METAL - $TlGaSe_2$ SEMICONDUCTOR - METAL STRUCTURE AS MEMRISTIVE SYSTEM

R.A. SULEYMANOV [1, 2, 3], MIR HASAN YU. SEYIDOV [1, 2] *, FAIK A. MIKAILZADE [1, 2], BUKET BILGEN KANDEMIR [1], YASIN ŞALE [1], TOFIG G. MAMMADOV [2]

[1]Department of Physics, Gebze Technical University, Gebze, Kocaeli 41400, Turkey
[2]Institute of Physics Azerbaijan National Academy of Sciences, AZ-1143 Baku, Azerbaijan
[3] Department of Electrical and Electronics Engineering, Antalya Bilim University, Antalya, Turkey
**Corresponding author. Adress: Department of Physics, Gebze Technical University, Gebze, 41400, Kocaeli, Turkey. Tel.: +90 262 605 1329; fax: +90 262 653 8490*
E-mail address: smirhasan@gyte.edu.tr (M-H.Yu.Seyidov).

The influence of electric field and current flow on the current - voltage *(I – V)* characteristics of $TlGaSe_2$ layered semiconductor was investigated by using a two - point probe measurement system. Switching in *I – V* characteristics associated with memory effect was observed in all samples selected from different batches. Experimental findings were analyzed by using a model of metal – insulator – semiconductor – insulator – metal (MISIM) structure having memristive behavior.

Keywords: memristor; current – voltage characteristics; metal – insulator – semiconductor – insulator – metal structure; Lambert W – function.
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1. INTRODUCTION

Memristor is the fourth fundamental two - terminal passive circuit component in addition to resistor, capacitor and inductor. It first was postulated by Leon Chua in 1971 and proposed as the missing electronic component [1]. As the name suggests, memristor behaves similar to a conventional resistor, but it has a memory, in the sense that instantaneous resistance of memristor depends on its past values.

For several decades, different types of memristors have been developed as solid - state semiconductor devices, by using polymers, in plants, trees, fruits, biological tissues and so on. The semiconductor memrestive switching devices usually demonstrate rectifying type current - voltage characteristic. The underlying reason is that, the semiconductor forms a Schottky contact with one of the metallic electrodes and an ohmic contact with the other. In this configuration, reversible changes in *I - V* characteristics can be induced by applying a threshold electric field or bias current.

As it is well known, the switching can be unipolar or bipolar. In unipolar resistive switching, the switching direction depends only on the amplitude of the applied voltage or current, but not on the polarity, whereas in the case of bipolar resistive switching, an inversion of the polarity is required to switch back the *I - V* characteristics. In the sequel, we will focus only on the bipolar resistive switching, which is of special interest in an application perspective.

In experimental investigations, the memristive behavior is defined by specific *I – V* characteristics. Pinched hysteresis loop on the *I – V* characteristics in a shape of bow tie is considered as a distinctive property of memristive behavior. In this paper, we present diode - like *I - V* characteristics of Metal - $TlGaSe_2$ - Metal structure followed by switching effect registered by using a current controlled method, within the temperature range of 77 – 300 K. In order to control the polarity of the diode, we applied an electrical training process. This training process changes the polarization direction of Metal - $TlGaSe_2$ - Metal structure from forward to reverse, and hence switch the charge transport characteristics as well.

We will demonstrate that, the diode polarity rectification as well as sign of switching voltage depend on sweeping direction of the applied external current, i.e. from negative to positive values or vice versa. In other words, the resistance of the structure depends on the past states through which the system has evolved, which clearly suggests that the structure ***remembers*** the direction of current sweeping and demonstrates memristive behavior [1 - 4]. The investigated system is also characterized by the pinched hysteresis loops, which was observed in all samples worked with.

The memristive effect is due to the displacement of charge while applying a bias electric field. The strength of the electric field is proportional to the inverse square of the layer thickness within which the charges are mobile. Clearly, memristive effect is possible if the thickness of the active layer is in nanometer scale. In this paper, we demonstrate for the first time that memristive behavior is possible in bulk devices, which exhibit similar characteristics to their nanoscale counterparts.

The MISIM – memristor structures were built by using bulk $TlGaSe_2$ thin plates having two electrodes fabricated from different metals in planar and sandwich geometry of contacts. The accuracy of thin insulating layers on both surfaces of $TlGaSe_2$ samples is of key importance for this type of model. We also point out the existence of a nonzero imprinted electric field within the $TlGaSe_2$ sample following electrical poling, which is considered as a key factor for memristive behavior. Thin insulating layer near the surface of the semiconductor could be polarized under applied electric field due to migration of some charged entities such as ions in oxide materials, thus resulting in memristive behavior.

131 H.Javid ave, AZ-13, Baku
ANAS, G.M.Abdullayev Institute of Physics
E-mail: jophphysics@gmail.com

The effect of polarization on the overall structure will depend greatly on the resistance of the $TlGaSe_2$ sample, which can change substantially depending on temperature, thus changing the distribution of voltage drop between insulating film and semiconductor. At low temperatures, when the resistance of semiconductor is sufficiently high, > 10^8 Ω, the system will behave as an ohmic resistor with additional voltage superimposed on the applied one. At room temperatures ~ 300 K the resistivity of semiconductor decreases substantially to ~ 10^6 Ω, and almost all applied voltage drops on the insulating layer. This mechanism provides diode behavior with controllable direction of rectification to the system.

We have obtained an analytical expression for *I* - *V* curves using Lambert W - function. This expression has been fitted to experimental data in order to obtain parameters of the electrically modelled diode circuit with a current source and series resistance.

2. EXPERIMENTAL PROCEDURE

For the Metal - $TlGaSe_2$ - Metal structure fabrication, initially undoped $TlGaSe_2$ single crystals grown by the modified Bridgman - Stockberger technology were used. $TlGaSe_2$ samples were picked from different batches. Their electrical resistivity was measured in dark, and was found to be larger than $10^6\ \Omega \cdot cm$ at ~ 300 K.

Different pairs of *Au*, *In*, and *Cu* - metallic contacts were prepared by evaporation on both sides of the freshly cleaved surfaces of the samples and were used to measure the conductivity along both directions, namely, parallel and perpendicular to the plane of layers. The measurements were performed by using three different $TlGaSe_2$ bulk samples, all having thicknesses around ~ 500 μm. The distance between the electrodes which were used for measuring the current in the direction parallel to the layers was ~ 2 mm. Samples were labeled and referred below as *F*, *Y*, and *Kh*. For example, *F Au* - *In* parallel refers to $TlGaSe_2$ sample from *F* - technological batch with the *Au* and *In* contacts deposited onto the top surface of the sample.

Samples were mounted on a cold finger and placed inside a Janis closed cycle helium cryostat. A control sensor (diode DT - 470) and a resistive control heater were mounted under the base and used to control the temperature by using a Lake Shore - 340 auto tuning temperature controller. Temperature of the samples was controlled within ~ 0.1 K accuracy by using a digital PID temperature controller.

I - *V* measurements were performed on three various structures fabricated from different $TlGaSe_2$ samples. Different pair of metallic electrodes of ~ 1.5 mm in diameter and about 100 nm in thickness were deposited on top and bottom layers of samples by thermal evaporation through a metal shadow mask. Electrical parameters were measured by using a two - probe method and a Keithley - 4200 semiconductor characterization system. *I* - *V* characteristics were registered at two different temperatures (300 and 140 K) in vacuum. The voltage bias was defined as positive when positive potential was applied to the *Au* electrode while the other electrode was connected to ground.

3. RESULTS

Typical *I* - *V* curves of all fabricated structures in a linear scale are shown in Fig. 1 (a - f). To study the resistance behaviors, the voltage bias was swept from – 40 V to + 40 V in both directions (indicated in Fig. 1 by arrows) and applied to the fabricated devices both at 300 and 140 K. Fig. 1 highlights that the resistance switching memory phenomenon can be observed during performing one cycle current sweep at room temperature. A high resistance state at 300 K is well maintained (cf. Fig. 1 (d - f)) when the positive current is increasing and until it reaches the set value. If current exceeds the set value, it dramatically increases, which puts the device in a low resistance state. The low resistance state can also be achieved by reversing the polarity of sweeping current, as depicted in Fig. 1 (a - c). It is easy to clarify that a resistance switching effect with memory during current sweep is not the only discernible peculiarity in Metal - $TlGaSe_2$ - Metal structure.

As it is seen from Fig. 1 all *I* - *V* curves registered at low temperature (140 K) are quasi - ohmic and highly asymmetric during forward and reverse biases at high temperature (300 K). Rectifying type current - voltage characteristics at room temperature was also observed for all samples independent of contacts and direction of current flow. As already mentioned above, the forward bias is defined as a positive ***dc*** voltage applied to the *Au* – electrode.

As illustrated in Fig. 1 (a - c), the *I* - *V* characteristics of fabricated structures registered at 300 K by sweeping current from positive to negative (as illustrated in Fig. 1 (a - c) by red arrows) demonstrate the rectifying behavior and resistance switching in the reverse bias region. Similarly, diode characteristics were observed by applying current from negative to positive with opposite rectification direction. In this case, resistance switching appears in the forward bias region, as shown in Fig.1 (d - f).

Another important effect was observed in the semi - logarithmic current – voltage curves shown in Fig. 1. Fig. 2 (a - b) demonstrates similar graphs, registered at different temperatures for *F Au* - *In* parallel $TlGaSe_2$ sample. Besides, the effects described above, which are correlated with the residual voltage, are clearly identified, especially at lower temperatures. The value and sign of this residual voltage as well as its temperature dependence can be clearly traced by the position of a “beak” corresponding to the voltage where current changes its sign. The sign of this voltage correlates with the sign of rectification, and temperature dependence of a “beak” shown in Fig. 2 (c) resembles the temperature dependence of conductivity of $TlGaSe_2$ crystals including non - monotonous behavior at low temperature range T < 160 K [5].

Described results clearly suggest that fabricated devices remember the direction of current sweeping or in other words the past states through which the system has evolved. Such behavior is characteristics of memristive systems [1].

It is well known that pinched hysteresis loop is a fingerprint of memristive behavior. Such behavior is demonstrated in Fig. 3 (a - c) for three different samples hiving different contacts, and in different directions of current flow parallel and perpendicular to the plane of layers. As it is seen from Fig. 3, starting, say, from 30 V and going towards 0 V a relatively high current is observed (ON - state); however, situation changes drastically if the polarity of the applied voltage is changed: resistance substantially increases (OFF - sate) and then sample switches into the ON - state again. Returning back from the ON – state, current demonstrates the similar behavior: now the OFF - state as well as subsequent switching is observed at positive voltages. Thus, the loop locks.

4. DISCUSSION

The following questions arise after the findings described above: a) why I - V characteristic is ohmic at low temperatures and diode type at higher temperatures?; b) what is the mechanism of rectification in these $TlGaSe_2$ devices?; c) why the direction of rectification depends on the direction of current sweep?; d) what is the nature of residual voltage observed during current sweep?; e) what is the physical mechanism of switching in $TlGaSe_2$ crystals?

We start our discussion from the questions a) and b), that is, from the different character of I - V characteristic at low (140 K) and high (300 K) temperatures. In order to find answers to these questions, one must explain the nearly ohmic behavior at low temperature and diode type behavior at high temperature. Below we will show that different types of I - V characteristics at low and high temperature can be explained based on the diode model having a high series resistance. The current - voltage characteristics of fabricated structures is modelled by using the Lambert W – function [7].

In brief, the Lambert W - function, $W(x)$, is defined as the solution to the following transcendental equation: $yexp(y) = x$ [7]. In this investigation, we present for the first time an analytical solution for $TlGaSe_2$ - diode circuit model, which is based on the Lambert W – function. According to this model, I - V characteristic of fabricated devices can be described by following equation:

$$I = (qI_0R_s/kT) \cdot W\left[(qI_0R_s/kT) \cdot exp\left(q(V + I_0R_s)\right)/kT\right], \quad (1)$$

where k, q, and T are the Boltzmann constant, electron's charge and temperature, respectively. R_s is the series resistance, V – is voltage and I_0 – is the diode reverse current. Taking I_0 and R_s as fitting parameters, I - V dependences of fabricate devices were calculated. Results are shown in Fig. 4 (b). Calculations give the ohmic behavior at 140 K and rectified diode - type behavior at 300 K.

The physical explanation of this effect is rather simple. The $TlGaSe_2$ crystal is considered as a semiconductor material with presence of thin or ultrathin insulated layers at the semiconductor - metal interfaces. As a rule, the value of active resistance of the semiconductor is always in series with the electrical resistance of the metal - semiconductor contacts. Semiconductor electrical resistance can significantly change under certain circumstances, such as temperature, external pressure or radiation absorption.

At low temperatures, when series resistance is very high, $>10^8\ \Omega$, approximately all voltage drops on the series resistance, which leads to an ohmic characteristic. At higher temperatures, when series resistance decreases by two order of magnitude, approximately all voltage drops on the barrier at the semiconductor - metal interfaces and diode type I - V characteristic is registered.

Apparently, the role of series resistance in Metal - $TlGaSe_2$ - Metal structure plays $TlGaSe_2$ semiconductor crystal. What is the mechanism of diode - type rectification of this device? To some extent, it is really a ***strange*** diode, as its rectification direction depends on the polarity of the applied voltage, independent of the contact materials.

For example, considering ***p*** - type conductivity of $TlGaSe_2$, upon starting an I - V measurement, if negative voltage is applied to the *Au* contact, this contact acts as a blocking contact. On the other hand, if positive voltage is applied to the same contact upon starting I - V measurement, it acts as an ohmic contact, (see Figs. 1 and 2). Therefore, one can use an electrical training process to control the polarity of this diode. This further suggests that, by changing the polarization direction of the external bias, one can switch the transport characteristics between forward and reverse diodes.

The blocking character of metal – ***p*** - semiconductor junction means that due to electron interchange between the metal and semiconductor, depletion region occurs near the metal semiconductor boundary with the electrical field directed from metal towards semiconductor. Thus, another contact must acts as an ohmic contact. It was shown in a number of our recent studies [9 - 11] that, the voltage applied to the metallic contact creates an intrinsic electric field near the surface of $TlGaSe_2$ samples. The direction of this field depends on the polarity of applied voltage, where it always opposes to the direction of applied electric field. In other words, independent of the contact material, it may acts as a blocking or ohmic contact. In order to explain such effect, we proposed the model of native thin insulating layer on the surface of $TlGaSe_2$ crystal [11]. The electric field created near the contact is due to polarization of the native insulating layer on the surface of the crystal. Independent of the mechanism of such polarization, we may conclude that considering the current flow in $TlGaSe_2$ semiconductor one must take into account that in a ***p*** – semiconductor, both holes and some charged entities are forced to move simultaneously while an external voltage is applied to the system. This ıs similar to the discussion in [2], which describes the first realization of memristive behavior in Pt - TiO_2 - Pt system.

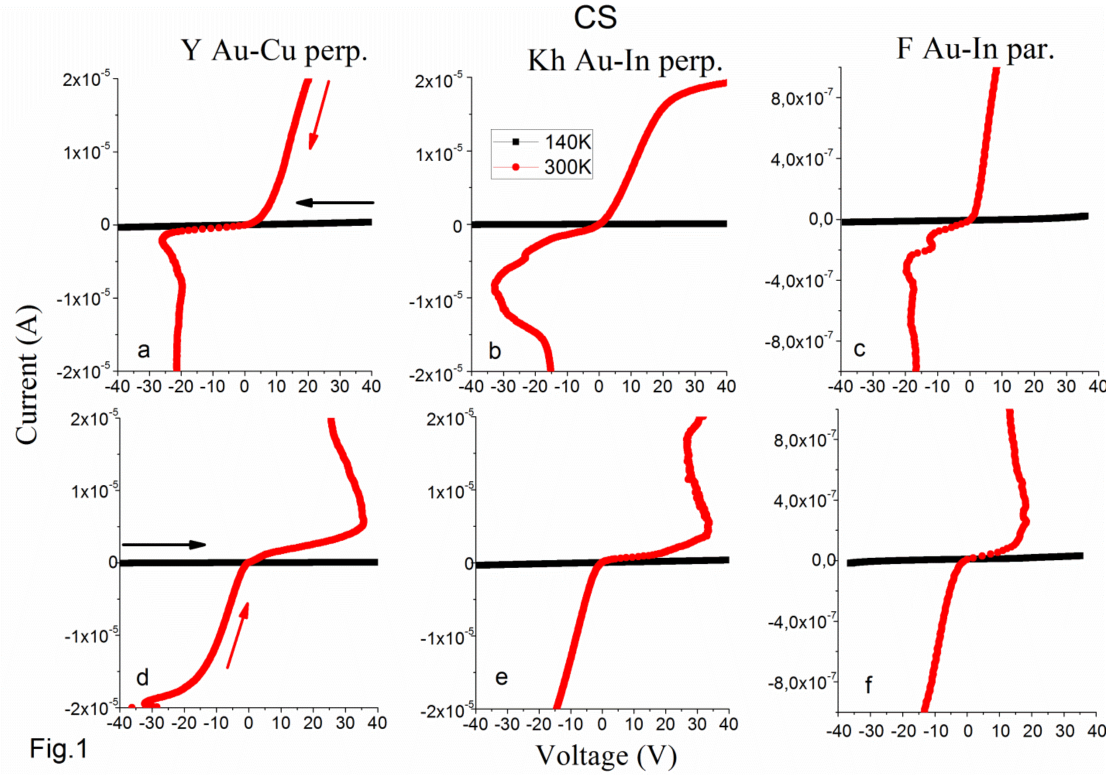

Fig. 1. I - V characteristics of different $TlGaSe_2$ samples measured by current sweep method in linear scale at two different temperatures; 140 and 300 K. Arrows indicate the direction of sweep.

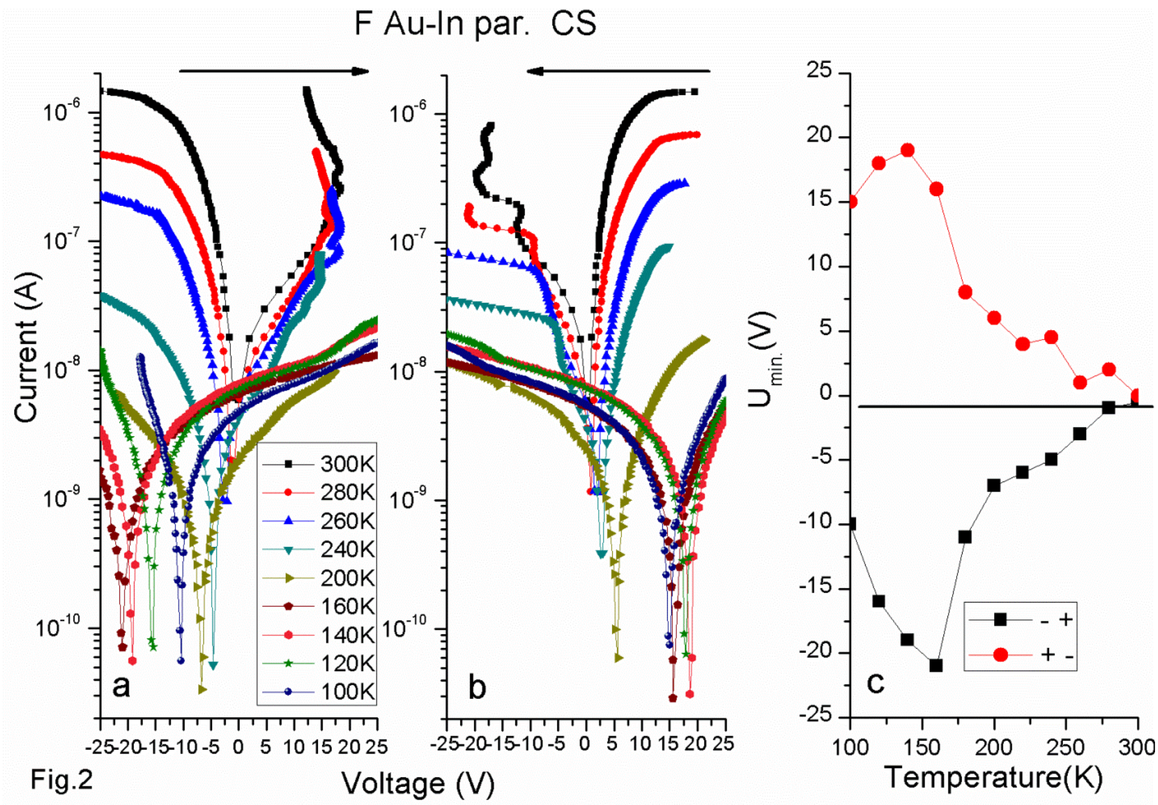

Fig. 2. a) and b) *I - V* characteristics of *F* – type $TlGaSe_2$ sample with *Au - In* metallic electrodes deposited on the top surface of crystal parallel to the layers. The measurements were carry out in current sweep method. *I - V* characteristics are displayed in logarithmic scale and corresponded to different temperatures. Arrows indicate the direction of sweep; c) The temperature dependences of "beak" position in Fig. 2 (a and b) for different direction of sweep.

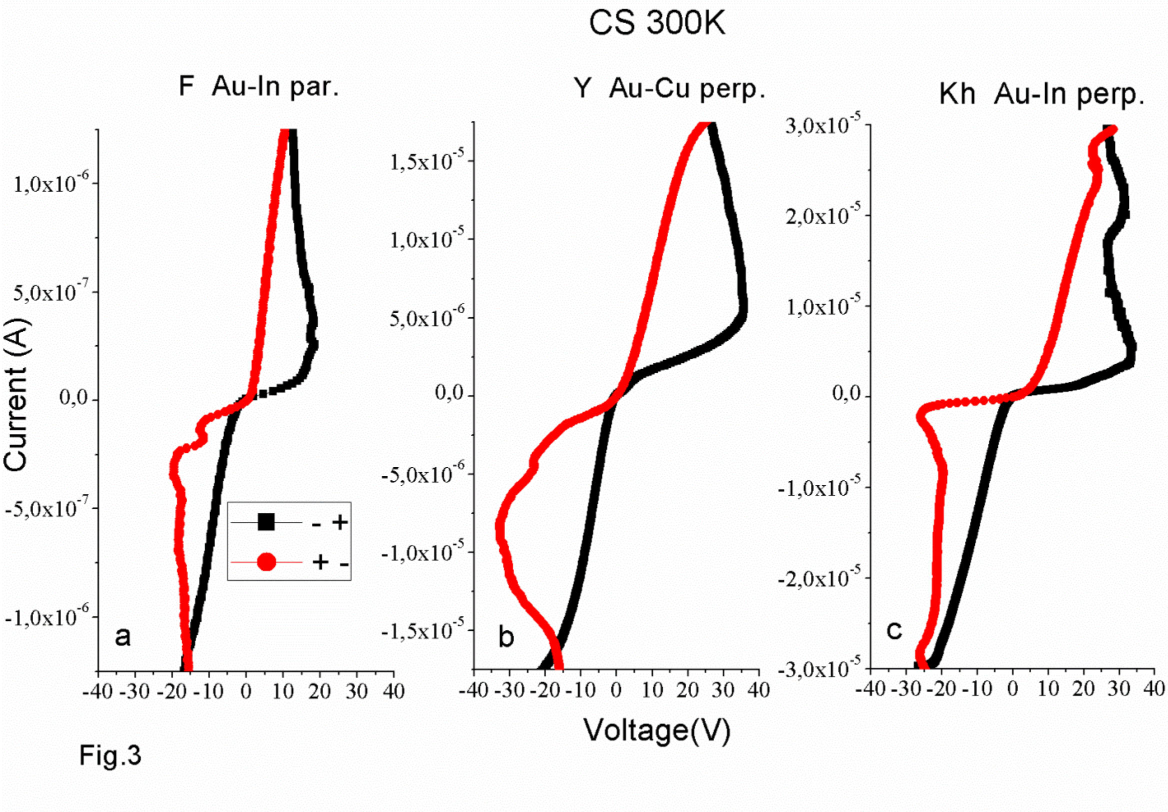

Fig. 3. The Pinched hysteresis loops registered for three different $TlGaSe_2$ samples by current sweep method at 300 K.

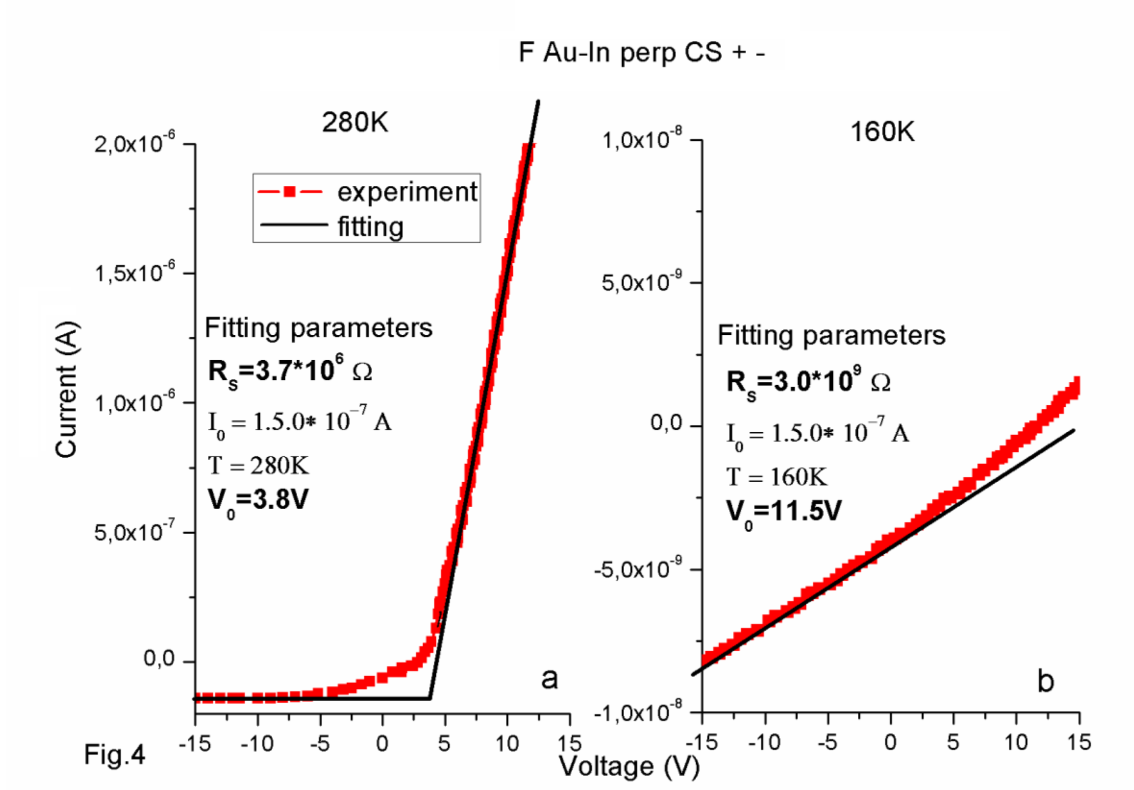

Fig.4. a) Experimental *I - V* characteristics of *Kh* - type $TlGaSe_2$ sample with *Au - In* metallic electrodes deposited on the top and bottom surfaces of crystal perpendicular to the layers. The measurements were carry out in current sweep method. *I - V* characteristics are displayed in linear scale at two different temperatures; 140 and 300 K. Sweep direction is from negative to positive values; b) – Results of fitting based on the diode model with series resistance. Calculations were made using formula (1). Fitting parameters are shown in figure.

Unlike our situation, it was established in [2,3] that charged entities mentioned above are charged oxygen vacancies which act above all as dopants. Moreover, it was shown in [11] that Pt - TiO_2 - Pt system behaves as a

Currently, we cannot claim whether or not the mechanism of charged ions migration within the electric field that is known in oxides [12 - 15] is applicable to native thin insulating layer proposed on the surface of $TlGaSe_2$ crystal. However, we can definitely state that, the observed memristive behavior in Metal - $TlGaSe_2$ - Metal structure is related with the migration of some mobile charged entities under the applied electric field. Such a model, which takes the memristive behavior of the investigated structure into account, makes the switching

5. CONCLUSIONS

In summary, we proposed the following model for the Metal - $TlGaSe_2$ - Metal structure: native thin insulating layer exists near the semiconductor surface, which can be polarized by applying an external electric field, due to migration of some charged entities such as ions in oxide materials. This layer provides the memristive behavior to this structure. The effect of such polarization on the overall structure will depend greatly on the resistance of the sample which can change

rectifier with controllable direction of rectification due to the electrical control of the chemical states in TiO_2-x such as the oxygen vacancy concentration at the interfaces between the TiO_2-x layer and Pt - electrodes.

phenomena quite understandable as well. As it is outlined in Chua's work [16]: all two - terminal non - volatile memory devices based on resistance switching are memristors, regardless of the device material and mechanism of operation. Apparently, the opposite proposition has also become true, because in the last decade, significant progresses has been made in understanding the resistive switching mechanisms based on the memristive type behavior independent of exact memory mechanism [17].

substantially with respect to temperature; thus changing the distribution of voltage drop between insulating film and semiconductor. At lower temperatures, when the resistance of semiconductor is sufficiently high, $> 10^8\ \Omega$, the system will acts as an ohmic resistor with additional voltage superimposed on the applied one, (see Fig.2). At higher temperatures close to 300 K the resistivity of semiconductor decreases substantially, $10^6\ \Omega$, and almost all applied voltage drops on the insulating layer thus providing diode behavior to the system with controllable direction of rectification.

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