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INFLUENCE OF EXFOLIATION ON THE PHOTOLUMINESCENCE PROPERTIES OF LAYERED GALLIUM SELENIDE SINGLE CRYSTALS

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Rezumat. *Soluții ce conțin nanofoi de GaSe cu dimensiuni controlate au fost obținute prin exfoliere, urmată de fragmentare asistată ultrasonic, utilizând apă și acetonă ca medii de dispersie. Analiza prin microscopie optică a evidențiat separarea eficientă a particulelor de GaSe în funcție de dimensiune prin centrifugare. Măsurătorile AFM au indicat o variație a dimensiunii nanofoilor între 50 și 130 nm. Spectrul de fotoluminescență al unui monocristal de GaSe prezintă o linie îngustă la 1,998 eV, caracteristică tranzițiilor bandă-bandă. În soluțiile cu nanofoi de GaSe, această linie este deplasată către energii mai mari, atingând 2,05 eV. De asemenea, în ambele soluții se observă o linie suplimentară în jur de 2,4 eV. Se atribuie prima tranziție nanofoilor cu dimensiuni de aproximativ 130 nm, iar semnalul de 2,4 eV este asociat reducerii dimensiunii acestora la 60 nm.*

Abstract. *GaSe nanosheet solutions with controlled dimensions were obtained through exfoliation followed by ultrasonic-assisted fragmentation, using water and acetone as dispersion media. Optical microscopy analysis revealed an efficient size-based separation of GaSe particles via centrifugation. AFM measurements showed that nanosheet sizes range from 50 to 130 nm. The photoluminescence spectrum of a GaSe single crystal exhibits a narrow line at 1.998 eV, characteristic of band-to-band transitions. In GaSe nanosheet solutions, this line shifts to higher energies, reaching 2.05 eV. Additionally, an extra line is observed around 2.4 eV in both solutions. The first transition is attributed to nanosheets of approximately 130 nm, while the 2.4 eV peak is associated with a reduction in nanosheet size to 60 nm.*

Keywords: Gallium Selenide, layered semiconductors, exfoliation, photoluminescence

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1. Introduction

With the discovering of graphene [1], interest in obtaining two-dimensional (2D) materials based on various semiconductors has increased. The gained interest appears to various layered semiconductor materials such as SnSe, SnS, SnS_2, $SnSe_2$, GaS and GaSe [2–6]. Single atomic materials or materials consisting of few atomic

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layers attempt interest due to his significant mechanical and electronic properties. The absence of dangling bonds over large surfaces areas ensures low charge dissipation in graphene and other (2D) non-graphene materials, making them suitable for applications in high-speed electronics, optoelectronics, sensors, energy generation and storage [7, 8]. But graphene application in electronics is limited by it zero band gap [1]. In this regard, in recent years, alternatives to graphene have been proposed and intensively studied, which have a similar two-dimensional structure but with nonzero band gap [8–11]. Among such materials, transition metal chalcogenides and dichalcogenides exhibit a layered structure with atoms bonded to each other to form 2D layers without dangling bonds, with the layers bounded to each other by weak van der Waals forces.

2D multilayer dichalcogenide nanomaterials are of interest due to their attractive properties and potential applications in optics, optoelectronics, and solar energy [8, 10–13]. Among these materials, gallium selenide has the weakest Van der Waals bonds, which allows obtaining layers of nanoscale sizes. In addition, this material has pronounced nonlinear properties [14] and can be used in terahertz region [5]. In gallium selenide single crystals, 4 excitonic series and photoluminescence are observed [15].

The layered crystals of gallium (II) chalcogenides in the present time are active used in laser optics as “active media” in phemtosecond pulse lasers and in CO_2 lasers due to their ability to generate broadband radiation in the near-IR region and in the millimeter-wavelength range [16–18]. It was shown that GaSe can be used in electrochemical cells for photovoltaic as solar cell material [19]. Beside this GaS, GaSe and solid solution on its base have photo- and electro-luminescence [20, 21], with high light response. This fact determines a possibility of using in optoelectronics devices as high-sensitive materials and photodetectors [22–24]. The wide application of these materials is due to the anisotropy of optical, electronic and optoelectronic properties, which is caused by the structural features of the bulk crystals.

2. Experimental details

GaSe nanosheets were obtained by exfoliating a thin layer from the bulk material using adhesive tape. The tape was then dissolved in acetone, and the resulting layers were fragmented by ultrasonic treatment. An alternative method involved mechanical exfoliation followed by ultrasonic fragmentation in water, eliminating the potential influence of acetone and adhesive residues on the analysis. Size separation of the GaSe nanostructures was performed through centrifugation at different speeds (3500 rpm and 7000 rpm). As a result, nanosheet solutions were prepared in both water and acetone. Three types of samples were obtained: without centrifugation, and with centrifugation at 3500 rpm and 7000 rpm. Images of the prepared nanoparticle solutions are presented in Figure 1.

Fig. 1. Photo of solutions of GaSe nanosheets in water (1, 2, 3) and acetone (4, 5, 6) obtained by ultrasonic fragmentation. Samples (1) and (4) were prepared without centrifugation, while samples (2) and (5) were centrifuged at 3500 rpm, and samples (3) and (6) at 7000 rpm.

For morphological analysis, samples were prepared on glass substrates. A drop of 1 microliter of water solution was placed on the substrate, which was then heated to allow for water evaporation. Nanosheet characterization on the glass substrate was performed using an optical microscope (Karl Zeiss) and a NanoStation II Atomic Force Microscope (AFM) with a Si cantilever operated in non-contact mode. The parameters were calculated using Gwyddion 2.56 software.

For optical characterization, the photoluminescence (PL) spectra of GaSe nanosheet solutions in water and acetone were recorded using a high-aperture MDR-2 monochromator at room temperature. As mentioned above the six samples were prepared: three from water solution and three from acetone solution. Each pair of samples differed by the centrifugation speed: the first pair was not centrifuged, the second pair was centrifuged at 3500 rpm, and the third pair at 7000 rpm. The samples were placed in quartz cuvettes and excited with laser light at a wavelength of 450 nm at room temperature. For comparison, the PL spectra of the initial single crystal were also recorded under identical excitation conditions.

3. Results and discussions

a. Morphology Study

As was mentioned, the samples were prepared on glass substrates. A drop of aqueous solution was deposited onto the glass, and the substrate was then heated to facilitate the evaporation of the water. After the evaporation process, the morphology of the resulting nanosheet samples was thoroughly examined using optical microscopy and atomic force microscopy.

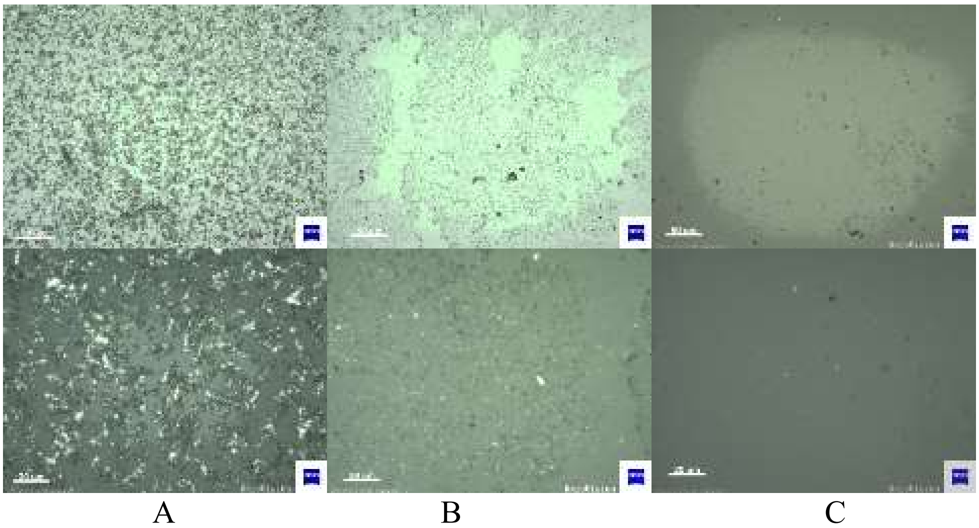

Fig. 2. Optical microscope images of samples prepared on glass: without centrifugation (A), centrifuged at 3500 rpm (B), and centrifuged at 7000 rpm (C).

Since the same volume of solution was applied to the glass for all three samples, the concentration of micro- and nano-sheets is highest in the sample without centrifugation and lowest in the sample subjected to centrifugation at 7000 rpm (see Figure 2). Centrifugation not only facilitates the separation of particles based on size but also affects their distribution and morphology. As shown in Figure 1, the particle sizes in the Figure 1C are smaller compared to those in the Figure 1B, indicating that higher centrifugation speeds lead to finer particle dispersion. This suggests that centrifugation at higher speeds promotes a more uniform size distribution by removing larger aggregates and facilitating the formation of smaller, more uniform sheets. However, as the centrifugation speed increases, the particle density decreases, due to the increased force separating the particles more effectively.

Figure 3 shows an example of the AFM topography of GaSe nanosheets after centrifugation at 3500 rpm and deposition on a glass substrate. It can be observed that as the scanning area increases, the surface roughness also increases. Specifically, for a 2×2 μm^2 area, the maximum particle size is 57 nm (see Figure 2a). For a scanning area of 5×5 µm, the maximum particle size increases to 64 nm, and for 10×10 μm^2 and 20×20 μm^2 areas, the particle size can reach 107 nm and 130 nm, respectively. Table 1 presents the main surface roughness parameters for the aforementioned sample. The roughness varies depending on the measurement area, ranging from 57 nm to 130 nm, indicating that particles with sizes from 50 nm to 150 nm are present.

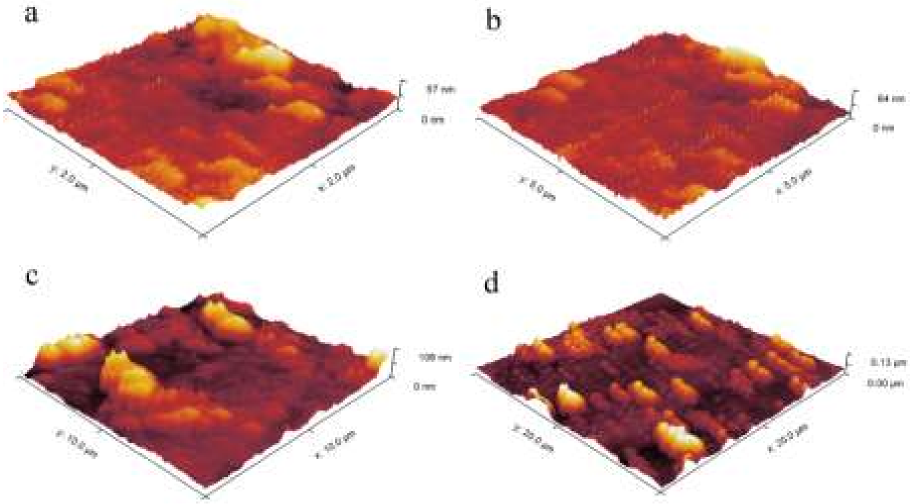

Fig. 3. AFM topography of GaSe nanosheets at centrifugation 3500 rpm for 2×2 μm^2 (a), 5×5 μm^2 (b), 10×10 μm^2 (c) and 20×20 μm^2 (d) areas.

Table 1. Surface roughness parameters of GaSe nanosheets deposited on a glass substrate at different AFM scanning areas

AFM Scale	RMS roughness (Sq)	Mean roughness (Sa)	Skew (Ssk)	Excess kurtosis	Maximum height (Sz) (nm)
2×2 μm^2	7.38	5.62	0.7760 Ssk>0	0.9736	57
5×5 μm^2	5.95	4.28	1.346 Ssk>0	4.235	64
10×10 μm^2	17.22	12.75	1.389 Ssk>0	1.918	107
20×20 μm^2	19.95	14.61	1.741 Ssk>0	2.108	130

b. Photoluminescence spectroscopy

Figure 4 shows the PL spectra of the bulk GaSe crystal and solutions of GaSe nanosheets. In the PL spectrum of the bulk GaSe crystal, a sharp line is observed at 1.998 eV, which corresponds to a band-to-band transition or excitonic emission [15]. In both solutions, this line shifts to higher energies, with the maximum energy around 2.05 eV. The emission line positions are indicated by arrows in Figure 4. In the PL spectra of the water solutions, a weak line is observed around 2.4 eV. In the case of sample 3 (acetone solution at a centrifugation speed of 7000 rpm), no PL lines were detected.

The line at 2.05 eV is associated with larger nanosheets (approximately 130 nm), which retain a structure similar to that of the bulk material, while the line at 2.4 eV is attributed to smaller nanosheets (approximately 60 nm).

The PL spectra of water solutions show more pronounced lines, due to better dispersion and more uniform distribution of nanosheets, which enhances the optical properties. On the other hand, for sample 3, where no PL line was observed, it is possible that the nanosheets were fragmented into even smaller particles or lost their ordered crystalline structure at the higher centrifugation speed, leading to the absence of clear PL signals.

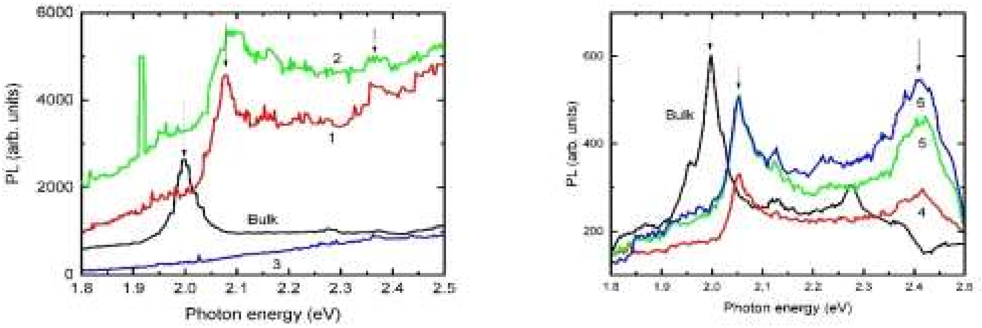

Fig. 4. PL spectra of single crystal GaSe (bulk) and of water (left) and acetone (right) solutions of GaSe nanosheets without centrifugation (1, 4) and with centrifugation with speed 3500 rpm (2, 5) and 7000 rpm (3, 6).

These results suggest that the solvent (water or acetone) and centrifugation speed significantly influence the size, dispersion, and optical properties of GaSe nanosheets, with potential applications in optoelectronics and sensing, where precise control over nanosheet size and morphology is crucial.

Conclusions

Nanosheets of GaSe were successfully obtained from a single-crystal sample in aqueous and acetone solutions, exhibiting a range of nanoparticle sizes. Surface roughness analysis of the nanoparticles deposited on a GaAs substrate, using optical and atomic force microscopes, revealed sizes varying from 57 nm to 130 nm. This suggests that, after ultrasonic fragmentation of the GaSe layer, particles ranging from tens of microns to tens of nanometers were dispersed into the solution. Centrifugation at speeds of 3500 rpm and 7000 rpm allowed for the separation of particles with sizes between 50 nm and 200 nm. The luminescence spectra of the studied solutions displayed lines corresponding to nanoparticles of different sizes. The line at 2.05 eV can be attributed to larger nanoparticles (around 130 nm), while the line around 2.4 eV corresponds to smaller nanoparticles, approximately 60 nm in size.

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