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ANISOTROPY OF ELECTRICAL AND PHOTOELECTRICAL PROPERTIES OF GaSe SINGLE CRYSTALS INTERCALATED WITH Cu ATOMS

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Abstract: In this study, the current–voltage characteristics, temperature dependence of electrical conductivity, and spectral distribution of photocurrent in layered GaSe single crystals intercalated with Cu atoms were investigated in directions parallel and perpendicular to the “C” axis. It was established that after Cu intercalation, the current increased by approximately 30–40 times along the “C” axis and by 10–20 times in the perpendicular direction. This behavior is explained by the formation of additional localized energy levels in the interlayer region and the increase in the concentration of free charge carriers due to the incorporation of Cu atoms.

It was observed that γ-irradiation leads to a decrease in electrical conductivity and an increase in activation energy. At an irradiation dose of 15 kGy, the activation energy increased from 0.10 eV to 0.29 eV along the “C” axis and from 0.14 eV to 0.36 eV in the perpendicular direction.

The spectral distribution of photocurrent revealed maximum photosensitivity in the 560–610 nm region. After Cu intercalation, the photocurrent intensity decreased by approximately one order of magnitude. The obtained results demonstrate that Cu intercalation and γ-irradiation significantly affect the charge transport mechanism and the anisotropy of the electrical and photoelectrical properties of GaSe single crystals.

Keywords: intercalation, anisotropy, γ-irradiation, electrical conductivity.

1. Introduction

The investigation of new functional semiconductor crystals and the comprehensive study of their structural, electrophysical, photoelectric, optical, and related properties are of particular importance in modern materials science and nanoelectronics. The rapid development of electronics, optoelectronics, and sensor technologies forms the basis for the discovery of new materials and technological innovations [1, 2]. Such materials enable the fabrication of more efficient, energy-saving, and multifunctional devices, thereby meeting global scientific and industrial demands [3]. In this context, hexagonal p-type GaSe single crystals have emerged as one of the most promising materials attracting considerable attention. The unique properties of GaSe make it a potential candidate for applications in nanoscale devices, photodetectors, and even quantum computing systems [4, 5].

The layered structure of GaSe crystals makes them highly suitable for various modification techniques such as implantation, intercalation, and doping. This layered configuration provides favorable conditions for the incorporation of atoms or molecules into the interlayer spaces, allowing purposeful modification of the material properties [6, 7]. Consequently, GaSe modified with different functional additives offers broad possibilities for the fabrication of multilayered and composite structures [7, 8]. Such structures may play an important role in radiation-resistant devices, space technologies, nuclear energy systems, and military applications, as they improve both the stability and functionality of the material. Overall, these properties make GaSe a strategic material for solving modern technological challenges.

It should be noted that intercalation processes in GaSe crystals lead to certain changes in their crystallographic and electronic structure [9, 11]. These modifications alter the anisotropic properties of the material and expand its application potential, while simultaneously introducing new challenges [10]. A comprehensive investigation of these changes is of great importance for understanding their nature and mechanisms, since this contributes to the optimization of the material and the elimination of potential limitations [9–14].

In the present study, the anisotropy of the electrophysical and photoelectric properties of Cu-intercalated GaSe single crystals is investigated. Although intralayer electronic processes in A^3B^6-type crystals have been studied extensively, the influence of changes in the electronic structure within the interlayer region on anisotropic properties has not yet been sufficiently explored, which motivated the present study [4, 10–14]. This issue is essential for realizing the full potential of the material, since the role of the interlayer region is particularly important in controlling the overall properties of layered semiconductors.

Such an approach provides an opportunity for the objective evaluation of the influence of Cu intercalation on the measurable parameters of GaSe crystals. The analysis based on experimental data will make it possible to assess the induced modifications in the material and verify theoretical models. Comparative analysis with future investigations will contribute to identifying new possibilities for technological applications of the material. This may open up new prospects for the broader use of GaSe in nanoelectronics, sensor technologies, and radiation protection, while also contributing to the general field of materials science.

2. Materials and methods

Layered semiconductor GaSe single crystals belonging to the A^3B^6 group were synthesized by the Bridgman–Stockbarger crystal growth method. During the crystallization process, the temperature gradient was maintained at 20–30 K/cm, while the growth rate was 0.13 mm/h. The obtained single crystals exhibited p-type conductivity with a resistivity of $\rho = 2\times10^9$ Ω·cm at room temperature. In order to reduce the concentration of Se vacancies, excess Se was added during the crystal growth process. The degree of conductivity anisotropy with respect to the crystal axis was approximately 10^2.

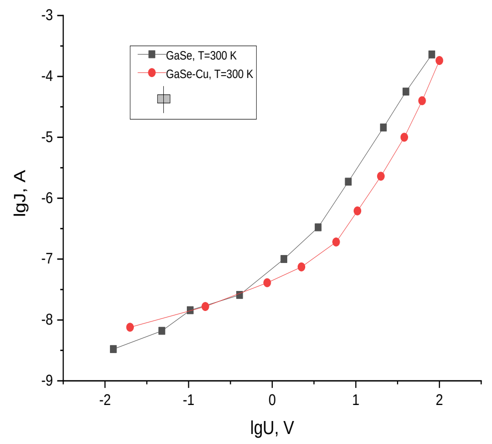
Microstructural and X-ray phase analyses showed that the obtained single crystals possessed a homogeneous structure. For the investigations, samples with mirror-like surfaces and a thickness of 200 μm were prepared and scanned along the (0001) plane. The phase composition and crystal structure were confirmed by X-ray diffraction (XRD) and differential thermal analysis (DTA), revealing the formation of the bright-red GaSe phase.

The intercalation process was carried out electrochemically in a copper sulfate solution under a constant voltage regime (U = 1 V) for a duration of t = 1 h. Gamma irradiation was performed using an MRX γ-25 Co^{60} facility with a dose rate of 117.606 rad/s.

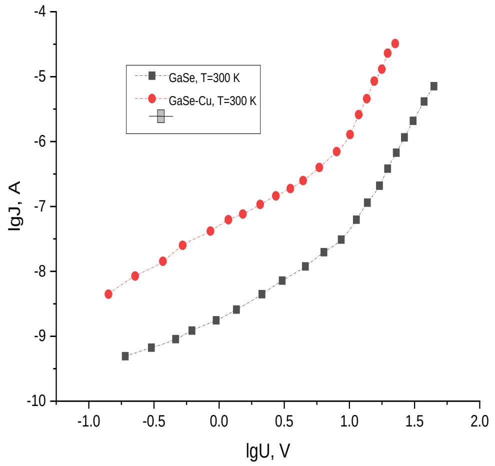
Electrophysical measurements were performed in the temperature range of 110–300 K. The applied voltage was regulated using a B7-27A voltmeter, while the current generated in the crystal was recorded by a B7-30 electrometer-amplifier. The photoelectric properties of the samples were investigated in the 200–2000 nm spectral range using a SF-4 spectrophotometer, and a 20 W lamp served as the source of monochromatic illumination. Ohmic contacts were used during the measurements, with silver paste employed for contact preparation. The contacts were deposited both parallel and perpendicular to the crystal surface.

3. Results and discussion

Figure 1 shows the anisotropy of the I–V characteristics measured in different directions for GaSe and Cu-intercalated GaSe crystals. The measurements were carried out both perpendicular to the layers and along the layer planes.



a)



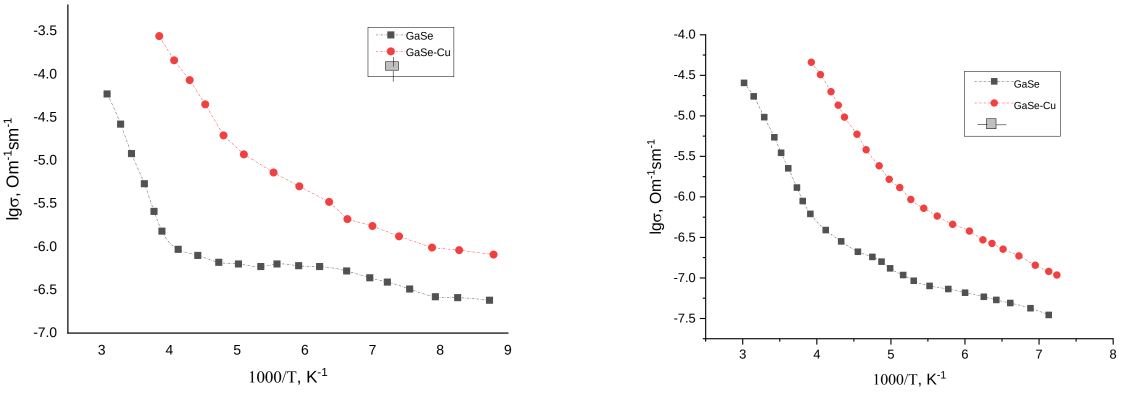
b)

Fig. 1. Anisotropy of the current–voltage characteristics (I–V characteristics) of GaSe and GaSe–Cu crystals: a) ∥ C; b) ⊥ C

As shown in Figure 1a (along the "C" axis), the current in the GaSe–Cu sample is approximately 1–2 orders of magnitude higher than that of pure GaSe over the entire voltage range. This increase is associated with the formation of additional localized energy levels in the interlayer region due to Cu atoms, resulting in an increase in the concentration of free charge carriers. Consequently, charge carrier transport along the "C" axis becomes easier, leading to enhanced conductivity.

Figure 1b (perpendicular to the "C" axis) demonstrates that the conductivity is generally higher in this direction, which is related to the more efficient movement of charge carriers along the layer planes. The graph shows that, particularly at high voltages, the current in the GaSe–Cu sample increases by approximately 10–20 times compared to pure GaSe. This indicates that Cu intercalation also increases the concentration of free charge carriers within the layers. However, the effect of Cu intercalation is more pronounced along the "C" axis, which can be explained by the fact that Cu atoms are mainly located in the interlayer spaces. Thus, the obtained results demonstrate that the electrical conductivity of GaSe crystals exhibits clear anisotropy and that Cu intercalation further enhances this anisotropy.

Figure 2 shows that the electrical conductivity of both GaSe and GaSe–Cu crystals increases with increasing temperature. The graphs demonstrate a decrease in conductivity with increasing 1000/T, indicating that the conductivity has a thermally activated character. As the temperature rises, the number of charge carriers transferred from the valence band to the conduction band increases, resulting in enhanced electrical conductivity.

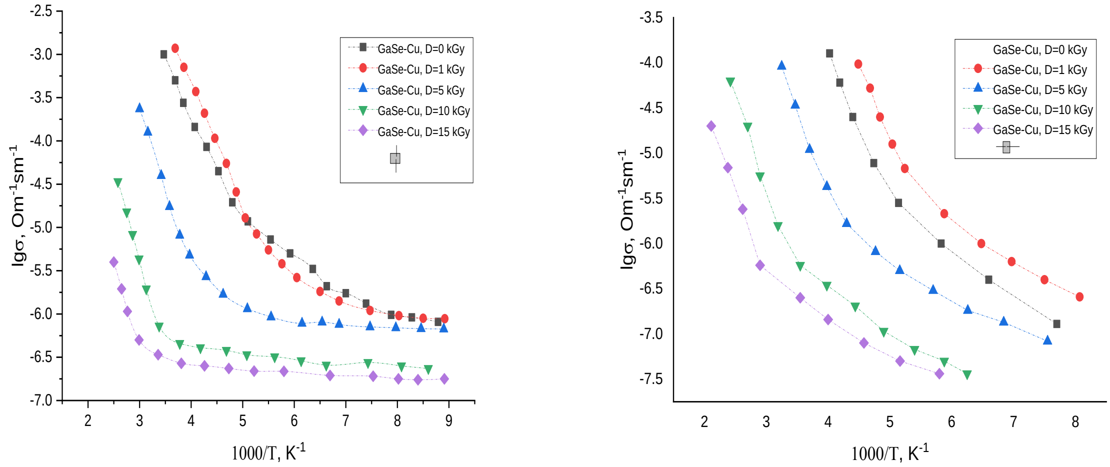


a) **b)**

Fig. 2. Anisotropy of the electrical conductivity of GaSe and GaSe–Cu crystals: a) ∥ C; b) ⊥ C

Along the "C" axis (Figure 2a), the conductivity of the GaSe–Cu crystal is approximately 1–2 orders of magnitude higher than that of pure GaSe throughout the entire temperature range. This increase is associated with the formation of additional localized energy levels in the interlayer region due to Cu atoms, which leads to an increase in the concentration of free charge carriers. At the same time, the change in the slope of the graph indicates that Cu intercalation also affects the activation mechanism of charge carriers.

In the direction perpendicular to the "C" axis (Figure 2b), the conductivity values are higher and the temperature dependence is more pronounced. Since charge carrier transport along the layer planes is more efficient in this direction, the conductivity increases. The conductivity of the GaSe–Cu sample being approximately 10–30 times higher than that of pure GaSe indicates that Cu intercalation increases the concentration of free charge carriers. Nevertheless, the different behavior of conductivity depending on the direction confirms that the electrical properties of GaSe crystals exhibit pronounced anisotropy.



a) **b)**

Fig. 3. Anisotropy of the electrical conductivity of γ-irradiated GaSe–Cu crystals at different irradiation doses: a) ∥ C; b) ⊥ C

Figure 3 shows the direction-dependent variation of the electrical conductivity of GaSe–Cu crystals under different doses of γ-irradiation and reflects the thermally activated character of conductivity in both directions. The systematic decrease in conductivity with increasing irradiation dose is associated with the formation of additional radiation-induced defects (donor-type) and trapping centers in the crystal due to γ-quanta.

Along the “C” axis (Figure 3a), the conductivity decreases progressively over the entire temperature range with increasing irradiation dose. While the activation energy for the unirradiated sample is approximately 0.10 eV, it becomes 0.13 eV for 1 kGy, 0.18 eV for 5 kGy, 0.24 eV for 10 kGy, and approximately 0.29 eV for 15 kGy. The increase in activation energy indicates that the trapping centers formed as a result of γ-irradiation hinder the thermal activation of charge carriers.

In the direction perpendicular to the “C” axis (Figure 3b), the temperature sensitivity of the electrical conductivity is higher, and the slopes of the graphs are steeper. In this direction, the activation energy is approximately 0.14 eV for the unirradiated sample, 0.19 eV for 1 kGy, 0.25 eV for 5 kGy, 0.31 eV for 10 kGy, and approximately 0.36 eV for 15 kGy. The higher values of activation energy indicate that the radiation defects generated by γ-irradiation more strongly impede charge carrier transport in the direction perpendicular to the “C” axis.

Thus, with increasing γ-irradiation dose, the electrical conductivity decreases while the activation energy increases. This behavior is associated with the increased concentration of n-type levels and trapping centers in the crystal.

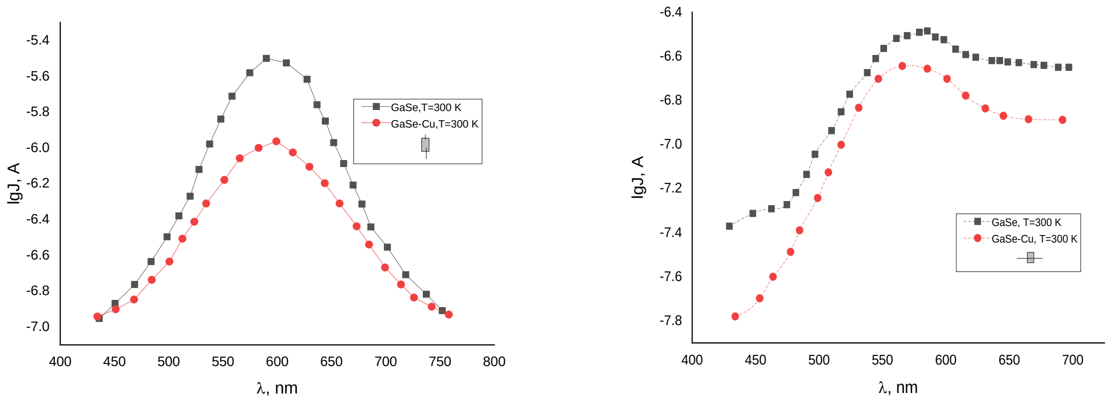


Fig. 4. Anisotropy of the spectral distribution of the photocurrent of GaSe and GaSe–Cu crystals at room temperature (U = 50 V): a) // C; b) ⊥ C.

Figure 4 shows the direction-dependent variation of the spectral distribution of the photocurrent in GaSe and GaSe–Cu crystals. In both directions, the main photosensitivity maximum is observed in the 560–610 nm region, which is associated with the fundamental absorption edge of the GaSe crystal and optical transitions occurring near the band gap. Due to the nonhomogeneous distribution of Cu atoms throughout the crystal volume, local potential fluctuations are formed in the interlayer regions. These fluctuations enhance the localization of charge carriers, lead to the formation of localized energy levels within the forbidden band, and significantly affect the spectral characteristics of photoconductivity.

The graphs show that both the photocurrent intensity and the changes in its spectral shape strongly depend on direction, indicating the anisotropy of the photoelectric properties. Along the “C” axis (Figure 4a), the photocurrent maximum reaches higher values, and the spectral peak is observed in a sharper form. In the GaSe–Cu sample, the maximum photocurrent decreases by approximately one order of magnitude compared to pure GaSe, which is associated with the localized levels and recombination centers formed as a result of Cu intercalation. These centers cause recombination of a portion of the photogenerated charge carriers, leading to a decrease in photocurrent.

In the direction perpendicular to the “C” axis (Figure 4b), the spectral distribution of the photocurrent is characterized by a broader maximum, and the decrease in photocurrent in the long-wavelength region is less pronounced. In this direction, the more efficient transport of charge carriers along the layer planes results in a more stable variation of the photocurrent. After Cu intercalation, the photocurrent also decreases in this direction, but the reduction is weaker compared to that along the “C” axis. This can be explained by the fact that Cu atoms are mainly located in the interlayer regions and therefore exert a stronger influence on charge carrier transport along the “C” axis.

Cu atoms located in the interlayer gaps increase the potential fluctuations along the “C” axis. As a result, exciton dissociation and charge carrier localization become more pronounced, which explains the photoconductivity anisotropy observed both along the “C” axis and in the direction perpendicular to it.

Thus, the obtained results demonstrate that, in addition to electrical properties, the photoelectric properties of GaSe crystals also exhibit pronounced anisotropy, while the localized levels formed due to Cu intercalation increase the recombination of photogenerated charge carriers, leading to a decrease in photocurrent.

4. Conclusion

The conducted investigations revealed that the electrical and photoelectric properties of Cu-intercalated GaSe single crystals exhibit pronounced anisotropy. The electrical conductivity along the “C” axis was found to be approximately 1–2 orders of magnitude higher, which is associated with more efficient charge carrier transport along the layer planes. After Cu intercalation, the I–V characteristics demonstrated that the current increased by approximately 30–40 times along the “C” axis and by 10–20 times in the direction perpendicular to the “C” axis. The increase in electrical conductivity is explained by the formation of additional localized energy levels in the interlayer region due to Cu atoms, leading to an increase in the concentration of free charge carriers.

It was established that γ-irradiation causes a decrease in electrical conductivity in both directions. At a dose of 15 kGy, the conductivity along the “C” axis decreases by approximately 2–3 orders of magnitude, while the activation energy increases from 0.10 eV to 0.29 eV. In the direction perpendicular to the «C» axis, the increase in activation energy from 0.14 eV to 0.36 eV indicates that γ-irradiation exerts a stronger influence on charge carrier transport in this direction. These changes are associated with the formation of radiation-induced defects and trapping centers.

The spectral distribution of the photocurrent showed that the maximum photosensitivity is located within the 560–610 nm region. After Cu intercalation, the maximum photocurrent decreased by approximately one order of magnitude, which was attributed to the enhanced recombination of photogenerated charge carriers. Thus, it was determined that Cu intercalation and γ-quantum irradiation modify the charge carrier transport mechanism in GaSe single crystals and significantly alter the anisotropy of conductivity and photosensitivity.

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АНИЗОТРОПИЯ ЭЛЕКТРИЧЕСКИХ И ФОТОЭЛЕКТРИЧЕСКИХ СВОЙСТВ МОНОКРИСТАЛЛОВ GaSe, ИНТЕРКАЛИРОВАННЫХ АТОМАМИ Cu

Р.С. Мадатов, Л.Э. Садыглы

Резюме: В данной работе исследованы вольт-амперные характеристики, температурная зависимость электропроводности и спектральное распределение фототока в слоистых монокристаллах GaSe, интеркалированных атомами Cu, в направлениях, параллельном и перпендикулярном оси «C». Установлено, что после интеркаляции Cu величина тока возрастает приблизительно в 30–40 раз в направлении оси «C» и в 10–20 раз в перпендикулярном направлении. Это объясняется образованием дополнительных локальных энергетических уровней в межслоевой области и увеличением концентрации свободных носителей заряда вследствие внедрения атомов Cu.

Показано, что γ-облучение приводит к уменьшению электропроводности и увеличению энергии активации. Установлено, что при дозе 15 kGy энергия активации возрастает от 0.10 eV до 0.29 eV в направлении оси «C» и от 0.14 eV до 0.36 eV в перпендикулярном направлении.

В спектральном распределении фототока максимальная фоточувствительность наблюдается в области 560–610 nm, при этом после интеркаляции Cu интенсивность фототока уменьшается примерно на один порядок. Полученные результаты показывают, что интеркаляция Cu и γ-облучение существенно изменяют механизм переноса носителей заряда и анизотропию электрических и фотоэлектрических свойств монокристаллов GaSe.

***Ключевые слова*:** интеркаляция, анизотропия, γ-облучение, электропроводность.

Cu ATOMLARI İLƏ İNTERKALASİYA OLUNMUŞ GaSe MONOKRİSTALINDA ELEKTRİK VE FOTOELEKTRİK XASSƏLƏRİN ANİZATROPİYASI

R.S. Mədətov, L.E. Sadıqlı

Xülasə: Bu işdə Cu atomları ilə interkalasiya olunmuş laylı GaSe monokristallarının cərəyan–gərginlik xarakteristikaları, elektrik keçiriciliyinin temperatur asılılığı və fotocərəyanın spektral paylanması “C” oxuna parelel və perpendikulyar istiqamətdə araşdırılmışdır. Müəyyən edilmişdir ki, Cu interkalasiyasından sonra cərəyanın “C” oxu istiqamətində təxminən 30–40 dəfə, perpendikulyar istiqamətdə isə 10–20 dəfə artdığı müəyyən edilmişdir ki, bu da Cu atomlarının laylararası oblastda əlavə lokal enerji səviyyələri yaratması və sərbəst yükdaşıyıcılarının konsentrasiyasını artırması ilə izah olunur. γ-şüalanma nəticəsində elektrik keçiriciliyinin azalması və aktivləşmə enerjisinin artması müşahidə edilmiş, 15 kGy dozada aktivləşmə enerjisinin “C” oxu istiqamətində 0.10 eV-dan 0.29 eV-a, perpendikulyar istiqamətdə isə 0.14 eV-dan 0.36 eV-a qədər artdığı müəyyən olunmuşdur. Fotocərəyanın spektral paylanmasında maksimum fotohəssaslıq 560–610 nm oblastında müşahidə edilmiş, Cu interkalasiyasından sonra fotocərəyanın intensivliyinin təxminən bir tərtib azalması qeydə alınmışdır. Alınmış nəticələr Cu interkalasiyası və γ-şüalanmanın GaSe monokristallarında yükdaşıyıcıların daşınma mexanizmini və elektrik-fotoelektrik xassələrin anizatropiyasını əhəmiyyətli şəkildə dəyişdirdiyini göstərir.

Açar sözlər: interkalasiya, anizatropiya, γ-şüalanma, elektrik keçiriciliyi.