FEATURES OF TRANSMISSION SPECTRA OF GaSe THIN FILMS AND NANOPARTICLES SYNTHESIZED BY LASER ABLATION

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The transmission spectra of GaSe thin films and nanoparticles obtained by laser ablation of a solid target in a liquid medium were experimentally studied. X-ray diffraction analysis showed that the crystalline structure of the nanoparticles is the same as that of the bulk material. It is shown that in GaSe nanoparticles the process of laser light absorption on structural defects is absent. It is shown that the observed luminescence is caused by radiative recombination of free excitons.

INTRODUCTION

One of the most intensively developing areas in the natural sciences is the study of small-sized objects - nanoparticles. Great scientific and practical interest in nanoparticles is because many of their physical, chemical, and thermodynamic properties differ significantly from the properties of their constituent atoms or molecules and the properties of macroscopic matter, which opens up great opportunities for obtaining new materials and creating new technologies based on them [1]. One of the most common methods for obtaining nanoparticles is pulsed laser ablation (PLA) of solid targets located in a vacuum, ambient gas, or liquid [2]. Laser ablation is a simple, fast, and direct nanoparticle synthesis method. This method does not require long periods for chemical reactions, as well as high temperatures and pressures or multi-step processes typical of chemical synthesis. The ILA method applies to a virtually unlimited combination of target materials and liquids, which allows NP synthesis in a selected medium. The properties of the generated NPs - shape, size, size distribution, composition, and structure for each target material - depend on the parameters of the laser used for ablation (radiation wavelength, pulse duration and repetition rate, pulse energy), as well as on the environmental conditions (vacuum, fixed gas pressure, or liquid). Currently, semiconductor nanoparticles attract much attention from researchers. Quantum-size effects, which occur in particles smaller than the Bohr radius of an exciton, play a key role in the manifestation of semiconductor nanoparticles' electronic and optical properties [3]. The dependence of optical properties on the size of nanoparticles opens up opportunities for creating new generations of solar cells, lasers, LEDs, luminescent labels, and photocatalysts on their basis [4].

Studies of optical phenomena in poorly studied, but at the same time very promising gallium selenide (GaSe) nanoparticles are of great interest. GaSe semiconductor crystals, due to their layered structure (covalent bonding along the layers and weak van der Waals bonding between the layers), high nonlinear polarizability, optical homogeneity, high exciton binding energy (~20 meV), and the presence of a natural mirror surface, have become one of the main elements of optoelectronics [5-8]. On the other hand, it is known that stacking faults existing in GaSe crystals greatly affect their physical properties and lead to the localization of electron wave functions in the direction perpendicular to the layers [9].

This work is devoted to an experimental study of the transmission spectra of thin films and GaSe nanoparticles synthesized by laser ablation.

EXPERIMENTAL PROCEDURE

The target material was a bulk nominally undoped GaSe crystal grown by the Bridgman method. Samples with a thickness of ~100 μm were prepared by mechanical cleavage. A pulsed Nd:YAG laser with built-in 2nd and 3rd harmonic generators designed to generate radiation with wavelengths of 1064, 532 and 335 nm was used as a radiation source. The laser pulse duration was 10 ns with a maximum power of ~12 MW/cm^2. The radiation intensity was varied using calibrated neutral light filters. The transmission spectra of GaSe thin films and nanoparticles were studied using an automatic M833 double-dispersion monochromator (spectral resolution of ~0.024 nm at a wavelength of 600 nm), with computer control and a detector recording radiation in the wavelength range of 350-2000 nm.

Laser radiation with a wavelength of 1064 nm, focused by a positive lens (f=11 cm), was used to ablate a GaSe crystal with a diameter of 1.5 cm. Laser ablation of the GaSe crystal was carried out in a quartz cuvette containing 5 ml of PVP (polyvinylpyrrolidone), without adding any surfactants. The ablation process was carried out at normal pressure with a laser energy of 135 mJ per pulse and an ablation time of 10 min.

X-ray structural analysis showed that the crystalline structure of the nanoparticles is the same as that of the bulk material (hexagonal). The sizes of the

nanoparticles calculated using the Debye-Scherrer formula [10] varied in the range of (2-20) nm.

EXPERIMENTAL RESULTS AND THEIR DISCUSSION

Figure 1 shows the dependencies of the transmittance of thin films and GaSe nanoparticles on the pump power of laser radiation. As can be seen from the figure, with an increase in the excitation intensity, a decrease in the transmittance of thin films is observed (curve 1). With an increase in the radiation intensity from 1 to 10 MW/cm^2, the transmittance decreases by ~35%. It should be noted that in this case, the position of the line width in the transmission spectrum remains virtually unchanged. Unlike thin films, in a colloidal solution of GaSe nanoparticles, an inverse dependence is observed; with an increase in the pump power, the transmittance increases by ~10 times.
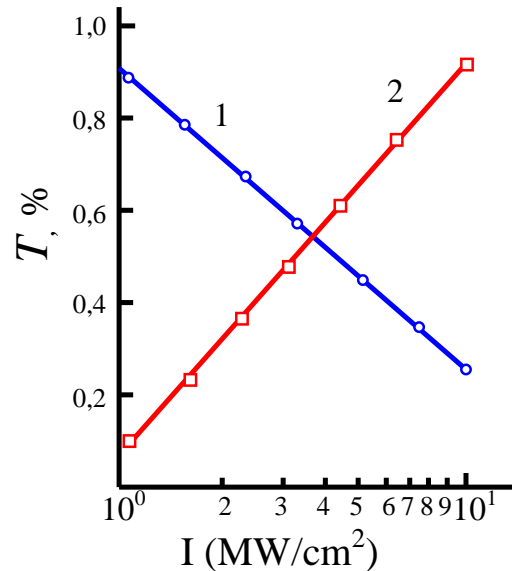

Fig. 1. Dependences of the transmittance of thin films (curve 1) and nanoparticles (curve 2) of GaSe on the pump power of laser radiation.

Of particular interest is the elucidation of the mechanism of laser radiation absorption in thin films and GaSe nanoparticles. In our case, the magnitude of the laser radiation quantum ($\hbar\omega$=1.17 eV) is less than the band gap of thin films (Eg =2.11 eV [11]) and even less than the band gap of GaSe nanoparticles (Eg=2.64 eV [12]), which turned out to be 0.53 eV larger than in thin films. When excitation of semiconductors by laser light with an energy lower than the band gap ($\hbar\omega$ < Eg), impurity and nonlinear absorption associated with 2- and 3-photon excitations can occur. In the case of layered semiconductors such as GaSe, absorptions associated with structural defects cannot be ignored. As our studies have shown, in the transmission spectra of GaSe thin films, absorption lines associated with impurity levels are absent. Two-photon absorption in the presence of structural defects and a low absorption coefficient (α~10^{-2} cm^{-1}) at the existing excitation intensities is also unlikely. In our opinion, the most probable process of laser radiation absorption is absorption by structural defects. In GaSe crystals, the distance between layers is ~(3-4) A^0, and group defects arising as a result of structural disorder occur in approximately each of the 15 layers [9]. Therefore, it can be assumed that when thin GaSe films are exposed to laser radiation with a quantum energy of $\hbar\omega$ < Eg, absorption occurs in the bulk of the substance, where group defects are randomly distributed in the defect layer, perpendicular to the optical axis "c". This assumption is also supported by our experiments on the study of the photoconductivity of GaSe at high laser excitation intensities [13, 14]. It was shown that the anisotropy of nonequilibrium carrier transport in different crystallographic directions is caused by the presence of group defects.

In GaSe nanoparticles, absorption associated with group defects is not observed. In this case, light absorption occurs not in the bulk of the substance, but in the surface layer with a thickness comparable with the thickness of the layer group, equal to ~(2-20) nm. Figure 2 shows the photoluminescence spectrum of GaSe nanoparticles excited by the second harmonic of the Nd:YAG laser ($\hbar\omega$=2.34 eV).

As can be seen from the figure, the maximum of the nanoparticle emission corresponds to the wavelength λ=473 nm (2.62 eV). The half-width of the emission line is ~10 A0. In our opinion, the observed luminescence is due to the radiative recombination of free excitons. This is evidenced by the stability, narrowness of the line and the location of the maximum (2.62 eV) from the width of the forbidden zone (2.64 eV) by 0.02 eV, equal to the binding energy of excitons in GaSe.
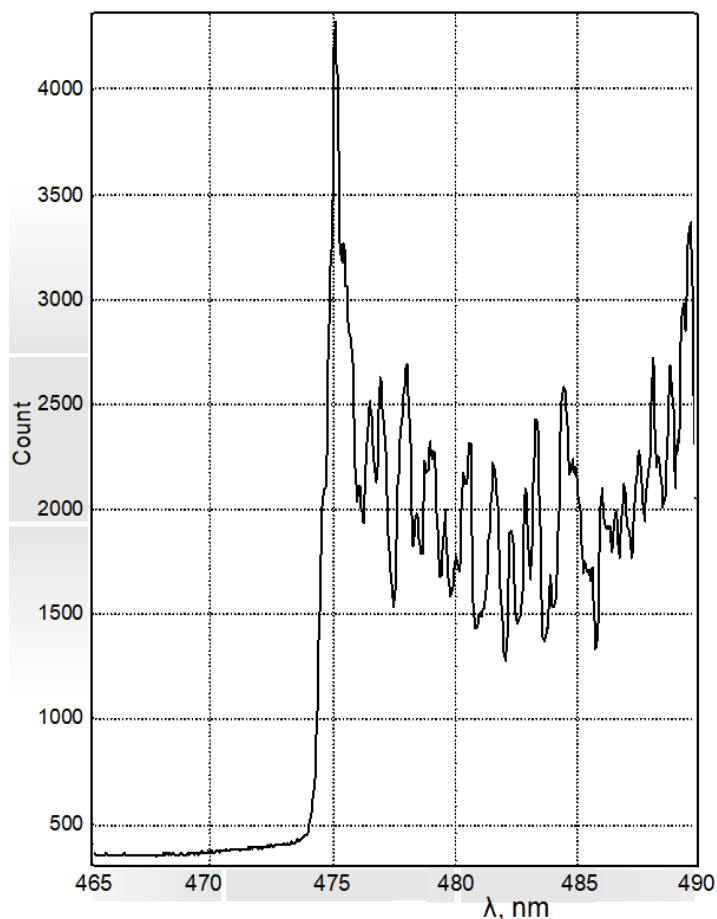
Fig. 2. Photoluminescence spectrum of GaSe nanoparticles excited by the second harmonic of a Nd:YAG laser ($\hbar\omega$=2.34 eV).

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