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ELEMENTS OF OPTOELECTRONICS BASED ON p-GaSe<Er> CRYSTALS

A.Sh. Abdinov [1] **R.F. Babayeva** [2]

1. Department of Physical Electronics, Baku State University, Baku, Azerbaijan, abdinov_axmed@yahoo.com
2. Department of Engineering and Applied Science, Azerbaijan State University of Economics (UNEC), Baku, Azerbaijan, babayeva.rena@unec.edu.az

Abstract - The features of the current passage phenomena under various modes, as well as photoconductivity and injection electroluminescence under various external and intracrystalline conditions in pure (in particular, undoped) and erbium (Er) doped ($N \approx 10^{-5} \div 10^{-1}$ at.%) single crystals of layered p-GaSe semiconductor are experimentally investigated. On the basis of statistical and comparative analysis, a scientific explanation of the obtained experimental results is proposed and the possibility of creating a multifunctional optoelectronic element based on crystals of this semiconductor is shown, which combines the functions of a triac, light-controlled parameters, electroluminescent glow and current switches with an S-shaped current-voltage characteristic.

Keywords: Electroluminescence, Current Passing, Photoconductivity, Injection, Switching Effect, Doping, Spectral Distribution.

1. INTRODUCTION

The unique functional features of optoelectronic devices open up wide opportunities for their use in various areas of modern human life - from household appliances, medicine, various fields of ground-based scientific research, up to space technology [1]. Therefore, the field of research on the search for suitable physical effects and active materials for this field of electronics, the identification of their new functional capabilities is expanding day by day and promises many more interesting things.

In this aspect, in addition to traditional elementary and binary, semiconductors with more complex chemical compositions, band and crystalline structures are also quite interesting and promising. These semiconductors include binary and ternary compounds, as well as solid solutions of selenides with a layered crystalline structure [2]. In experimental studies of the electrical, photoelectric, and luminescent properties of these semiconductors, along with the detection of theoretically unpredictable physical effects, the possibility can also be revealed of creating fundamentally new functional elements based on them for various areas of electronics, including for optoelectronics and photoelectronics.

In this paper, we report the results obtained by us in a joint experimental study of the current transmission process under various modes, as well as intrinsic photoconductivity and injection electroluminescence under various external conditions in pure (in particular, undoped) and Er doped containing the introduced impurities in the range of $N \approx 10^{-5} \div 10^{-1}$ at.% gallium selenide single crystals (p-GaSe).

2. OBJECTS AND RESEARCH TECHNIQUE

The compound of gallium selenide (GaSe) is synthesized by joint fusion of the constituent components in a stoichiometric ratio of substances at a certain temperature regime. Metallic gallium (Ga) and granular selenium (Se) served as components of the base material (GaSe), and metallic erbium (Er) was taken as an impurity. Both groups of materials used - both impurity (Er) and composite components (Ga, Se) had high (99.999 %) purity.

The phase and crystal structure of the obtained products (pure and erbium-doped gallium selenide crystals) were checked by complex thermographic and X-ray structural analyzes [3]. It was found that all of them are single-phase, belong to ε-GaSe with lattice parameters a=3.744 Å, c=15.902 Å [4] and have a high degree of single crystallinity.

The measurements were carried out at temperatures T=77÷300 K, electric field strength $\sim 5 \cdot 10^{1} \div 4.0 \cdot 10^{3}$ V⁄sm, wavelength λ=0.30÷2.00 μm and intensity $\Phi = 1 \cdot 10^{1} \div 5 \cdot 10^{2}$ Lx of light.

Contact materials were tin (Sn), indium (In), and silver paste. On each sample of both groups of crystals (pure and Er doped) under different conditions (at different temperatures, in the dark and under the influence of light) and modes (under the regime of currents limited by the space charge [5] and under the switching effect [6]), current-voltage characteristic (CVC), as well as the spectral distribution of photoconductivity (PC), and also the spectral distribution, dependence on the magnitude of the electric voltage applied to the sample (electric field strength), the value of the current strength and the temperature of the brightness of electroluminescence (EL).

3. EXPERIMENTAL RESULTS

It was found that in all the samples in the temperature range T<200 K at the strengths of the electric field (E) acting on the sample, equal to some $E_{s.i}$ (switching strength), the effect of bistable switching (BSE) occurs [6], with symmetric with respect to the voltage applied to the sample by an S-shaped CVC (a "triac" effect is observed [7]) (Figure 1, curve 1); starting from the value $E=E_{i.i}$ (tension ignition EL), electroluminescence is observed [8]; for samples with different values of the initial value (which takes place at a boiling liquid nitrogen temperature of -77 K) ρ_0, and the content of the introduced impurity - N (in samples of pure and doped crystals, respectively) at 77 K, the value of $E_{i.i}$ varies within ~ $(10^2\div10^3)$ V/cm. When $E_{1\text{-}2}\le E<E_{s.i}$ (where $E_{1\text{-}2}$ is the value of the intensity of the electric field, at which the dark static CVC goes from the linear section to the first quadratic [6]) the "pre-breakdown part" of the CVC consists of currents characteristic of the mode, limited by volume charges (SPC) [6], several alternating power-law sections.

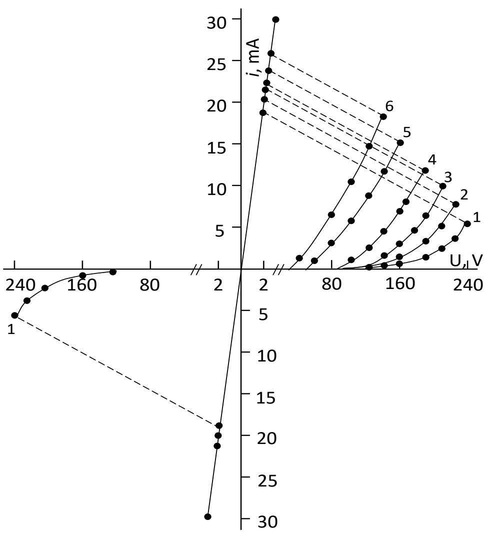

Figure 1. Static CVC of p-GaSe:Er with N=10^{-1} at.%
at T, K: 1-77; 2-100; 3-150; 4-200; 5-250; 6-300

The value of $E_{s.i}$ is expediently controlled by the action of light (Figure 2, curves 1 and 2) - a "photo trigger" effect is observed [9, 10]. In both groups of crystals, at the strengths of the electric field applied to the test sample $E_{i.i}\le E<E_{s.i}$, the dependence of the brightness of the electroluminescence (B_λ) on E obeys a power law ($B_\lambda \sim E^k$) with an exponent $k\approx3\div6$ for various samples, and at electric field strength $E=E_{s.i}$, in addition to the switching effect in the conductivity of the sample (Figure 3, curve 1), there is also switching in the brightness of the electroluminescence - the value of B_λ drops sharply to zero (Figure 3, curve 2). With an increase in the temperature and intensity of the light incident on the sample, the "pre-breakdown part" of the CVC gradually "smoothes out", and the value of $E_{s.i}$ decreases (Figure 1, curves 1-6 and Figure 2, curves 1, respectively). The dependence of the value of the switching strength on the wavelength of the light incident on the test sample (Figure 2, curve 2) correlates well with the spectrum of intrinsic photoconductivity in the test sample (Figure 2, curve 3). In samples of pure crystals, the values of the ignition intensity and the brightness of the electroluminescence depend on the initial value of the specific dark resistance (ρ_0) and with increasing ρ_0, the value of $E_{i.i}$ smoothly increases, and B_λ decreases.

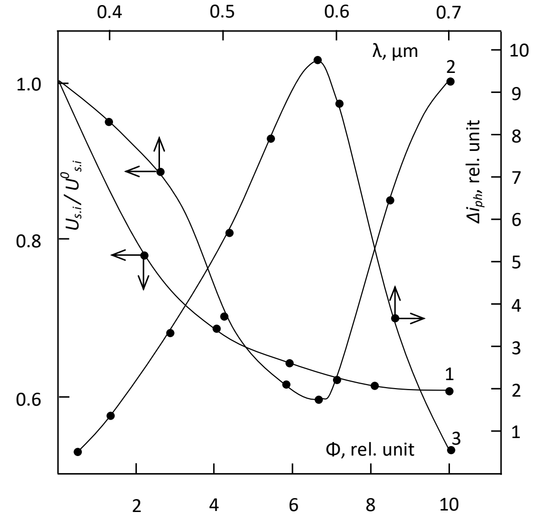

Figure 2. Dependence of switching voltage on intensity (curve 1) and light wavelength (curve 2), photoconductivity spectrum (curve 3) in p-GaSe: Er crystals at 77 K
λ, μm: 1-0.58; Φ, in rel.ed: 2 and 3 - 10; N = 10^{-1} at.%

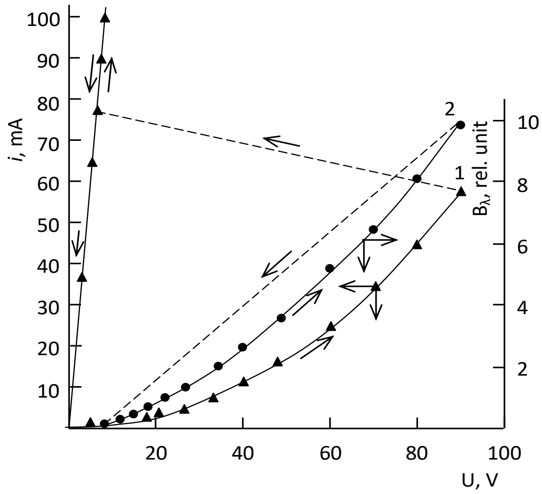

Figure 3. Dark current-voltage characteristic (curve 1) and current-voltage characteristic of electroluminescence (curve 2) in erbium-doped p-GaSe crystals with 10^{-1} at.% at 77 K, Φ = 0

In Erbium-doped crystals, with an increase in the content of the introduced impurity, first (up to a value of $N\approx5\times10^{-4}$ at.%) the value of $E_{s.i}$ (or switching voltage - $U_{s.i}$)) increases by ~ 15-20%, and then, decreasing, approaches the value that occurs in the most low-resistance pure crystals. The values of $E_{i.i}$ and B_λ also depend on the value of N. Both dependences have a non-monotonic character - with an increase in the value of N, they initially deviate by ~20÷25% from that in the lowest-ohmic pure crystals; at $N\approx5\times10^{-4}$ at.% the dependence $E_{i.i}(N)$ passes through its maximum and dependence $B_\lambda(N)$ - through a minimum.

The spectral distribution of electroluminescence does not depend on doping, in all studied samples it covers the wavelength region $0.58 \leq \lambda \leq 1.10$ µm and has maxima at wavelengths $\lambda_{M1} \approx 0.600$ µm (basic), $\lambda_{M2} \approx 0.590$ µm, $\lambda_{M3} \approx 0.615$ µm, $\lambda_{M4} \approx 0.650$ µm and $\lambda_{M5} \approx 0.825$ µm (additional). With an increase in the strength of the external electric field applied to the test sample, the maximum detected at $\lambda_{M4} \approx 0.825$ µm gradually shifts towards shorter wavelengths up to ~ 0.740 µm (Figure 4). For various samples, the energy value determined from the sharply decaying short-wavelength part of the spectrum of electroluminescence at 77 K from the side of short wavelengths corresponds to the value of the band gap of p-GaSe crystals, found from the spectral distribution of the optical absorption coefficient (~ 2.05 eV), and the energy value found from the main maximum of the spectral distribution of electroluminescence turns out to be less than ε_g, by almost 0.15 eV.

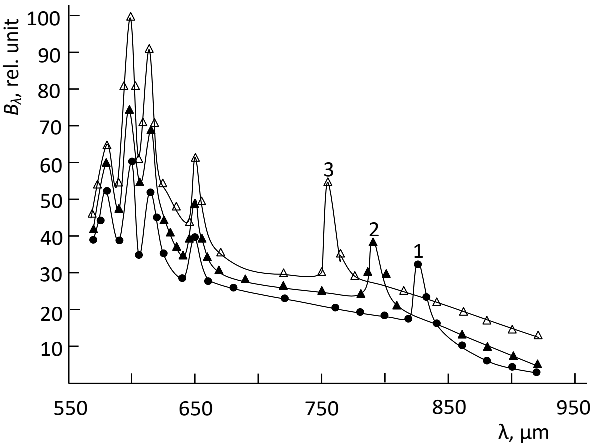

Figure 4. Spectral distribution of electroluminescence in erbium-doped p-GaSe crystals at different strengths of an electric field applied to the sample, $N=10^{-1}$ at.%; T=77 K; $E/E_{i.i}$: 1- 1.2; 2- 2.5; 3- 5.0

The luminescence brightness of electroluminescence (B_λ) in samples of both groups of crystals at temperatures $T \leq 110 \div 125$ K does not depend on temperature, and then decreases exponentially with increasing temperature. In this case, the activation energy of electroluminescence radiation for all the samples (regardless of the values of ρ_0 and N) is ~ 0.60 eV, which is in good agreement with the energy depth of occurrence of slow r-recombination centers in p-GaSe crystals [10].

The results obtained on samples with different electrical contacts show that the switching effect and electroluminescence in them are mainly associated with the individual features of the p-GaSe crystals themselves, and contact phenomena play only an auxiliary (igniting) role. In samples with highly injecting electrical contacts, both phenomena are more pronounced. The most stable and reproducible characteristics are observed in Er doped ($N \approx 10^{-1}$ at.%) samples soldered with indium electrical contacts in the open air without flux (Figures 1-4).

4. DISCUSSION

A statistical analysis of the experimental results obtained, taking into account the information available in the scientific literature on the electronic properties of p-GaSe crystals, as well as on the switching effect and injection electroluminescence in semiconductors, allows us to say that the current passage in the samples of both groups of p-GaSe crystals in the pre-breakdown region of the current-voltage characteristic, it is predominantly determined by the mode of the SCLC in the presence of two groups of sticking levels in the forbidden band of this semiconductor [5].

With an increase in the value of the strength of the electric field applied to the test sample, a gradual curvature of the edges of the energy bands and local levels occurs. At an electric field strength $E=E_{s.i}$, due to the collective tunnel transition of the injected charge carriers trapped at shallow levels of adhesion to the free energy band, the conductivity of the sample, as well as the current density through it, increases abruptly. The latter, in turn, leads to pinning of the current flowing through the sample.

As a result, a filamentous highly conductive channel is formed between the electrical contacts, which shunts the high resistance of the rest of the sample. Therefore, the sample is abruptly transformed into a low-resistance state. As the temperature rises and the sample is exposed to light from the region of intrinsic absorption, the process of filling the traps is accelerated and, therefore, the value of $E_{s.i}$ decreases, and the pre-breakdown part of the current-voltage characteristic is smoothed compared to the initial one.

As in pure [8], in samples of erbium-doped p-GaSe crystals, electroluminescence also has an injection nature. With the switching effect due to the formation of a shunting intercontact highly conductive filamentous channel, firstly, the voltage drop across the test sample sharply decreases (the intensity of the electric field applied to the test sample becomes much less than the ignition intensity of the electroluminescence), and secondly, due to the concentration of free charge carriers only in this filamentous channel of the sample, the process of injection of nonequilibrium minority charge carriers from electrical contacts into the sample volume, where those directly responsible for the generation of radiation centers of recombination stops. Both of these factors lead to a sharp quenching (decrease in brightness) of electroluminescence during the switching effect.

In erbium-doped p-GaSe crystals, with a change in the content of the introduced impurity, the degree of spatial inhomogeneity of the samples changes [11, 12], which, in turn, causes the experimentally found dependences of the the content of the introduced impurity. With an increase in N, the influence of the spatial inhomogeneity of the sample on the photoconductivity, the switching effect and electroluminescence radiation first (at $N_{REE} \leq 5 \times 10^{-4}$ at.%) increases, and then (at $N_{REE} > 5 \times 10^{-4}$ at.%) due to gradual partial overlap of space charge regions of neighboring random large-scale defects (RLSD) is weakened [13], and the situation approaches the corresponding one in pure crystals with the smallest ρ_0.

When doped erbium ions, in addition to changing the size of the space charge regions of the RLSD, also entering the layers and due to the covalent bond between the ions with the same origin in neighboring layers, to some extent increases the interlayer bond, which in turn increases the mechanical strength of the sample. Apparently, it is for this reason that in samples of erbium-doped p-GaSe crystals with an introduced impurity content of $N \geq 10^{-2}$ at.%, the values of individual parameters and characteristics of photoconductivity, the switching effect and electroluminescence radiation become more stable, reproducible, and their experimentally discovered features are satisfactorily explained on the basis of the theory of spatially homogeneous crystalline semiconductors with different centers of attachment, capture, and recombination [14-17], which we verified by more than 50 measurements on the same sample and by comparing experimental results for more than 20 different samples p-GaSe<Er> with the content of the introduced impurity $N \approx 10^{-2} \div 10^{-1}$ at.%.

From these data, it follows that on the same sample of p-GaSe crystals with a resistor structure (which does not have any rectifying electrical contacts), switching in electrical conductivity and brightness of electroluminescence are simultaneously combined, as well as the "photo-emistor" effect (purposeful control of the parameters of the symmetric *S*-shaped current-voltage characteristic by the action of photoactive-inducing photoconductivity, light [7, 9]).

Since among the basic functional elements of optoelectronics with their wider applied capabilities are optocouplers with an S-shaped current-voltage characteristic [7, 9, 18], the prospects of functional elements with such a combination of three different functions are beyond doubt. Moreover, this does not require complex technological operations, which are necessary in the case of creating regenerative optocouplers consisting of several interconnected *p-n* or other rectifying electric transitions [18]. These results indicate that the crystals of the layered semiconductor p-GaSe<Er> with the content of the introduced impurity $N \approx 10^{-2} \div 10^{-1}$ at.%. in addition to solar photovoltaic converters [19, 20], they are also promising materials for optoelectronics.

5. CONCLUSIONS

A joint experimental study of the current-voltage characteristic, the switching effect (BSE) and electroluminescence (EL) in the same sample of erbium-doped layered semiconductor crystal p-GaSe, allows to more reliably clarify the physical mechanism and features of current conductivity, BSE, and EL in this semiconductor;

The combination on the same sample of erbium-doped p-GaSe semiconductor crystal with a resistor structure of the switching effects in the electrical conductivity of electroluminescence, as well as the possibility of targeted control of the parameters of the conductivity switching effect by the action of light, make it possible to recommend this semiconductor for creating multifunctional optoelectronic elements, in particular light sources and receivers with S-shaped current-voltage characteristic without any rectifying contact structures;

By optimal doping (with the content of the introduced impurity $N \approx 10^{-2} \div 10^{-1}$ at.%) of gallium selenide crystals with erbium, it is possible to provide high stability, reproducibility and more favorable for optoelectronics parameters of the elements of BSE, EL, and “photosimistors” based on them.

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BIOGRAPHIES

Ahmed Shahvaled Abdinov was born in Behrud, Ordubad, Azerbaijan on May 30, 1945. In 1968 he graduated from the Physics Department of Baku State University, Baku, Azerbaijan. He defended the Ph.D. thesis and the Doctoral thesis in 1972 and 1979, respectively. Since 1981 he is a Professor. Since 1992 occupies a position of Head of the "Physical Electronics" Department at Baku State University. He is the author of over 430 scientific papers on semiconductor physics. His researches are related to the study of the electronic properties of complex semiconductor materials and contact structures based on them.

Rena Fikrat Babayeva was born in Baku, Azerbaijan on December 30, 1969. In 1991 she graduated from the Physical Faculty of the Baku State University, Baku, Azerbaijan. She defended the Ph.D. thesis and the Doctoral thesis in 1997 and 2009, respectively. She occupies position of Professor of the Engineering and applied science Department at the Azerbaijan State University of Economics (UNEC), Baku, Azerbaijan. She is the author of more than 240 works on semiconductor physics. In particular, her researches include the study of the electronic properties (electrical, optical, photoelectrical, luminescent, etc.) of semiconducting A^3B^6 compounds with a layered structure.