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ANALYSIS OF MORPHOLOGICAL CHANGES ON THE SURFACE OF LAYERED GaSe SEMICONDUCTOR CRYSTALS AS A RESULT OF GAMMA IRRADIATION

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Abstract: In this study, the surface effects of layered GaSe single crystals were investigated using Atomic Force Microscopy (AFM) before irradiation, after thermal annealing, and at low (Dγ = 0.5 kGy) and high (Dγ = 1 kGy) gamma irradiation doses. It was determined that gamma irradiation induces observable changes in the surface morphology.

At low irradiation doses (Dγ < 0.5 kGy), structural defect ordering occurs due radiation-stimulated defect diffusion. At higher doses (Dγ > 0.5 kGy), the dissociation of complexes leads to the formation of point defects that accumulate around specific centers. These results indicate that changes on the GaSe crystal surface can be controlled depending on the irradiation dose.

Keywords: surface morphology, gamma irradiation, GaSe, thermal annealing.

1. Introduction

In the manufacturing technology of modern semiconductor devices, various types of radiation, especially those involving radiation-stimulated diffusion processes, have found widespread application. Through these processes, the diffusion of atoms and point defects within crystal structures can be controlled. Gallium selenide (GaSe), a III-VI group semiconductor, possesses a layered structure and exhibits unique optoelectronic and structural properties that distinguish it from other bulk crystals. These characteristics make it a promising material for the development of devices with high photosensitivity in the visible spectrum and for the detection of elementary particles [1].

The high resistance of GaSe crystals to ionizing radiation and the anisotropy in their crystal structure make the investigation of surface morphological changes under radiation exposure particularly relevant. In particular, the targeted control of structural defects and understanding their morphological characteristics can broaden the application areas of these crystals. Therefore, the aim of this study is to investigate the radiation-induced changes occurring on the surface of layered GaSe monocrystals and to analyze their dependence on the radiation dose.

$A^{III}B^{VI}$ compounds, particularly GaSe monocrystals, exhibit specific properties compared to other bulk crystals, making them promising materials for the development of photoconverters, highly photosensitive detectors in the visible spectral range, and detectors for elementary particles and high-energy electromagnetic radiation. These unique characteristics have spurred interest in studying the surface changes induced by gamma radiation [2–6]. The growing interest in these compounds is mainly due to their resistance to ionizing radiation and their pronounced anisotropic properties [7–11].

Although various structures based on $A^{III}B^{VI}$ compounds have been intensively studied in recent years, the lack of developed methods for the targeted control of structural defects limits the practical applications of these crystals [2,6–8]. In this regard, investigating the effects of radiation on the surface morphology of GaSe crystals is essential, as controlling the distribution of surface defects can enhance photosensitivity in the ultraviolet and visible spectral regions. Moreover, understanding how gamma irradiation affects the radiation resistance and controllability of physical properties in these materials enables the prediction of the performance characteristics of diodes fabricated from them [12–18]. Therefore, studying the radiation-induced surface changes in GaSe monocrystals and comparing them with unirradiated samples is of significant interest.

2. Sample Preparation and Measurement Methodology

The investigated layered GaSe monocrystal, a compound from the $A^{III}B^{VI}$ group, was grown under laboratory conditions using the Bridgman–Stockbarger directional crystallization method. GaSe belongs to the III–VI family of semiconductor crystals. For direct (G–G) and indirect (G–M) transitions, the band gap of the monocrystal is 2 eV, and the concentration of defects is approximately 10^{17} cm^{-3} [19].

The obtained crystal exhibits p-type conductivity. At room temperature, its specific resistivity measured parallel and perpendicular to the layers was $2\times10^{7}\,\Omega\cdot cm^{-1}$ and $1 \times 10^{5}\ \Omega\cdot cm^{-1}$, respectively. The surface of the GaSe monocrystal was examined using Atomic Force Microscopy (AFM) in contact mode, employing a NanoEducator scanning probe microscope with a horizontal resolution capability of 50 nm.

AFM requires only a very small amount of sample. Since AFM is designed to study the topography, relief, and surface characteristics at the nanoscale, the analyzed sample surface must be extremely clean.

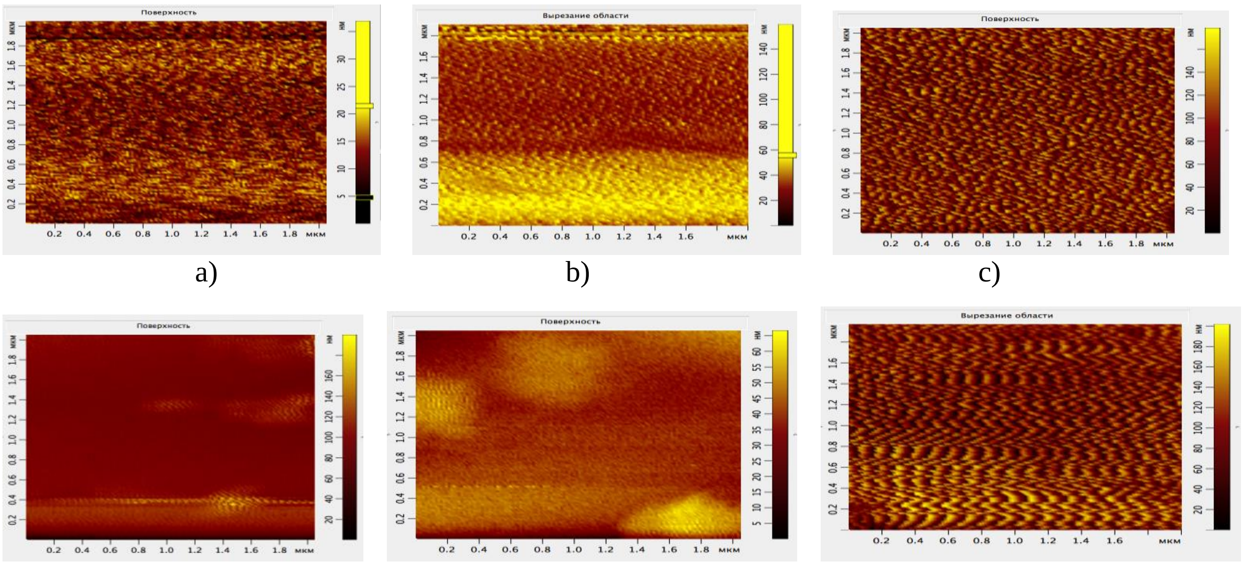
The aim of this study is to analyze the surface images of GaSe layered monocrystals—before irradiation, after thermal annealing, and after exposure to low ($D\gamma$ = 0.5 kGy) and high ($D\gamma$ = 1 kGy) doses of gamma radiation—using Atomic Force Microscopy.

3. Experimental results and discussion

Atomic Force Microscopy (AFM) technology enables the investigation of the electrical properties of nanostructures and defects [20]. Figures 1, 2, and 3 present the two-dimensional (2D), three-dimensional (3D), and histogram surface representations of the GaSe layered monocrystal obtained using the NanoEducator atomic force microscope.

In the 2D format, the width and length dimensions of the crystal surface are clearly displayed (Figure 1). In both 2D and 3D images, darker regions represent gallium (Ga) atoms, while lighter regions correspond to selenium (Se) atoms. As seen in Figure 1(a), the initial (unirradiated) 2D surface image of the GaSe monocrystal reveals a certain degree of surface roughness, which appears periodically. The raised and recessed areas observed are attributed to the spatial distribution of Se (raised) and Ga (recessed) atoms on the surface.

The influence of thermal annealing on surface processes is evident in Figures 1(b) and 2(b). After thermal annealing at 100 °C for 60 minutes, the 2D surface image (Figure 1b) indicates an increased presence of Ga atoms on the crystal surface. This change suggests a rearrangement or redistribution of atoms under thermal treatment, which likely plays a role in surface stabilization and defect regulation.



a) b) c) d) e) f)

Fig. 1. 2D Surface Images of GaSe Monocrystals Captured by Atomic Force Microscopy (AFM):
a — initial (untreated) sample; b — initial sample after thermal annealing at 100 °C for 60 minutes;
c — sample irradiated at 0.5 kGy gamma dose; d — sample irradiated at 1 kGy gamma dose;
e — thermally annealed (100 °C, 60 min) and irradiated at 0.5 kGy gamma dose;
f — thermally annealed (100 °C, 60 min) and irradiated at 1 kGy gamma dose.

Compared to the initial sample, the 2D surface image of the GaSe monocrystal after gamma irradiation at a dose of $D\gamma$ = 0.5 kGy shows a gradual disappearance of the previously observed periodic surface irregularities. This indicates a certain ordering of defects on the crystal surface as a result of irradiation. As known, the obtained GaSe crystal is a p-type semiconductor with an inherently high defect density. Upon exposure to a 0.5 kGy gamma dose, opposite-type (donor-type) defects are introduced into the structure, partially compensating for the existing acceptor-type defects. This compensation process manifests as a smoother surface morphology, as seen in Figure 1(c).

Such changes demonstrate that low-dose irradiation can regulate the surface structure of the crystal without causing significant disruption, thereby enhancing its radiation resistance potential. This is a crucial factor for future device applications, especially in sensors and detectors.

After exposure to a low dose of 0.5 kGy, the surface morphology of the GaSe crystal irradiated at a higher dose (1 kGy) was examined. At this elevated dose level (1 kGy), an increase in surface roughness is observed (Figure 1(d)). This can be attributed to the migration of defects, leading to their accumulation around favorable centers.

Subsequently, the surface images of the p-type GaSe monocrystal were analyzed following thermal annealing and subsequent irradiation at doses of 0.5 kGy and 1 kGy, respectively (Figures 1(e) and 1(f)). After thermal annealing and 0.5 kGy irradiation, both the number and size of surface defects decrease, resulting in a more homogeneous morphological structure. This observation indicates that defects become more ordered under these conditions.

However, in the sample subjected to thermal annealing followed by 1 kGy irradiation, surface roughness increases again, and the surface appears significantly more deformed. This suggests that the higher radiation dose induces new defect complexes and structural distortions, ultimately degrading the surface quality. Therefore, it can be concluded that thermal annealing combined with low-dose irradiation promotes defect ordering, whereas high-dose exposure disrupts structural integrity.

In contrast to the 2D format, the 3D representation also includes height information in addition to width and length. To assess the effect of thermal annealing on surface processes, the 3D image reveals that after annealing at 100 °C for 60 minutes (Figure 2(b)), a significant increase in recessed regions is observed compared to the initial sample. As previously mentioned, this is attributed to an increased presence of Ga atoms on the surface.

The surface smoothness after 0.5 kGy irradiation is more clearly observed in the 3D image. Considering that darker regions correspond to gallium (Ga) atoms and lighter regions represent selenium (Se) atoms, the 3D surface map after 0.5 kGy irradiation (Figure 2(c)) indicates a predominance of Se atoms on the surface.

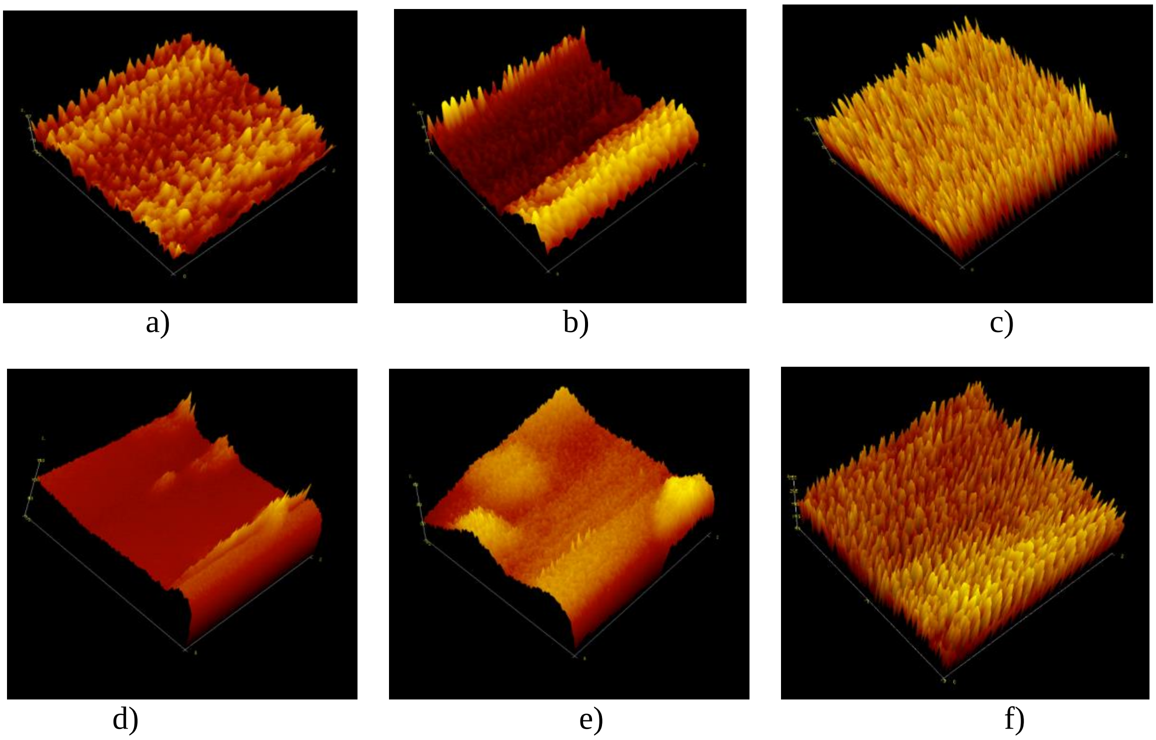


Fig. 2. 3D surface images of GaSe monocrystals:
a — initial sample; b — initial + thermally annealed at 100 °C for 60 minutes; c — irradiated at 0.5 kGy; d — irradiated at 1 kGy; e — thermally annealed at 100 °C for 60 minutes + irradiated at 0.5 kGy; f — thermally annealed at 100 °C for 60 minutes + irradiated at 1 kGy.

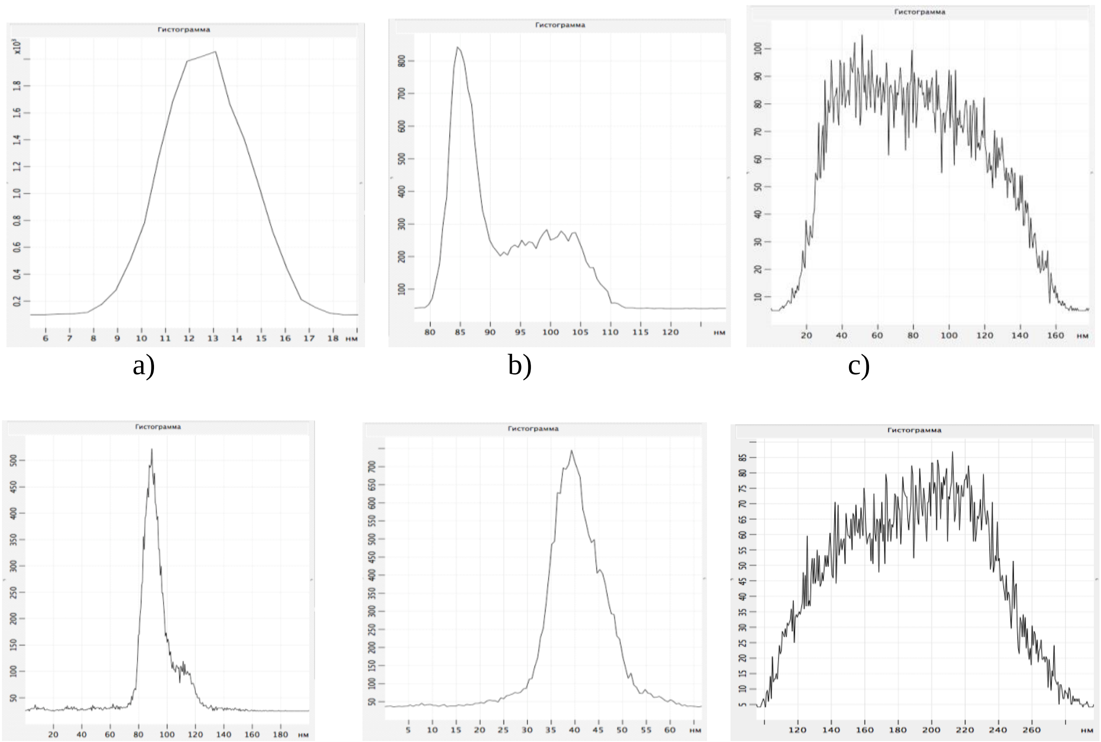
The confirmation of the three-dimensional surface profiles is reflected in the histograms (Figure 3). From the histogram, it is evident that after irradiation at a gamma dose of $D\gamma = 0.5$ kGy, larger defect clusters break down into smaller-sized defects. Specifically, low-dose (0.5 kGy) gamma irradiation leads to the fragmentation of pre-existing large and disordered defect agglomerates in the crystal, resulting in the formation of smaller and more ordered defects.

At low irradiation doses, the formation of point defects leads to radiation-stimulated processes, in which the mobility of atoms or defects within the crystal increases under the influence of radiation. These newly formed point defects interact with pre-existing large defects, resulting in enhanced ordering. In other words, local structural alignment and homogeneity are established within the crystal. As a result of these processes, the degradation of parameters remains minimal, indicating that the samples exhibit high resistance to gamma radiation (Figure 3c). A comparative analysis of the histograms reveals that on the surface of the GaSe monocrystal irradiated with 1 kGy, stable layers are formed. These layers are characterized by the presence of nanoparticles ranging in size from 80 nm to 120 nm (Figure 3d). When comparing the effects of low and high gamma doses (Dγ = 0.5 kGy and Dγ = 1 kGy) on the p-type GaSe sample, it is observed that at the lower dose (0.5 kGy), the surface becomes smoother due to the ordering of defects, whereas at the higher dose (1 kGy), defect migration leads to increased surface irregularities.

As previously noted, in the initial sample, the surface roughness is more pronounced in the 3D format compared to the 2D image. This roughness is mainly caused by a single type of nanoparticle with a size of approximately 13 nm and a count of 2000 (Figure 3a). From the histogram of the thermally annealed sample (annealed for 60 minutes at 100 °C), the rough region is determined to have a size of about 85 nm, with around 800 nanoparticles present in the sample (Figure 3b).

The histogram of the irradiated sample (Figure 3c) shows that larger and more disordered defects are fragmented into smaller and more ordered ones. This is attributed to the radiation-stimulated diffusion process activated by the low-dose (0.5 kGy) gamma irradiation. During this process, newly generated point defects interact with pre-existing large defects, facilitating their rearrangement and contributing to improved structural ordering. As a result, surface homogeneity increases, and the morphology becomes smoother and more organized. This effect is a significant factor enhancing the radiation resistance of GaSe crystals.

The histogram of the sample irradiated at a 1 kGy gamma dose shows that stable but larger-sized surface layers have formed. The sizes of the nanoparticles mainly range between 80 nm and 120 nm (Figure 3d). This phenomenon is attributed to the high radiation dose (1 kGy), which leads to the formation of complex defects. These defects migrate and accumulate around favorable centers, resulting in renewed surface roughness. In this case, instead of defect compensation, the aggregation of newly formed defects dominates, leading to a degradation in surface quality.



a) b) c) d) e) f)

Fig. 3. Figure 3. Histograms of GaSe monocrystals:
a — initial sample; b — initial + thermally annealed at 100 °C for 60 minutes; c — irradiated at 0.5 kGy; d — irradiated at 1 kGy; e — thermally annealed at 100 °C for 60 minutes + irradiated at 0.5 kGy; f — thermally annealed at 100 °C for 60 minutes + irradiated at 1 kGy.

In Figures 3e and 3f, histograms (distribution curves of surface elements by size) of the p-type GaSe crystal after thermal annealing and subsequent gamma irradiation at doses of 0.5 kGy and 1 kGy (D = 50 kGy and 100 kGy) are presented. In the sample that was both thermally annealed and irradiated at 0.5 kGy, a single dominant type of nanoparticle is observed—with an average size of 40 nm and a quantity of 700 particles (Figure 3e).

In contrast, the histogram of the crystal irradiated with a 1 kGy gamma dose after thermal annealing shows a broader distribution range of nanoparticle sizes, spanning from 120 nm to 250 nm. Moreover, the number of nanoparticles decreases significantly—by a factor of 8.2—down to just 85 particles, compared to the 0.5 kGy case.

A comparative summary of the histogram analysis results for GaSe monocrystals is presented in Table 1, based on Figures 3a to 3f.

Table 1

Comparative analysis of GaSe monocrystal surface morphology under different treatment conditions

Figure	Sample Condition	Nanoparticle Size (nm)	Nanoparticle Count (pcs)	Surface Morphology	Nature of Defects	Final Result
3a	Initial	13	2000	Irregular, rough	Large defect clusters	Disordered, high surface roughness
3b	Thermally annealed (100°C, 60 min)	85	800	Relatively smooth	Scattered defects	Dominance of Ga atoms
3c	Irradiated at 0.5 kGy	< 40	20–100	Homogeneous, smooth	Point-like, ordered defects	Defects compensated
3d	Irradiated at 1 kGy	80–120	50–500	Irregular	Migrated defects	Formation of complex clusters
3e	Annealed + irradiated at 0.5 kGy	40	700	Highly homogeneous	Compensated point defects	Optimal morphological structure
3f	Annealed + irradiated at 1 kGy	120–250	85	Very rough	New complex defects	Surface degraded, low quality

4. Conclusions

Based on the obtained results, it can be concluded that the surface morphology of the GaSe crystal changes depending on the gamma irradiation dose, and that the distribution and size of defects in layered crystals can be deliberately controlled under gamma exposure. The energy absorbed by defects accelerates the disintegration of randomly distributed defect clusters and the redistribution of point defects through diffusion within the material. This enables control over parameters such as charge carrier concentration, mobility, and relaxation time in defective crystals.

Radiation-induced defects (Frenkel pairs), unlike structural defects, are mobile and capable of migration. In defective crystals, these radiation-induced defects may interact with structural defects, resulting in partial compensation or the formation of stable complexes.

The surface morphology of GaSe layered single crystals strongly depends on both the applied γ-irradiation dose and the conditions of thermal annealing. Low-dose irradiation (0.5 kGy) causes the decomposition of large, disordered defect structures into smaller, more ordered ones, resulting in a smoother and more homogeneous surface. Conversely, high-dose irradiation (1 kGy) leads to defect migration and the formation of new complex structures, thereby degrading the surface quality. When low-dose irradiation is combined with thermal annealing, defect ordering becomes more efficient, leading to an optimal surface morphology. This not only enhances the radiation resistance of the crystal but also opens up significant opportunities for the effective application of these materials in sensor and detector technologies. Thus, the combined application of radiation and thermal annealing presents a promising approach for controlling the surface structures of GaSe crystals.

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АНАЛИЗ МОРФОЛОГИЧЕСКИХ ИЗМЕНЕНИЙ НА ПОВЕРХНОСТИ СЛОИСТЫХ ПОЛУПРОВОДНИКОВЫХ КРИСТАЛЛОВ GaSe, ВЫЗВАННЫХ ГАММА-ОБЛУЧЕНИЕМ

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Резюме: В данной работе с использованием атомно-силового микроскопа (АСМ) исследованы поверхностные эффекты слоистого монокристалла GaSe до облучения, после термического отжига, а также при низкой (Dγ = 0,5 кГр) и высокой (Dγ = 1 кГр) дозе облучения. Установлено, что после воздействия γ-квантов наблюдаются изменения морфологии поверхности. При низкой дозе облучения (Dγ < 0,5 кГр) происходит упорядочение структурных дефектов в результате радиационно-стимулированной диффузии. При дозе облучения Dγ > 0,5 кГр наблюдается накопление точечных дефектов вокруг соответствующих центров вследствие диссоциации комплексов. Полученные результаты свидетельствуют о возможности управлять изменениями на поверхности кристаллов GaSe в зависимости от дозы облучения.

Ключевые слова: морфология поверхности, гамма-облучение, GaSe, термический отжиг.

GaSe LAYLI YARIMKEÇİRİCİ KRİSTALLARIN SƏTHİNDƏ QAMMA ŞÜALANMA NƏTİCƏSİNDƏ FORMALAŞAN MORFOLOJİ DƏYİŞİKLİKLƏRİN ANALİZİ

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Xülasə: İşdə GaSe laylı monokristalının səth effektləri Atom güc mikroskopu (AGM) vasitəsilə şüalanmadan əvvəl, termik dəmlənmiş, aşağı (D_{γ} = 0,5 kGy) və yuxarı (D_{γ} = 1 kGy) şüalanma dozasında araşdırılmışdır. Müəyyən edilmişdir ki, γ-kvantlarla şüalanmadan sonra səth morfologiyasında dəyişikliklər müşahidə olunur. Aşağı şüalanma dozasında (D_{γ} < 0,5 kGy defektlərin radiasion-stimullasdırıcı diffuziyası nəticəsində struktur defektlərin nizamlanma prosesi baş verir), D_{γ} > 0,5 kGy şüalanma dozasında isə komplekslərin dissosasiyası nəticəsində yaranan nöqtəvi defektlərin uyğun mərkəzlər ətrafında toplanması müşahidə olunur. Bu nəticələr GaSe kristal səthindəki dəyişikliklərin şüalanma dozasından asılı olaraq idarə oluna bildiyini göstərir.

Açar sözlər: səth morfologiyası, qamma şüalanma, GaSe, termik dəmlənmə.