round-bottom flask equipped with a reflux condenser. The mixture was heated under the protective nitrogen atmosphere to the toluene boiling point. Afterward, 1 g of 3-Mercaptopropyltrimethoxysilane was added. The obtained white suspension was stirred and refluxed for 22 h. After cooling, the suspension was filtered and washed with hexane to eliminate the excess of 3-Mercaptopropyltrimethoxysilane. The modified ZnS nanoparticles were dried at 40 ^{o}C for 12 h and and pressed into tablets (8 mm in diameter and 3 mm thick) by using a cold isostatic press (P = 3 t cm^{-2}).

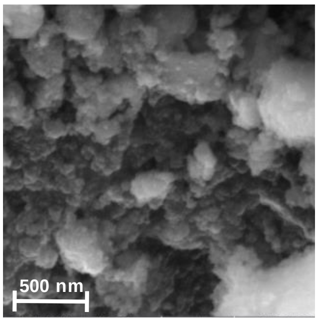
3. Results and discussion

3.1. SEM analysis

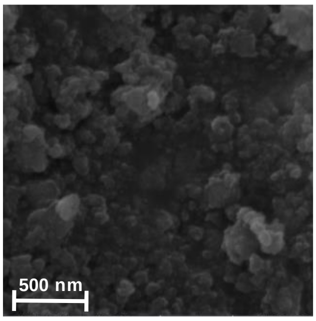
The ZnS nanoparticles structure is presented in Fig. 1a. The SEM micrographs show that synthesized nanomaterial is composed of a mixture of well-defined isolated nanoparticles and spherical nanoparticles clusters 17-30 nm in size. Macroscopic defects like pinhole, peeling, or cracks were not observed. The SEM analysis also revealed that the cold isostatic pressing, utilized as the tablet's preparation method, did not affect the structure and morphology of the obtained samples.

The micrographs showing the surface-modified ZnS nanoparticles are given in Figs. 1b and 1c. A significant difference was observed in the morphology of powder (Fig. 1b) and tablet (Fig. 1c) made from that powder. The SEM images of surface-modified ZnS powder show similar characteristics as the SEM images of pure ZnS. However, in this case, the formed clusters are slightly larger (about 40 nm) due to the obtainment of ZnS nanoparticles / 3-Mercaptopropyltrimethoxysilane core-shell structure.

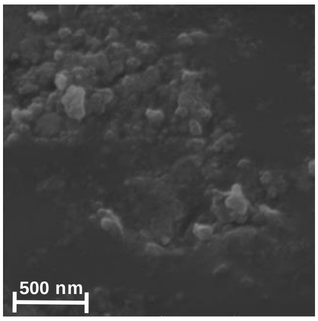
Nevertheless, after making the tablets, areas without ZnS nanoparticles were formed on the sample surface. On the ZnS surface a 3-Mercaptopropyltrimethoxysilane formed secondary dipole-dipole bonds, which are weaker than primary bonds and during sample pressing these bonds could be broken. The remaining silanol and R groups are available for further bonding with the matrix and they are present in condensed or in free form. Thus, at the same time the presence of ZnS nanoparticles / 3-Mercaptopropyltrimethoxysilane core-shell structure, and tablet surface layer with predominant 3-Mercaptopropyltrimethoxysilane with just a few ZnS nanoparticles can be observed. Having all this in mind it can be assumed that this type of modification of the ZnS nanoparticles with 3-Mercaptopropyltrimethoxysilane is most suitably described by the quasi core-shell structure [7]. The characteristics of both quasi core-shell structure parts, *i.e.* semiconductor nanoparticles and organic coating, were preserved in the obtained system and the appearance of a resulting effect was examined by far-infrared spectroscopy.



a)



b)



c)

Fig. 1. SEM micrographs: a) ZnS nanoparticles, b) surface modified ZnS powder nanoparticles, and c) surface modified ZnS nanoparticles after the tablet obtainment

3.2. Far-infrared spectroscopic analysis

The experimental far-infrared spectrum of ZnS powders obtained during milling for 10 min was recorded in the spectral range of 90-600 cm^{-1} at room temperature and in Fig. 2 is presented as a blue line.

The obtained spectrum shows all characteristics of the ZnS nanoparticles already described in the literature [13]. The far-infrared spectrum of the surface-modified ZnS nanoparticles, recorded in the spectral range of 90-600 cm^{-1} at room temperature, is presented in Fig. 2 as a red line. Even though the spectra given in Fig. 2 were recorded under the same conditions, differences in the ZnS nanoparticles and surface-modified ZnS nanoparticles spectra are clearly visible and can be observed throughout the wavelength range.

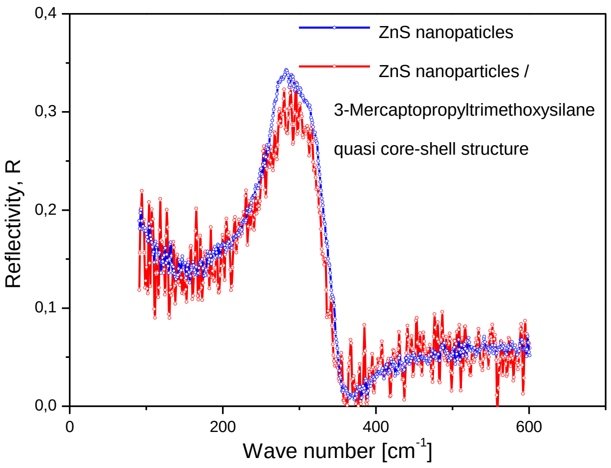


Fig. 2. Experimental far-infrared reflection spectra of ZnS nanoparticles (blue line) and ZnS nanoparticles / 3-Mercaptopropyltrimethoxysilane quasi core-shell structure (red line) (color online)

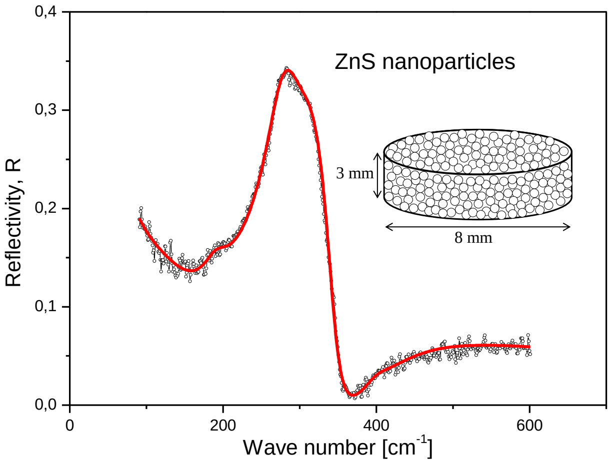


Fig. 3. Far-infrared reflection spectra of the ZnS nanoparticles. The experimentally obtained data points are depicted as circles. The theoretical spectra obtained using the model defined by Eq. (1) and the fitting procedure is given as solid line. Inset: Schematic overview of the sample (color online)

A detailed analysis of the ZnS nanopowder, obtained by mechanochemical synthesis during milling for 10 min, was previously reported [13] and therefore was not the subject of the present research. The previously reported spectrum is presented in Fig. 3 to associate the results of the previously reported and present research and in that way gives a good introduction into the present work, while a schematic overview of the tablet obtained during this study is given as the insert in Fig. 3. In summary, the presented solid line was obtained using the effective medium theory, *i.e.* Maxwell-Garnet mixing rule, as follows [15]:

$$\varepsilon_{eff} = \varepsilon_1 + 3f\varepsilon_1 \frac{\varepsilon_2 - \varepsilon_1}{\varepsilon_2 + 2\varepsilon_1 - f(\varepsilon_1 - \varepsilon_2)} \qquad (1)$$

Approximation presented in (1) describes a homogeneous matrix ε_1 (in this case air with ε_1 = 1) in which spherical nanoparticles with permittivity ε_2 are randomly arranged to occupy a volume fraction *f*. The reflection coefficient, in this case, is given as:

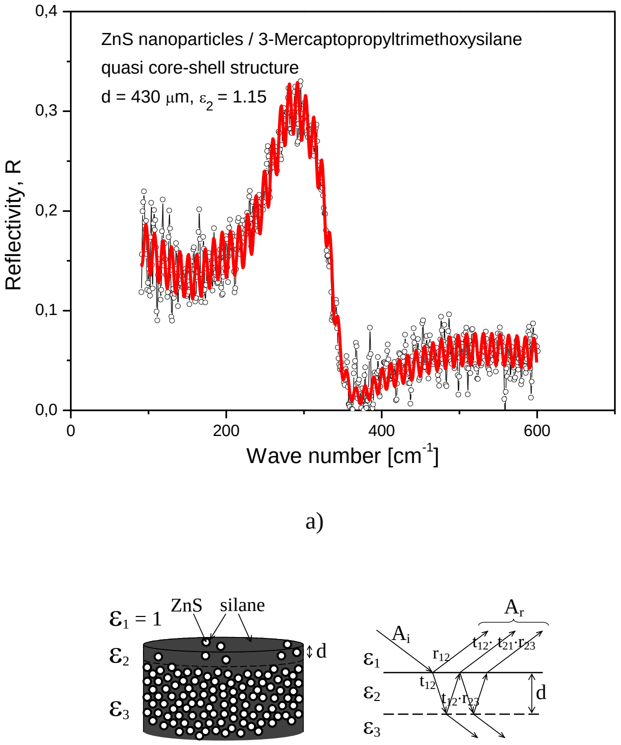
$$R = \left(\sqrt{\varepsilon_{eff}} - 1\right) / \left(\sqrt{\varepsilon_{eff}} + 1\right) \qquad (2)$$

To describe the optical properties of ZnS nanoparticles, ε_2, the dielectric function that includes the interaction between LO phonon and a plasmon, described in more detail elsewhere [16], was used:

$$\varepsilon(\omega) = \varepsilon_\infty \frac{\prod_{j=1}^{2}\left(\omega^2 + i\gamma_{lj}\omega - \omega_{lj}^2\right)}{\omega(\omega + i\gamma_P)\left(\omega^2 + i\gamma_t\omega - \omega_t^2\right)} \prod_{m=1}^{s} \frac{\omega^2 + i\gamma_{LOm} - \omega_{LOm}^2}{\omega^2 + i\gamma_{TOm} - \omega_{TOm}^2} \qquad (3)$$

The key parameters (*f* and γ_t), described in the previous report [13], were obtained in this way as $f = 0.75$ and γ_t = 190. Twice degenerated A1 and E1 TO modes at approximately 270 cm^{-1}, and mode at approximately 348 cm^{-1}, associated with the A1 and E1 symmetry of LO modes, were registered. Weak modes registered at ~ 190 cm^{-1}, 450 cm^{-1}, and 510 cm^{-1} originated from the cubic ZnS and correspond to sums and differences of two phonons [13].

The situation is much more complicated in the case of surface-modified ZnS nanoparticles. The far-infrared spectra of ZnS nanoparticles/3-Mercaptopropyltrimethoxysilane quasi core-shell structure, recorded in the spectral range of 90-600 cm^{-1}, are presented in Fig. 4a. The experimentally obtained data are presented as circles.



a)

b)

Fig. 4. a) Far-infrared reflection spectra of the ZnS nanoparticles / 3-Mercaptopropyltrimethoxysilane quasi core-shell structure. The experimentally obtained data points are depicted as circles. The theoretical spectra obtained using the model defined by Eq. (4) and the fitting procedure is given as solid line. b) Schematic overview of the sample and scheme of the model described by Eq. (4)

The SEM analysis results (Fig. 1c) indicate the presence of an inhomogeneous layer on the tablet surface. This layer mostly consists of 3-Mercaptopropyltrimethoxysilane. The schematic representation of our sample is given in Fig. 4b showing a three-layer structure, where:

(a) medium 1 is air (ε_1=1),

(b) medium 2 is a layer with thickness *d* present at the tablet surface with dielectric constant ε_2 (due to the optical properties of 3-Mercaptopropyltrimethoxysilane [17] it can be assumed that ε_2 is a constant), and

(c) lower optically thick layer, described during the analysis of ZnS nanopowders (Fig. 3), is here, instead of as air, presented as 3-Mercaptopropyltrimethoxysilane with a dielectric constant ε_2 that surrounds ZnS nanoparticles, while the layer itself is described by $\varepsilon_3 = \varepsilon_{eff}$ according to the Maxwell-Garnet mixing rule given in Eq. (1).

In this case, the reflectivity can be determined as described in [18]:

$$R_A = \frac{A_r}{A_i} = \frac{r_{12}e^{-i\alpha} + r_{23}e^{i\alpha}}{re^{-i\alpha} + r_{12}r_{23}e^{i\alpha}} \tag{4}$$

where $r_{ij} = (n_i - n_j)/(n_i + n_j) = \left(\sqrt{\varepsilon_i} - \sqrt{\varepsilon_j}\right)/\left(\sqrt{\varepsilon_i} + \sqrt{\varepsilon_j}\right)$ are the Fresnel coefficients, A_i and A_r represent amplitudes of the incident and reflection beams, respectively, *n* is the complex index of refraction, ε is the dielectric constant and $\alpha = 2\pi\omega d(\varepsilon_2)^{1/2}$ is the complex phase change related to the absorption in the crystal layer with the thickness *d*. Reflectance, *R*, is given as $R = |R_A|^2$.

The parameters for ε_3=ε_{eff} are determined based on data presented in Fig. 3. The interference parameter is affected only by the surface layer properties. The thickness of the layer 2 (*d*), affects the period of oscillations. The ε_2 value directly determines the oscillations intensity. The theoretical model obtained in this manner is in very good agreement with the experimental results. The best fitting is attained when parameters are as follows: *d* = 430 μm and ε_2 = 1.15. It must be underlined that this model predicts the existence of interference oscillations in the whole spectral range.

A similar result can be achieved by using thin films on different bases. However, in the case of thin films, agglomeration of nanoparticles would occur, as well as their inhomogeneous distribution within the film. Due to the type of organic component, the structure obtained in the manner described in this paper, has the advantage that at the same time the separation of nanoparticles and their homogeneous distribution is performed. Thus, nanostructures of desired characteristics are formed.

This implies that the effect of interference is directly related to the organic surface layer properties and that it is modulated by the ZnS nanoparticles' properties. This finding opens new directions of research and potential applications. First of all, with a suitable semiconductor and organic coating selection, it is possible to simultaneously control the parameters and the range of interference, which is of great importance for interferometry applications. On the other hand, nanocomposites that contain such surface-modified semiconductor nanoparticles can give qualitatively new application directions.

4. Conclusion

Results of the present study showed that the ZnS nanoparticles / 3-Mercaptopropyltrimethoxysilane core-shell structure was formed during the synthesis. However, this obtained structure is quite unstable and during the tablets formation under the pressure of 3 t cm^{-2} it was transformed into a state similar to the colloidal nanocrystals, *i.e.* the resulting material shows the properties of quasi core-shall structures. The formed nanostructure shows characteristics of both compounds, the organic and semiconductor. In addition to these characteristics, the effect of interference has been registered. This effect is directly related to the organic surface layer properties. This interference is modulated by the ZnS nanoparticles' properties. The nanostructure obtained in this way is very suitable for use in interferometry, but also as a compound of nanocomposites suitable for nanoscales photonic and nanoelectronics applications.

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