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Photoelectrical properties of layered GaS single crystals and related structures

M. Caraman [a], V. Chiricenco [b], L. Leontie [c,*], I.I. Rusu [a]

[a] Bacau University, 157 Calea Marasesti, 600115 Bacau, Romania
[b] Moldova State University, 60 A Mateevici Street, Chisinau MD-2009, Republic of Moldova
[c] Faculty of Physics, "Al.I. Cuza" University, 11 Carol I Boulevard, 700506 Iasi, Romania

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Abstract

The photoconductivity of pure and Cu-doped layered gallium monosulfide (GaS) single crystals, and of Ni–GaS(Cu)–In and GaS(Cu)–ZnO structures, is investigated. The activation energies of surface states were found as 0.10 eV, 0.40 eV and 17 meV, ~400 meV for GaS and GaS(Cu), respectively. Cu acceptor levels are localized at 0.44 eV and 0.52 eV above the valence band of GaS. ZnO–GaS(Cu) heterojunctions show remarkable photosensitivity in the wavelength range of 250–700 nm.
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1. Introduction

High-resistivity semiconductors in both single crystals and thin films are largely used in the technology of microelectronic and optoelectronic devices [1]. The area of practical applications considerably enlarges if respective materials possess also electrical and optical anisotropy. These characteristics are fully illustrated by III–VI layered semiconductors, to whom gallium monosulfide (GaS) belongs. The unit hexagonal cell of GaS consists of two packages of S–Ga–Ga–S type. Besides, its symmetry axis C_6 is perpendicular to (0 0 0 1) planes.

Gallium monosulfide has proved a promising material for electronics, in chemical and electrical passivation of GaAs surface [2,3]. It is also known as a parent substance for gallium–lanthanum–sulphide (GLS) chalcogenide glasses, with important applications in the nonlinear integrated optics [4–9].

The practical utilization of GaS layers in optoelectronics is conditioned by the possibility of obtaining layers with controlled electrical resistivity, without significant modification of optical and photoelectrical properties. This goal can be achieved by doping GaS single crystals with groups II and I impurities, which in certain conditions leads to an increase in majority carrier concentration.

The study of photoconduction in GaS was reported by a rather limited number of authors [10–12] so far.

In the present work, we investigate the photoconductivity (PC) characteristics of Ni–GaS–In, Ni–GaS(Cu)–In and ZnO–GaS(Cu)–Ni structures in wide spectral and temperature ranges.

* Corresponding author. Tel.: +40 232 201165; fax: +40 232 201150/201.
E-mail address: lleontie@uaic.ro (L. Leontie).

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2. Experimental

Gallium monosulfide was synthesized from its component elements. Ga (99.999), containing 10^{-5}% Al, $<10^{-6}$% Bi, $<10^{-6}$% Cd, 10^{-5}% Mg, 6×10^{-7}% Mn, 10^{-6}% Cu, 2×10^{-6}% Ni, 2×10^{-6}% Pb, 5×10^{-5}% Zn, 3×10^{-6}% C, 5×10^{-5}% Fe, 6×10^{-5}% Si, $<10^{-4}$% Sn and S in stoichiometric proportions were used. The synthesis was performed in a vacuum furnace at temperature 1120 °C, for 6 h. The melt was mixed by a electromechanical buzzer ($\nu = 70$ Hz).

The investigated GaS single crystals were grown by Bridgman method. From bulk single crystal two types of layers have been splitted, with crystal axis (C_6) perpendicular and parallel to single crystal surface, respectively. Both undoped and Cu-doped single crystalline GaS layers with thickness in the range (12–20 μm), showing n-type electrical conductivity have been investigated. Cu doping was accomplished by thermal diffusion (at 720 K, for 30 min, under a vacuum of 2×10^{-5} Torr) of metal, which was formerly deposited onto single crystal lateral surface by thermal vacuum evaporation. As measured from atomic emission spectra, Cu concentration in investigated samples was 0.11 at.%.

The Ni and In electrodes were deposited onto freshly splitted crystal surfaces by thermal evaporation under vacuum of $\sim 5 \times 10^{-5}$ Torr. The thin films of ZnO have been grown onto (0 0 0 1) surface of GaS(Cu) single crystals by d.c. magnetron sputtering method, in an atmosphere of 90% O_2 and 10% Ar. The current density in the gas discharge was up to 10 mA cm^{-2}. The optical transmittance in temperature range of 78–293 K was measured by using a SPECORD M-40 spectrophotometer, with an energy resolution of 0.5 meV. The sample temperature was measured with a copper–constantan thermocouple. The optical transmittance (at 500 nm) of as-deposited ZnO films, with thickness between 1.50 μm and 5.00 μm, was ~73%, while their resistivity laid in the range (250–1300 Ω cm^{-2}) at room temperature.

The d.c. current–voltage (I–V) characteristics were measured in both dark and illumination conditions. The electric field was directed along the C_6 crystal axis. The ohmicity of the electrodes was verified and confirmed by linearity of I–V characteristics over a wide bias range.

A wolfram filament lamp at temperature 3270 K was used for illumination. The light from the lamp passed through a 3 mm thick blue-green filter SZS-22. The power density of the light beam was about 22 mW/cm^2. The integral illuminance (without absorptional light filter) was about 1000 lx.

The spectral dependences of short-circuit (SC) photocurrent and of photoconductivity [13] were measured by means of a spectrometric installation based on a MDR-2 type monochromator. The signal on the charging resistor was registered by a selective У2-8 amplifier, tuned on the frequency of sinusoidal light pulses, 42 Hz. A Xe-arc lamp of DKCS-250 type was used as light source with cvasi-continuous spectrum. The energy of monochromatic incident beam was measured by means of a Vth-1 type thermoelement with quartz window. The photoresponse relaxation curves were registered by means of a S8-14 memory oscilloscope.

3. Results and discussion

Fig. 1 presents the I–V characteristics for the single crystalline layers of GaS and GaS(Cu), with thickness of 9 μm and 12 μm, respectively. As one can easily see, the shape of current–voltage dependences does not depends on the polarity of applied voltage and they are linear (regions a) for electric fields up to $\sim 10^4$ V/cm. The linear aspect of the above I–V curves, as well as their form at reverse bias, indicate that in the presence of an external electric field, Ni and In form electron injecting contacts into GaS and GaS(Cu).

The linearity of $I(V)$ dependences for a wide range of voltages leads to conclusion that the concentration of injected electrons is small as compared to that of thermally generated carriers from donor shallow levels. In this case the current density is determined by the relation:

$$J = en\mu \frac{V}{d}, \tag{1}$$

where n is the concentration of thermally generated carriers, μ their mobility, V the applied voltage and d is the gap between electrodes.

At field intensities $E \geq 10^4$ V/cm, the $I(V)$ dependence of Ni–GaS–In structures becomes parabolic in both dark and illumination conditions (regions b, Fig. 1). This attests the presence of the space-charge-limited current (SCLC), due to the volumic charge localized in the vicinity of metal electrodes [14].

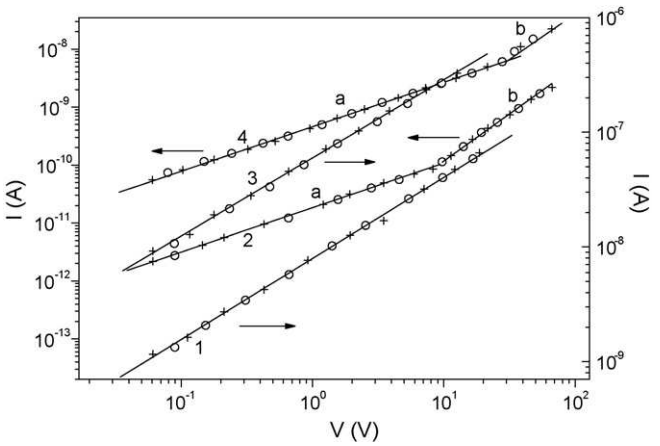


Fig. 1. Current–voltage characteristics of Ni–GaS(Cu)–In (1 and 3) and Ni–GaS–In (2 and 4) single crystalline layers, at temperature 293 K. 1 and 2: dark characteristics; 3 and 4: light characteristics. Structure bias: (○) Ni(+), In(−); (+) Ni(−), In(+).

In the SCLC domain, the current density is described by the quadratic, Mott type law [15]:

$$J \sim V^2 \exp\left[-\frac{E_t}{kT}\right], \tag{2}$$

where E_t denotes trap energy (measured relative to the bottom of conduction band, CB), k the Boltzmann's constant, V the applied voltage across the sample and T is the absolute temperature.

As experiments demonstrated, the $I(L)$ dependence for GaS(Cu) single crystals is linear for illuminance (L) values from ∼10 lx up to (1–2)× 10^3 lx, at both room temperature and 78 K.

By studying the temperature dependence of photocurrent, was demonstrated that in temperature range from 78 K up to almost room temperature, the thermal activation of photoconductivity for both GaS and GaS(Cu) samples takes place (Fig. 2).

For GaS single crystals in temperature interval 78–200 K a slow photocurrent increase is observed, and at temperatures $T \geq 200$ K this rise becomes exponential, showing two slopes. Such photocurrent increase with temperature can be due to both transformation of deep trapping levels into recombination levels with large lifetimes for nonequilibrium charge carriers, and release of charge carriers trapped on surface levels.

The temperature dependence (e.g. rise) of photocurrent obeys the law [14]:

$$n = B \exp\left(-\frac{E_t}{2kT}\right), \tag{3}$$

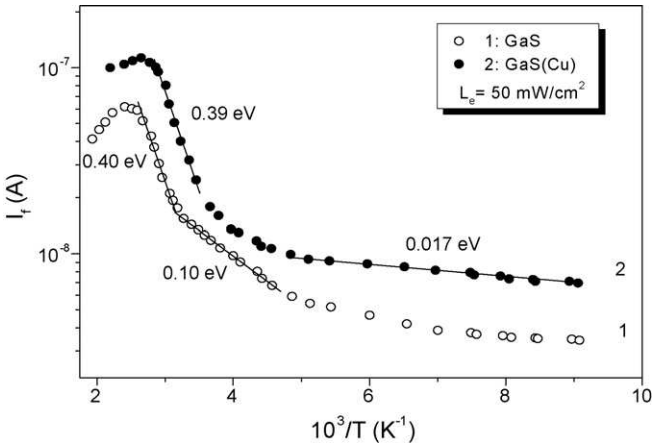


Fig. 2. Photocurrent versus reciprocal temperature for GaS (1) and GaS(Cu) (2) crystals. Exciting level: 50 mW/cm^2.

where n denotes the concentration of photogenerated charge carriers, B is a parameter including concentration of surface levels, E_t the mean energy of trapping level and k is the Boltzmann's constant.

The registered two slopes in dependence $\log I_f = f(10^3/T)$ from Fig. 2 attests that thermal activation of photocurrent in undoped GaS single crystals is conditioned by two levels with thermal activation energies of 0.10 eV and 0.40 eV, respectively.

An exponential photocurrent increase in temperature range of 110–350 K was also evidenced in the case of Cu-doped GaS crystals (Fig. 2). For temperatures lying between 110 K and 200 K, the photocurrent activation is determined by the ionization of low energy surface states ($E_t \approx 17$ meV), while at temperatures $T > 250$ K, by the level with an activation energy of about 0.40 eV (0.39 eV, more precisely).

The deep surface levels ($E_t \approx 400$ meV) in both undoped and Cu-doped GaS crystals are of the same nature and are probably determined by structural defects located at interface between S–Ga–Ga–S packages, since, as was stated in [16], the impurity ionized atoms are localized just on the surface of respective stratified packs.

For a wide temperature range, photocurrent activation in Cu-doped GaS crystals is determined by ionization of low energy surface centres ($E_t \approx 17$ meV); these centres do not become manifest in undoped GaS and therefore one can assume that they are created by Cu impurity atoms.

The diminution of photosensitivity in case of GaS and GaS(Cu) samples at temperatures over 400 K (Fig. 2) can be determined by complete ionization of trapping levels, as well by exponential increase of majority carrier concentration as a result of thermal electron transitions from valence band (VB) into the conduction band.

The spectral distribution of photoconductivity in the case of Cu-doped GaS crystals, in the photon energy range $h\nu \geq E_g^i$ (E_g^i is the width of forbidden band at respective temperature), actually coincides to photoconductivity spectrum of undoped crystals [17]. Comparison between PC spectra of undoped [17] and Cu-doped GaS (Fig. 3) shows that presence of Cu impurities can be attested by two particularities located at 2.06 eV and 1.98 eV, in the domain of absorption impurity band. At temperature 78 K the band from the impurity photoconductivity spectrum is located in the energy domain 2.20–2.60 eV and also is manifest in the absorption spectrum [18]. The concordance between absorption and photoconductivity spectra allows us to assume that Cu impurity atoms form localized states in the vicinity of valence band limit of GaS crystals from which, as a result of indirect optical transitions, nonequilibrium charge carriers are generated into the conduction band. Since at room temperature (Fig. 3, curve 2) the energy corresponding to most probable transitions from impurity states is equal to 2.06 eV and 1.98 eV and taking into account that the indirect gap of GaS is equal to 2.5 eV [10] at 293 K, we can determine the energy of localized Cu states as 0.44 eV and 0.52 eV, with respect to the top of the valence band.

Fig. 4 shows the spectral curves of short-circuit current (I_{SC}) for untreated and thermally treated GaS(Cu)–ZnO heterojunctions. Respective structures were illuminated through ZnO layer, which is optically transparent in a wide wavelength range. As one can see, in the case of untreated heterojunctions (curve 1), the spectrum shows an outlined

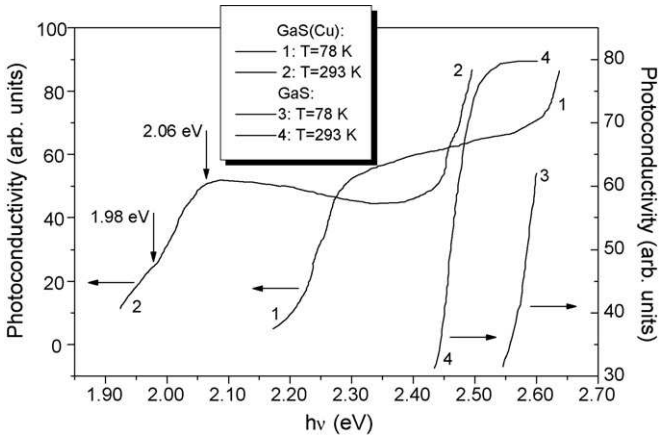


Fig. 3. Spectral distribution of photoconductivity for Cu-doped and undoped GaS crystals in the domain of fundamental absorption threshold. 1 and 3: $T = 78$ K; 2 and 4: $T = 293$ K.

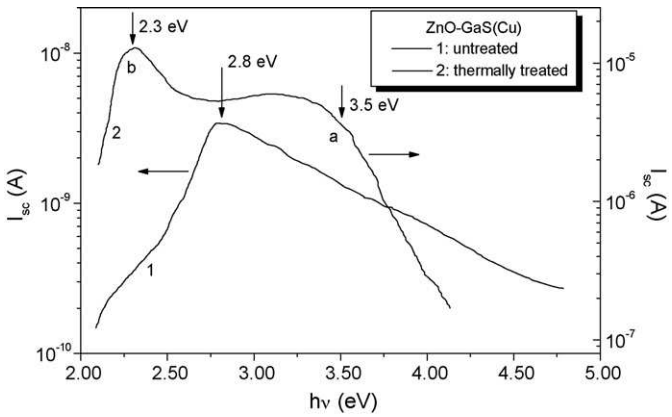


Fig. 4. Spectral distribution of short-circuit current in ZnO–GaS(Cu) heterojunctions. 1: untreated; 2: heat-treated in air, 30 min at $T = 650$ K.

maximum, with an energy position (photon energy) $h\nu = 2.8$ eV, which surpasses by 0.3 eV the indirect gap. Besides, this spectrum evidences a continuous photoresponse in the range $h\nu < E_g^i$, which is determined, as results from the comparison with photoconductivity spectra of GaS(Cu) crystals (Fig. 3), by indirect electron transitions via Cu localized states.

The maximum at 2.8 eV (Fig. 4, curve 1) attests that the generation of nonequilibrium charge carriers takes place in a thin GaS layer by the vicinity of ZnO–GaS junction. The rapid decrease of I_{SC} at increasing photon energy indicates a large density of recombination centres localized in respective layer by junction interface.

The heat treatment for 30 min at ∼650 K in air, applied to GaS(Cu)–ZnO heterojunctions, results in a rise in the photocurrent through the junction of 2–3 orders of magnitude and, as one can see from Fig. 4 (curve 2), the shape of $I_{SC}(h\nu)$ dependence changes essentially. Thus, the plateau by 2.15–2.45 eV, existing in the case of untreated junctions (curve 1), turns up into a predominant band with maximum (b) at 2.3 eV.

In the UV range a wide maximum (a) located at ∼3.5 eV is evidenced, followed by an I_{SC} fall as photon energy increases. The rapid drop of photocurrent for exciting (photon) energies $h\nu > 3.5$ eV can be mainly explained by taking into account the small value of mean free path of nonequilibrium charge carriers from polycrystalline ZnO layer, as well as the large recombination rate of photogenerated electrons in single crystalline GaS(Cu) layer.

Fig. 5 presents *I–V* characteristics of ZnO–GaS(Cu)–Ni structures at room temperature in dark conditions (curve 1), as well as under illumination (curve 2) in the range (330–620 nm) using a halogen lamp with a wide band filter of SZS-21 type. The power density of incident beam was ∼50 mW/cm^2. The illumination was performed through polycrystalline ZnO layer, whose transmittance at $\lambda > 400$ nm was ∼80%. The shape of these characteristics is quite

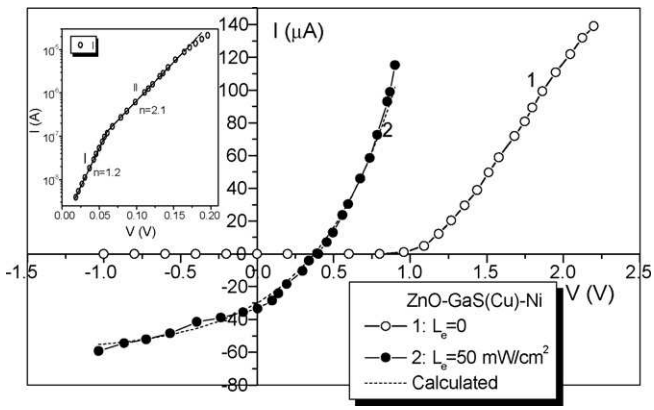


Fig. 5. Current–voltage characteristics of ZnO–GaS(Cu)–Ni heterostructures. Irradiance: (1) $L_e = 0$; (2) $L_e = 50$ mW/cm^2. Dotted curve-calculated characteristics, according to Eq. (4); fitting parameters: $I_f = 30.0$ μA, $I_s = 29.5$ μA and $A = 21$. *Inset*: dark current–voltage characteristics, forward bias, $V < 0.20$ V.

similar to that of typical p–n junctions. The current–voltage dependence of illuminated heterojunction is described by [19]:

$$I = I_s\left[\exp\left(\frac{eV}{AkT}\right) - 1\right] - I_f, \tag{4}$$

where I_s denotes the current of minority charge carriers through heterojunction, I_f the photocurrent and A is the quality factor of junction. Values of three indicated parameters have been provided by the best-fit curve also indicated (dotted curve) in Fig. 5: $I_f = 30.0$ μA, $I_s = 29.5$ μA and $A = 21$.

From the last figure it can be observed that dark and light I–V characteristics differ own to the value of coefficient A, which is lower in the case of darkness. A more pronounced current increase at forward polarity can be due to (i) modification of the energy spectrum of localized (in the forbidden band of GaS(Cu) crystals) states, which is directly related to the concentration variation of recombination centres as a result of light absorption, and (ii) photoinjection, since the majority carrier concentration in ZnO and GaS(Cu) under illumination is larger than that of equilibrium charge carriers produced by junction. When illuminating with a calibrated beam of 50 mW/cm^2, the photoelectromotive force reaches ∼0.4 V, and I_{SC} is equal to 38 μA.

The inset of Fig. 5 shows the dark I–V characteristics in forward bias, for voltage range $V < 0.20$ V. In region I, for $V < 0.06$ V, diode quality factor is $n \approx 1.2$, indicating a predominant diffusion of minority charge carriers through the heterojunction. At voltages $V > 0.08$ V (region II, $n \approx 2.1$), moreover recombination of minority carriers within junction region becomes important, probably owing to structure defects in the surface layer of GaS.

In the case of reversed polarity, the current through junction is determined by two competitive phenomena, charge leakage through surface states and tunneling through junction.

4. Conclusions

For electric fields of intensity $E \leq 10^4$ V/cm the current–voltage characteristics in both GaS and GaS(Cu) single crystals are linear. At intensities $E > 10^4$ V/cm, $I(V)$ dependences turn out into quadratic and have been interpreted on the basis of Mott model.

By analysing the temperature dependence of integral photocurrent, the activation energies of surface states have been determined as 17 meV and about 400 meV for GaS(Cu), and 0.10 eV and 0.40 eV for undoped GaS crystals.

The spectral characteristics of photocurrent for GaS(Cu) single crystals in the energy range $h\nu < E_g^i$ is determined by two acceptor levels due to Cu impurity atoms, localized within energy gap of GaS at 0.44 eV and 0.52 eV above the valence band.

ZnO–GaS(Cu) heterojonctions show remarkable sensitivity in the energy range of 2–4 eV. Their annealing at ∼400 K, in air, leads to an increase in sensitivity by 2–3 orders of magnitude by comparison to untreated junctions.

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