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SWITCHING EFFECT WITH MEMORY IN $TlIn_{1-x}Ga_xSe_2$, $TlIn_{1-x}Ce_xSe_2$ CRYSTALS

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Abstract

The paper presents the results of a study of current-voltage characteristics of $TlIn_{1-x}Ga_xSe_2$, $TlIn_{1-x}Ce_xSe_2$ single crystals grown by Bridgman – Stockbarger method in a static mode at different temperatures. The contact was silver paste. It was revealed that these crystals have switching properties with memory, with decreasing temperature the threshold voltage values increase, the threshold current decreases, and the area of negative differential resistance expands. Upon partial substitution of indium atoms with gallium and cerium atoms in the $TlInSe_2$, lattice, the threshold voltage value decreases. The values of threshold current and threshold voltage are managed by varying the composition of crystals under study and temperature of the surrounding medium.

Keywords*: switching effect, threshold voltage, negative resistance, crystals* $TlIn_{1-x}Ga_xSe_2$, $TlIn_{1-x}Ce_xSe_2$.

I. INTRODUCTION

The switching effect was first revealed in amorphous semiconductors [1–3]. This discovery stimulated many researchers to work in this direction. Subsequent studies have shown that the switching effect is also present in two-component crystalline semiconductors of the $A^{III}B^{VI}$ type, such as GaSe, Ga_2Te_3, InTe [4-6]. This effect was also detected in ternary and quaternary compounds of the type AIIIBVI, as well as in solid solutions based on them [7–13].The use of semiconductor devices, the principle of operation of which is connected with the switching effect or devices with negative resistance (NR), allows us to significantly simplify circuit solutions, since the feedback is carried out not by external circuits, but by the device itself, due to the presence of internal positive feedback. Therefore, the use of devices with the NR makes it possible to significantly increase reliability while simultaneously reducing the size, weight of electronic equipment and reducing power consumption. The advantages of devices with negative resistance are most fully manifested when used in microelectronics. NR-based semiconductor devices are essentially elementary solid functional circuits, since due to the presence of NR they can perform the functions of amplifiers, generators, converters, etc. For this, it is usually sufficient to attach the load and the power supply to them. By creating several devices with NR in one semiconductor plate and carrying out a volume connection between them, it is possible to obtain more complex functional circuits [14].

The main advantages of semiconductor switches are the following: symmetry of current-voltage characteristics (CVC), which allows switching regardless of signal polarity, memory effect, i.e., it can be in any of two possible states indefinitely when disconnected from power sources. The presence of switching with memory is determined by the composition of the active material and the electric mode of transferring the device from one state to another. Insensitivity to radiation levels at which bipolar devices fail, simplicity of design and the ability to combine switch technology with hybrid and monolithic integrated circuit technology are of great interest to such devices, and the limited number of switches is a common problem of such devices and a temporary obstacle for their mass use in technology.

Of particular interest is the effect of switching with memory. Such switches are stable in the closed and open states when they are removed from the voltage. The manufactured device is in high resistance. The effect of molding, in contrast to switches without memory, is absent. The effect of switching with memory occurs at certain values of time and amplitude of the current passing through the element in the open state, and its mechanism is associated with a reverse glass-crystal phase transition in the current channel [2, 3]. Therefore, in order to ensure high reliability of the memory elements, it is recommended to provide such a mode of operation when a simpler glass-to-crystal transition is implemented. Memory cells allow you to raise the working temperature, to provide photolithography. The study of the current – voltage characteristics makes it possible to understand the causes of a sharp change in the electrical conductivity of the samples under study when they are transferred from a state of high resistance to a state of high conductivity, as well as the reasons leading to the known instability of threshold switches and to develop devices with threshold voltage stability no worse than 1-2%. These urgent tasks by now do not have a satisfactory solution.

Currently, intensive research is underway to identify new materials with switching properties with memory. As early as the middle of the last century, intensive work was started on obtaining and studying ternary compounds of the type $A^{III}B^{III}C_2^{VI}$ and it was revealed that these compounds have high photo- and strain-sensitivity coefficients and have switching properties with memory. Subsequently, with a partial substitution of three valent indium atoms in lattices $TlInC^{VI}_2$ such as lanthanide atoms, a new class of semiconductor $TlIn_{1-x}Ln_xC_2$ materials was obtained. It was found that these materials also have switching properties [15-18]. In connection with the foregoing, this work is devoted to the study of the current – voltage characteristics in crystals $TlIn_{1-x}Ga_xSe_2$, $TlIn_{1-x}Ce_xSe_2$.

II. METHOD & MATERIAL

For the synthesis of $TlIn_{1-x}Ga_xSe_2$ and $TlIn_{1-x}Ce_xSe_2$ crystals, elements of In- A.C.S. purity were used, Se - A.C.S., Ga-99.996, Tl-99.99, Ce-99.996 wt.%. The ampoules were first cleaned with a mixture of HF and distilled water. After chemical cleaning, the ampoule was filled with highly purified elements of the crystal under study, placed in a furnace, and then, in order to reduce the risk of explosion of the ampoule, the mixture at a speed of 0,600C/min. heated to 950 – 10500C depending on the composition. Then, in order to homogenize the alloy, it was kept at this temperature for 10 to 12 hours, depending on the composition. During the synthesis, ampoules were often shaken in order to better mix the components. Then, the temperature, with a speed of 2.50C / hour, was reduced to 900-10000C and kept for 10-12 hours to homogenize the melt and cooled to room temperature.

Single crystals of $TlIn_{1-x}Ga_xSe_2$ and $TlIn_{1-x}Ce_xSe_2$ alloys obtained by the Bridgman-Stockbarger methods with mirror verges, were prepared for the study of the volt-ampere characteristic (VAC) without any additional processing. Studies were conducted in the temperature range of 100-400K, the sample temperature was measured with a chromel - alumel thermocouple. The contacts were silver paste deposited on parallel surfaces of the sample. The samples of rectangular crystals were prepared with a smooth and mirror surface placed between two metal electrodes.

III. RESULT & DISCUSSION

The results of the study are shown in Figures 1-4. As follows from fig. 1, for the studied ternary compounds with increasing voltage I (U), the characteristic decayed and was strictly non-linear and S-shaped. It was revealed that in the ohmic region the temperature of the sample remains constant, and in the region of negative differential resistance increases to a temperature T, usually greater than the ambient temperature. S-shaped characteristic in the field of high currents with a better pronounced area of negative resistance then becomes the critical current (threshold current). Part of the negative differential resistance on the instrument curve is more pronounced at low ambient temperatures. The transition from low to high conductivities on the curve is almost abrupt at low temperatures.

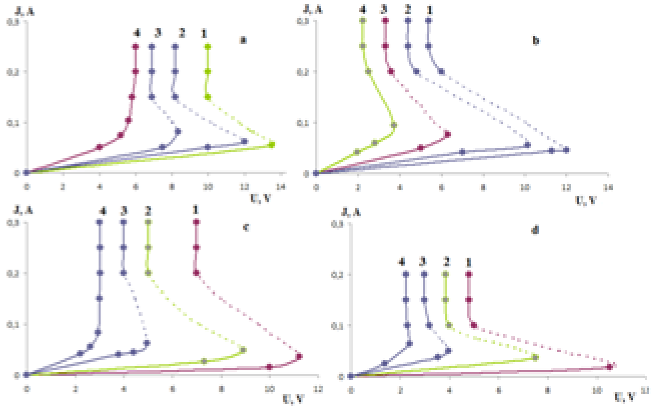

Fig. 1. Current-voltage characteristics of $TlIn_{1-x}Ce_xSe_2$*, crystals: a-x=0.02; b-x=0.04; c-x=0.06; d-x=0.08; at different temperatures 1-80K; 2 - 120K; 3 - 220K; 4-300K*

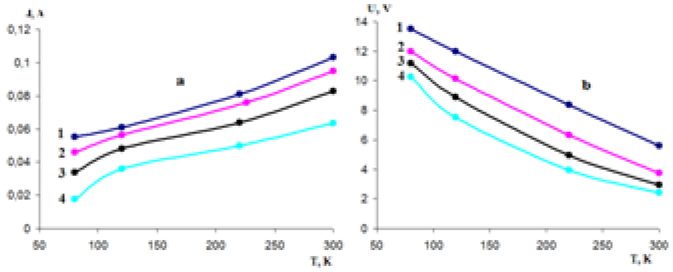

Fig.2. Temperature dependences of the threshold voltage (a) and threshold current b) of $TlIn_{1-x}Ce_xSe_2$*, crystals 1-x = 0.02; 2 = 0.04; 3 = 0.06; 4x = 0.08;*

In solid solutions $TlIn_{1-x}Ga_xSe_2$, $TlIn_{1-x}Ce_xSe_2$ with partial replacement of indium atoms with gallium and cerium atoms in the $TlInSe_2$ lattice, the threshold switching gradually decreases.

This is apparently due to the fact that indium atoms are partially replaced by those atoms, which, unlike indium atoms, have a less likely tendency to form a sp^3- hybrid bond and contribute to an increase in the metal fraction of the chemical bond. And this is due to the fact that with partial replacement gallium and cerium atoms of indium decreases the shift of the maximum of the electron density to the cores of selenium atoms, i.e. the possibility of completing the outer electron shells of the atom to a stable configuration s^2p^6 is reduced. In this regard, the ionicity of chemical bond decreases, i.e. the statistical weights of the configurations s^2p^6 decrease and the threshold voltage in $TlIn_{1-x}Ga_xSe_2$, $TlIn_{1-x}Ce_xSe_2$ crystals decreases.

The obtained CVC characteristics of these crystals are identical. This is due to the fact that the crystal structure and the type of chemical bond between the atoms of the crystals studied, as well as the initial one $TlInSe_2$, is almost the same. In this regard, we limit ourselves to discussing the results of the study $TlInSe_2$. For this phase, in each ohmic region of CVC, the electrical conductivity was determined and the temperature of the samples was measured.

Our results show that the area controlled by current is corrected by increasing the temperature of the sample. An analysis of the results shows that with a decrease in the ambient temperature, migration to high values occurs, and with an increase in the ambient temperature, a weak appearance of the NR region on the I–V characteristic appears. These results prove that truly electrothermal processes are responsible for the appearance of a domain of NR in $TlIn_{1-x}Ga_xSe_2$, $TlIn_{1-x}Ce_xSe_2$, crystals.

In electrothermal processes, small local deviations from a uniform distribution of imperfections, leading to high current densities in these areas, are allowed. This increase in current density is usually accompanied by the formation of a high-current density of the filament in the samples. In these “channels,” the increased current density is the result of an increase in dissipation energy, leading to Joule heat. Due to the increase in temperature, the electrical conductivity also increases and allows the flow of high current. The steady state of this behavior will be achieved when the heat dissipation is equal to the heat loss.

The steady state of the CVC and the characteristics of their NR region can be interpreted by the electrothermal approximation. At low current values, this corresponds to the norms.

The temperature dependence of the current-voltage characteristics is an important factor for determining the commutation material for technological applications. The choice of material for storing information depends on the change in the properties of switching with temperature. Therefore, the I–V characteristics of $TlIn_{1-x}Ga_xSe_2$, $TlIn_{1-x}Ce_xSe_2$, single crystals were studied at different temperatures (Fig. 2, 4.).

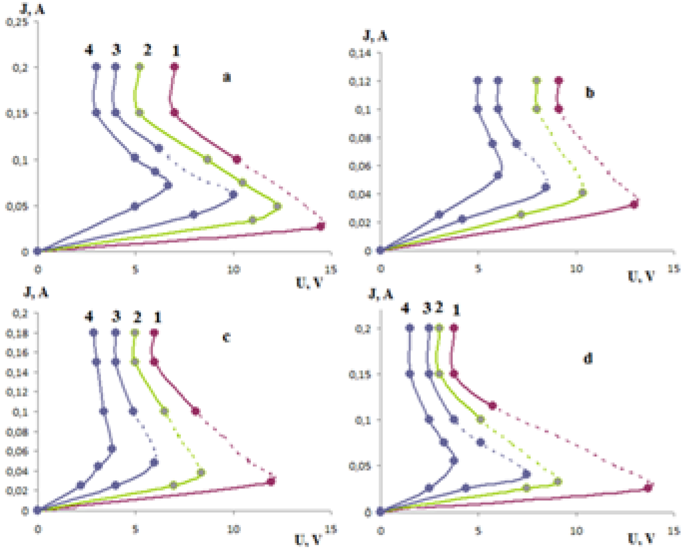

Fig. 3. Current-voltage characteristics of the crystals $TlIn_{1-x}Ga_xSe_2$,*: a-x=0.02; b-x=0.04; c-x=0.06; d-x=0.08; at different temperatures 1-80K; 2 - 120K; 3 - 220K; 4-300K*

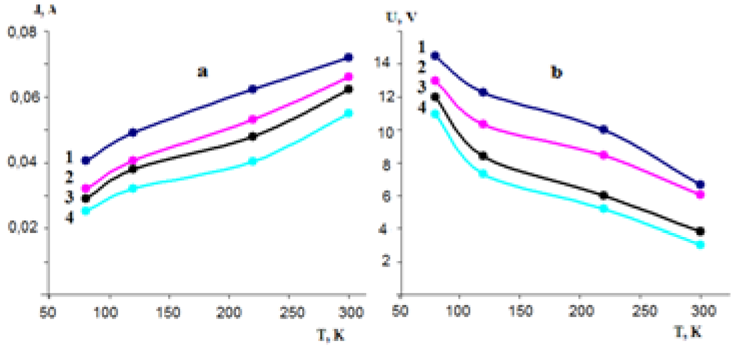

Fig.4. Temperature dependences of the threshold voltage (a) and threshold current b) of crystals $TlIn_{1-x}Ga_xSe_2$, *1-x=0.02; 2-x=0.04; 3-x=0.06; 4 -x=0.08;*

The figures show that with decreasing temperature the threshold voltage increases, and the threshold current decreases. Obviously, the threshold voltage increases for the reason specified in the works for other compounds [7, 12]. The part of the CVC, showing a negative slope, is an area of (NDR) negative differential resistance. Its main characteristics are its width, slope, threshold voltage and threshold current, as well as holding voltage and holding current. Therefore, in the holding branch, the electrothermal balance between Joule heat produced in the volume and heat flux in the electrodes seems to play an important role in maintaining a high current density, while decreasing the ambient temperature the critical voltage Vth at which the slope dI / dV first becomes negative offset to higher voltage values, and the corresponding current (threshold current) shifts to lower current values. The switching and threshold voltage can be explained using the electrothermal model [6,7,18]. The temperature of the semiconductor rises due to Joule heating. Since the process of conduction in the material is thermally activated, the conductivity of the sample will increase when it is heated, this will allow more current to flow through the heated areas and provide more Joule heating, which will further increase the current density. Ultimately, the temperature increase will be sufficient to initiate thermal breakdown due to the strong temperature dependence of the conductivity. As follows from the experimental results, as well as, based on the electrothermal model, the temperature strongly influences both the shape of the current-voltage curves and the threshold voltage Vth. According to this assumption, the threshold current decreases with increasing threshold voltage. As can be seen, the current – voltage characteristics strongly depend on the ambient temperature of the samples under study. From these curves, the variation of the threshold voltage V_{th} and the threshold current I_{th} with the ambient temperature (Fig. 2, 4) is constructed. Increasing the ambient temperature of the samples $TlIn_{1-x}Gd_xSe_2$ increases the threshold current, while it reduces the threshold voltage. This indicates that the electrothermal mechanism is involved in the switching process. The dissipated power was calculated in the investigated crystals ($P_{th}=V_{th}\times I_{th}$). The power required to change a material from a state of high resistance to a low-resistance state is called the threshold power P_{th}. The threshold power also depends on the ambient temperature. The calculation showed that P_{th} decreases with increasing temperature, as shown in Fig.5. This led us to the assumption that as the temperature of the number of random collisions and scattering between charge carriers increases, the rate of thermal generation of free charge carriers is less than the recombination rate and the effect of trapping centers increases with increasing temperature. All these factors led to a decrease in the threshold power as the temperature rises. Thus, this result is quite logical, since the power required to initiate switching decreases with increasing temperature. It seems almost obvious that switching in massive samples is due to thermal effects, although a purely thermal model cannot fully explain the observed switching characteristics by Joule heat, especially in the conducting state, they cannot be neglected.

In the case of the electron-thermal mechanism of the switching effect, the combined effect of the electric field and temperature on the semiconductor, which is transferred from the high-resistance state to the low-resistance state, is taken into account.

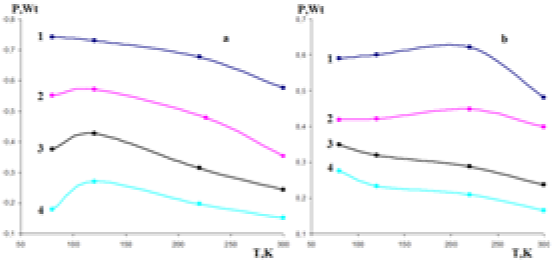

Fig.5. Temperature dependences of the electric power of crystals a) $TlIn_{1-x}Ce_xSe_2$, and *b)* $TlIn_{1-x}Ga_xSe_2$, *1-x=0.02; 2-x=0.04; 3-x=0.06; 4 -x=0.08*

The thermal mechanism of the effect is determined mainly by the heat capacity, thermal conductivity, and the dependence of the resistance of the active region of the sample on temperature. In the study of crystals of the above type, it turned out that at low voltages the characteristics I(U) are linear and, accordingly, ohmic contact (Fig. 1, 3). At high voltages, the characteristics turned out to be non-linear and possessed S-figurative form. For the crystals studied, the S -figurative curve in the region of high currents with a better-expressed region of the NDR subsequently became the critical (threshold) current. Part of the NDR on the I(U) curve is more pronounced at low ambient temperatures. An analysis of the results showed that a decrease in the voltage of the direct transition at each subsequent switching and a substantial nonlinearity of the current–voltage characteristics in sub threshold electric fields is characteristic of all the crystals we studied. The superlinear section of the I–V characteristic is well described by a three-term polynomial in the form,

$$I=aU+bU^2+cU^3, \qquad (1)$$

where the numerical values of the coefficients are easily determined and different for different compositions. These results prove that truly electro - thermal processes are responsible for the appearance of the NDR in crystals $TlIn_{1-x}Ga_xSe_2$, $TlIn_{1-x}Ce_xSe_2$. Small local deviations from homogeneous distribution of imperfections leading to high current densities in these areas. This increase in current density is usually accompanied by the formation of a high-current density of the filament in the samples. In these “channels”, the increased current density is the result of an increase in dissipation energy leading to Joule heat. Due to the increase in temperature, the electrical conductivity also increases and allows the flow of high current. The steady state of this behavior will be achieved when the heat dissipation is equal to the heat loss. The steady state of the I–V characteristic and the characteristics of their NDR region can be interpreted by the electrothermal approximation. At low current values, this corresponds to the norms. Increasing the heating of the internal part of the sample leads to an increased concentration of free carriers in this region due to the semiconductor nature of $TlIn_{1-x}Ga_xSe_2$, $TlIn_{1-x}Ce_xSe_2$ crystals. A high filament can be created in the inner side of the sample. The results obtained for studying the current-voltage characteristics of $TlIn_{1-x}Ga_xSe_2$, $TlIn_{1-x}Ce_xSe_2$ crystals make it possible to conclude that when creating high-speed switching devices, as elements of microelectronics and computer technology, samples of small thickness should be obtained that are less sensitive to temperature and which there is practically no dependence of the threshold voltage on the thickness of the active region of the switching element. Thus, investigating the current – voltage characteristics of the above crystals, with different conditions found that the major phase of said switching characteristics can be controlled depending on the contact material, temperature, the dimensions and the composition.

I would like to especially note that we have obtained the results of studying the CVC of ternary analogs TlSe and solid solutions based on them in good agreement with the results of [7, 12].

IV. CONCLUSION

Studies of the current-voltage characteristics of $TlIn_{1-x}Ga_xSe_2$ and $TlIn_{1-x}Ce_xSe_2$ crystals in the static mode revealed that these phases have switching properties with memory. With increasing temperature the threshold voltage decreases and threshold current increases. The area of negative differential resistance is narrowed. It is revealed that the current-voltage characteristics of the studied solid solutions are symmetric with respect to the polarity of the applied voltage and current. The obtained experimental results show that the switching phenomena observed in TlIn$_{1-x}$Ga$_x$Se$_2$ and TlIn$_{1-x}$Ce$_x$Se$_2$ crystals are very sensitive to the effects of external factors. These materials can be used as switching elements and memory elements in electronic devices.

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