Synthesis of spherical zinc sulfide nanoparticles produced by femtosecond laser ablation and deposited on a silicon substrate under the action of an electrostatic field

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Abstract. In this paper we consider the synthesis of spherical zinc sulfide (ZnS) nanoparticles (NPs) deposited on a silicon substrate by femtosecond laser ablation of ceramic target under the action of an electrostatic field in argon gas atmosphere. The use of an electrostatic field in the process of ablative synthesis of NPs allows, in addition to capturing particles, to carry out predicted deposition of nanomaterials on the substrate, while carrying out the ablation products from the region of laser beam propagation. The morphology and structural characteristics of synthesized ZnS NPs were investigated using scanning electron microscopy and X-ray diffraction analysis. The size distribution of ZnS NPs were studied using dynamic light scattering technique. Obtained NPs have a spherical shape and are characterized by a hexagonal phase of wurtzite ZnS.

1. Introduction

Semiconductor compounds of group II-VI have been the subject of research by scientists for the past few decades and are currently a fairly well-studied and widespread class of materials that are widely used in various optoelectronic devices based on them, such as: light-emitting diodes, flat-panel displays, lasers, electroluminescent light sources, solar cells, sensor devices [1-4].

The compounds of group II-VI are mostly direct-gap semiconductors, possess and are formed by combining an element of the zinc subgroup (Cd, Zn, Hg), which is a metal, with an element of group VI (O, S, Se, and Te), which in turn is a non-metallic element. Semiconductor compounds of group II-VI cover the area of wavelengths from the ultraviolet (UV) to the infrared (IR) range of the spectrum, while these compounds have high optical absorption and emission coefficients, which in turn makes it possible to effectively use them as the basis of a variety of light-emitting devices. Zinc sulfide (ZnS) is deservedly one of the most important representatives of the group II-VI of semiconductor compounds and plays a significant role in the problems of nanoplasmonics and polaritonics, this is due to the possibility of creating a wide variety of quantum-dimensional structures with different morphologies. Such quantum-dimensional structures based on ZnS have high thermal and chemical stability, which together makes these compounds very demanded. A great interest in ZnS quantum dots is caused by the dependence of the optical properties of particles on their size characteristics. By varying the size of the formed particles, as well as the chemical composition, it becomes possible to regulate the photo- and electroluminescent properties [5].
However, there are certain difficulties associated with the formation of high-quality thin films on the surface of substrates, as well as the synthesis of quantum-size structures and particles with the required morphology, for example, an ideal spherical shape of particles with the desired granulometric composition. Semiconductor materials of group II-VI can be obtained by various methods, among which: chemical methods, including the hydrothermal method [6, 7], high-temperature thermolysis [8, 9], spray pyrolysis [10, 11], chemical bath deposition (CBD) [12, 13]; physical methods, including the method of molecular beam epitaxy (MBE) [14], radio frequency cathode deposition [15], thermal evaporation [16, 17], etc.

Of particular interest is the use of the method of pulsed laser sputtering (PLD) [18] and the method of pulsed ablation processing in argon gas atmosphere for obtaining thin coatings, as well as the synthesis of different types of nanomaterials [19-22]. Laser ablation processing is a unique tool that allows you to customize the impact parameters. Changing the modes of exposure to the laser beam, the properties of the medium in which the processing takes place, allows us to obtain quantum-sized particles of various morphologies that have a unique set of properties. A variation is pulsed ablative processing in liquids [23]. Thus, using ablation processing of a ceramic target in water, it was possible to obtain ZnS NPs with a uniform size distribution [24].

2. Experiments
In this study spherical ZnS NPs were obtained by pulsed laser ablation processing of a ceramic ZnS target (made by hot isostatic pressing, purity 99.99%) using a femtosecond Yb:KGW laser system with a wavelength of 1.03 microns, a pulse duration of 280 fs, a pulse energy of up to 150 µJ, and a pulse repetition rate of 10 kHz. Figure 1 shows the scheme of the experimental setup for producing ZnS NPs by pulsed laser ablation processing under the action of an electrostatic field.

![Figure 1. Scheme of the experimental setup for producing NPs by pulsed laser ablation processing under the action of an electrostatic field: 1 – Yb:KGW femtosecond laser; 2 – laser radiation; 3 - beam attenuation system; 4, 5, 6, 7 - system of turning mirrors; 8 – galvo scanner head; 9 – flat-field lens; 10 – vacuum chamber; 11 - electrical conductor entry units; 12 - xyz linear stage ; 13 - high-voltage source; 14 – gas bottle (Ar); 15 – turbomolecular pump.](image-url)
When the radiation of a femtosecond Yb:KGW laser system passes through a beam attenuation system, the pulse energy is set at the required level. Then, passing through a system of turning mirrors, the radiation is directed to a galvo scanner head equipped with a flat-field lens (focal length 200 mm). With the aid of the galvo scanner head, the laser beam is moved along a given trajectory at a required speed and focused the radiation passing through the transparent quartz window of the isolated from the external environment vacuum chamber onto a ceramic ZnS target. Figure 2 shows the schematic image inside view of the vacuum chamber.

![Figure 2. Schematic image inside view of the vacuum chamber.](image)

During laser ablation processing, a focused laser beam interacts target surface, accompanied by the creation of a plasma plume as a result of this interaction, the target's material is removed. The volume of the vacuum chamber is filled with high-purity argon (purity 99.9999%), the ceramic target was located between high-voltage electrodes on which are arranged in a vertical position parallel to each other substrates made of single-crystal silicon Si (100). In the area between the high voltage electrodes, an electrostatic field was created, the intensity of which in the course of experiments was 5-15 kV/cm. Before starting the experiments, silicon substrates were prepared by ultrasonic cleaning.

The use of an electrostatic field in the process of ablative synthesis of NPs allows, in addition to capturing particles, to carry out predicted deposition of nanomaterials on the substrate surface of the substrate, while carrying out the ablation products from the region of laser beam propagation. As a result, the ablated particles do not fall under the repeated exposure of laser radiation, no coagulation of ablation products caused by the action of a laser erosion plume is not observed, the deposition of ablated particles is carried out directly on silicon substrates, behind which are installed high-voltage electrodes, which are energized, which makes it possible to obtain materials of a given size with a narrow size distribution.

3. Results and discussion
In the course of experiments on pulsed laser ablation processing of the ZnS target, several samples were obtained, the variable parameter was the scanning speed of the laser beam, while the parameter of pulse
duration, pulse repetition rate and energy of laser pulses remained unchanged. The morphology of synthesized ZnS NPs were obtained using scanning electron microscope (SEM) MIRA3 TESCAN. To estimate the sizes of NPs obtained under various processing modes, a particle size analyzer HORIBA LB-550 were used, the principle of operation of which is based on the analysis of the nature of the scattering of the radiation beam transmitted through the sample (dynamic light scattering technique), as a result, the histograms of the particle distribution were constructed. Figure 3 shows the SEM image of obtained ZnS NPs (a) and particle size distribution histogram of ZnS NPs (b), NPs were obtained at a scanning speed of 1 mm/s.

![Figure 3](image)

*Figure 3.* (a) SEM image of obtained ZnS NPs. (b) Particle size distribution histogram of ZnS NPs.

Figure 3 shows that as a result of pulsed ablation processing under the action of an electrostatic field in argon gas atmosphere, the obtained NPs have a spherical shape, there are no defects on the particle surface in the form of inhomogeneities, satellites. The characteristic size of particles obtained at a scanning speed of 1 mm/s is in the range of values from 2 to 160 nm, the main fraction is in the range of 15-30 nm.

Figure 4 shows the SEM image of obtained ZnS NPs (a) and particle size distribution histogram of ZnS NPs (b), NPs were obtained at a scanning speed of 50 mm/s.

![Figure 4](image)

*Figure 4.* (a) SEM image of obtained ZnS NPs. (b) Particle size distribution histogram of ZnS NPs.
The characteristic size of particles obtained at a scanning speed of 50 mm/s is in the range of values from 1 to 160 nm, the main fraction is in the range of 10-20 nm. It can be seen that the obtained NPs also have a spherical shape, it is important to note that with an increase in the scanning speed, the dispersion of the formed particles decreases. A decrease in the dispersion and average particle size is due to a decrease in the probability of repeated entry of ablation products into the region of laser radiation propagation and the region of propagation of the laser erosion plume.

Structural characterization of the synthesized ZnS NPs was carried out using a D8 ADVANCE diffractometer. Figure 5 shows the X-ray diffraction (XRD) pattern of spherical ZnS NPs formed on a silicon substrate.

![XRD pattern of ZnS NPs](image)

**Figure 5.** XRD pattern of ZnS NPs formed on a silicon substrate.

Figure 5 shows a set of peaks at 27.06°, 28.66°, 30.67°, 39.79°, 47.65°, 51.91°, 56.52° which correspond to (100), (002), (101), (102), (110), (103), (112), these peaks are similar to the set of peaks that are indicated in the JCPDS card (№ 36-1450). Which suggests that the obtained XRD pattern is characteristic of the hexagonal phase of wurtzite (w) ZnS [27-29]. The (002) diffraction peak is highly dominant compared to the rest of the peaks.

4. Conclusion

In this study, to form spherical ZnS NPs, we used the method of pulsed laser ablation processing of the ceramic target under the action of an electrostatic field in argon gas atmosphere. The use of an electrostatic field in the process of ablation synthesis made it possible to carry out the predicted deposition of nanomaterials on the substrate surface, while carrying out the ablation products from the area of the laser radiation propagation. The morphology and structural characteristics of synthesized ZnS NPs were investigated using SEM and XRD analysis. SEM and XRD analysis showed that the particles have a spherical shape, while the structural characteristics of the particles are similar to those reported in the JCPDS card № 36-1450 and are typical for hexagonal wurtzite-type ZnS. An increase in
the scanning speed during pulsed ablation processing led to a significant change in the size distribution of synthesized particles. The decrease in size distribution and average particle size due to a decrease in the probability of repeated entry of ablation products into the region of laser radiation propagation and the region of propagation of the laser erosion plume.

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