Interpretation of Switching Properties of $InGaSe_2$ Single Crystal

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(Received May 12, 2011; in final form July 31, 2011)

The goal of this paper is to present experimental results of the switching effect and analyze qualitatively the influence of various factors, such as temperature, light illumination and sample thickness on switching behavior of the high quality ternary chalcogenide semiconductor $InGaSe_2$. Current-controlled negative resistance of $InGaSe_2$ single crystals has been observed for the first time. It has been found that indium gallium diselenide single crystals exhibit bistable or memory switching. The switching process takes place with both polarities on the crystal and has symmetric shapes. Current–voltage characteristics of Ag–$InGaSe_2$–Ag structures exhibit two distinct regions, high resistance OFF state and low-resistance ON state having negative differential resistance. $InGaSe_2$ is a ternary semiconductor exhibiting S-type I–V characteristics. The specimen under test showed threshold switching with critical field of the switching being 10^3 V/cm at room temperature.

PACS: 78.20.–e, 78.66.–w, 73.61.Ga, 74.25.Gz

1. Introduction

The switching effect was observed for the first time in amorphous chalcogenide material by Pearson et al. [1] and by Ovshinsky [2, 3]. This discovery caused quite a stir in the international scientific field and induced many researchers to study these phenomena. In recent years, it has been observed that the switching effect is not only characteristic of these amorphous materials but is present also in many crystalline materials like InTe, GaSe and Ga_2Te_3 from the $A^{III}B^{VI}$ binary semiconductor compounds [4–6]. It is also present in a large part of the ternary chalcogenide semiconductor compounds, such as $TlGaTe_2$ [7, 8], $TlInSe_2$ [9], and $TlInTe_2$ [10]. For many years, the properties of layered crystals have constituted a major research area in solid state physics.

Our investigated material $InGaSe_2$ was found to be a promising material among ternary semiconducting chalcogenides because of its relative low threshold voltage. Consequently our investigated material $InGaSe_2$ can be used as switching devices, memories storages and photovoltaic devices. $InGaSe_2$ is a layered compound and the interest in this material is stimulated not only by its fundamental properties but also by possible practical applications [11]. In addition, its quasi-two-dimensional, structural anisotropy, as well as its peculiar optical and photoconductive properties have attracted investigators in an effort to acquire a better insight in the physics of these compounds.

The $A^{III}B^{III}C_2^{VI}$ chalcogenide semiconductors belong to the $A^{III}B^{VI}$ type layered structure semiconductors [12]. Although the ternary semiconducting chalcogenides have been investigated extensively in recent years, very few investigations have been performed on $InGaSe_2$. The crystal structure of this compound is reported [13], some information about the electrical and optical properties was investigated [14], and also the electrical and thermoelectric power was published [11]. This material just like other ternary semiconductor compounds could have many possible applications ranging from use in solar cells to nonlinear effect such as S-type characteristics with voltage oscillations in the negative resistance region and switching and memory effects.

Negative differential resistance (NDR) and electrical switching effects attracted the interest of many researchers. This is due to possible technological applications, such as switching and memory devices, oscillators' thermistors, etc. In view of the absence of published observations of these phenomena in this compound and also in view of recent interest in this group of compounds, the author undertook such work and reports here his investigation of switching effect and some factors affecting it. A lot of work has been done to establish the mechanism of switching process, but at present there still exists some uncertainty about the actual physical content of these theories. Since then, the characterization and utilization of this negative-resistance behavior has received considerable attention. These investigations are essential for the understanding of the materials and consequently open up also new possibilities of practical applications.

2. Experimental details

2.1. Apparatus and method of crystal growth

In the present research we used techniques based on the Bridgman method. The requirement was that the freezing isotherm should move systematically through

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the molten charge. Generally, in the Bridgman technique, this can be satisfied by moving the crucible (TSM) or the furnace itself (THM) or by changing the furnace temperature. Among these probabilities we selected the case of changing the furnace temperature. This selection was done to avoid difficulties produced from the movement of the crucible or that expected in the case of the furnace movement. Changing the furnace temperature needs much efforts and manpower to do this. But in order to overcome this problem, we used digital programmable muffle furnace to control and change the temperature accurately. With the aid of the facilities available in the furnace a program of three stages can be done. $InGaSe_2$ crystals were prepared by direct melting of the initial elements taken in the stoichiometric ratio and introduced in sealed quartz ampoules under vacuum of 10^{-5} Torr. The silica tube has a trapped tip at the bottom to facilitate seeding in the growth process. The quartz capsules were cleaned using first a mixture of HF and distilled water (1:2 by volume) and then pure ethanol and hot distilled water. The ampoule is coated internally with a thin layer of the pyrocarbon to prevent the produced ingot from adhesion with silica tube.

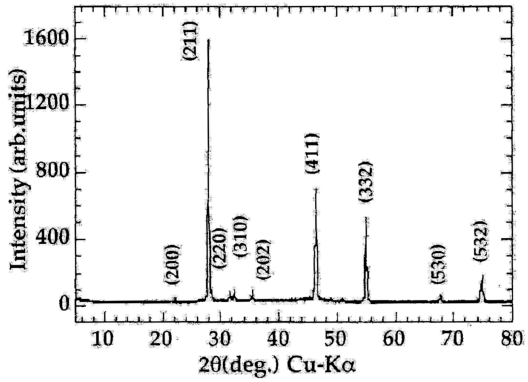

Fig. 1. X-rays powder diffraction chart for $InGaSe_2$.

The ampoule with its charge was introduced in the furnace where the following programs were used:

1. The first program began from the set point 373 K to 1223 K with a rate of 25 K/h. Then the temperature was held constant for 10 h to give a chance to the reaction to begin.

2. The second one was from 1223 K to 938 K, where the last temperature represents the crystallization temperature [13] via rate of 5 K/h. Then the temperature was kept constant for 24 h to ensure crystallization.

3. The third program was suggested for solidification, i.e. cooling the melt slowly down to room temperature. The total time for crystallization program was 80 h. The obtained chart and results indicate that the product is single phase with tetragonal structure ($\alpha = \beta = \gamma = 90°$) and its lattice constant is $a = 8.003$ Å and $c = 6.538$ Å as shown in Fig. 1. Our X-rays powder diffraction (XRD) data have shown a good agreement with standard international center for powder diffraction data JCPDS No. 77-1921. X-ray pattern proves that there is no any other phase except $InGaSe_2$. After the end of the crystallization program the product ingot has a cylindrical form inside the silica ampoule. We must doff the ingot from its container. Differential thermal analyses (DTA) were performed to assure the presence of the crystalline phase in the prepared ingot as obtained from XRD and there is no other phase except $InGaSe_2$.

2.2. Instrumentation for switching investigation

All samples used in this work were freshly cleaved from the grown ingot, in the same ampoule and no further polishing treatments were required, because of the natural mirror-like cleavage faces. They were rectangularly shaped with parallel faces. A dc current source was connected to the ends of the rectangularly shaped samples, so that the current flow is perpendicular to the crystallographic c-axis. Steady-state measurements were made with a series resistor of value 0–100 kΩ, depending on the original resistance of the sample. Contact was made to the opposite faces of the crystal by means of silver paste. The gap between the electrodes is equal to the thickness of the crystal. A pointed contact holder was used in the measurements of the switching phenomena. The I–V characteristics were measured, using a simple circuit containing a dc power supply, current meter and series load resistance. The applied voltage can be increased steadily up to the point where the crystal switched, after which the series resistor limited the applied voltage for preventing crystal destruction. We studied M–$InGaSe_2$–M structure in sandwich form. The resistivity of a virgin $InGaSe_2$ was of the order of 1.8 MΩ. Measurements above room temperature were done by placing the sample holder in a thermally controlled furnace (±1 K). Measurements below room temperature were done using liquid nitrogen. All measurements were carried out under vacuum. The environment temperature of the specimen under test was measured by means of calibrated spot-welded chromel–alumel thermocouple junction and was as small as possible to active high response to the measured temperature. The junction was located very near to the specimen to active real measurements of the environment temperature. The investigation was carried out in the temperature range 173–353 K, in order to show the influence of ambient temperature on switching behavior. White light was focused on the sample surface for studying the effect of light intensity on the switching behavior. In order to investigate the effect of light intensity on the switching phenomena at 300 K, samples with appropriate thickness were mounted in a cryostat equipped with suitable windows and clamped in its holder provided with apertures to allow the passage of the radiation. The intensity

of the radiation was measured with a luxmeter from 20 to 1200 lx. Sample with thickness varying from 0.15 to 0.375 cm were used to investigate the influence of the sample thickness on the switching characteristics. Details of the experimental procedures and apparatus were published earlier [14].

3. Results and discussion

The general behavior of the current–voltage characteristics obtained with dc supplies for virgin sample of $InGaSe_2$ single crystals has the characteristic shape as given schematically in Fig. 2. It is symmetric with respect to the polarity and consists of a low conductivity branch in which the conductivity is relatively low nearly field independent and a high conducting branch or switching, in which the current follows essentially the load line. In this last branch the current increases with a marked decrease in the voltage across the specimen giving the negative resistance region. Moreover, we observe for the same branch that the specimen becomes in the low resistance or memory state. The memory state persists if the current is decreased slowly to its zero value. However, if the current was forced to decay suddenly, the specimen returns to the high resistance state.

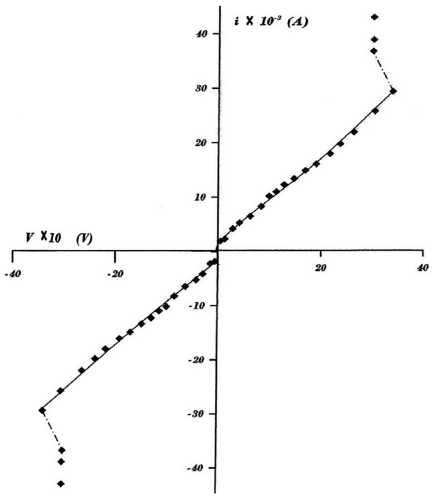

Fig. 2. Symmetrical CVC of $GaInSe_2$ relative to the polarity.

The specimen under test showed threshold switching with critical field of the switching being 1.435×10^3 V/cm at room temperature. We observe in $GaInSe_2$ crystals, a current controlled negative resistance (CCNR) process that occurs in filaments, so that when the crystal goes into negative resistance, currents of the order of a few mA are collected in a small zone of the crystal, this zone has the diameter of a few μm. This can be observed by the optical microscope after the memory effect has been obtained in the sample. This can give place to a high Joule effect which causes drastic transformations in the material. At present, we do not have information about

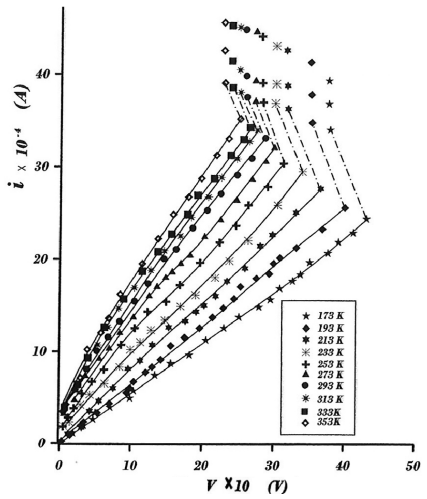

Fig. 3. Current–voltage characteristics at different values of temperature for $GaInSe_2$ single crystal.

these changes, but our idea is that in these compounds, the memory-switching effect takes place by two processes following each other in time — an electric process which can give place to the negative resistance (Lambert's effect) and a Joule effect in localized zone which gives place to the memory effect.

Figure 3 represents the current–voltage characteristics (CVC) of the investigated sample at different temperatures extending from 173 K to 353 K. It is shown that temperature has a significant effect on the I–V behavior. The part of the I–V curves exhibiting the negative slope is usually called the NDR. The ohmic and NDR regions are apparent in these curves. The width of the NDR region, slope, threshold voltage, and threshold current values ($V_{\rm th}$ and $I_{\rm th}$) are the main characteristic features of this region. If we are decided about the mechanism governing the NDR regions, we have to study the temperature distribution along this part of the I–V curve; i.e. we have to look for a change in the sample temperature T at every measured point of this region. Generally, two processes of quite different origin and character may govern the phenomenon: pure electronic or electrothermic processes. In electronic processes the high conductivity state connected with the appearance of the NDR region is due to an increase in the non-equilibrium majority carriers *and/or* to an increase in their mobility. This can be attributed to different mechanisms, such as the Crunn effect, tunneling effect, carriers' injection, etc. Generally speaking, electronic processes are not connected directly with an increase in the sample temperature T in the NDR region. In electrothermal processes it is assumed that small local deviations from the homogeneous distribution of the imperfections lead to a higher current density in these regions. Such elevated current densities are usually accompanied by the formation of high-current density filaments in the sample. Anyhow, according to the electrothermal model, it is assumed that a high current

density filament exists in the sample. In this "channel" the elevated current density results in increased power dissipation, leading to a Joule heating. The steady state of this feed path is reached when the heat dissipation is equal to heat losses. Many mechanisms can be considered responsible for the onset of electrothermal processes. Impact ionization seems to be the most significant. The effect of ambient temperature on the switching parameter ($V_{\rm th}$) and ($I_{\rm th}$) of $InGaSe_2$ is shown in Fig. 4.

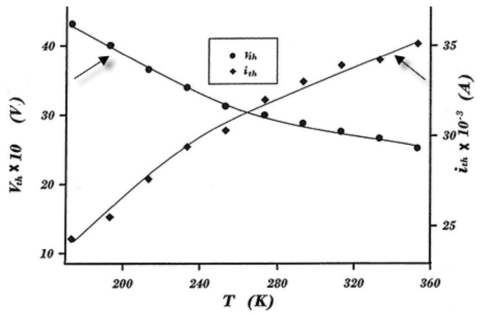

Fig. 4. Ambient temperature effect on threshold current and voltage for $GaInSe_2$ single crystal.

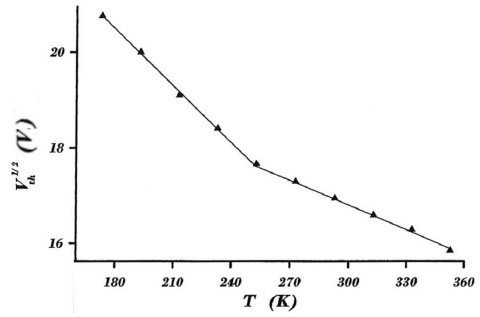

Fig. 5. Temperature dependence of $V_{\rm th}^{1/2}$ for $GaInSe_2$ single crystal.

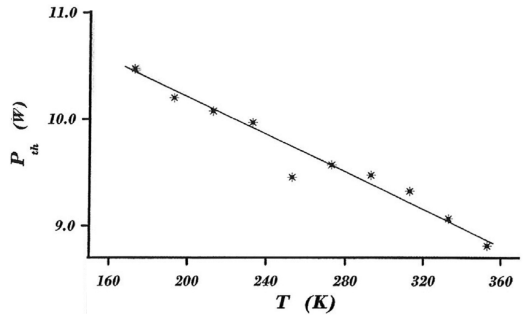

Fig. 6. Relation between $P_{\rm th}$ and temperature for $GaInSe_2$ sample.

We observe from this relation that while $I_{\rm th}$ increases continuously with increasing the ambient temperature, continuous decrease in $V_{\rm th}$ can be observed. Both relations are not linear. The dependence of $V_{\rm th}^{1/2}$ on T is plotted in Fig. 5 on the basis of the thermal field. This figure obeys the following relation [15]:

$$V_{\rm th}^{1/2} = \left(\frac{\pi\varepsilon_0\varepsilon_\infty d}{e}\right)^{1/2}(\phi - cT)\,, \qquad (1)$$

Where ε_0 is the permittivity of vacuum, ε_∞ is the electron component of permittivity, d is the distance between the electrodes, c is a constant, e is the electron charge, ϕ is the depth of the potential well and T is the absolute temperature. This shows that the switching in Ag–$InGaSe_2$–Ag structures from high to a low resistivity state occurs under the simultaneous action of a field and temperature [16, 17]. This must be supported by the dependence of threshold field on the thickness of the active region. The power necessary to change the material from the high-resistance state to the low-resistance state is called threshold power ($P_{\rm th}$). Calculation showed that the magnitude of $P_{\rm th}$ sharply decreases with temperature increase with a linear relation. The threshold power depends as seen from the figure on the ambient temperature. So this result is quite logical, since the power necessary for initiate switching decreases with temperature increase as shown in Fig. 6. The effect of surrounding temperature on the sample resistance ratio was also determined. The OFF and ON state resistance ratio ($R_{\rm OFF}/R_{\rm ON}$) depends on temperature which decreases as temperature increase as seen in Fig. 7.

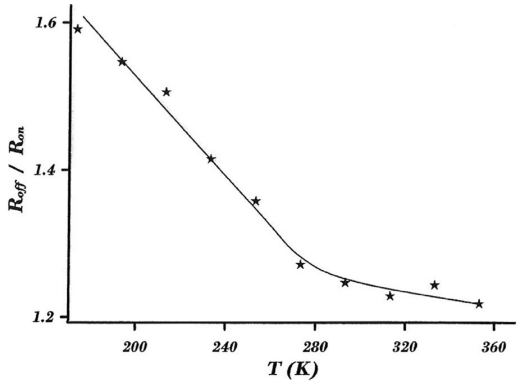

Fig. 7. Effect of surrounding temperature on the sample resistance ratio ($R_{\rm OFF}/R_{\rm ON}$) of $GaInSe_2$.

The effect of light intensity on the CVC is represented in Fig. 8 which shows the I–V characteristics of $InGaSe_2$ at room temperature at different values of illumination doses. As observed from the curve in the figure the behavior of the CVC has the general form of switching with S-shape. It is evident from this figure that the I–V characteristic as a whole are shifted toward lower potentials with an increase in the intensity of the incident light. This means that in case of weak illumination, the threshold voltage is larger and the threshold current value is smaller than the value obtained in case of intense light. Consequently the threshold voltage $V_{\rm th}$ decreases linearly

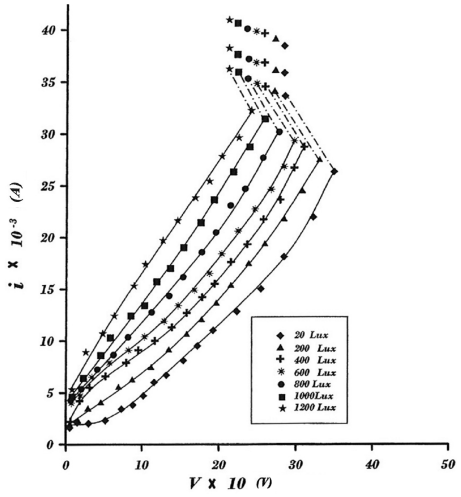

Fig. 8. The effect of light intensity on I–V characteristics of $GaInSe_2$ specimen.

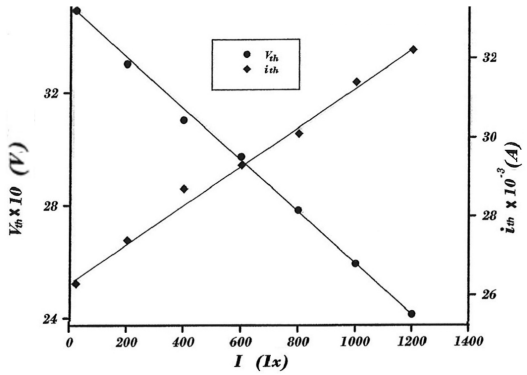

Fig. 9. Dependence of I_{th} and V_{th} on light illumination for $GaInSe_2$ compound.

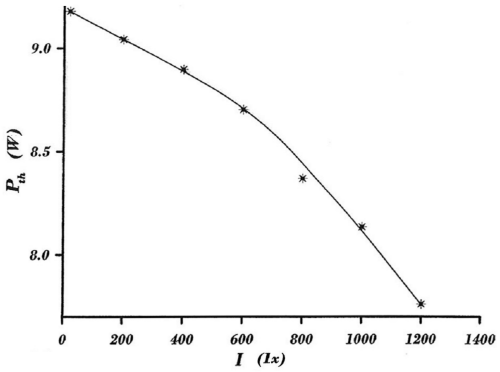

Fig. 10. Effect of light intensity on threshold power P_{th} for $GaInSe_2$ compound.

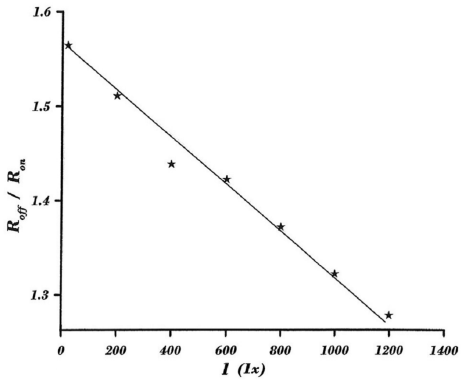

Fig. 11. Relation between R_{OFF}/R_{ON} of $GaInSe_2$ on light intensity.

with increasing the light intensity, while the threshold current I_{th} increases also linearly with the increasing of light illumination as shown in Fig. 9.

The relation between threshold power P_{th} with light intensity is presented graphically in Fig. 10. As we notice, P_{th} decreases linearly with increasing of light intensity. This may be due to photogeneration processes which take place under illumination of the sample and lead to low power for switching as the intensity dose increases. The dependence of the resistance ratio (R_{OFF}/R_{ON}) on the illumination intensity was also determined. This ratio decreases linearly as the light intensity increases as shown in Fig. 11. To show the real effect of sample thickness on the I–V characteristics we plotted Fig. 12, where the sample thickness varied in the range from 0.15 to 0.375 cm, and the width of the dashed lines which represent the variation from OFF to ON state decreases with thickness. This result indicates that the switching can be easily controlled with sample thickness. It is also observed from the curves that the holding voltage (V_h) decreases with increasing sample thickness, while holding current (I_h) increases with increasing sample thickness. Investigation of the effect of the sample thickness on switching phenomena is useful for a chosen specimen whose resistance is changed from high value (OFF state) to a very low value (ON state) by lowest switching power.

Figure 13 shows the effect of sample thickness on switching phenomena of P-type $InGaSe_2$ at room temperature. The curves indicates that the threshold potential and current changes with the thickness of the active region. It is clear from the curves in Fig. 13 that the threshold voltage decreases rapidly and linearly with increasing sample thickness, while the threshold current increases exponentially with sample thickness.

Figure 14 shows the dependence of the threshold field on the thickness of the sample. It is clear that E_{th} decreases with sample thickness. This indicates that the electric field has a profound influence on the ability of the samples to undergo transits from the OFF state to an effective region of negative differential resistivity. The variation of the threshold power P_{th} with sample thickness was plotted in Fig. 15. It is seen that the power required for switching decreases as the thickness of the $InGaSe_2$ crystal increases. This result indicates that the switching

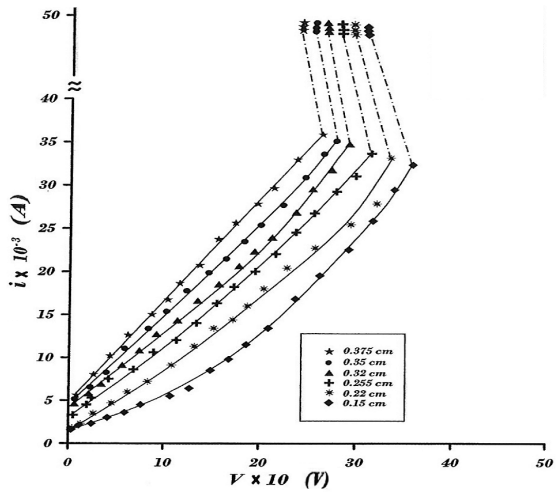

Fig. 12. Effect of the specimen thickness on switching phenomena for $GaInSe_2$ single crystal compound.

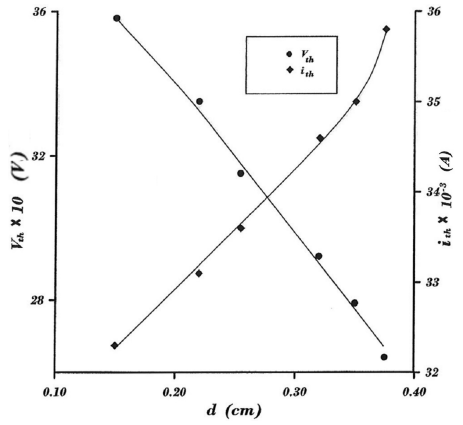

Fig. 13. Variation of $V_{\rm th}$ and $I_{\rm th}$ with $GaInSe_2$ compound as the sample thickness.

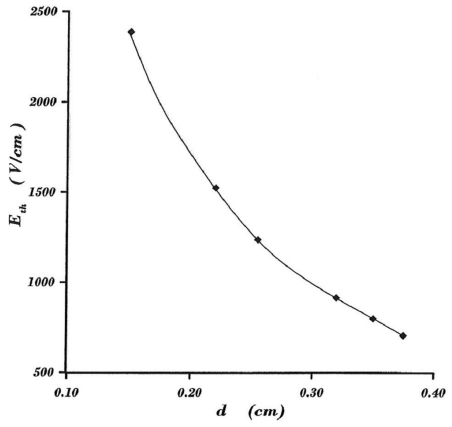

Fig. 14. The dependence of the threshold field $E_{\rm th}$ on the thickness of $GaInSe_2$ compound.

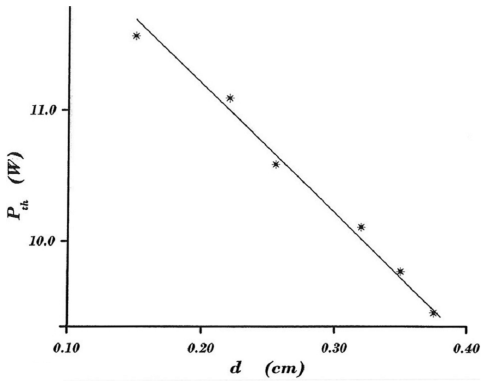

Fig. 15. Variation of threshold power $P_{\rm th}$ with sample thickness of $GaInSe_2$ single crystal compound.

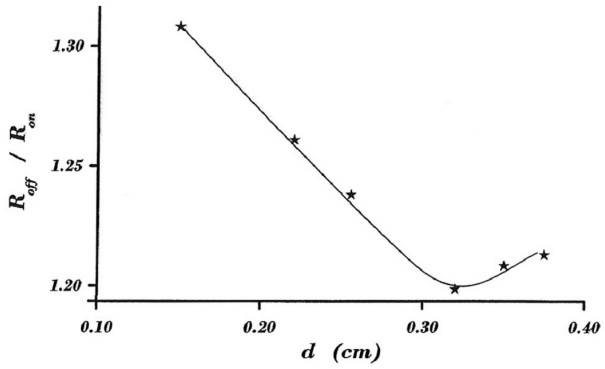

Fig. 16. Effect of sample thickness of $GaInSe_2$ compound on the ratio $R_{\rm OFF}/R_{\rm ON}$.

can be easily controlled with specimen thickness. The ratio between OFF and ON state resistivity decreases rapidly with thickness and reaches a very low value at higher thickness; this behavior is plotted in Fig. 16.

4. Conclusions

The major features for the switching in $InGaSe_2$ single crystal can be summarized as follows:

- From the I–V characteristic we can see that the process takes place with both polarities on the crystal and has symmetrical shape.
- When the applied voltage exceeds threshold voltage, the unit switches along the load line to the conducting state.
- The specimen under test shows threshold switching with critical field of the switching being 1.435×10^3 V/cm at room temperature.
- The I–V characteristic in the OFF state shows a region in which the current varies linearly with the applied voltage. Finally the current increases

strongly with voltage up to a point where the crystal switches to the ON state and a sudden current enhancement is observed.

- The memory switching effect in such crystals is an effect which appears after the negative resistance process. In case when the sample is brought into negative resistance, if we use in the circuit a very low resistance so that the rate between the threshold voltage and the series resistance is higher than a certain current value $I_{\rm th}$ the crystal goes into conduction state and there it remains even if it is taken away from the circuit.
- The memory state persists if the current is decreased slowly to its zero value, however, if current was forced to decay suddenly, the specimen returns to the high resistance state.
- The switching behavior as well as switching parameter ($I_{\rm th}, V_{\rm th}, P_{\rm th}$ and $R_{\rm OFF}/R_{\rm ON}$) are sensitive to the temperature, light intensity and sample thickness.

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