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Charge transport in bismuth orthogermanate crystals

T.M. Bochkova, S.N. Plyaka
Dnepropetrovsk National University, 49050, Dnepropetrovsk, Ukraine
Phone:+38 (056) 776-83-18; e-mail: tbochkova@meta.ua

Abstract. Current-voltage relations in bismuth orthogermanate crystals with Ag, Pt, In-Ga electrodes have been measured in the modes of double and unipolar injection of charge carriers. It has been shown that $Bi_4Ge_3O_{12}$ is relaxation type semiconductor. The appearance of the regions with negative differential resistance or sublinear rise of the current in $I-V$ characteristics is connected with the injection of the minority charge carriers and recombination processes in the space charge layer.

Keywords: bismuth orthogermanate, current-voltage characteristics, relaxation type semiconductors.

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1. Introduction

Bismuth orthogermanate ($Bi_4Ge_3O_{12}$, BGO) single crystals are used in technology as an effective scintillation material for registration of high-energy ionizing radiation in detector systems. These crystals have considerable advantages over analogs. They are transparent, colorless, nonhygroscopic. The high γ-quantum detection efficiency, relatively short decay time and small afterglow provide a wide application of $Bi_4Ge_3O_{12}$ in high-energy physics and positron computer tomography [1, 2]. The problem of the improvement of the resistance to radiation damage for scintillation crystals is very actual and connected with the production of high quality crystals. They have not to contain impurities and structural defects that can be transformed into color centers or create spatial layers with changed properties under the influence of external factors, namely: irradiation, electric fields, temperature changes. The scientists try to solve this problem, as a rule, by technological means using chemical and physical purification of raw materials, the modification of available crystal growth methods and development of the new ones [3, 4]. Investigation of the effect of impurities and radiation defects on the scintillation characteristics of $Bi_4Ge_3O_{12}$ crystals is another main line [4-7]. But study of their electrical properties is also sufficiently informative relative to the nature of the local centers, their energy and spatial distribution, charge transport mechanisms and recombination processes.

This work is continuation of the dc and ac conductivity investigations in bismuth orthogermanate crystals [8-10], in which it has been shown that high-resistance $Bi_4Ge_3O_{12}$ crystals should be considered as heavily compensated semiconductors. Charge carrier transport is realized by phonon-assisted quantum mechanical tunneling of the carriers from one localized state to another. There is gradual transition from pair jumps near the Fermi level to multiple hopping that shifts to higher temperatures with the frequency increase. Existence of this transition indicates that distribution of localized states in the forbidden energy gap is quasi-continuous. It has been also found that in the direct current both electrons and holes are mobile, and there are distinctions in values of donor and acceptor concentrations for electrons and holes at temperatures above 200 ºC. It allows to suggest the presence of two channels of charge percolation parted by recombination barriers.

This paper presents the results of further investigation of the charge carrier transport in high quality $Bi_4Ge_3O_{12}$ crystals by means of measurements of the current-voltage characteristics under the conditions of unipolar and double injection of charge carriers.

2. Experiment

Bismuth orthogermanate single crystals were grown by Czochralski method from platinum crucibles in air. The starting materials were “OSCh”-grade Bi_2O_3 and GeO_2 oxides. The double recrystallization technique was used. The obtained single crystals were colorless, transparent and contained uncontrolled impurities in amounts up to 10^{-4} mass% (according to data of the spectral analysis).

The applied electrodes were of Pt (evaporation in vacuum), Ag (cathode sputtering) and In-Ga (liquid eutectic). The thickness of the samples used was about 0.5 mm. The measurements of $I-V$ characteristics were performed in the electric field 10^2 to 10^4 V/cm and within the temperature range 25 to 400 °C according to the standard technique described in [10].

3. Results and discussion

$Bi_4Ge_3O_{12}$ crystals belongs to wide band-gap semiconductors. The dark dc conductivity is about 10^{-14} $Ohm^{-1}\cdot cm^{-1}$ at room temperature and increases with heating. The width of the forbidden band obtained from optical measurements exceeds 4.5 eV [1]. $I-V$ characteristics measured in a wide temperature range in the samples of bismuth orthogermanate with Ag, Pt, In-Ga contacts differ in details, quite possible, due to different levels of the charge carrier injection, but their common features allow to consider them in the complex. The main feature is the existence on the $I-V$ characteristics observed not only the regions with linear ($I \sim U^m$, $m = 1$) and superlinear ($I \sim U^m$, $m > 1$) rise of the current but also the regions with sublinear ($I \sim U^m$, $m = 1/2$ or $0 < m < 1$) dependence of the current and regions with negative differential resistance (NDR) of *n*-type. $I-V$ characteristics of $Bi_4Ge_3O_{12}$ sample with Ag electrodes are shown in Fig. 1.

Two temperature ranges are available on presented curves. In the former, up to the temperature ~ 150 ºC, the ohmic, quadratic regions and regions with the sharp rise of the current are observed. All the regions are shifted to lower electric fields with heating. The presence of the quadratic region testifies to the ohmic character of the contacts and shows that the concentration of injected carriers becomes of the same order of magnitude with the concentration of the equilibrium carriers. Such behavior of $I-V$ characteristics is typical for the case of the space charge limited currents (SCLC).

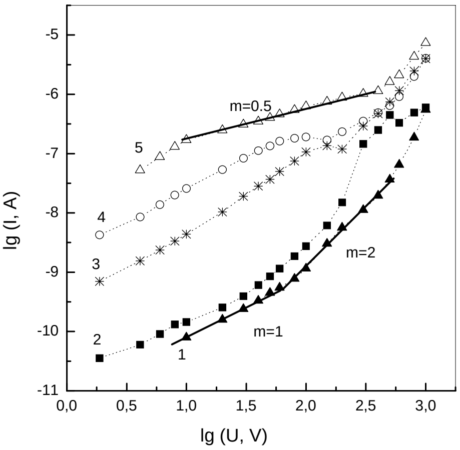

Fig. 1. Current-voltage characteristics of $Bi_4Ge_3O_{12}$ crystals with Ag electrodes: 1 – 100 ºC, 2 – 150 ºC, 3 – 225 ºC, 4 – 250 ºC, 5–300 ºC.

In the second temperature range, at 150-250 ºC, one can observe the regions with NDR. And at the temperatures above 250 ºC, we can see the extensive sublinear regions ($m = 1/2$), which are again replaced by the ohmic and superlinear dependences.

Bismuth orthogermanate is a high-resistance semiconductor with hopping conductivity, therefore it can belong to semiconductors of the relaxation type [11]. It means that the minority charge carrier lifetime τ_0 that defines the diffusion length of the minority carriers is less than the dielectric relaxation time τ_d (maxwellian time). For classic semiconductors (such as Si, Ge), the opposite relation $\tau_0 > \tau_d$ is valid. But for $Bi_4Ge_3O_{12}$, the conductivity of which varies from 10^{-13} up to 10^{-10} $Ohm^{-1}\cdot cm^{-1}$ in the studied temperature range, the dielectric relaxation time that can be estimated as $\tau_d \sim \varepsilon\varepsilon_0/\sigma$ is equal $\sim 10^1 – 10^{-2}$ s, respectively. It can considerably exceed the lifetime of minority carriers.

If the injection of the minority carriers of charge takes place, the restoration of the system into the equilibrium state is realized by means of the relaxation and recombination processes. According to [11], in relaxation type semiconductors quasi-Fermi levels that describe the nonequilibrium electron and hole concentrations coincide on the expiry of τ_0 due to recombination of charge carriers long before restoration of the system to equilibrium by maxwellian relaxation.

So, recombination in the space charge region (SCR) may be a cause of NDR appearance and sublinear regions in $I-V$ characteristics. The theory of charge carrier recombination in SCR of a *p-n* junction for the first time was considered by Sah, Noyce and Shockly in [12] where a model of single energy level uniformly distributed Shockly-Read-Hall recombination centers was used for developing the specific dependence of the recombination current density J on the voltage U

$$J \sim \exp(eU / 2kT). \qquad (1)$$

The modern theory of the recombination processes in SCR of the semiconductor structures, in which the electrons and holes are spatially distributed in the localized centers and have to tunnel through potential barriers for the recombination, is more complex. In particular, it is established that the recombination rate reaches the saturation under the assumption of low probability of tunneling and only with the rise of this probability the classic dependence of the recombination (1) is observed [13].

In bismuth orthogermanate, electrons are dominant charge carriers at room temperature. It was determined as a result of investigation of the thermoelectric power [14] and exoelectron emission [15]. Consider $I-V$ characteristics of $Bi_4Ge_3O_{12}$ crystals measured under conditions of asymmetrical contacts, when one of them is metal and another is made with the thin layer of dried orthophosphoric acid between the metal and the crystal. The use of orthophosphoric acid, that is ionic conductor, allows to eliminate the double injection. In Figs 2 and 3, the families of $I-V$ characteristics measured under conditions of unipolar injection of electrons (the metal electrode is cathode) and holes (the metal electrode is anode) are presented. The platinum is used as the metal for electrodes in experimental results shown in these figures.

In both cases at the temperatures above 100 ºC, one can see the linear ($I \sim U^2$) and the quadratic regions ($I \sim U^2$) that is the criterion of the injected space charge appearance and testifies to the ohmic character of Pt contact. $I-V$ characteristics allows, in accordance with SCLC formulas, to calculate values of the specific conductivity, effective drift mobility, concentration of the equilibrium charge carriers and dielectric relaxation time τ_d. The calculated data to a considerable extent confirm the experimental results obtained earlier [8-10]. In both cases, the values of the concentrations and mobilities of charge carriers are rather close and very small. The conductivity and mobility have an activation character. All these features are attributed to the hopping conductivity. In Fig. 4, the temperature dependences of $Bi_4Ge_3O_{12}$ conductivity calculated from $I-V$ curves are displayed. These are conductivities σ_h, σ_l, computed respectively from the high-field (appearing above 200 ºC) and low-field ohmic regions of $I-V$ characteristics inherent to $Bi_4Ge_3O_{12}$ crystals with symmetrical Pt electrodes as well as conductivities σ_p, σ_n computed from $I-V$ characteristics of crystals with asymmetrical electrodes.

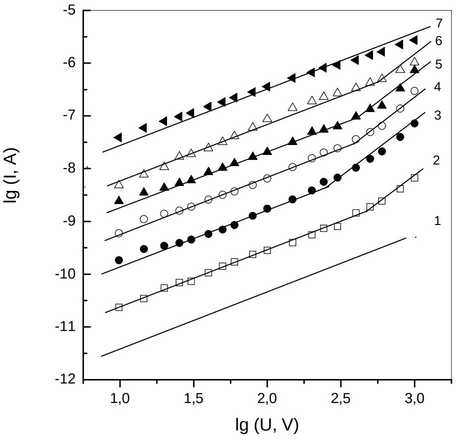

Fig. 2. Current-voltage characteristics of $Bi_4Ge_3O_{12}$ crystals with injecting Pt electrode that were measured in the mode of unipolar injection of electrons: 1–75ºC, 2–125ºC, 3–175ºC, 4–200ºC, 5–225ºC, 6–250ºC, 7–300ºC.

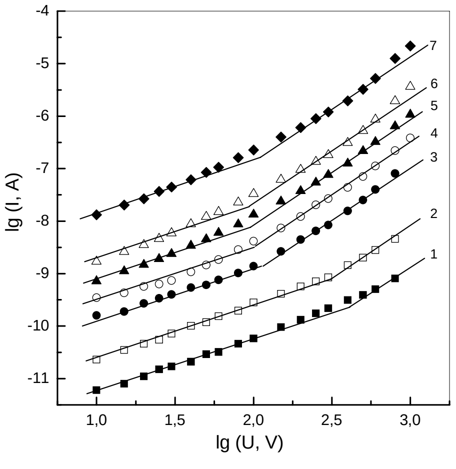

Fig. 3. Current-voltage characteristics of $Bi_4Ge_3O_{12}$ crystals with injecting Pt electrode that were measured in the mode of unipolar injection of holes: 1 – 100 ºC, 2 – 125 ºC, 3 – 175 ºC, 4 – 200ºC, 5 – 225 ºC, 6 – 250 ºC, 7 – 300 ºC.

From this figure, one can see that σ_l, σ_p, σ_n identically increase with the temperature up to ~150-175 ºC (activation energy $E_\sigma \sim 0.5$ eV). Above this temperature, the value of the activation energy is changed: for σ_l and σ_n – $E_\sigma \sim 0.95$ eV; for σ_h and σ_p – $E_\sigma \sim 0.70$ eV. The temperature dependences of the mobility give the activation energy 0.85 eV for holes and 0.70 eV for electrons (The insert in Fig. 4). Two regions are also observed in the temperature dependences of equilibrium concentrations of the charge carriers (Fig. 5). These concentrations decrease exponentially up to 175 ºC ($E_n \approx -0.2$ eV, $E_p \approx -0.3$ eV) and then, in the case of the hole injection, the concentration remains at the constant level, in the case of electron injection, the concentration increases with the temperature ($E_n \approx 0.25$ eV). The values of dielectric relaxation time τ_d calculated from $I-V$ curves are equal 67 s for electrons; 19.1 s for holes at 100 ºC and $2.4 \cdot 10^{-2}$ s for electrons; $6.6 \cdot 10^{-2}$ s for holes at 250 ºC. The calculation of the activation energy for the conductivity, mobility and concentration of the equilibrium charge carriers in both cases satisfies classic equations

$$\sigma_n = en\mu_n, \quad \sigma_p = ep\mu_p \qquad (2)$$

in all the temperature ranges.

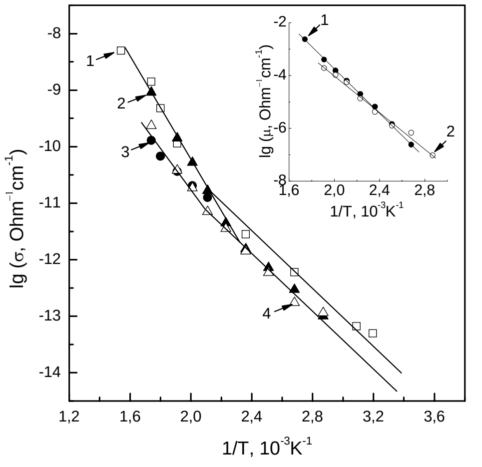

Fig. 4. Temperature dependences of the conductivity and mobility of charge carriers in $Bi_4Ge_3O_{12}$ crystals: 1 – σ_l; 2 – σ_n ; 3 – σ_h ; 4 – σ_p. In the insert: 1 – holes; 2 – electrons.

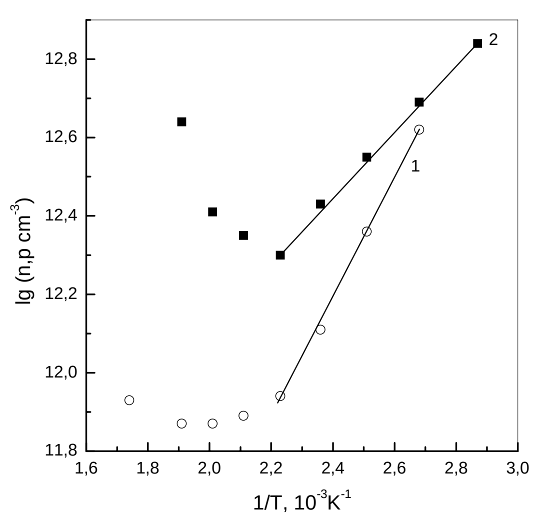

Fig. 5. Temperature dependences of the charge carrier concentration in $Bi_4Ge_3O_{12}$ crystals: 1 – holes; 2 – electrons.

As it was aforesaid, the investigated nominally pure $Bi_4Ge_3O_{12}$ crystals are heavily compensated semiconductors. It means that the concentrations of donors and acceptors are close, and charge carrier concentration is small. The carriers are in the most deep energy states created by pairs of nearest impurity centers. Moreover, the energy bands of the semiconductor are modulated by large scale potential caused by fluctuations of the charged impurity concentration. Screening these impurities by charge carriers is weak, because the carriers get into the deep potential wells and Fermi level fall additionally by an order of magnitude as to the modulation amplitude of the potential η that increases with decrease of the density of charge carriers [16]

$$\eta = \frac{e^2 \cdot N_t^{2/3}}{\varepsilon\varepsilon_0 \cdot n_c^{1/3}} \, . \qquad (3)$$

Here, N_t is the total concentration of donors and acceptors, and n_c is the average density of charge carriers.

In $Bi_4Ge_3O_{12}$, both electrons and holes are mobile. The activation energy of charge carrier jumps is counted from the Fermi level to the percolation one. It is obvious that for comparatively low temperatures $Bi_4Ge_3O_{12}$ is semiconductor of *n*-type, the Fermi level is close to the maximum of density of states corresponding to isolated donor position. With the increase of temperature, the equilibrium concentration of the mobile charge carriers decreases due to recombination, and the hole component of current, that has its own percolation level, is considerable. So, the activation energies of the conduction for electrons and holes are different at high temperatures.

The obtained data enabled us to interpret the current-voltage characteristics of bismuth orthogermanate with two symmetrical electrodes as follows. In the first temperature range (up to 150 ºC), injection of the majority charge carriers (electrons) is realized, and SCLC phenomenon is observed. In the second range (above 150 ºC), injection of the minority charge carriers (holes) is noticeable and becomes the dominant mechanism with the further increase of the temperature. According to [11], after injection of Δp holes into bismuth orthogermanate, restoration of the equilibrium law of mass action takes place during the time of τ_0, and as a result – the reduction of the local concentration of the majority carriers (electrons) is observed. In the moment of this process finishing, the product pn satisfies the equation

$$pn = (n_0 + \Delta n)(p_0 + \Delta p) = n_i^2 = p_0 n_0, \qquad (4)$$

where n_0, p_0, n, p are equilibrium and nonequilibrium concentrations of electrons and holes, respectively; n_i is the concentration of electrons or holes in an intrinsic specimen; Δn is the concentration of electrons which are pulled into the space charge region. The value of Δn from (4) is

$$\Delta n = -n_0 \Delta p \,/\, (p_0 + \Delta p). \qquad (5)$$

If the hole injection level is so high that $\Delta p > p_0$, we shall obtain $\Delta n \to -n_0$. It means that mobile electrons in the space charge region can quite vanish.

Reduction of the local concentration of mobile electrons leads to the increase of the resistance of crystal. The layer depleted with electrons is positioned in close proximity to the anode which injects the holes. It is expanded into the bulk of semiconductor following the narrow recombination front. The sublinear dependence of the current on voltage ($I \sim U^{1/2}$) is observed in $I - V$ curves. The voltage rise increases the space charge in the depleted layer leading in certain cases to the creation of NDR region due to the negative gradient in the majority carrier concentration.

The temperature increase leads to the gradual decrease of the voltage at which the depleted with electrons region occupies the interelectrode space entirely, and the crystal sample becomes spatially homogeneous again. The sign of the majority carriers of charge is changed. Now these are holes. This process corresponds to the second ohmic (high-field) region in $I - V$ characteristics. With further temperature increase one can observe the high-field regions of quadratic and more steep rise of the current, i.e. SCLC phenomenon but only for the holes. Thus, the existence of regions with NDR and sublinear rise of the current in $I - V$ characteristics of bismuth orthogermanate crystals may be caused by the so-called process “recombination space-charge injection” [17].

Among other reasons that could result in these $I - V$ characteristics, there is transformation of the current controlled by the bulk properties of the sample into the current controlled by the electrode processes near the blocking contacts. In these cases, the ideal $I-V$ characteristic $I \sim U^{1/2}$ is observed.

However, the existence of the quadratic dependencies in the same $I-V$ curves testifies about charge carrier injection from the electrodes into the sample, and therefore, the contacts are ohmic. Secondly, from the obtained $I-V$ curves with sublinear regions one can see that calculations of the resistance for high-field linear regions give the considerably higher values then for the low-field ones (Fig. 1). Thirdly, for the justification of the stated affirmations let us again come back to Fig. 4. An observed good coincidence of the values and activation energies for σ_h and σ_p, σ_n and σ_1 shows that the proposed model is valid.

Conclusions

Thus, bismuth orthogermanate is the semiconductor of relaxation type, the conduction processes in which are very different from the ones taking place in the classic inorganic semiconductors (Si, Ge). $Bi_4Ge_3O_{12}$ has such electrical properties as high resistance, low mobility of charge carriers, its activation rise with temperature, very low density of mobile charge carriers, large time of dielectric relaxation, hopping mechanism of the conduction, power character of the increase of the conductivity in alternative field, sublinear $I-V$ dependences. These features are characteristic rather for high-resistance organic semiconductor crystals (such as anthracene, naphthalene) or amorphous semiconductors (such as chalcogenide glasses). The existence of double injection into the crystal at the application of usual Ag, Pt, In-Ga contacts gives an opportunity to study waves of the space charges of different type (both enriched and depleted with the charge carriers), to investigate the recombination mechanisms and control the processes of heterovalent impurity ion charge exchange in this practically important material.

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