

FABRICATION AND CHARACTERIZATION OF GaSe NANOPARTICLE/Si HETEROSTRUCTURES PREPARED BY PULSED LASER ABLATION IN LIQUID

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GaSe nanoparticles were synthesized using the pulsed laser ablation in liquid (LAL) technique and deposited onto n-type silicon substrates to form GaSe nanoparticle/Si heterostructures. The LAL method enabled the production of high-purity nanoparticles without the use of chemical precursors or surfactants. The structural, morphological, compositional, and vibrational properties of the obtained heterostructures were systematically investigated using X-ray diffraction (XRD), scanning electron microscopy (SEM), energy-dispersive X-ray spectroscopy (EDS), and Raman spectroscopy. XRD analysis revealed the presence of crystalline hexagonal GaSe nanoparticles along with the dominant diffraction peak of the Si substrate. SEM observations showed the formation of nanoparticles with sizes ranging from tens to several hundreds of nanometers distributed across the silicon surface. EDS measurements confirmed the presence of Ga and Se elements, verifying the successful deposition of GaSe nanoparticles. Raman spectroscopy identified characteristic phonon modes of GaSe, including A_{1g} and E_{2g} vibrations, confirming the preservation of the layered crystal structure after laser ablation. The results demonstrate that the pulsed laser ablation in liquid method is an effective approach for the synthesis of GaSe nanoparticles and the fabrication of GaSe nanoparticle/Si heterostructures. The obtained structures show promising potential for future optoelectronic and photodetector applications.

Keywords: Nanoparticles, pulsed laser ablation, X-ray diffraction, scanning electron microscopy, energy-dispersive X-ray spectroscopy, Raman spectroscopy, phonon modes, quantum confinement, surface effects.

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1. INTRODUCTION

Gallium selenide (GaSe) is a layered III–VI semiconductor that has attracted considerable attention due to its unique structural, optical, and electronic properties. It crystallizes in a hexagonal structure consisting of covalently bonded Se–Ga–Ga–Se atomic layers held together by weak van der Waals forces [1–3]. This layered nature enables GaSe to exhibit strong anisotropy, high optical absorption coefficients, and excellent photoresponse characteristics over a wide spectral range. Owing to its direct band gap of approximately 2.0 eV in multilayer form and favorable carrier transport properties, GaSe has emerged as a promising material for applications in optoelectronic devices, including photodetectors, nonlinear optical devices, and energy conversion systems [4,5].

In recent years, particular interest has been focused on GaSe in nanoparticle form. Compared to bulk crystals, GaSe nanoparticles offer several advantages, such as increased specific surface area, enhanced light–matter interaction, and size-dependent optical and electronic properties due to quantum confinement and surface effects. These features make GaSe nanoparticles highly attractive for applications in photodetection, sensing, and nanostructured optoelectronic systems. [6,7] Furthermore, the nanoscale dimensions facilitate efficient charge separation and transport when combined with semiconductor substrates, enabling the formation of heterostructures with improved functional performance. Various chemical synthesis methods

have been employed to prepare GaSe nanoparticles, including chemical vapor deposition, solvothermal synthesis, hydrothermal methods, and colloidal chemical routes. Although these techniques allow controlled nanoparticle growth, they often suffer from several limitations, such as complex processing steps, the use of toxic precursors, residual chemical contamination, and difficulties in achieving high purity and stoichiometric control. In addition, post-synthesis purification and high-temperature processing are often required, which can further complicate the fabrication process and affect material quality [8,9].

Pulsed laser ablation in liquid (LAL) has emerged as a powerful alternative technique for the synthesis of semiconductor nanoparticles. This physical method enables the direct production of high-purity nanoparticles without the use of chemical precursors or surfactants. During LAL, intense laser pulses interact with a solid target immersed in a liquid medium, resulting in the ejection of material and the formation of nanoparticles [10,11]. The LAL technique offers several important advantages, including simplicity, environmental friendliness, high purity of the produced nanoparticles, and preservation of the original crystal stoichiometry. Moreover, nanoparticles synthesized by LAL are typically free from chemical contamination, making them highly suitable for optoelectronic applications [12]. In addition to nanoparticle synthesis, the integration of GaSe nanostructures with semiconductor substrates is of particular interest for the development of heterostructure-based devices. Silicon (Si), being the most widely used semiconductor in modern

electronics, provides an excellent platform for forming heterostructures with GaSe. The combination of GaSe nanoparticles and Si substrates enables efficient interfacial charge transfer and offers significant potential for photodetector and optoelectronic device applications [13].

In the present work, GaSe nanoparticles were synthesized using the pulsed laser ablation in liquid method and subsequently deposited onto n-type silicon substrates. The structural, morphological, compositional, and vibrational properties of the obtained GaSe nanoparticle/Si heterostructure were systematically investigated. The results confirm the successful formation of crystalline GaSe nanoparticles and their integration with the silicon substrate, demonstrating the effectiveness of the LAL technique for the preparation of GaSe-based heterostructures.

2. EXPERIMENTAL DETAILS

2.1 Synthesis of GaSe nanoparticles

GaSe nanoparticles were synthesized using the pulsed laser ablation in liquid (LAL) technique. High-quality GaSe single crystals grown by the Bridgman method were used as the ablation targets. Due to the layered structure of GaSe, thin plate-like targets were obtained by mechanical cleavage from bulk crystals, resulting in optically smooth, mirror-like surfaces with a typical thickness of approximately 100 μm . This ensured uniform and stable interaction between the laser beam and the target surface during the ablation process. The ablation experiments were performed using a pulsed Nd:YAG laser system (LQ529B) equipped with harmonic generation modules. In the present work, the fundamental wavelength of 1064 nm was employed. The laser operated with a pulse duration of 10 ns, pulse energy of 135 mJ, and repetition rate of 10 Hz. The laser fluence was controlled using calibrated neutral density filters to ensure reproducible ablation conditions. The GaSe target was placed at the bottom of a quartz cuvette filled with distilled water, which served as the liquid medium for nanoparticle formation. The laser beam was focused onto the target surface, and ablation was carried out for approximately 10 minutes. During laser irradiation, the intense interaction between the laser pulses and the GaSe target led to material ejection, plasma formation, and subsequent rapid cooling in the liquid environment, resulting in the formation of GaSe nanoparticles suspended in the liquid. After the ablation process, a stable colloidal suspension of GaSe nanoparticles was obtained. The obtained GaSe nanoparticle colloidal solution was transferred onto the silicon substrates using a drop-casting method. The solution was allowed to spread naturally over the substrate surface and was subsequently dried under ambient atmospheric conditions at room temperature without the use of additional heating or vacuum treatment. This process resulted in the formation of GaSe nanoparticle layers on the Si substrate surface.

2.2 Characterization techniques

The structural properties of the synthesized GaSe nanoparticles and GaSe nanoparticle/Si

heterostructures were investigated using X-ray diffraction (XRD) analysis performed on a Rigaku MiniFlex 600 diffractometer employing Ni-filtered Cu $K\alpha$ radiation with a wavelength of $\lambda = 1.5406 \text{ \AA}$. The measurements were carried out in the θ - 2θ scanning mode to identify the crystalline phases and evaluate the structural characteristics of the deposited nanoparticle layers. The surface morphology, microstructural features, and elemental composition of the GaSe nanoparticle films deposited on silicon substrates were examined using a Vega Tescan scanning electron microscope (SEM) equipped with an energy-dispersive X-ray spectroscopy (EDS) system. SEM analysis provided detailed information on particle morphology, size distribution, surface coverage, and nanoparticle-substrate interaction, while EDS measurements were used to determine the elemental composition and verify the presence of Ga and Se elements, as well as to assess the chemical purity of the samples. Raman spectroscopic analysis was performed using an EnSpectr R532 Raman spectrometer (Enhanced Spectrometry Inc., USA) with a laser excitation wavelength of 532 nm. The Raman measurements were used to identify characteristic phonon modes, confirm the crystalline structure, and evaluate the structural integrity of the synthesized GaSe nanoparticles. The obtained spectra were also compared with the known Raman features of bulk GaSe crystals to verify the successful formation of GaSe nanoparticles.

3. RESULT AND DISCUSSIONS

3.1 XRD analysis of GaSe/Si

The crystal structure and phase composition of the GaSe nanoparticle/Si heterostructure were investigated by X-ray diffraction, and the obtained pattern is shown in Fig. 1. The XRD pattern is dominated by an intense diffraction peak located at $2\theta \approx 69.52^\circ$, which is attributed to the (400) reflection of the single-crystal silicon substrate [14]. The high intensity and sharp nature of this peak confirm the excellent crystallinity and preferred orientation of the Si substrate. In addition to the substrate-related peak, several weak diffraction peaks are observed at approximately $2\theta \approx 22.84^\circ$, 33.55° , and 61.98° . These reflections can be attributed to the crystalline phase of hexagonal GaSe, indicating the successful formation of GaSe nanoparticles on the silicon surface [15]. In particular, the peak observed at $2\theta \approx 33.55^\circ$ corresponds to the (004) crystallographic plane of layered GaSe, which is one of the characteristic reflections of its hexagonal structure. The presence of this peak provides clear evidence of the crystalline nature of the deposited GaSe nanoparticles. The relatively low intensity of the GaSe diffraction peaks compared to that of the silicon substrate can be explained by the nanoscale thickness and limited volume fraction of the GaSe nanoparticle layer, as well as the strong diffraction contribution from the underlying single-crystal Si substrate. Such behavior is typical for nanoparticle-based thin films deposited on highly crystalline substrates. Furthermore, the

broadening and reduced intensity of the GaSe peaks are associated with the nanoscale dimensions of the synthesized particles and possible structural disorder, which are common features of nanoparticles produced by the pulsed laser ablation in liquid method. The absence of additional impurity peaks indicates that the synthesized GaSe nanoparticles possess good phase

purity within the detection limits of the XRD technique.

Overall, the XRD results confirm the successful synthesis of crystalline GaSe nanoparticles and their deposition onto the Si substrate, leading to the formation of a GaSe nanoparticle/Si heterostructure.

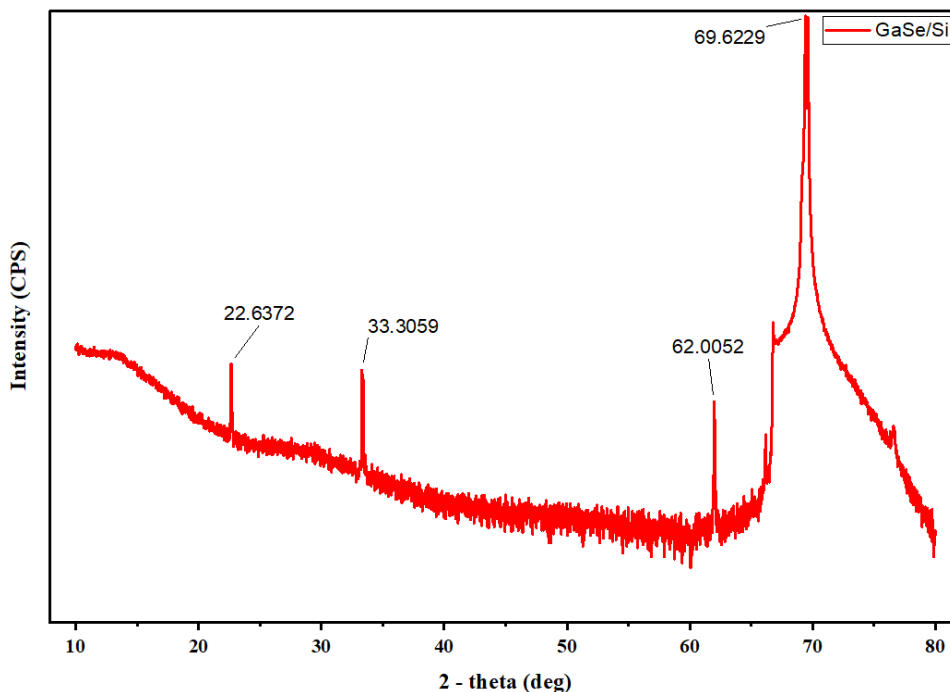


Fig.1. XRD pattern of GaSe nanoparticle/Si heterostructure.

3.2 SEM and EDS analysis

The surface morphology and microstructural characteristics of the GaSe nanoparticle/Si heterostructure were examined using scanning electron microscopy, and the corresponding SEM image is presented in Fig. 2(a). As seen in the figure, the silicon substrate surface is covered with a large number of GaSe nanoparticles distributed over the entire surface. The nanoparticles exhibit both isolated and agglomerated configurations, forming clusters of different sizes. The formation of such agglomerates is typical for nanoparticles synthesized by the pulsed laser ablation in liquid method due to the high surface energy and strong interparticle interactions. The particle size varies from tens to several hundreds of nanometers, indicating the successful formation of nanoscale GaSe particles. In addition, the SEM image clearly shows that the nanoparticles are in direct physical contact with the silicon substrate, which is essential for the formation of GaSe nanoparticle/Si heterostructures. The non-uniform but continuous distribution of nanoparticles suggests the successful deposition of GaSe nanoparticles onto the substrate surface via the drop-casting method.

The elemental composition of the synthesized structures was analyzed by energy-dispersive X-ray spectroscopy, and the corresponding spectrum is shown in Fig. 2(b). The EDS results confirm the presence of gallium (Ga) and selenium (Se), verifying the formation of GaSe nanoparticles. The measured weight percentages of Ga and Se were found to be 20.7 wt% and 21.8 wt%, respectively, indicating good compositional consistency of the synthesized material. In addition, a strong silicon (Si) signal (40.5 wt%) is observed, which originates from the underlying substrate, confirming the nanoscale thickness of the deposited GaSe nanoparticle layer. Furthermore, the presence of oxygen (17.0 wt%) can be attributed to the native oxide layer on the silicon surface and possible surface oxidation of the nanoparticles during synthesis and exposure to ambient conditions. Such oxygen-related signals are commonly observed in nanoparticle systems prepared in liquid environments.

Overall, the SEM and EDS analyses confirm the successful synthesis and deposition of GaSe nanoparticles onto the silicon substrate, as well as the formation of a GaSe nanoparticle/Si heterostructure with nanoscale features.

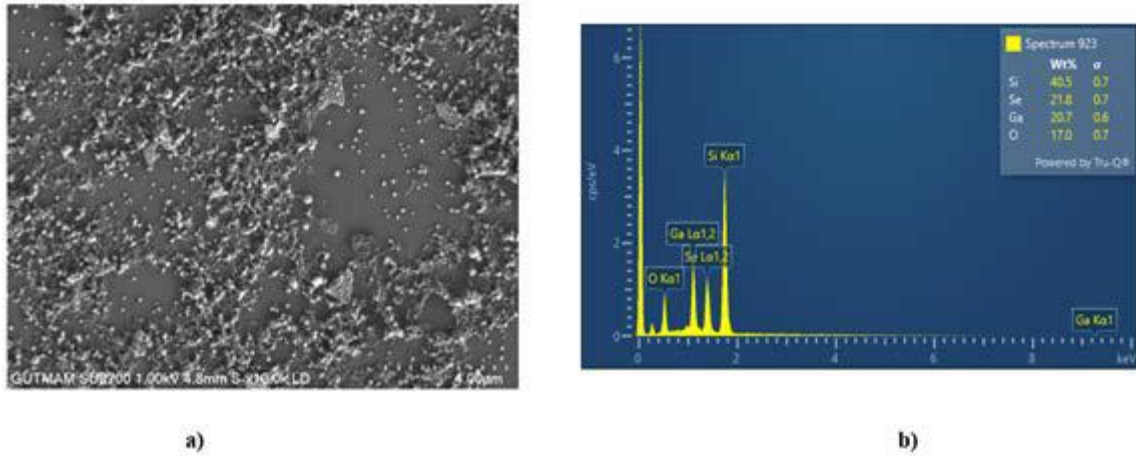


Fig. 2. (a) SEM image showing the surface morphology and distribution of GaSe nanoparticles on the silicon substrate. (b) EDS spectrum and elemental composition of GaSe nanoparticle/Si heterostructure.

3.3 Raman analysis

The vibrational and structural properties of the synthesized GaSe nanoparticles deposited on the Si substrate were investigated by Raman spectroscopy, and the obtained spectrum is presented in Fig. 3. The Raman spectrum exhibits several characteristic phonon modes corresponding to the crystalline structure of GaSe, confirming the successful formation of GaSe nanoparticles via the pulsed laser ablation in liquid method. The prominent Raman peak observed at approximately 135.6 cm^{-1} corresponds to the A_{1g}^1 mode, which is associated with the out-of-plane vibrations of Se atoms in the layered GaSe structure. Another characteristic peak located at 212.7 cm^{-1} is attributed to the E_{2g}^2 mode, corresponding to in-plane vibrational motion within the GaSe layers. The strong and sharp peak observed at 236.1 cm^{-1} is related to interlayer vibrational modes and is commonly observed in GaSe nanostructures, particularly in nanoparticle and few-layer systems, where interlayer interactions and size-related effects influence phonon behavior. Additionally, the peak at

308.2 cm^{-1} corresponds to the A_{1g}^2 mode, which represents another out-of-plane vibration of the GaSe layered structure. The presence of these characteristic Raman modes confirms that the crystal structure of GaSe is preserved after laser ablation and nanoparticle formation [16]. Several additional peaks observed at 315.9 cm^{-1} , 441.4 cm^{-1} , and 464.0 cm^{-1} can be attributed to size confinement effects, structural disorder, and defect-related vibrational modes, which are commonly observed in nanoparticle systems due to their reduced dimensions and increased surface-to-volume ratio. These features further confirm the nanoscale nature of the synthesized material. Furthermore, the Raman peak observed at 522.6 cm^{-1} corresponds to the first-order optical phonon mode of crystalline silicon [17], confirming the presence of the Si substrate and the formation of the GaSe nanoparticle/Si heterostructure.

Overall, the Raman results clearly confirm the successful synthesis of crystalline GaSe nanoparticles and the preservation of their layered structure after the pulsed laser ablation process (table 1).

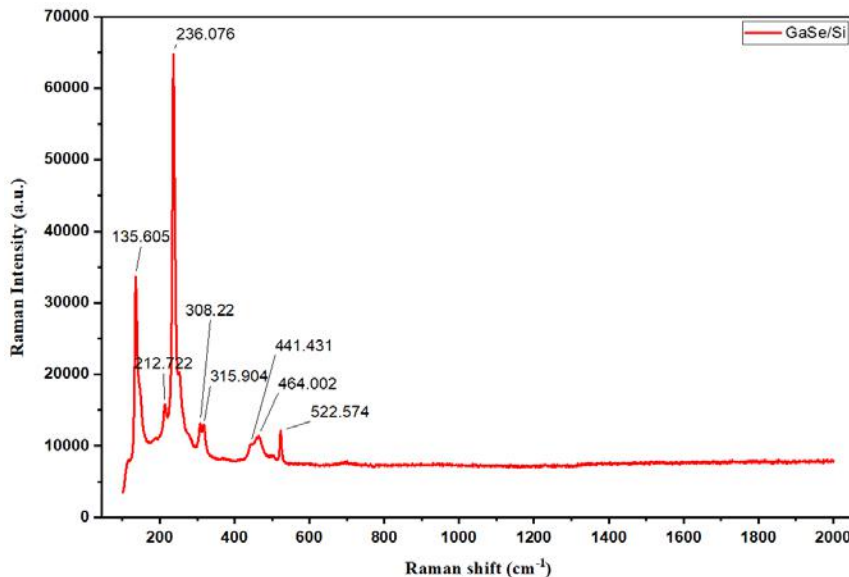


Fig.3. Raman spectrum of GaSe nanoparticle/Si heterostructure obtained using 532 nm laser excitation.

Table 1.

Raman peaks and their assignments

Raman shift (cm ⁻¹)	Assignment	Vibrational mode	Physical meaning
135.6	GaSe	A _{1g} ¹	Out-of-plane vibration of Se atoms
212.7	GaSe	E _{2g} ²	In-plane vibration of GaSe layers
236.1	GaSe	Interlayer mode	Interlayer interaction / nanoparticle effect
308.2	GaSe	A _{1g} ²	Out-of-plane lattice vibration
315.9	GaSe	Defect-related mode	Structural disorder / size effect
441.4	GaSe	Higher-order mode	Multi-phonon or defect-related vibration
464.0	GaSe	Size-related mode	Nanoparticle phonon confinement
522.6	Si substrate	TO phonon mode	Crystalline Si substrate

4. CONCLUSION

In this work, GaSe nanoparticles were successfully synthesized using the pulsed laser ablation in liquid method and deposited onto n-type silicon substrates to form GaSe nanoparticle/Si heterostructures. The applied LAL technique enabled the production of high-purity nanoparticles without the use of chemical precursors, demonstrating its effectiveness as a simple and environmentally friendly synthesis method. The XRD analysis confirmed the crystalline nature of the synthesized GaSe nanoparticles, with characteristic diffraction peaks corresponding to hexagonal GaSe observed alongside the dominant Si substrate reflection. SEM observations revealed the formation of nanoscale GaSe particles with sizes ranging from tens to several hundreds of nanometers, distributed over the silicon surface and forming direct nanoparticle–substrate interfaces. The EDS results verified the presence of Ga and Se elements and confirmed the successful

deposition of GaSe nanoparticles on the Si substrate. Raman spectroscopy further confirmed the preservation of the layered crystal structure of GaSe, with characteristic A_{1g} and E_{2g} phonon modes clearly observed. Additional Raman features indicated nanoscale effects and structural modifications associated with nanoparticle formation. The combined structural, morphological, compositional, and vibrational analyses confirm the successful synthesis of crystalline GaSe nanoparticles and the formation of GaSe nanoparticle/Si heterostructures. These results demonstrate that the pulsed laser ablation in liquid method is a reliable and efficient technique for the fabrication of GaSe nanostructures integrated with silicon substrates.

The obtained GaSe nanoparticle/Si heterostructures show strong potential for future applications in optoelectronic devices, particularly in photodetectors and nanoscale semiconductor heterostructure systems.

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