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Electroluminescence of *p*-GaSe⟨REE⟩ Single Crystals

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Abstract—We have studied the electroluminescence (EL) properties of *p*-GaSe⟨REE⟩ single crystals doped with $N \leq 0.1$ at % gadolinium or dysprosium and exhibiting a switching effect (SE). The results demonstrate that, at such values of *N*, EL and SE parameters and characteristics are independent of the chemical nature of the rare-earth dopant (gadolinium or dysprosium). Rare-earth doping levels in the range $N \approx 10^{-2}$ to 10^{-1} at % ensure high stability and reproducibility of the EL and SE parameters. We have examined the feasibility of using *p*-GaSe⟨REE⟩ single crystals for the fabrication of high-performance light switches and sources with S-shaped current–voltage characteristics.

Keywords: switching effect, electroluminescence, local levels, incorporated impurity, rare-earth element

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INTRODUCTION

Dynamic development of optoelectronics requires a detailed understanding of the electronic properties and potential practical applications of semiconducting materials with electroluminescence properties in the visible range of the optical region of electromagnetic radiation. In connection with this, there is currently great interest in studying electroluminescence, especially injection luminescence, in various semiconductors. Recent years have seen particular interest in nanomaterials (for example, porous silicon [1–5]), whose physical properties can be tuned over a wide range by varying their geometric parameters at a given chemical composition. At the same time, there are certain difficulties in producing visible sources based on such materials, which are associated primarily with the low quantum yield of their luminescence, the instability of their emission, the nonuniform intensity distribution over their surface, their slow response, and their short service life. Moreover, such structures (electroluminescent elements) are commonly produced using various types of electric contact (*p*–*i*, *n*–*i*, *p*–*n*, *p*–*p*, and *n*–*n* homo- and heterojunctions). However, the fabrication of such structures is typically limited by technological difficulties, so only a limited range of materials are used for this purpose, with a limited spectral region of emission.

The emergence of novel potential practical applications has aroused considerable interest in the electroluminescence behavior of long-known semiconductors. One such semiconductor is single-crystal *p*-GaSe, a III–VI compound with a layered structure. This semiconductor is promising for the fabrication of various optoelectronic devices [6–8], including electroluminescent light sources operating in the visible spectral region and low-dimensional structures with unique properties [9–15]. In particular, disk-shaped gallium selenide quantum dots one tetrahedral layer in thickness offer good photostability and high luminescence quantum yield. Single-crystal *p*-GaSe layers exhibit injection electroluminescence (EL) [16] and various switching effects (SEs) (bistable and threshold switching) [17], with the possibility of combining them in a single sample [18]. The latter makes this semiconductor a potentially attractive material for the fabrication of light switches and sources with S-shaped current–voltage (*I*–*V*) characteristics. At the same time, the presence of various random defects (RDs), including macroscopic defects (MDs) [19], influences the stability and reproducibility of the electroluminescence properties of pure (nominally undoped) *p*-GaSe single crystals, limiting their utility for many practical applications.

A variety of approaches have been used to reduce the influence of defects on the electronic properties of *p*-GaSe single crystals. It is well documented that it can be reduced by not only heat treatment and ionizing radiation but also slight doping (to a level $N \leq 0.1$ at %) with some rare-earth elements (REEs). The effect is assumed to be due to MD “consolidation.” This and previously reported results [20, 21] suggest that the stability and reproducibility of the electroluminescence properties of *p*-GaSe single crystals can be enhanced by doping with REEs.

The objectives of this work were to prepare a high-performance material (with stable and reproducible parameters) for the fabrication of light switches and sources with S-shaped *I–V* characteristics based on *p*-GaSe⟨REE⟩ single crystals by investigating the SE and EL in a single sample and clarify the mechanism underlying the influence of low rare-earth doping levels on these effects.

EXPERIMENTAL

The GaSe compound was synthesized by melting a mixture of 99.999%-pure constituent components. To dope it, an appropriate amount of gadolinium (Gd) and dysprosium (Dy) was added to the starting mixture. These REEs were chosen for a number of reasons. First, extensive studies (see, for example, Abdinov et al. [20] and Abdinov and Babaeva [21]) have been concerned with the preparation and various physical properties of Gd- and Dy-doped *p*-GaSe single crystals, which allows the experimental data obtained by us to be accounted for. Second, the electronic configuration and chemical reactivity of these REEs, their stability in dry air, and their electrochemical similarity to Ga, as well as their melting points and their atomic and ionic radii [22–24], make them highly suitable for doping GaSe. Two distinct REEs were employed as dopants because we wanted to understand how the chemical nature of the dopants influenced the EL in the semiconductor under study. If the doping effect on its EL is associated not with processes directly related to the local energy levels (centers) produced by incorporated impurities but with structural changes in the host semiconductor under study, its EL will be independent on the chemical nature of the dopant.

The single crystals grown from the synthesized material by the Bridgman method [25] were *p*-type. The structure, phase composition, and elemental composition of the grown ingots and the surface condition on natural cleavage planes were determined by a variety of techniques using DSK-910, ADVNCA-8D, SINTECP 21, and DRON-4-07 (CuK_α radiation, scan step of 0.05°, angular range 8°–135°) instruments and a Carl Zeiss scanning electron microscope (SEM) equipped with an energy dispersive X-ray spectrometer system.

Samples in the shape of rectangular parallelepipeds were prepared by cleaving from different ingots and from different portions of a particular large single-crystal ingot. The 77-K dark resistivity of the undoped samples (ρ_0) ranged from ~5×10^4 to 10^8 Ω cm, and the *N* and ρ_0 of the doped samples ranged from 10^{-5} to 10^{-1} at % and from ~5×10^3 to 10^9 Ω cm, respectively. The highest (~10^9 Ω cm) and lowest (~5×10^3 Ω cm) values of ρ_0 were obtained at $N \approx 5 \times 10^{-4}$ and $N \approx 10^{-1}$ at %, respectively.

Electrical contacts were made by indium or tin solder and by firing silver paste on freshly cleaved surfaces in air.

Measurements were performed between 77 and 300 K at electric field strengths of up to ~3.5 kV/cm in the wavelength range 0.30–2.00 μm using an experimental setup built around a modified KSVU-23 system. For all of the samples, we measured a static *I–V* characteristic under open-circuit conditions, the spectral distribution of the electroluminescence brightness, and the EL brightness as a function of electric field strength (*E*), electric current (*i*) through the sample, and temperature (*T*). The electric circuit included dc sources.

RESULTS AND DISCUSSION

At $T \le 200$ K, the *p*-GaSe⟨REE⟩ single crystals with $N = 10^{-5}$ to 10^{-1} at % exhibited EL starting at a certain electric field strength, E_{th} (electroluminescence threshold field), like undoped crystals. The E_{th} corresponds to a region of the *I–V* characteristic where noticeable injection takes place, increases with increasing *T* and ρ_0, and depends on the material of the electrical contacts. The lowest E_{th} and highest emission brightness (B_λ) are observed in the samples with indium contacts.

EL emerges near the "negative" contact and, with increasing *E*, gradually extends toward the "positive" contact. The EL parameters and characteristics (E_{th} and B_λ, as well as the variation of B_λ with λ, *T*, *V*, and *i*) in the *p*-GaSe⟨REE⟩ single crystals were found to be independent of the chemical nature of the incorporated impurity at the *N* values examined. The wavelength range ($0.58 \le \lambda \le 1.10$ μm) and position ($\lambda \approx 0.60$ μm) of the main peak and the positions of additional peaks ($\lambda_1 \approx 0.67$ μm and $\lambda_2 \approx 0.82$ μm) in the spectral dependence of B_λ (EL spectrum) for the *p*-GaSe⟨REE⟩ single crystals coincide with those for undoped GaSe single crystals (Fig. 1). The sharp short-wavelength drop in the EL spectrum corresponds to a band gap of ~2.04 eV [18], and the main and additional emission bands correspond to recombination centers at $\varepsilon_{r1} \approx \varepsilon_\upsilon + 0.20$ eV and $\varepsilon_{r2} \approx \varepsilon_\upsilon + 0.54$ eV, respectively. Note that the EL brightness rises as a power law function of voltage and as a linear function of current (Fig. 2). *N* influences only the brightness of individual emission bands and E_{th}. Both dependences have a nonmonotonic character.

With increasing REE content, E_{th} first rises (at $N \leq 10^{-4}$ at %) by ~25–30% compared to the value for the lowest resistivity undoped crystals (E_{th0}) and then gradually decreases (in the range $10^{-4} < N \leq 10^{-1}$ at %), becoming lower than E_{th0} at $N \approx 10^{-1}$ at % (Fig. 3, curve *1*). With increasing N, B_λ first decreases (at $N \leq 10^{-4}$ at %) by ~30–40% relative to that in the lowest resistivity undoped crystal ($\rho_0 \approx 5 \times 10^4\ \Omega$ cm) and then rises sharply (in the range $10^{-4} < N \leq 10^{-1}$ at %), exceeding it by a factor of 1.5–2.5 at $N \approx 10^{-1}$ at % (Fig. 3, curve *2*). With increasing temperature, B_λ remains essentially constant in the range $T \approx 160$–170 K, with thermal quenching of EL at higher temperatures. The temperature of complete EL quenching is ~200 K in all of the p-GaSe⟨REE⟩ samples under investigation (Fig. 4).

When the applied voltage reaches the switching voltage ($V \approx V_{sw}$) [17, 18], the transition of the material to a low-resistivity state (Fig. 5, curves *1*, *2*) is accompanied by abrupt EL quenching (Fig. 5, curves *3*, *4*). Note that, at $V \approx V_{sw}$, the samples with transverse and longitudinal contacts have not only identical I–V curves but also identical $B_\lambda(V)$ curves. At $V = V_{sw}$, the EL brightness in the samples reaches a maximum, whereas the onset of the switching effect sharply changes the situation. The samples having transverse contacts (Fig. 5, curves *1*, *3*) undergo a transition from a high-resistivity to a low-resistivity state in a time $\tau \leq 10^{-8}$ s, and their B_λ drops to zero at roughly the same rate. In the region of a negative differential resistance in their I–V curves, during the switching process (Fig. 5, curve *3*) the B_λ of the samples with longitudinal electrical contacts first gradually decreases by ~30–40% relative to that at $V = V_{sw}$ and drops sharply to zero at higher voltages (EL quenching) (Fig. 5, curve *4*). In both cases, no EL is observed while the material is in its low-resistivity state.

With increasing N, the switching field first increases (at $N \leq 10^{-4}$ at %) by ~20–25% relative to that in undoped crystals (E^0_{sw}) and then drops (in the range $10^{-4} < N \leq 10^{-1}$ at %), becoming ~10–15% lower than E^0_{sw}. In all of the p-GaSe⟨REE⟩ samples with $N \approx 10^{-2}$ to 10^{-1} at %, the switching parameters and characteristics are almost identical, stable, and reproducible.

The stability of SE and EL parameters and characteristics was verified by performing 200 tests of a given sample and their reproducibility was verified by comparing results for a hundred of different p-GaSe⟨REE⟩ samples with $N \approx 0.1$ at %.

The present results can be adequately accounted for in terms of the recombination of injected minority carriers (electrons) at r-centers of recombination [26] and the sharp decrease in the voltage drop across the sample under study as a result of the SE [17].

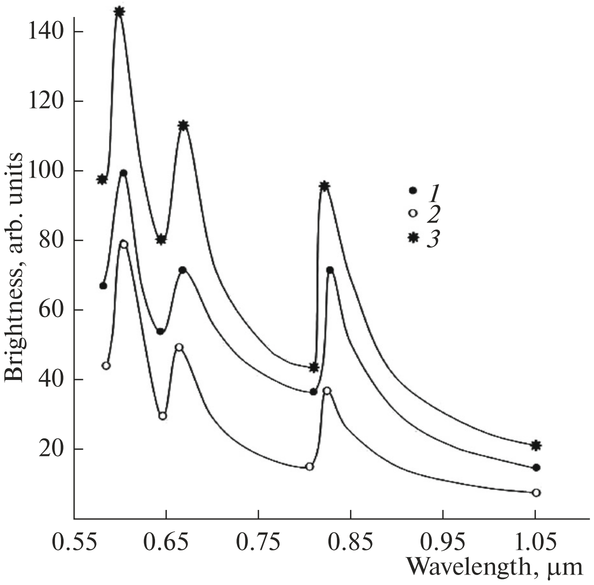

Fig. 1. EL spectra of (*1*) undoped and (*2*, *3*) rare-earth-doped p-GaSe single crystals: $T = 77$ K, $E = 4E_{th}$, $i = 30$ mA, $N =$ (*2*) 10^{-3} and (*3*) 10^{-1} at %.

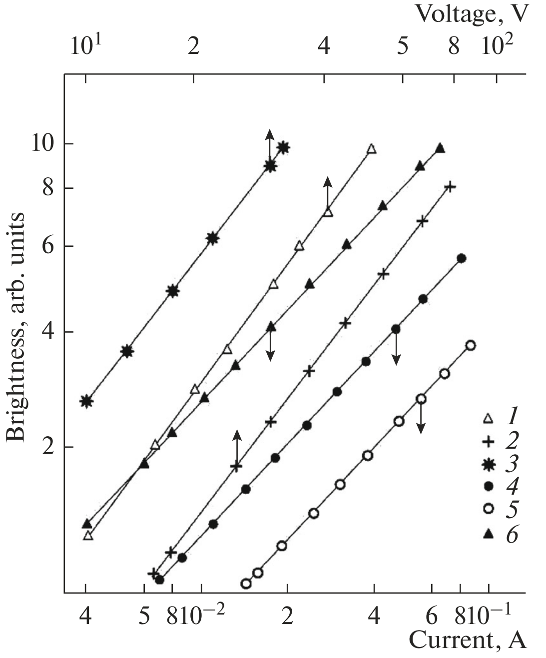

Fig. 2. EL brightness as a function of (*1–3*) voltage and (*4–6*) electric current for the p-GaSe⟨REE⟩ single crystals: $T = 77$ K; $\lambda = 0.60$ μm; $N =$ (*1*, *4*) 0, (*2*, *5*) 10^{-3}, and (*3*, *6*) 10^{-1} at %.

The observed variations in EL parameters and characteristics from sample to sample and their dependence on the history of the samples and doping

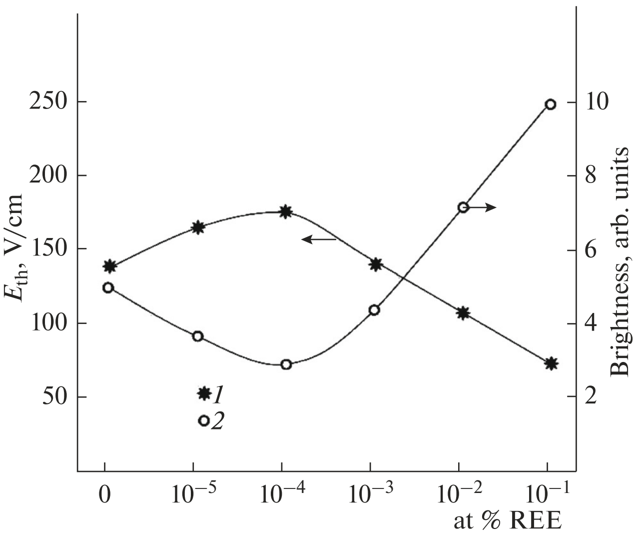

Fig. 3. (*1*) EL threshold field and (*2*) EL brightness as functions of the doping level for the *p*-GaSe⟨REE⟩ single crystals: $T = 77$ K, $\lambda = 0.60$ μm.

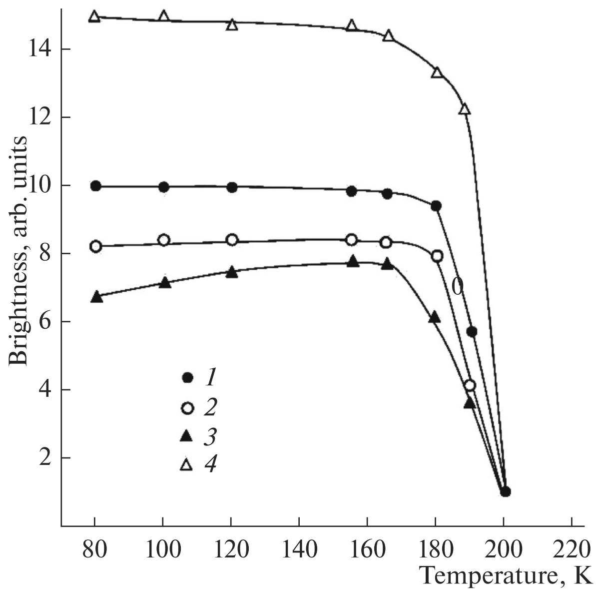

Fig. 4. Temperature dependences of EL brightness for the *p*-GaSe⟨REE⟩ single crystals: $E = 4E_{th}$; $i = 30$ mA; $\lambda = 0.60$ μm; $N = (1)$ 0, (*2*) 10^{-5}, (*3*) 10^{-4}, and (*4*) 10^{-1} at %.

level are most likely related to the presence of random MDs in *p*-GaSe [19]. In the case of doping with REEs, the internal electric field causes the incorporated impurity ions to concentrate at RDs, thereby increasing their size. As a consequence, raising the RE doping level in the range $N \leq 10^{-4}$ at % increases spatial inhomogeneity and, accordingly, the effect of MDs on minority carrier injection and generation–recombination processes. In the range $10^{-4} < N \leq 10^{-1}$ at %, because of the increase in RD size the distance between neighboring MDs is comparable to the diffusion length and, hence, to the carrier mean free path. This is accompanied by MD "consolidation," and, like heavily doped semiconductors, the *p*-GaSe⟨REE⟩ single crystals gradually approach a quasi-ordered state [27].

Moreover, the increase in the degree of covalent bonding between rare-earth ions located in neighboring layers leads to an increase in interlayer bonding in the crystal. These two processes, in turn, lead to an increase in B_λ and improve the stability and reproducibility of EL parameters and characteristics in *p*-GaSe⟨REE⟩. The fact that the EL and SE parameters and characteristics of the material are independent of the chemical nature of the dopant suggests that, in the range $N \leq 0.1$ at %, accumulating at RDs the rare-earth dopant atoms change only the surrounding space charge region (SCR), without producing impurity levels. Because of this, the effect of rare-earth doping on EL in this range of doping levels is associated with changes in the random electron potential in the material under investigation. In particular, at low doping levels, the SCRs of neighboring RDs do not overlap and the random potential is high. At high values of N, the overlap of the SCRs of neighboring RDs leads to a reduction in spatial inhomogeneity in the structure of the semiconductor host in the sample under investigation [27]. In this model, intracenter processes directly related to the electron configuration or chemical nature of dopant atoms and the interaction of injected charge carriers with impurity centers should show up at higher doping levels, as supported by previously reported results [28].

The thermal quenching of EL in the semiconductor under investigation is obviously due to the thermal depletion of *r*-centers, which is accompanied by a reduction in recombination rate and, accordingly, in B_λ.

EL quenching in the case of an SE can be accounted for by the sharp decrease in the voltage drop across the sample and filamentation of the current flowing through it.

CONCLUSIONS

p-GaSe single crystals doped with Gd and/or Dy to $N \leq 0.1$ at % exhibit an SE and EL in the range $T \leq 200$ K, like undoped crystals of this semiconductor.

The possibility of combining an SE and EL in a single *p*-GaSe⟨REE⟩ sample allows one to fabricate light switches and sources with S-shaped *I*–*V* characteristics based on single crystals of this semiconductor by a simple process.

EL parameters and characteristics in *p*-GaSe⟨REE⟩ with $N \leq 0.1$ at %, as well as their stability and repro-

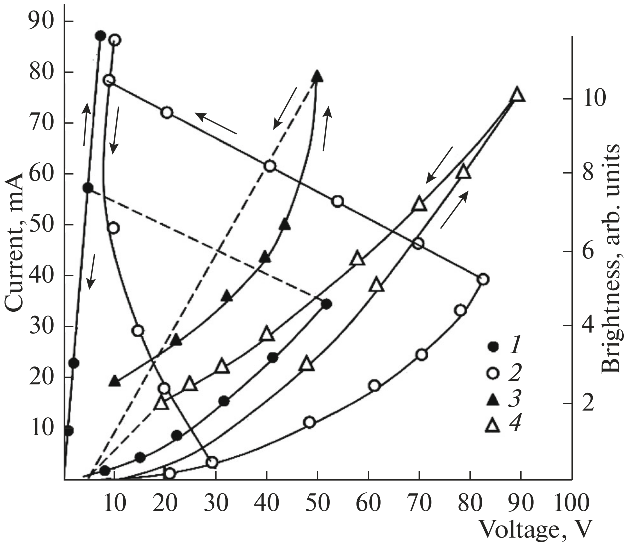

Fig. 5. (*1*, *2*) *I*–*V* curves and (*3*, *4*) EL brightness as a function of voltage for the *p*-GaSe⟨REE⟩ single crystals in the cases of (*1*, *3*) bistable and (*2*, *4*) threshold SEs: $T = 77$ K, $N = 10^{-1}$ at %, $\lambda = 0.60$ μm.

ducibility, are independent of the chemical nature of the rare-earth dopant and can be controlled by varying the doping level.

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