Properties of gallium selenide doped with sulfur from melt and from gas phase

O.V. Voevodina, A.N. Morozov, S.Yu. Sarkisov, S.A. Bereznaya, Z.V. Korotchenko, D.E. Dikov

Siberian Physico-Technical Institute
1 Revolution sq. 634050, Tomsk, Russia
Phone/ Fax: +7/3822/41-3636, e-mail: voevodin@elefot.tsu.ru

Abstract -**This paper presents the results of investigation on influence of doping with sulfur and annealing in sulfur atmosphere on properties of promising nonlinear optical gallium selenide crystals, grown by the Bridgman method from melts with content of sulfur 0.01-3 mass % and annealed in sulfur atmosphere.**

I. INTRODUCTION

Gallium selenide crystal (GaSe) is known as one of the most promising materials for nonlinear optical applications in mid- and far-IR regions. GaSe allow realizing the maximal number of parametrical laser radiation frequency converters of existing lasers, operating within near- and far-IR and also submillimeter and millimeter spectral ranges. The interest to coherent terahertz radiation sources on its base is now very high [1]. The basic merits of this layered material are: the high birefringence B=0.375; the broad region of spectral transparency 0.65-18.0 µm; a high value of nonlinear susceptibility of the second order d_{22}=23.0-54.4 pm/V up to 75 pm/V; the thermal conductivity in the direction perpendicular to the optical axis 0.118 W/cm/K (along this axis – 0.021 W/cm/K); a simple method of making surfaces of optical quality by cleaving; besides, minimal optical losses in terahertz spectral region among known nonlinear optical crystals.

The set of positive properties brings gallium selenide to the best five mid-IR nonlinear optics' materials. Nevertheless, the possibilities of practical application of GaSe are still limited by a low microhardness and cleavage. Because of this, the problem of finding the new possibilities to improve gallium selenide properties is actual. So at SphTI the works on growing and investigation of doped and pure gallium selenide and production of optical elements on its base (Fig. 1) are conducted.

The doping of the crystals with isovalent impurities is one of the possible ways to improve optical and mechanical properties of gallium selenide [2,3,4]. Along with the technological problem solution, the characterization of the crystals by different physical methods is an actual task. In this connection, the electrical, optical, mechanical and photoelectric properties of gallium selenide doped with sulfur were investigated. To distinguish the changes of properties connected with sulfur, especially in the interlayer space, experiments on annealing in S vapor were conducted.

Fig. 1. Ampoules with synthesized compound, cleaved crystals and an optical element (Siberian Physico-Technical Institute, Materials Science Laboratory)

II. EXPERIMENTAL

The doping of GaSe, grown by the Bridgman method, was made from the melt. The experiments on annealing were made in quartz ampoules at sulfur vapour pressures of approximately 3.2 atmospheres for 1-2 weeks.

In first experiment the temperature was 500 ^{0}C. At this temperature sulfur is presumably in the form of S_8 rings and does not intercalate intensively to the interlayer space. In the second experiment the temperature was high (800 ^{0}C) and the content of monoatomic and diatomic molecules of sulfur was sufficient. But at this temperature material's decomposition may be considerable so we observed the formation of 200 µm orange-yellow film on the samples' surfaces. We consider this film to be a solid solution $GaSe_{1-x}S_x$.

The physical properties were measured using standard schemes. The electrical contacts were made by indium evaporation onto samples' surfaces.

III. EXPERIMETAL RESULTS

A. Electrical properties

The measurements of Hall effect have shown in the concentration range from 0.01 to 0.1-0.5 mass % (Fig. 2) that: the hole type conductivity is preserved; parameters lies within the values being observed for undoped gallium selenide (conductivity $5 \cdot 10^{-3}$-$1 \cdot 10^{-2}$ $\Omega^{-1}cm^{-1}$, mobility 20-25 $cm^2V^{-1}s^{-1}$, carrier concentration 10^{15}-10^{16} cm^{-3}, at
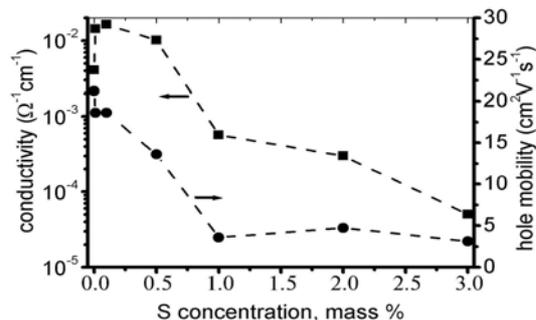
Fig .2. Concentration dependences of conductivity and hole mobility (300 K).

300 K). At sulfur concentrations 1-3 mass % the noticeable decrease of the mobility (up to 3-9 $cm^2V^{-1}s^{-1}$) and carrier concentration (up to $1\cdot10^{14}$ cm^{-3}) and, as the result, the conductivity of the material (approximately up to 10^{-5} $\Omega^{-1}cm^{-1}$) is observed (Fig. 2, 3).

The reduction of gallium selenide conductivity along the cleavage planes (001) with increasing sulfur content may be caused by the acceptor concentration decrease. It is known, that the structure of GaS compound is identical to that of gallium selenide β-polytype, and crystals GaS are characterized by the n-type conductivity that is explained by presence mainly of anion vacancies [5]. It is possible, that with growing content of more light anions the areas of β-polytype in GaSe crystals, containing greater amount of anion vacancies and smaller amount of cation vacancies, are appeared there. The results of approximation of the obtained experimental hole concentration temperature dependences according to the electroneutrality equation for a single-level model approved such an assumption, though they are not absolutely reliable as require a high precision of measurements and good conformity of the assumed model to processes in the crystal.
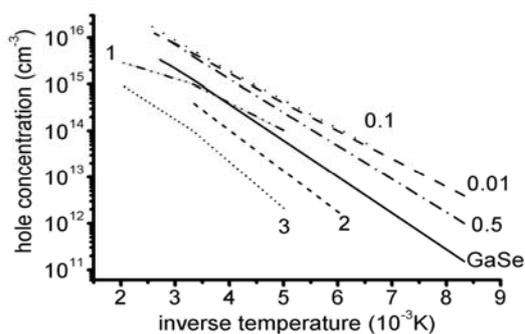
Fig. 3. Hole concentration temperature dependences

For most of the undoped samples and samples with low content of sulfur the obtained negative values of the exponent in mobility temperature dependence are higher then the well-known theoretical value -3/2 for scattering on heat lattice oscillations and lie within 1.9-2.2. It is consistent with Schmid model for scattering on homopolar optical phonons in layered crystals [6].
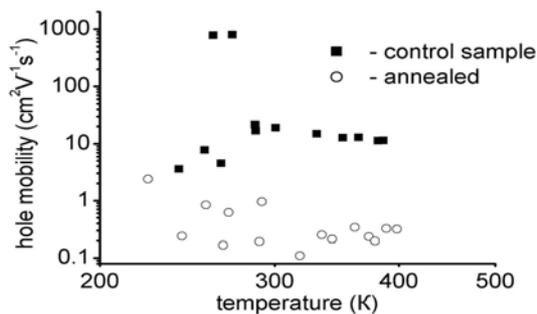
Fig. 4. Mobility temperature dependences in control and annealed samples

The annealing resulted in conductivity and hole mobility decrease (Fig. 4). The influence was like that in the case of doping from the melt. So it may be connected with interlayer sulfur. As for samples from the second experiments, they were so high-resistant that it was impossible to measure Hall emf on the background of low-frequency noise. It should be noted that measurements are often hampered by low frequency noise, typical for gallium selenide.

B. Optical properties

The calculation of band gap from spectra of edge absorption assuming indirect transitions has shown, that with increasing dopant concentration from 0.1 mass % to 3 mass % the energy gap increases linearly (Fig. 5). It is not an unexpected result taking into account the fact that sulfur is able to form continuous series of solid solutions $GaSe_{1-x}S_x$ in gallium selenide. Besides, according to our data doping with S enhances optical transparency of the material.

In the spectral region 14-25 μm along with the peaks of phonon absorption A_1=67 meV, A_2=63 meV, A_3=59 meV, A_4=54 meV being observed in undoped samples two new peaks appear B_1=78.7 meV and B_2=73.8 meV instead of peak at 77 meV (Fig. 6). The absorption coefficient values corresponding to the peaks B_1 and B_2 increase with increasing impurity concentration.

The annealing results in disappearing of phonon peaks and slight transmittance decrease (Fig. 7). The films obtained in the second experiment were nearly opaque, may be because of scattering on the rough surfaces.
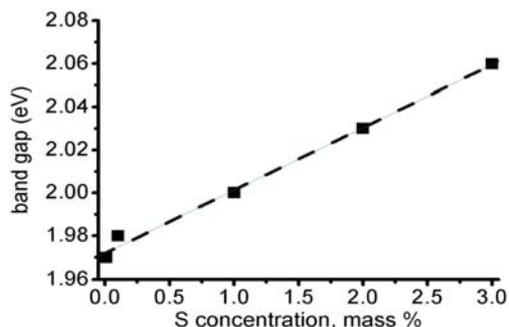
Fig. 5. Dependence of forbidden band width on concentration of S (300 K)

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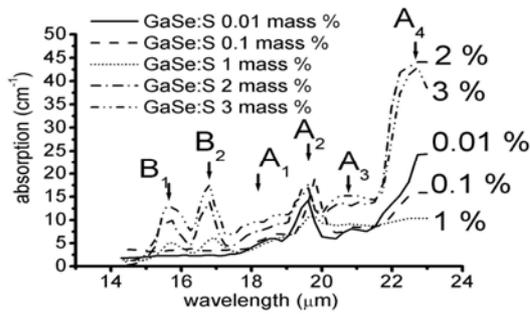
Fig. 6. Phonon absorption spectra in GaSe:S (300 K)
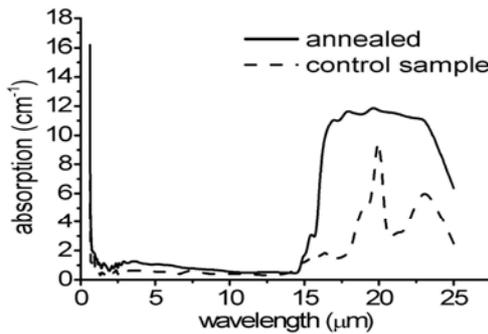
Fig. 7. Absorption spectra in control and annealed at 500 ^{0}C samples (300 K).

C. Photoelectric properties

The investigations of photocoductivity in GaSe:S crystals in spectral region 350-2000 nm have shown a complex character of the dependences on temperature and concentration (Fig. 8). Usually, it was possible to separate the investigated curves into three bands: a band of intrinsic photoconductivity 400-600 nm and two bands of impurity photoconductivity 600-900 nm and 900-1700 nm. Each of remarked regions has its own characteristic features in behavior at changing temperature and sulfur concentration.

The long-wave intrinsic photoconductivity edge shifts to a shorter wavelength region with increasing doping degree. A short -wave-border shift towards the shorter
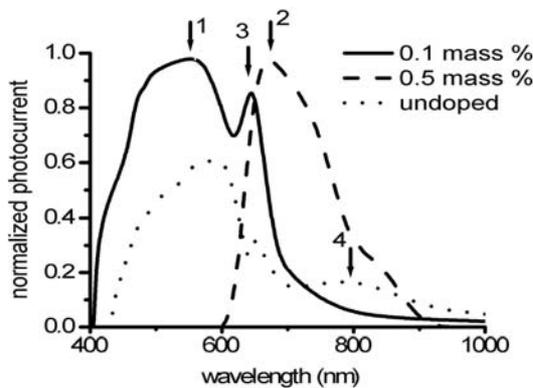
Fig. 8. Photoconductivity spectra typical for gallium selenide crystals doped with sulfur in the short-wave spectral region: 1 – intrinsic photoconductivity band; 2, 3, 4 – impurity photoconductivity peaks

wave region was observed, that may be explained by decreasing recombination center concentration on the surface of the crystals. Such a behavior of an intrinsic photoconductivity is especially noticeable at higher doping impurity concentrations 0.5-3 mass %. It is connected with solid solution GaSe$_{1-x}$S$_x$ formation and the subsequent long-wave fundamental absorption edge shift at band gap broadening.

The shift of intrinsic photoconductivity long-wave border at temperature reduction to 100 K is determined by the temperature forbidden band gap changing, which can be described by the relations E_g=2.08—4.8·10^{-4}·T – for undoped samples and E_g=2.26—5.5·10^{-4}·T – for samples with sulfur content 3 mass %.

The photoconductivity band in the region 600-900 nm reduced partly or disappeared at temperature reduction to 100 K. That allows connecting the photoconductivity peaks at 640-650 nm and 800 nm with defects, forming the acceptor levels, for example gallium vacancies or interstitial selenium atoms. Their activation energies found by the red border, equal 1.85 eV and 1.5 eV, respectively. The ionization energy of the acceptor level, found from the electrical measurements, is equal to 0.12 eV. The sum of energies obtained from the electrical and photoelectric measurements 1.97 eV is close to the GaSe forbidden band width value.

It should be pointed out that the photoconductivity band in the region 600-900 nm increases its intensity at sulfur concentration increase within 0-1 mass % (T = 300 K) and is absent on the spectral curves, corresponding to the samples with concentrations 2 and 3 mass %. That is, the extrinsic photoconductivity value correlates to impurity concentration in an interval of concentrations. That may be explained by that the extrinsic photoconductivity in the region 600-900 nm is determined by release of the electrons localized on cation vacancies and interstitial atoms as a result of recharging from donor levels being formed at sulfur introduction in the interval 0.01-1 mass %.

The broad spectral photoconductivity band 900-1700 nm being clearly observed in undoped and low-doped samples decreases its intensity with increasing sulfur content. At sulfur concentration increase to 3 mass % the photoresponse can decrease by 3 orders of magnitude from intrinsic photoconductivity value. The nature of photoconductivity in the range 900-1700 nm stays unrevealed. Perhaps, the photoconductivity in this spectrum region is connected with structural distortions in crystal matrix. Low-temperature measurements of photoconductivity at 100 K has shown an increasing photocurrent in all the samples being investigated. So the photocurrent of samples, doped with sulfur within 2 mass % and 3 mass %, changes by one order of magnitude. At the same time, the photocurrent temperature changing for the samples with sulfur concentration 0.01-1 mass % can reach several orders of magnitude. It is seen from the electrical measurements that the mobility temperature dependence can not give such a significant photocurrent changing.

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Therefore the temperature photocurrent changing is determined mainly by a charge carrier life time changing.

A new peak with maximum at λ=880 nm appeared on the spectrum of annealed sample (Fig. 9). It may be regarded as an evidence of sulfur introduction to the material and impurity levels formation. On the spectrum (Fig. 10) of a sample annealed at 800 ^{0}C the long-wave border of photoresponse is related to GaSe forbidden gap.
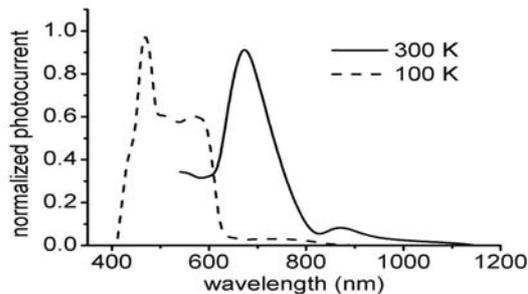
Fig. 9. Photocurrent for sample annealed at 500 ^{0}C.
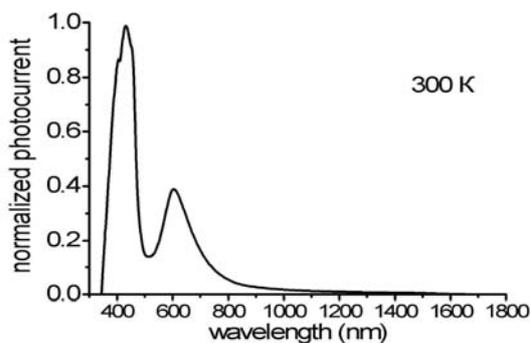
Fig. 10. Photocurrent for sample annealed at 800 ^{0}C.

The shot-wave border correspond to the energy approximately 2.6 eV. We explain it by solid solution $GaSe_xS_{1-x}$ formation.

It should be noted, that in many GaSe:S samples the residual conductivity increasing the current by an order of magnitude after switching illumination off was observed. The residual conductivity disappears after thermal quenching of the sample or reduces by 50-80 % by short-term supply of voltage exceeding nominal by 20-30 V.

D. Mechanical properties

The data on the microhardness of doped from the melt and annealed GaSe crystals are given in Table I. In general, it is possible to reckon for doped crystals that the microhardness grows with increasing sulfur concentration in gallium selenide. As for annealed samples, in the first experiment on annealing the microhardness did not increase considerably. In the second experiment it became higher by one order of magnitude but most likely it was that of the film.

So, the doping with sulfur renders an appreciable influence on the mechanical properties of gallium selenide despite of the fact that atoms of sulfur mainly introduce to the anion sublattice, replacing selenium

TABLE I
MICROHARDNESS OF DOPED AND ANNEALED SAMPLES

sample	impurity concentration in the melt (mass %)	temperature of the annealing (K)	average microhardness (kg/mm^2)
pure GaSe	0	-	7.4
doped from the melt	0.01	-	9.6
doped from the melt	0.1	-	10
doped from the melt	0.5	-	8.9
doped from the melt	1	-	10.4
doped from the melt	2	-	15.2
doped from the melt	3	-	14.5
annealed in sulfur atmosphere	-	500	7.9
annealed in sulfur atmosphere	-	800	47.7

to explain stronger binding between the layers by partial stacking of layers to the β-polytype in which anions are located closer to cations (directly above them), that results in appearance of some ionic component in bonds along with weak van der Waal forces. Also sulfur in the interlayer space can form bonds with selenium atoms of adjacent layers.

IV. DISCUSSION

Sulfur forms a continuous series of solid solutions $GaSe_{1-x}S_x$ in a wide concentration range therefore first of all changes in the properties of doped gallium selenide are connected with introduction of sulfur into selenium sublattice. This assumption is confirmed by the executed measurements of optical properties of GaSe:S crystals in the regions of fundamental absorption edge and phonon absorption. According to them, doping with sulfur leads to the increase of the forbidden band width and to change of multiphonon absorption spectrum, connected with change of elastic constants of lattice.

Homogenizing influence of sulfur impurity on the set of uncontrollable native defects of GaSe crystals may be pointed out. The reduction of nonselective absorption in the transparency range of the crystals and also an absence of selective absorption near the edge of the fundamental absorption testify to it.

The residual conductivity (RC) and the low-frequency noise observable in the experiments on research of the photoconductivity, usually are connected with the presence of inhomogeneities in crystals, forming potential barriers [7]. These effects, probably, are connected with non-uniform distribution of native defects or uncontrollable impurity on crystal volume (it is possible, with formation of clusters), since noise and RC are observed as in the undoped, so in the material doped with sulfur.

On the basis of the researches performed, it is possible to recommend sulfur as homogenizing impurity improving optical quality and mechanical properties of gallium selenide, and also expanding transparency range of this material.

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One of the main objectives of annealing was to intercalate GaSe with sulfur and compare the influence of it on the mechanical and other properties with material doped from the melt. To intercalate GaSe with S is not simple using annealing. It requires finding of optimal parameters of the process. In spite of the fact that we have obtained some characteristic changes in the properties such as the new photoconductivity peak or electrical properties changing, we plan to perform some more experiments. Also X-ray analysis of films and annealed samples is prepared.

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