Investigation of the optical properties of monocrystalline silicon with a deposited layer of spherical zinc sulfide nanoparticles

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Abstract. In the present work zinc sulfide (ZnS) nanoparticles (NPs) were synthesized on silicon wafer by femtosecond pulsed ablation processing of ZnS bulk target using an electrostatic field in argon gas atmosphere. The morphology, size distribution and structural characterization of obtained ZnS NPs were investigated using scanning electron microscope (SEM), dynamic light scattering (DLS) technique and X-ray diffraction (XRD). Dominant size of obtained NPs lies in the range 10-20 nm, NPs are in spherical shape, particles of other shape and agglomerates of particles are absent. XRD investigation of synthesized NPs identified hexagonal wurtzite structure. There is a structural phase transition from the sphalerite ZnS bulk (target) structure to the structural phase of wurtzite (obtained NPs). The optical characterization of synthesized by laser ablation ZnS NPs was carried out using a photoluminescence (PL) measurement. ZnS NPs show a strong broad PL emission spectra covering the entire visible electromagnetic spectra region (range from 380 to 800 nm) centered at 513.7 nm.

1. Introduction

Close attention to II-VI semiconductor compounds materials is due to its unique optical properties and accordingly the possibility of creating a wide variety number of high-performance optoelectronic devices based on the synthesized materials. The II-VI semiconductor nanomaterials can be synthesized by various methods, including thermal evaporation, chemical vapor deposition, sputtering, pulsed-laser deposition, metal organic, laser ablation processing, electron beam evaporation, photochemical deposition and a number of others methods [1-8]. Laser ablation synthesis method, by flexible adjustment of the exposure mode, makes it possible to obtain nanomaterials of narrow dispersion from a wide range of materials [9, 10]. The use of femtosecond laser systems for the synthesis of nanomaterials allows processing irrespective of the absorption capacity of the processed materials [11, 12]. By changing the processing environment, introducing the necessary impurities, it is possible to obtain, including shell particles.

ZnS is one of the most important semiconductor compound of the group II-VI materials. ZnS is a chemically stable material and under normal conditions it is a wide-band semiconductor. ZnS exist in two primary crystal structures: sphalerite (or zinc blende (β-ZnS)) and wurtzite, in the case of cubic sphalerite phase with a band gap of 3.72 eV and 3.77 eV in the case of hexagonal wurtzite phase [13].
In addition, the properties of ZnS can be rearranged, for example, by varying the size of the resulting nanomaterials, doping with metallic elements (such as Cu, Fe, Mn, etc.), also allows control of the optical and electrical properties [14]. Recent advances on modification of ZnS and on synthesis quantum-dimensional materials have enabled to be effectively used in various applications: luminescent devices, scintillators, light-emitted diodes (LEDs), saturable absorbers, second harmonic generators of laser radiation transparent conductors, UV photodetectors, solar cells, etc. [15-20]. Hexagonal wurtzite-type ZnS nanomaterials due to its wider intrinsic band gap is more preferable for application in optoelectronic devices. In case of infrared transparent ceramic application of ZnS, the cubic sphalerite phase is more preferred than wurtzite, which in turn is related to crystallographically and optical properties of sphalerite (isotropic).

2. Experiments
We synthesized ZnS NPs via pulsed laser ablation processing of a ZnS target using a femtosecond laser Yb:KGW (wavelength 1030 nm, pulse width 280 fs, maximum pulse energy 150 µJ per pulse, pulse repetition rate 10 kHz). Figure 1 shows the scheme of the experimental setup for pulsed laser ablation synthesis of nanomaterials under the action of an electrostatic field [11, 21]. The working chamber was filled with high-purity argon, the ZnS target was placed between high-voltage electrodes (created an electrostatic field with intensity 15 kV/cm) on which are arranged in a vertical position parallel to each other silicon single-crystal wafer (100). Schematic representation of the working chamber (inside view) presented in figure 1 (b).

Femtosecond laser radiation from an Yb: KGW source is directed through a system of turning mirrors to an optical head. The laser beam is swept along the plane by galvanometer scanners, the beam is focused by a flat-field lens with a focal length of 200 mm, the spot diameter on the surface of the sample being processed is 40 µm. The scanning speed of the beam over the surface was previously determined.
and amounted to 50 mm/s, this scanning speed makes it possible to carry out the synthesis of NPs of the required dispersion. Scanning was carried out over an area of 4x4 mm, scanning over the surface allows you to stay in the focal plane of the focusing system for a long time. Attenuation of laser radiation to the required value is carried out using a polarization attenuator installed on the axis of beam propagation; the pulse energy on the sample surface is 120 mJ. Laser radiation acts on the surface of a ZnS bulk target (obtained by the chemical vapor deposition (CVD) method) and introduced through a quartz window into the inner volume of the working chamber filled with argon to the required pressure. The use of an electrostatic field in the process of NPs ablative synthesis allows to carry out continuous synthesis in an isolated chamber. Forced deposition of NPs, obtained as a result of laser ablation makes it possible to exclude deposition on the internal volume of the chamber, including the opening windows. Under the action of an electrostatic field, the predicted deposition of nanomaterials on the surface of the wafer is carried out. The deposition of ablated particles was carried out directly on silicon wafer, behind which electrodes are installed, to which a voltage of 30 kV is applied, which makes it possible to obtain materials of a given size with a narrow size distribution. Ablation products leave the area of laser beam propagation, do not fall under repeated exposure to laser radiation, an increase in the efficiency of ablation treatment is observed, there is no coagulation of ablation products caused by the action of the laser erosion plume.

Dynamic light scattering (DLS) technique is used to estimate the size distribution of obtained ZnS NPs (particle size analyzer HORIBA LB-550), the morphology of synthesized ZnS NPs were investigated using scanning electron microscope (SEM) (MIRA3 TESCAN). The structural studies of synthesized ZnS NPs were characterized by X-ray diffraction (XRD) using a Bruker D8 ADVANCE diffractometer with Cu Kα radiation source and LynxEye XE detector (measurement were carried out with 20 range from 10 to 60 degrees). The optical characterization of synthesized by laser ablation ZnS NPs was carried out using a photoluminescence (PL) measurement. The excitation source was an ultraviolet He-Cd laser (PLASMA) operating at wavelength 325 nm. PL spectra were measured and recorded in the temperature range 220 – 300 K using a composite-grating spectrometer Ocean Optics HR4000.

3. Results and discussion

As a result of SEM study and DLS analysis, the images of NPs were obtained and the histogram of the particle distribution were obtained. Figure 2 shows the SEM image of ZnS NPs, synthesized via pulsed laser ablation processing and particle size distribution histogram of obtained ZnS NPs (the red line in figure 2 is the approximated lognormal distribution).

**Figure 2.** (a) SEM image of synthesized ZnS NPs. (b) Particle size distribution histogram of ZnS NPs and fitted lognormal distribution (red line).
It can be seen that the obtained NPs have a spherical shape, particles of other shape and agglomerates of particles are absent. The ablated material takes on the correct spherical shape as a result of passing through the melting stage. The characteristic size of synthesized NPS is in the range of values from 1 to 160 nm, the dominant size lies in the range 10-20 nm (processing mode: scanning speed of 50 mm/s, pulse energy 120 µJ).

The result of XRD study (XRD patterns) of ZnS bulk (target) and ZnS NPs synthesized on a silicon wafer presented in figure 3.

![Figure 3. XRD patterns of ZnS bulk (target) and ZnS NPs synthesized on a silicon wafer.](image)

In the case of ZnS bulk (target) the four diffraction peaks can be well indexed to the (111), (200), (220), (311) lattice planes of the sphalerite ZnS, respectively (strong resemblance to JCPDS card № 65-9585) [22]. In the case of ZnS NPs, there are nine diffraction peaks at 27.06, 28.66, 30.67, 39.79, 47.65, 51.91, 55.73, 56.52, 57.71 which can be indexed to (100), (002), (101), (102), (110), (103), (200), (112), (201) lattice planes of the wurtzite-type ZnS [23-25], respectively (strong resemblance to JCPDS card № 36-1450). In our case the (002) and (102) peaks are most intense. Recrystallization of the crystal lattice and transition from the structural phase of sphalerite ZnS bulk to the structural phase of wurtzite (obtained NPs) are observed. This transition is characteristic when exposed to high temperatures and pressures in the region of the formation of the laser erosion plume. In paper [12], Wang et al. describes the transition of the structural phase of single-crystal ZnSe wafer sphalerite as a result of laser ablation with a femtosecond laser to the structural phase of wurtzite (fabricated ZnSe NPs), this transfer occurs as a result ultrahigh localized ablation pressure due to the rapid injection of high laser energy within a femtosecond time scale.

Figure 4 shows the temperature dependent PL spectra of ZnS NPs on a silicon wafer (temperature range from 220 to 300 K).
To vary the temperature at which the PL measurement is performed, the wafer was placed in a closed cycle helium cryostat. It is noticed that the emissions can also be observed at room temperature, but it has a low intensity, due to the influence of thermal effect, with increasing temperature the intensity of the PL pronounced reduced (thermal quenching of luminescence) [26]. ZnS NPs show a strong broad PL emission spectra covering the entire visible electromagnetic spectra region (range from 380 to 800 nm, centered at 513.7 nm (green emission peak arise due to zinc vacancies $V_{Zn}$ defect states and the presence of several peaks at the wavelength of 422 nm (associated with interstitial sulfur lattice defects $I_S$), 448.6 nm (blue emission peak arise due to interstitial zinc lattice defects ($Zn_i$)), 490 nm (associated with sulfur vacancies $V_S$), 544.6 nm (arise due to transfer of trapped electrons on sulfur vacancies to interstitial sulfur states) [13, 27, 28].

4. Conclusion

In summary ZnS NPs have been synthesized using pulsed laser ablation processing of ZnS target under the action of an electrostatic field in argon gas atmosphere. The use of an electrostatic field in the process of NPs ablative synthesis allows to carry out continuous synthesis in an isolated chamber. Ablation products leave the area of laser beam propagation, do not fall under repeated exposure to laser radiation, an increase in the efficiency of ablation processing is observed, there is no coagulation of ablation products caused by the action of the laser erosion plume. The morphology and the structural studies of synthesized ZnS NPs were investigated using SEM and XRD analysis. Dominant size of obtained NPs lies in the range 10-20 nm, NPs are in spherical shape, particles of other shape and agglomerates of particles are absent. XRD analysis revealed the crystalline nature of obtained NPs and correspond to hexagonal phase of wurtzite ZnS. As a result of laser ablation processing, the structural phase transition
from cubic sphalerite (ZnS target) to the structural phase of hexagonal wurtzite in the case of synthesized particles is observed. PL measurement demonstrate that obtained ZnS NPs have a strong broad PL emission spectra covering the visible electromagnetic spectra region centered at 513.7 nm (green emission peak) and the presence of several peaks at the wavelength of 422 nm, 448.6 nm, 490 nm and 544.6 nm. Thermal quenching of the luminescence takes place, i.e. with an increase in temperature, the PL intensity noticeably decreases.

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