Rev. Adv. Mater. Technol., 2022, vol. 4, no. 2, pp. 77–88 DOI: 10.17586/2687-0568-2022-4-2-77-88

Current Filamentation and Switching Effect in Chalcogenide Glassy Semiconductors: A Review

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Article history

Received June 09, 2022
Received in revised form
June 21, 2022
Accepted June 26, 2022
Available online June 30, 2022

Abstract

A review on current filamentation and switching effect in chalcogenide glassy semiconductors (CGSs), which are promising materials for the development of phase change memory devices, is presented. First, a history of the research on CGSs and their properties is considered. Next, formation of a current filament in CGSs is discussed and the scale of heat release in the material as well as the geometric shape of the filament is analyzed. Finally, various hypotheses developed for the explanation of the switching effect in CGSs are reviewed. It is shown that the most relevant model of the switching effect in CGS is the model of multi-phonon tunneling ionization of the so-called 'negative-U centers'. This model is based on the assumption that an avalanche-like increase in current at a certain point in time is associated with mass tunneling of electrons located on atoms, occuring due to thermal vibrations of atoms.

Keywords: Chalcogenide glassy semiconductors; Switching effect; Memory effect; Current filament

1. INTRODUCTION

Currently, we live in an era of the development of new data storage devices, which will be more capacious than the means for data storage of the previous generation. These new materials include compounds based on chalcogenide glassy semiconductors (CGSs). These are semiconducting glasses incorporating elements of the VI group of the periodic table, such as sulfur, selenium, and tellurium. These materials possess amorphous structure and are covalently bonded materials, which experience externally driven amorphous-to-crystalline phase changes. Recording information in these materials is carried out by exploiting the so-called 'phase change' memory (PCM) effect. The PCM system undergoes a phase transition from an amorphous state to a crystalline state and vice versa (switching effect), and is able to remain stable in the new state (memory effect).

Switching is achieved in CGSs by heating them with the use of an electrical current or a laser beam. In order to transfer the system from an amorphous state to a crystalline state and vice versa, it has to be heated and then cooled.

With the switching effect, a region of existence of a negative differential conductivity is observed. This shows in current–voltage characteristics as an '*S*-shaped' part; for such a system the uniform distribution of current is unstable, and a current filamentation (analogous to 'current crowding') occurs. The two phenomena, switching and filamentation, can be linked to each other, especially in relatively 'large' CGS samples. This paper briefly reviews the works on current filamentation in CGSs. Section 2 introduces the basics of CGSs. Section 3 provides information on current filamentation in various media, and on the influence of various external factors on the properties of current filaments. This information helps to look at the phenomenon of filamentation more broadly. Section 4 discusses the switching effect in CGSs and considers one the latest theories of the occurrence of this phenomenon, which relates to the multi-phonon tunneling ionization of the negative-U centers.

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2. CHALCOGENIDE GLASSY SEMICONDUCTORS AND THEIR ELECTRICAL PROPERTIES

Before we discuss the appearance of current filaments, it is first necessary to provide general information on the CGSs. Since their discovery, these materials have been of genuine interest not only for researchers, but for the electronic industry as well. The switching effect observed in these materials means that a CGS-based device can change its resistance abruptly by several orders of magnitude, and this process can be controlled and repeated many times. The switching effect (Fig. 1a) was first demonstrated in 1963 by Kolomiets and Lebedev (USSR) in the chalcogenide compound Tl-As-Se(Te) [1]. In 1968 Ovshinsky (USA) et al. demonstrated the reversibility (more than 10^4 cycles) of this effect in STAG ($Si_{12}Te_{48}As_{30}Ge_{10}$) compounds [2].

According to Fig. 1a, the material will switch from a high-resistance state to a low-resistance state in a short switching time ($t_{sw} < 1$ ns) when a voltage above the threshold voltage V_{th} is applied to the sample. The system can remain in the electronic state into which it has passed, and it is this phenomenon that is called the memory effect (Fig. 1b). The memory effect is accompanied by a first-order phase transition from a crystalline state to an amorphous state. The transition takes some time and it is generally believed that it occurs while the voltage is applied to the sample. In the first approximation, it is considered that this time is proportional to t_{sw} and does not exceed 100 ns [3], though it does depend on the chemical composition of CGS and on the external conditions. The ability of CGSs to change their phase state under the action of an electric field and to return to the previous state led engineers to the idea of using these materials for data storage. In 1971 a light-driven memory cell based on Te-Ge-Sb-S was developed [4]. In 2011 Samsung developed a 8 Gb memory cell implemented in a 58-nm manufacturing process technology [5]. Around 2012 the development of 3D XPoint PCM-based data storage technology was started by Intel and Micron (formerly Numonyx). 3D XPoint architecture differed from previous offerings of PCM, and used chalcogenide materials for both selector and storage parts of the memory cell that were faster and more stable than traditional PCM materials like GeSbTe (GST). Until recently 3D XPoint-based solid-state drives (SSDs) and memory components with the so-called Intel Optane technology were widely available commercially, yet in July 2022 Intel announced the winding down of the Optane division, which effectively discontinued the development of 3D XPoint. Thus, the mass introduction of CGS-based PCM devices into electronics and the displacement of data storage units based on standard memory remains a matter of the near future.

The parameters of a memory cell depend on the cell size; typically, the resistance in the amorphous state is 1 MΩ (state "0"), and resistance in the crystalline state is 1 kΩ (state "1"). The voltage applied to the cell during reading does not exceed hundreds of millivolts, and the reading time is several tens of nanoseconds.

In 1987 Yamada et al. proposed using the Ge-Sb-Te compound for data recording and storage, which stimulated commercial interest in $Ge_2Sb_2Te_5$ [6]. Of all the CGSs, this compound is now one of the most frequently studied. In the 1970s Gelmont and Tsendin studied the non-linear heat equation for a hypothetical thin film (which can be considered as that with thermodynamic characteristics of $Ge_2Sb_2Te_5$) and found that when a constant voltage was applied, a current filament was forming, which was a strong non-uniform dependence of the current density on the coordinate [7]. The equation that Gelmont and Tsendin derived described the distribution of heat in a disk-shaped semiconductor, after which the current contained in the filament I_c was determined:

$$I_c = \frac{8\pi\kappa T_m^2}{F\Delta E}, \tag{1}$$

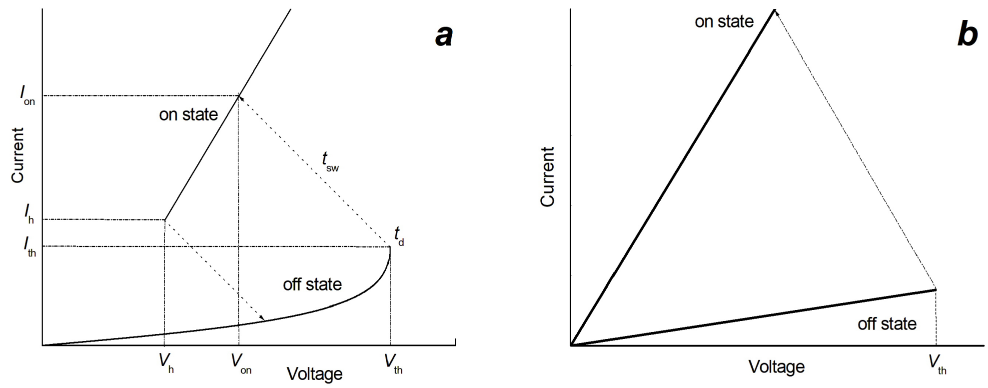

Fig. 1. Switching effect (*a*) and memory effect (*b*). I_h and V_h are holding current and voltage, respectively, t_d is delay time, and V_{on} и I_{on} are on-state voltage and current, respectively.

where T_m is the maximum temperature, which is the temperature at the center of the disk, F is the electric field, ΔE is the activation energy, κ is the thermal conductivity.

Sovtus et al. [8] later derived an approximate formula that described analytically the distribution of heat in such a model, taking into account time and coordinates, and have shown that the temperature in this model has the form:

$$T \propto e^{-ax^2-bt}, \tag{2}$$

where a and b are constants, t is time and x is the coordinate.

In Refs. [7,8] it was suggested that as a result of current filamentation, the temperature at the center of the filament for a film with a thickness of 1 μm might reach 1000 °C. However, when performing calculations, the value of the activation energy ΔE had to be taken smaller than that obtained experimentally for the sake of achieving the agreement between the calculations and the experimental data.

A large number of experiments have been carried out with CGSs based on Ge, Sb and Te. Within the framework of this review, it is impossible to mention all the combinations made up from these elements. We only mention that in what follows, in the text of the review, CGSs will be generally understood as compositions of the GST type. These include, for example, GeTe, Sb_2Te_3, $GeSb_2Te_4$, $GeSbTe_7$, and the above mentioned $Ge_2Sb_2Te_5$. The latter, as previously mentioned, is of the greatest interest for both the research and the industry. The reasons for this are the higher number of switching cycles possible and the longer post-switching phase transition compared to the other GST structures (this means greater stability and reduced tendency to phase transition at the room temperature). GST has not only a crystalline and an amorphous state, but also within the crystalline state in $Ge_2Sb_2Te_5$ there can be a transition from a state with a cubic lattice to a state with a hexagonal lattice. Under normal atmospheric pressure, this change occurs at temperatures from 200 °C to 365 °C [9]. Figure 2 shows the current-voltage characteristics (*I–V* characteristics) of GST glasses, which are of particular interest because of what happens in them at high applied switching voltages. *I–V* characteristics have three segments. The thickness of the glasses in the case considered is $L \sim 1$ μm. At the low fields $F < 10^3$ V/cm, the dependence of current I on voltage U is linear, at the intermediate fields $10^3 < F < 10^4$ V/cm it is quadratic, and at upon further increase of the field it becomes exponential [10]. With the specified L value, the magnitude of the applied voltage was several volts.

The transition from the linear (Ohm type) law to the nonlinear *I–V* characteristic is often believed to occur due to the Frenkel-Poole effect, when in a strong electric field electron tunneling from impurity trap centers is observed,

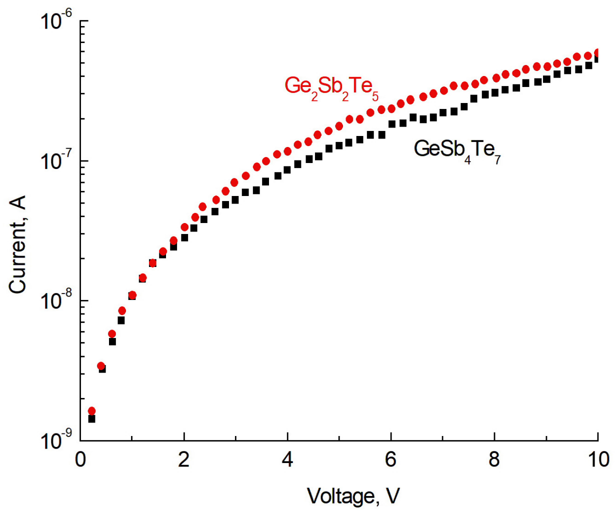

Fig. 2. Current–voltage characteristics of GST samples at 300 K (replotted using the data from Ref. [10]).

and also, according to a number of assumptions, due to multi-phonon tunneling ionization, which will be discussed in Section 4. The conductivity in CGS at strong fields and high temperatures depends on the magnitude of the applied voltage exponentially.

Experiments devoted to the investigation of other electrical and physical properties of CGS involved studying the dependence of the V_{th} on the film thickness and the external temperature and that of the filament radius on the applied electric field and film thickness. The dependence of the current density, through which the filament radius can be calculated, on the film thickness ($j \sim L^{-1.4}$) was established by Kostylev [11]. The effect of an external electric field on the growth of the filament is discussed in more detail in Section 4.

3. CURRENT FILAMENTATION IN CHALCOGENIDE GLASSY SEMICONDUCTORS. PHASE CHANGE MEMORY

Current filamentation is in fact a widely known phenomenon, which manifests not only in amorphous glasses consisting of germanium, tellurium, antimony, indium, arsenic, etc. In this Section, we will discuss some experiments and hypotheses related to this topic. Once again, it would not be superfluous to recall that a current filamentation may be related to the switching effect, when the system passes from a high-resistance state to a low-resistance state. In CGSs, this effect manifests itself as reversible, as the system is able to return from one state to the other many times. For example, in Ref. [3] 10^{10} transitions were demonstrated.

The structure of the filament in all materials is described by the heat conduction equation:

$$\rho c \frac{dT}{dt} = \Delta T + Q,$$

where ρ is the material density, c is the heat capacity, and Q is heat.

In Ref. [12] the numerical simulation of current filamentation in amorphous carbon was carried out. The current filamentation in this material is accompanied by the transition of carbon from an amorphous form to a graphite structure. A similar change is the exact phenomenon that is observed in GST [13]. Interestingly, current filament formed in carbon structures could take a helical shape, as was shown with methods of quantum molecular dynamics [12]. The current filament tended to curl into this shape due to the effect of magnetic and electric fields, and its behavior was also described by the equations of hydrodynamics.

If we turn to earlier papers, where some data on current filamentation in CGSs were obtained and reported on, Refs. [14–16] should be referred to. Ref. [14] describes the manifestation of current filamentation in $Si_{12}Te_{48}As_{30}Ge_{10}$. The equation by which the authors of Ref. [14] described the current filament was again that of heat conduction. It was shown that the filament formation could be explained using thermal and electronic-thermal models. In thick films, the model was electronic-thermal, and in thin films, only heat should have been taken into account.

In Ref. [15] an important matter was pointed out, namely, that the current filament is characterized by the presence of an 'S-like' section (a portion with negative differential conductivity) of the I–V characteristic, which appears to be due to the capturing of charge carriers by traps. The filament was described using terms used in plasma physics. The author of Ref. [15] proposed the following pattern of the development of the filament formation: in the conductor, when current flows, a pinch effect occurs, that is, the compression of the current by its own magnetic field, while inside the current filament there remain some traps onto which the charge carriers are captured. The two processes are filament compression and recombination, which can balance each other. However, if equilibrium is not reached, then the current formation will collapse with the emission of light. The filament was experimentally investigated in GaP. It is noted that the appearance of the filament was also accompanied by instability, for example, two filaments were formed simultaneously, which overlapped, while current fluctuations with up to 1 MHz frequency appeared in the system.

Ref. [16] describes one more possible shape of a filament in a semiconductor, a conical one. It forms at the interface between amorphous and crystalline semiconductors, such as $GaTe_3$ and n-Si. The study of Ref. [16] was carried out mainly experimentally and the heat conduction equation was not considered. However, some formulas were written to describe the current inhomogeneity. The following formula determined the filament radius:

$$r_c = \frac{d_{\mathrm{Si}}}{2}\left[\left(1 + \frac{4\rho_{\mathrm{Si}}}{\pi d_{\mathrm{Si}} R_{\mathrm{Si}}}\right)^{1/2} - 1\right], \tag{3}$$

where d_{Si} is the thickness of the Si epitaxial layer, ρ_{Si} is the resistivity of silicon, R_{Si} is the impedance of the silicon semiconductor. A potential barrier formed in the region where the current filament was formed, which, as the authors of Ref. [16] indicated, persisted upon transition to a low-resistance state.

Research on current filamentation currently continues. Of great interest are the time-dependent characteristics of the current filament. Ref. [17] describes voltage fluctuations in a semiconductor structure, which can be caused by the destruction of a current filament. The structure was a "sandwich", and in various structures, materials like $Ge_2Sb_2Te_5$, $Ge_{15}Sb_{15}Te_{70}$, and $Ge_{15}Sb_5Te_{80}$ were used. The most suitable shape of the filament in Ref. [17] was recognized as a cylinder whose diameter exceeded its height. According to the calculations, the filament radius turned out to be of the order of 1 μm. Heat removal occurred through the side contacts, and the destruction of the current filament was accompanied by a sharp cooling of the sample. An example of a dependence of the temperature of the current filament on time is shown in Fig. 3. This time dependence of the filament temperature was restored from the experimental data obtained by measuring the time dependence of the filament resistance. In calculations performed for obtaining the dependence, it was considered that that the temperature at the maximum voltage $U_{\max}$ was 30 °C. In this case, the temperature after the switching turned out to be ~ 320 °C, i.e., it was close to the temperature of the phase transition of the GST to the crystalline

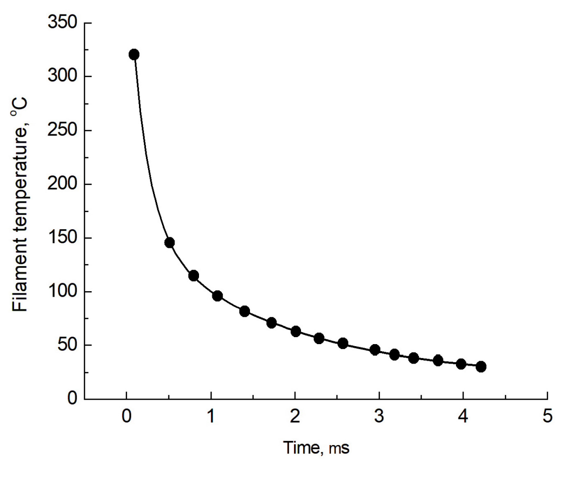

Fig. 3. Time dependence of the current filament temperature (replotted using the data from Ref. [17]). The solid line is only a guide for an eye.

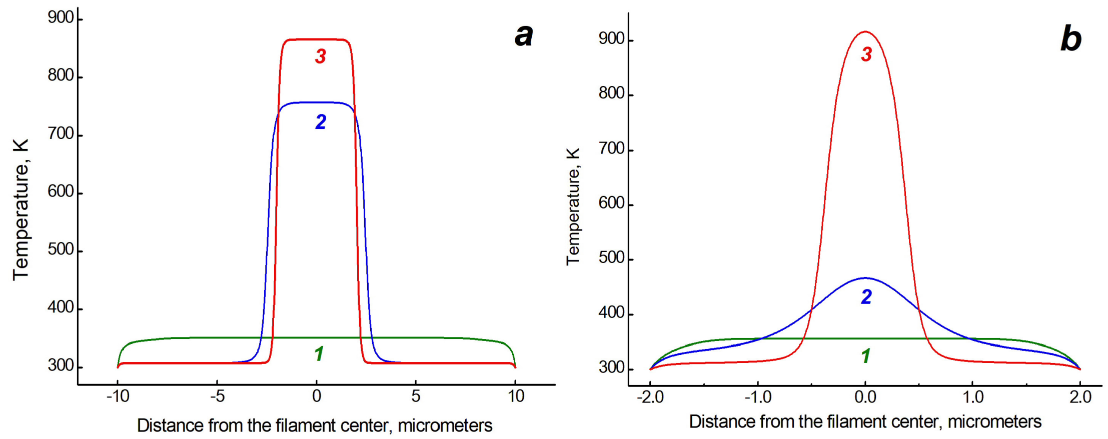

Fig. 4. Calculated temperature distribution in a 'large' (*a*) and 'small' (*b*) homogeneous CGS samples at various characteristic time points: 2 μs (*1*), 4.2 μs (*2*) and 10 μs (*3*) (*a*), and 0.4 μs (*1*), 0.6 μs (*2*) and 2 μs (*3*) (*b*) (replotted using the data from Ref. [18]).

state. Close values of the filament temperature were found for other currents through the sample and, correspondingly, other oscillation periods observed in the experiment. These estimates confirmed the assumption of the authors of Ref. [17] that the voltage oscillations they observed in the experiment were associated with the appearance of the hot current filament in the sample and its subsequent cooling. The current filament formed during switching, and when the voltage supply was interrupted, decreased its temperature according to an exponential law with time.

This result turned out to be in full agreement with the results of Ref. [18], where similar filament dimensions were obtained numerically. The thickness of the CGS sample to which the voltage was applied was 50 nm. The typical dimensions of the filament can be assessed using Fig. 4 for 'large' and 'small' (radius < 2 μm) samples. Here, for modeling the current filament, the following parameters were used by the authors of Ref. [18]: ΔE = 0.28 eV, the product of density and thermal capacity $\rho c = 2{\cdot}10^6$ J/(m^3·K), κ = 0.5 W/(m·K), heat exchange coefficient $\lambda = 4{\cdot}10^6$ W/(m^2·K), CGS film thickness L = 50 nm, ambient temperature T_0 = 300 K. Another subject of interest is the study of quantum effects that may occur during the formation of the filament [19].

Current filamentation occurs not only in amorphous semiconductors, but in crystalline ones, too. For example, in Ref. [20] Bi_2Te_3 crystals doped with copper were studied. The authors of Ref. [20] referred to current filamentation as to the "skin effect," a phenomenon in which the main current flows in the near-surface layer of the material; according to them, copper atoms diffused into the same surface layer. Whether current filamentation is beneficial or detrimental, one can answer by studying the behavior of the filament directly in devices, for example, in magnetically controlled transistors [21]. The filament in a *p–n–p* transistor [21] had a conical shape and was represented by a current of holes propagating from the emitter to the base contact. The density of holes along the edges of the filament decreased exponentially depending on the radius of the filament. The magnetic field, due to the Lorentzian deviation, controls the magnitude of the current filament. The redistribution of the current in the sample manifests when negative differential dependence of the emitter current on the voltage between the emitter and the base contact occurs. In Ref. [22] current filament in a Si diode was studied. The equation of thermal conductivity for the adiabatic process, which is filamentation, was solved. The adiabaticity of the process was manifested in the fact that the heat release was much higher than the heat removal from the transistor to the environment. The heat conduction equation was written in the form:

$$\frac{dT}{dt} = \frac{\sigma U}{c\rho W^2}, \tag{4}$$

where W is the thickness of the base of the diode. The conductivity σ was described by a temperature-dependent polynomial $\sigma = aT^3 + bT^{11}$, where a and b were constants. Both experimental and theoretical studies showed that the silicon diode would be destroyed under the action of the current concentrated in the filament, which would heat the diode up to the melting temperature.

In Refs. [23,24] a team of authors considered in detail the process of alleged current filamentation that occurred when information was recorded in GST films located between two electrodes. According to the results of those studies, a crystalline region of a semiconductor with low resistance was formed inside the current filament, while outside the filament there was an amorphous high-resistance region. Of particular interest in Ref. [23] was the statement that the current filament was dynamic, namely, it reduced its radius at the moment of switching.

Kroll thoroughly analyzed current filamentation in Ref. [25]. A model of switching in semiconductors was considered, the conductivity of which varied according to the law (electronic-thermal model):

$$\sigma = \sigma_0 \exp\left(-\frac{\Delta E}{kT} + \frac{F}{F_0}\right), \tag{5}$$

where k is the Boltzmann constant, σ_0 and F_0 are initial conductivity and electric field, respectively. This is a widely used formula that describes conductivity in various classes of semiconductors including CGSs. Kroll solved the heat balance equation for a cylindrical $Ge_{15}Te_{85}X_4$ sample, where X was a multi-element additive. The values of the electric field at which breakdown occurred and their dependences on the thickness of the semiconductor and the ambient temperature were calculated. It was shown that a current filament indeed could form in a region with a negative differential resistance. It should be noted that, according to the results of that research, for film thicknesses from 100 μm to 1000 μm, switching depended solely on the distribution of heat in the semiconductor and the electric field played practically no role in the breakdown. In Ref. [26] the team of authors also witnessed current filamentation in a GST semiconductor sample under Joule heating.

Nakashima and Kao in 1978 studied a sample of $Si_{12}Ga_{10}As_{30}Te_{48}$ with indium electrodes [27]. A formula was obtained for V_{th}:

$$V_{th} = \left(\frac{8\kappa k}{\sigma_0 \Delta E}\right)^{\frac{1}{2}} T \exp\left(\frac{\Delta E}{2kT_0}\right). \tag{6}$$

The sample was also exposed to the beam of a helium-neon laser (400 mW/cm^2). The beam did not affect the spatial dimensions of the current filament formed during switching, but increased the switching current, due to which the transition to the low-resistance state occurred at a lower applied voltage. When the supply of the light was stopped at a constant external applied voltage, the system returned to its original state.

Madatov et al. [28] exposed the CGS sample made of germanium monosulfide GeS, also a promising recording medium, to γ-radiation. The samples were grown in ampoules at a pressure of about 10^{-4} mm Hg, some of the samples were doped with rare earth elements such as Nd, Sm, or Gd. The samples were bombarded with gamma quanta, the source of which was ^{60}Co. The results promised to be of interest, since rare earth impurities significantly increased the resistance of the sample, and exposure to γ-radiation in the range of up to 100 KRad reduced the switching voltage. At high fluxes of gamma rays, the switching effect did not appear. The authors of Ref. [28] have mentioned that they considered current filamentation to be a phenomenon accompanying the switching effect.

Concluding this Section, one can summarize that current filamentation in CGS is an acknowledged and a fairly well-studied phenomenon. Being manifested in other semiconductors and metal structures, as well as in metal-semiconductor hybrid structures, filamentation can damage the device by heating it to the melting temperature. The current filament can take on a variety of shapes: cone-shaped, cylindrical, or helical. In the latter case, a rapidly destructible filament may be formed with the emission of light.

The heat conduction equation is used to describe the non-uniform distribution of current in a semiconductor, as according to some beliefs, its occurrence mainly has the thermal nature. However, this is not solely a thermal phenomenon. In the next section, it will be shown that the current filamentation that occurs in CGS can be the result of a multi-phonon tunneling ionization. According to the experimental results, current filamentation can manifest itself under the switching effect in CGSs with a low-resistance crystalline region forming inside the filament. The current filament is not a fixed formation, it is able to grow and shrink. However, the switching effect is not always ascribed to the formation of a current filament.

4. SWITCHING IN CHALCOGENIDE GLASSY SEMICONDUCTORS

4.1. Initial hypothesis

This Section mainly represents a summary of the results presented in Refs. [29,30]. Thermal and electronic-thermal breakdowns were considered to be the very first switching models. In the first case, it was believed that the increase in current density in a certain region of the semiconductor is directly related to the heat release in this region and to the exponential dependence of the conductivity on the temperature. At the same time, there was no mention of current filamentation, switching occurred in a certain homogeneous volume due to a sharp increase in conductivity during heating. This model was first developed by Wagner [31] and was considered in Refs. [32,33] and in many other works. We only note that the '*S*-shape' of the *I–V* characteristics (see Fig. 1a) cannot be explained solely within the boundaries of the thermal model.

Under electronic-thermal breakdown, the semiconductor conductivity also depended exponentially on the applied electric field [34].

In addition to the thermal and electronic-thermal models of the switching effect, there exist some other models:

- a model based on impact ionization of negative-U centers;

- a model based on hopping conduction over localized states;
- a nucleation model;
- electronic models (electronic phase transition model, double carrier injection model).

To date, there is no unified theory of the switching effect that would explain the '*S*-shape' of the *I–V* characteristics and the transition from a high-resistance state to a low-resistance state. For example, in Ref. [28] it was reported that the thermal breakdown model is not applicable for semiconductors at low temperatures (those of the order of 200 K). One of the first authors to consider thermal breakdown as the cause of the switching effect was Eaton [35]. He studied switching in As-Te-I glasses and found a strong dependence of the breakdown field strength on temperature. However, as it turned out experimentally, the theory of thermal breakdown is suitable only for the case of rather thick (thickness greater than 10 μm) films. This is its main difference from the electronic-thermal model.

In 1970 Warren and Male [34] considered the process of current flow in a semiconductor, in which the conductivity depended on temperature and voltage exponentially; see Eq. (5). To date, not only dependences of a similar type for conductivity on the field strength have been proposed, but also dependences of another type, for example, a dependence of the form:

$$\sigma = \sigma_0 \exp\left(-\frac{\Delta E}{kT} + aF^2\right), \tag{7}$$

where a is a constant that describes the electron tunneling between adiabatic terms. This type of conductivity was proposed by Bogoslovskiy and Tsendin [29] and is associated with the presence of the negative-U centers in a semiconductor. It will be discussed in more detail below, after the consideration of purely electronic models of the origin of the switching effect.

An interesting model was proposed by Savransky [36]. This model is based on the Auger effect involving two or more electrons. According to the Savransky model, the electrons located at the negative-U center affect each other, and when one electron leaves the center as a result of interaction with a heated lattice or a third electron, the interaction energy of two electrons at the center passes to another electron and transfers it to the conduction band. Ryvkin [37] also studied the origin of the emergence of the '*S*-shape' of *I–V* characteristics. In one of his works, he suggested that potential fluctuations are present in an amorphous semiconductor due to disorder in the position of atoms. Because of this, the material is a series of *n*- and *p*-regions and has the '*S*-shape' of the *I–V* characteristics.

Considering the nature of the origin of the '*S*-shaped' *I–V* characteristic and the current filament, it is necessary to refer to the scale of physical quantities that are encountered in solving problems associated with the design of cells in which switching is observed.

Popov et al. [38] analyzed in detail the engineering side of the problem of the switching effect. Ref. [38] did not explicitly mention current filamentation, but discussed a crystalline filament, which was formed when current flowed simultaneously with the transition from a high-resistance state to a low-resistance state. The magnitude of the current increased with switching by 2–3 orders. The authors of Ref. [38] proposed three types of cells based on GST and $C_8H_{20}O_4Si$ and $C_4H_{16}O_4Si_4$ dielectrics. For example, in cell 1, the GST element was represented as a film with a thickness of 550 nm. The heat released during the flow of current through the cell was calculated according to the Joule-Lenz law and was of the order of 10^{-11} J. Given that the released power was of the order of 10^{-3} W, the switching time was approximately 10^{-8} s.

4.2. Models that take into account the presence of negative-U centers. Multi-phonon tunneling ionization.

Models that were taking into account the influence of negative-U centers first appeared in 1975 with Anderson's hypothesis [39]. Negative-U centers are sites, defects, atoms of dopants, etc., on which electrons are located. Electrons affect each other with the forces of the Coulomb repulsion, yet they are also affected by the semiconductor lattice. Under certain conditions, the interaction of the electron with the lattice can prevail over the Coulomb repulsion and the electrons are able to gather in pairs similar to the Cooper pairs in superconductors. In contrast to superconductivity, electron pairing in Anderson's model occurs at room temperature. A pair of electrons can be considered as a boson, and the current of these pairs, as a superfluid Bose gas, which manifests in the form of a sharp increase in current at a certain voltage (switching effect). In this case, both electrons can be in the conduction band. The repulsion of electrons leads to the fact that a pair of electrons is shifted towards one of the negative-U centers, while the neighboring center, having given an electron to its electron pair, is thus positively charged. Of the two negative negative-U centers, one positive center is formed, with a hole, and one negative, with a bound pair of electrons. This process can be described by the equation:

$$2D^0 \rightarrow D^+ + D^-. \tag{8}$$

CGSs are interesting because, in addition to current filamentation, another type of a high current density manifestation in them is also possible, which is superconductivity [40–42]. It was observed experimentally in $Ge_{33}As_{12}Se_{55}$ [40], Ge_2Se_3 [41], and As_2Te_3 [42]. The concentration of negative-U centers and, consequently, the conductivity depend on pressure; at elevated pressure, the band gap decreases and at a high pressure of 140 kbar [40], the semiconductor acquires superconducting properties. At the same time, it was suggested that superconductivity was associated with the interaction of electrons located at negative-U centers and in the valence band [43]. In Ref. [44], an analysis was made of the thermodynamic parameters of a phonon gas, and it was shown how the phonon pressure increases in the region that can be spatially attributed to the current filament (in that paper, the current filament was represented as a cylinder with a uniform temperature distribution).

At present, the main reason for the flow of large currents in semiconductors, be it current filamentation or superconductivity, is considered to be associated with negative-U centers. Let us consider in more detail the model of impact ionization of negative-U centers. The model of impact ionization was developed even before the appearance of the term 'negative-U centers'. Zabrodsky, Ryvkin and Shlimak [45] suggested that in some cases conduction proceeds via hopping mechanism based on electron tunneling transitions from one energy level to another. Some localized electronic states near the Fermi level were considered to be the levels in question. In a strong electric field, electrons that populate the excited levels are ejected, which is accompanied by a sharp increase in the current and results in '*S*-shaped' *I–V* characteristics. The impact ionization model implies that the electrons involved in the flow of current will interact with other electrons that are in a bound state (in the case under consideration, at negative-U centers) and will transfer these bound electrons to the conduction band. There are a number of models similar to the above model, for example, the model with thermally stimulated hopping conduction through localized states. In this model, electron tunneling occurs between certain states (defects, impurity atoms, free electronic bonds) and is enhanced in an applied external electric field (the Frenkel-Poole effect) [46]. This idea differs from the one based on negative-U centers in that the description of the motion of electrons is given without negative correlation energy. We can mention that CGSs are frequently doped, for example, with bismuth, tin, or indium [47]. Doping has a positive effect on the probability of filament formation. In Ref. [48], the observation of the switching effect in the $Ge_{0.15}Se_{0.85-x}Ag_x$ $(0 < x < 0.2)$ structure was described in detail. In particular, the authors of Ref. [48] mentioned that at low concentrations of silver ($x = 0.08$) the switching effect was not observed up to an applied voltage of 1100 V. The current filamentation was one of the scenarios. The filament was formed in the region where the Ag_2Se crystalline phase appeared due to the migration of silver ions in the studied CGS. The

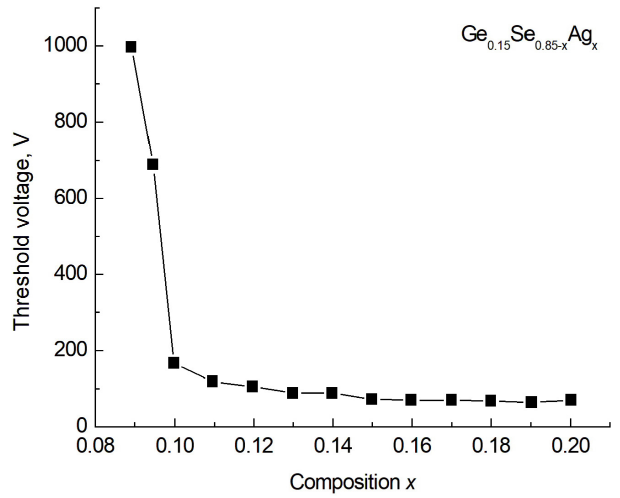

Fig. 5. Dependence of the threshold voltage on silver concentration in $Ge_{0.15}Se_{0.85-x}Ag_x$ alloy (replotted using the data from Ref. [48]).

conductivity of the Ag_2Se phase is higher than that of chalcogenide glass; this is precisely what the authors used to explain the growth of the current filament. The geometric characteristics of the filament have not been studied, but Fig. 5 describes the experiment quite informatively.

However, the above theory only includes interactions of electrons with each other and with ions. Therefore, today one of the most advanced theories of current flow in amorphous semiconductors can be considered to be the theory of negative-U centers with the multi-phonon tunneling interaction. In this theory, the nuclei of atoms, which play the role of negative-U centers, are considered as harmonic oscillators. Electrons are located on these atoms, which, from the classical point of view, are located in the field of inertial forces, since the nucleus performs thermal oscillations with acceleration $\omega^2 x$ (ω is frequency). In the above model, electrons are treated using quantum mechanics, and their binding energy dependence on the coordinate is described by a polynomial of the first degree. As a result of harmonic oscillations, an electron can (via tunneling) leave the negative-U center with which it is associated. In this case, the negative-U center is ionized, and its energy increases, since the energy of an electron at the center is negative. There can be more than one tunneling electron, so it should be taken into account that subsequent electrons will tunnel in the electric field of an ionized atom. In addition, the Frenkel-Poole effect will appear, which means reducing the potential barrier in the applied electric field. Ionization is called 'multi-phonon', because in order to ionize the center by removing an electron from it, an energy of the order of several tenths of an electron volt is needed, which is much more than the energy of a single phonon at a temperature comparable to the Debye temperature for CGSs. Tunneling of an electron occurs when several phonons affect the negative-U center. It was reported in Ref. [30] that the expression for the ionization probability ε of the negative-U center in an external electric field looks like:

$$\varepsilon(F) \sim \exp\left(\frac{F^2 q^2 \tau^2}{3\hbar m}\right), \quad (9)$$

where τ is the tunneling time, q is the elementary charge, $\hbar$ is Planck's constant, m is the electron mass. According to this formula, the logarithm of the ionization probability is proportional to the square of the electric field. However, this formula turned out to be inapplicable for centers with a binding energy of the order of 0.3–0.5 eV; according to Bogoslovskiy [30], the linear dependence of the logarithm of the ionization probability of the center on the applied external field turned out to be more accurate. The conductivity in this case depends exponentially on the applied electric field. Ionization is accompanied by mass tunneling of electrons from the negative-U centers, which leads to the appearance of an '*S*-shaped' section of the *I–V* characteristics and a transition to a high current over time ~ 10^{-14} s. This results in a switching effect. Yet the effect does not appear in the whole cell, but only in some part of it, that is, the current is actually filamented (here, by the cell we mean a memory cell based on GST). Current filamentation occurs in the region with the lowest resistance, and the difference in resistance arises from the inhomogeneity of the amorphous phase.

The current density depends on the applied electric field in different ways. In Ref. [30] it was shown that with an electric field $F = (2–8)\times10^7$ V/m, the current density in the filament is proportional to $F^{1/2}$. When the field increased up to $F = (8–18)\times10^7$ V/m, the current density becomes proportional to F. Also, the current density in the filament depends on the thickness of the film L, the experimental dependence states that $J \sim L^{-1.4}$; the theoretical dependence has a slightly different form, $J \sim L^{-0.9}$.

Thus, the switching effect in CGSs can be explained by multi-phonon tunneling ionization, and the current filamentation that accompanies the switching effect can be described in terms of heat release. Thermal effects have not been discussed in detail in this Section, although the behavior of phonons and the release of heat are closely related to each other.

It should be briefly explained how the parameters of the filament can be derived from the heat equation. Often, the equation is considered in the form of a dependence on one variable, representing the filament as homogeneous (near the maximum heat release) with the corresponding equation:

$$\rho c \frac{dT}{dt} = j(T,F)F - \lambda \frac{T - T_0}{L}. \quad (10)$$

Finding the dependence $T(t)$ helps in determining the so-called delay time, which is the time it takes for the formation of a filament in the sample. In this equation, the thermal conductivity is assumed to be constant, however, during heating it can vary within small limits, given that it has a phonon and electronic nature. Similarly, the problem can be considered only for the stationary case of thermal conductivity depending on the coordinate. For example, in Ref. [8] it was proposed to find the second derivative with respect to the radial coordinate to determine the boundaries of a steady-state filament. It was assumed that in the coordinate that describes the filament boundary, the heat flux proportional to the first derivative and going along the radial coordinate, will have maximum value. Based on this, the dimensions of the current filament were calculated, whose radius appeared to be inversely proportional to $F^{1/2}$.

Finally, let us note that apart from filamentation models based on heat conduction and balance, electronic models of current filamentation in CGS were also developed. An example of such model was presented by Karpov et al. [49]. This model is based on the nucleation of conducting cylindrical crystallites in amorphous media. In this case, the filament was represented not by a flux of charged particles, but actually by a phase transition. Namely, in the model, the switching started with the field-induced nucleation of a shunting crystalline cylinder, which caused voltage drop and acted as a "lightning rod" concentrating the electric field. The stronger electric field facilitated nucleation of an additional conductive particle at the cylinder end making it longer, hence, further increasing the field, etc. This instability resulted in a conductive crystalline filament reaching through the entire amorphous region and stabilized by the electric field energy. The filament parameters were defined from the minimum of Helmholtz's free energy, and the minimum threshold voltage for the formation of the crystalline channel was:

$$V_{min} = L\sqrt{\frac{kT}{4R_0^3\,\varepsilon}}, \quad (11)$$

where R_0 is the channel radius and ε is dielectric permittivity. With channel radius 3 nm and film thickness 100 nm this minimum voltage equaled 1 V.

5. CONCLUSION

In this paper, we reviewed some works concerning current filamentation and the switching effect in chalcogenide glassy semiconductors (CGSs). Surely, current filamentation occurs not only in CGSs, and the switching effect is not a full-fledged synonym for filamentation. Still, in our review we paid attention to current filamentation that occurs during the switching effect in CGSs, as these materials are very promising for the development of memory devices, which should be more advanced than a magnetic disk or floating-gate-transistor memory.

Section 2 of the review briefly considered the history of the discovery of CGSs and the fact that they can exist in two phases — crystalline and amorphous. Section 3 considered formation of a current filament, the scale of heat release in the corresponding materials, and the geometric shape of the filament. Section 4 presented in detail the hypotheses that were put forward to describe the switching effect in CGSs. It was indicated that under certain conditions the switching effect leads to the formation of a filament. After analyzing various early hypotheses explaining this effect, it was shown that the most relevant model of the switching effect is the model of multi-phonon tunneling ionization at negative-U centers. This model is based on the assumption that an avalanche-like increase in current at a certain point in time is associated with mass tunneling of electrons located on atoms (including impurity atoms). The idea of electron tunneling at negative-U centers in the presence or absence of an external electric field was presented in detail. It was noted that when an external electric field is applied, the probability of an electron transition from a localized center to a higher energy level increases sharply. In the same Section, we also mentioned that the current redistribution can also be described by impurity diffusion processes, and not necessarily by multi-phonon processes. Study of current filamentation is a very relevant matter, since the current filamentation can destroy the material structure. On a smaller scale, filamentation can affect the quality of data recording, since it is accompanied by 'chaotic' current fluctuations, and thus, noise is generated. Analytical description of this noise has not yet been presented. In relatively large samples, it is impossible to completely avoid the growth of the current filament, and today's goal is to create devices with an optimal structure, in which the redistribution of current density could perform some key useful function.

REFERENCES

[1] B.T. Kolomiets, *Vitreous semiconductors (I)*, Phys. Status Solidi B, 1964, vol. 7, no. 2, pp. 359–372.

[2] S. Ovshinsky, *Reversible electrical switching phenomena in disordered structures*, Phys. Rev. Lett., 1968, vol. 21, no. 20, pp. 1450–1453.

[3] A.L. Lacaita, *Phase change memories: State-of-the-art, challenges and perspectives*, Solid-State Electron., 2006, vol. 50, no. 1, pp. 24–31.

[4] J. Feinleib, J. deNeufville, S.C. Moss, S.R. Ovshinsky, *Rapid reversible light-induced crystallization of amorphous semiconductors*, J. Appl. Phys., 1971, vol. 18, no. 6, pp. 254–257.

[5] P. Clarke, *Samsung preps 8-Gbit phase-change memory*, Electronic resource (accessed 29.05.2022).

[6] N. Yamada, E. Ohno, N. Akahira, K. Nishiuchi, K. Nagata, M. Takao, *High speed overwritable phase change optical disk material*, Jpn. J. Appl. Phys., 1987, vol. 26, no. S4, pp. 61–66.

[7] B.L. Gelmont, K.D. Tsendin, *Analytical theory of current filamentation at switching*, Sov. Phys. Semicond., 1976, vol. 10, no. 6, pp. 665–668.

[8] N.V. Sovtus, K.D. Mynbaev, *Parameters of lateral and unsteady cord currents in a cylindrical chalcogenide glassy semiconductor*, Semiconductors, 2019, vol. 53, no. 12, pp. 1651–1655.

[9] N. Yamada, E. Ohno, K. Nishiuchi, N. Akahira, *Rapid phase transitions of GeTe-Sb_2Te_3 pseudobinary amorphous thin films for an optical disk memory*, J. Appl. Phys., 1991, vol. 69, no. 5, pp. 2849–2856.

[10] P.N. Lazarenko, *Technology and electro-physical properties of thin films of materials of Ge-Sb-Te system, developed for change-phase-memory devices*, PhD Thesis, 2014, Moscow, Russia, 181 p. (in Russian).

[11] S.A. Kostylev, *Threshold and filament current densities in chalcogenide-based switches and phase-change-memory devices*, IEEE Electron Device Lett., 2009, vol. 30, no. 8, pp. 814–816.

[12] A.M. Popov, *Numerical simulation of the instability of the molecular nanostructure of a semiconductor at bifurcation points of I-V characteristics*, Comp. Nanotechnol., 2018, no. 4, pp. 41–47 (in Russian).

[13] A.V. Kolobov, P. Fons, J. Tominaga, A.I. Frenkel, A.L. Ankudinov, S.N. Yannopoulos, K.S. Andrikopoulos, T. Uruga, *Why phase-change media are fast and stable: a new approach to an old problem*, Jpn. J. Appl. Phys., 2005, vol. 44, no. 5S, pp. 3345–3349.

[14] N.P. Kalmykova, E.A. Smorgonskaya, V.Kh. Shpunt, *Electronic processes and the dynamics of the highly conductive filament formation in bulk samples of a chalcogenide vitreous semiconductor under high electric field*, J. Non-Crystal. Solids, 1987, vol. 90, no. 1–3, pp. 605–608.

[15] S.T. Voronin, A.F. Kravchenko, A.P. Sherstyakov, *Dynamic current-voltage characteristics of GaP:Fe p–i–n^+ structures under current filamentation*, Sov. Phys. Semicond., 1984, vol. 18, no. 4, pp. 413–416.

[16] A. Česnys, S.-A. Karpinskas, A. Urbelis, *Current-voltage characteristic and parameters of the current filament region of an amorphous gallium telluride-crystalline silicon barrier negistor structure*, Tech. Phys., 2002, vol. 47, no. 10, pp. 1263–1267.

[17] S.A. Fefelov, L.P. Kazakova, N.A. Bogoslovskiy, K.D. Tsendin, *Estimation of the temperature of the current filament that forms upon switching in GeSbTe*, Semiconductors, 2018, vol. 52, no. 12, pp. 1607–1610.

[18] N.A. Bogoslovskiy, K.D. Tsendin, *Dynamics of the current filament formation and its steady-state characteristics in chalcogenide based PCM*, Solid-State Electron., 2017, vol. 129, pp. 10–15.

[19] N.V. Sovtus, K.D. Mynbaev, *Analytical description of quantum effects at current filamentation in chalcogenide glasses*, Mater. Phys. Mech., 2020, vol. 46, no. 1, pp. 202–206.

[20] A.A. Shashkin, V.T. Dolgopolov, S.I. Dorozhkin, *Filamentation of the Hall current in a two-dimensional nonlinear electron system in a quantizing magnetic field*, Sov. Phys. JETP, 1986, vol. 64, no. 5, pp. 1124–1128.

[21] Ch.S. Rumenin, *The role of current filamentation in the magnetosensitivity of planar magnetotransistors*, Semiconductors, 1988, vol. 22, no. 9, pp. 1647–1650.
[22] I.V. Grekhov, A.E. Otblesk, *Heat and current non-stationary localization in direct-biased silicon diodes*, J. Tech. Phys., 1984, vol. 54, no. 9, pp. 1787–1792 (in Russian).
[23] S.A. Fefelov, L.P. Kazakova, D. Arsova, S.A. Kozyukhin, K.D. Tsendin, O.Yu. Prikhodko, *Voltage oscillations in the case of the switching effect in thin layers of Ge–Sb–Te chalcogenides in the current mode*, Semiconductors, 2016, vol. 50, no. 7, pp. 941–946.
[24] S.A. Fefelov, L.P. Kazakova, S.A. Kozyukhin, K.D. Tsendin, D. Arsova, V. Pamukchieva, *Current-voltage characteristics of thin $Ge_2Sb_2Te_5$ films taken using a measuring circuit with a current source*, Technical Physics, 2014, vol. 59, no. 4, pp. 546–550.
[25] D.M. Kroll, *Theory of electrical instabilities of mixed electronic and thermal origin*, Phys. Rev. B, 1974, vol. 9, no 4, pp. 1669–1706.
[26] G. Betti Beneventi, A. Calderoni, P. Fantini, L. Larcher, P. Pavan, *Analytical model for low-frequency noise in amorphous chalcogenide-based phase-change memory devices*, J. Appl. Phys., 2009, vol. 106, no. 5, art. no. 054506.
[27] K. Nakashima, K.C. Kao, *Conducting filaments and switching phenomena in chalcogenide semiconductors*, J. Non-Cryst. Solids, 1979, vol. 33, pp. 189–204.
[28] R.S. Madatov, A.S. Alekperov, O.M. Hasanov, *Changeover and memory effects in the layered GeS monocrystals*, Applied Physics, 2015, no. 4, pp. 11–15 (in Russian).
[29] K.D Tsendin, N.A. Bogoslovsky, *Physics of the switching effect and memory effect in chalcogenide glassy semiconductors*, Semiconductors, 2012, vol. 46, no. 5, pp. 577–608.
[30] N.A. Bogoslovsky, *Electronic-thermal model of switching and memory effects, based on multi-phonon tunnel ionization of negative-U centers in chalcogenide glassy semiconductors*, PhD Thesis, 2013, Saint-Petersburg, Russia, 112 p. (in Russian).
[31] K.W. Wagner, *The physical nature of the electrical breakdown of solid dielectrics*, J. Am. Inst. Electr. Eng., 1922, vol. 41, no. 12, pp. 1034–1044.
[32] K.D. Tsendin, A.B. Shmel'kin, *Conditions preventing thermal breakdown in semiconductor devices*, Tech. Phys. Lett., 2004, vol. 30, no. 6, pp. 525–528.
[33] T. Kaplan, D. Adler, *Thermal effects in amorphous-semiconductor switching*, Appl. Phys. Lett., 1971, vol. 19, no. 10, pp. 418–420.
[34] A.C. Warren, J.C. Male, *Field-enhanced conductivity effects in thin chalcogenide-glass switches*, Electron. Lett., 1970, vol. 6, no. 18, pp. 567–569.
[35] D.L. Eaton, *Electrical conduction anomaly of semiconducting glasses in the system As-Te-I*, J. Am. Ceram. Soc., 1964, vol. 47, no. 11, pp. 554–558.
[36] S.D. Savransky, *Model of conductivity transition in amorphous chalcogenides induced by Auger recombination*, J. Ovonic Res., 2005, vol. 1, no. 2. pp. 25–31.
[37] S.M. Ryvkin, *Switching mechanism in amorphous semiconductors*, JETP Lett., 1972, vol. 15, no. 10, pp. 448–450.
[38] A.I. Popov, S.M. Salnikov, Yu.V. Anufriev, *Conditions of steady switching in phase-transition memory cells*, Semiconductors, 2015, vol. 49, no. 4, pp. 498–503.
[39] P.W. Anderson, *Model for the electronic structure of amorphous semiconductors*, Phys. Rev. Lett., 1975, vol. 34, no. 15, pp. 953–955.
[40] I.V. Berman, N.B. Brandt, V.A. Alekseev, I.E. Kostyleva, V.I. Sidorov, O.P. Pyatkina, *Superconductivity near the dielectric-metal junction in amorphous α-$Ge_{33}As_{12}Se_{55}$*, JETP Lett., 1984, vol. 40, no. 11, pp. 1303–1305.
[41] I.V. Berman, N.B. Brandt, I.E. Kostyleva, S.M. Chudinov, V.A. Alekseev, *Superconductivity of amorphous α-$GeSe_{1.5}$ at high pressures*, Sov. Phys. Solid State, 1985, vol. 27, no. 9, pp. 2747–2750.
[42] I.V. Berman, N.B Brandt., I.E. Kostyleva, S.K. Pavlov, V.I. Sidorov, S.M. Chudinov, *Critical magnetic fields of amorphous As_2Te_3 near the insulator-metal transition*, JETP Lett., 1986, vol. 43, no. 1, pp. 62–65.
[43] K. Tsendin, A. Kapustin, I. Barygin, *Normal phase conductivity of glass-like semiconductors and high temperature superconductors with U-minus-centers under high pressure*, Izvestia: Herzen University Journal of Humanities & Sciences, 2006, no. 6(15): Physics, pp. 204–212 (in Russian).
[44] K.D. Mynbaev, N.V. Sovtus, *Non-equilibrium phonon gas in a chalcogenide semiconductor with exponential temperature dependence of conductivity*, Mater. Phys. Mech., 2022, vol. 48, no. 3, pp. 308–314.
[45] A.G. Zabrodskii, S.M. Ryvkin, I.S. Shlimak, *Mechanism of low-temperature impurity breakdown in compensated semiconductors and of switching in amorphous semiconductors*, JETP Lett., 1973, vol. 18, no. 8, pp. 290–292.
[46] D. Ielmini, *Threshold switching mechanism by high-field energy gain in the hopping transport of chalcogenide glasses*, Phys. Rev. B, 2008, vol. 78, no. 3, art. no. 035308.
[47] S. Kozyukhin, V. Kudoyarova, H.P. Nguyen, A. Smirnov, V. Lebedev, *Influence of doping on the structure and optical characteristics of $Ge_2Sb_2Te_5$ amorphous films*, Phys. Status Solidi C, 2011, vol. 8, no. 9, pp. 2688–2691.
[48] P. Pattanayak, S. Asokan, *Anomalous electrical switching behaviour in phase-separated bulk Ge–Se–Ag chalcogenide glasses*, Europhys. Lett., 2006, vol. 75, no. 5, pp. 778–783.
[49] V.G. Karpov, Y.A. Kryukov, S.D. Savransky, I.V. Karpov, *Nucleation switching in phase change memory*, Appl. Phys. Lett., 2007, vol. 90, no. 12, art. no. 123504.

УДК 538.953

Шнурование тока и эффект переключения в халькогенидных стеклообразных полупроводниках: обзор

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Аннотация. Представлен обзор по эффектам шнурования тока и переключения в халькогенидных стеклообразных полупроводниках (ХСП), являющихся перспективными материалами для создания устройств фазовой памяти. Вначале рассматривается история изучения ХСП и их свойств. Далее обсуждается формирование шнура тока в ХСП и анализируются масштабы тепловыделения в материале, а также геометрическая форма шнура. Наконец, рассмотрены различные гипотезы, разработанные для объяснения эффекта переключения в ХСП. Показано, что наиболее актуальной моделью эффекта переключения в ХСП является модель многофононной туннельной ионизации так называемых «U-минус» центров. Эта модель основана на предположении, что лавинообразное возрастание тока в определенный момент времени связано с массовым туннелированием электронов, находящихся на атомах, причем туннелирование происходит за счет тепловых колебаний атомов.

Ключевые слова: халькогенидные стеклообразные полупроводники; эффект переключения; эффект памяти; шнурование тока