Growth and memory switching effect in the quaternary thallium chalcogenide Tl₂GaInTe₄ semiconductor compound

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Abstract

High quality single crystal of the quaternary thallium chalcogenide Tl₂GaInTe₄ compound were grown by a modified Bridgman technique. 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 chalcogenide semiconductor Tl₂GaInTe₄. Current-controlled negative resistance of Tl₂GaInTe₄ has been observed for the first time. It has been found that Tl₂GaInTe₄ single crystal 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-Tl₂GaInTe₄-Ag structures exhibit two distinct region, high resistance OFF state and low resistance ON state having negative differential resistance. Tl₂GaInTe₄ is а quaternary semiconductor exhibiting S-type I-V characteristic. The specimen under test showed threshold switching with critical field of switching 116 V/Cm at 213K.

Keywords: quaternary chalcogenide, Tl₂GaInTe₄, switching, memory, NDR region, S-shape.

1- Introduction

In the past three decades, significant interest in chalcogenide semiconductors has been shown by various workers owing to their interesting physical properties as well as their wide technological applications.⁽¹⁾ The ternary semiconducting chactcogenides with the

formula TIBX₂ where B=Ga or In and X= S, Se or Te belong to the III-III-VI₂ family and have a low – dimensional layered or chain structure.^(2,3)TIGaTe₂ and TIInTe₂ have received a great deal of attention due to their optical and electrical properties in view of the possible optoelectronic device application.^(4,5)

Quaternary thallium chalcogenide $Tl_2GaInTe_4$ is formed from $TlGaTe_2$ - $TlInTe_2$ system having the ratio 1-1. The quaternary $Tl_2GaInTe_4$ crystal belongs to the new group of chain structure, has a band gap of 0.88 eV.

Electrical threshold switching and memory in semiconductor have a roused great interest in recent years. Among the materials in which these effects takes place there are chalcogenides. Some of the ternary and quaternary compounds are known to have nonlinear current- voltage (I-V) characteristics and switch from the high resistance ⁽⁽OFF⁾⁾ state for lower applied voltages, to the low resistance ⁽⁽ON⁾⁾ state for higher voltages.^(6,7) Therefore some of these compounds can be used as micro switches in electronic circuits to switch current passing through the circuit ((ON)) or ((OFF)) at the points of the circuit where they are incorporated. It is well known that the negative differential resistance (NDR) device can be used in many applications⁽⁸⁾, to create extremely fast and compact circuits. Hence researchers are trying to discover new materials and compounds which can be used for operation as bistable devices. The quaternary thallium chalcogenide $Tl_2GaInTe_4$ belong to the new group semiconductor exhibiting S-type I-V characteristics. The present authors have investigated the electrical conductivity and Hall coefficient.⁽⁹⁾ Also the thermoelectric properties of this compound was studied and reported. $^{(10)}$ previously by the same authors. In view of the absence of publication of these phenomena in this compound and also in view of recent interest in this group of compound, the author undertook such work and reports here his investigation of switching effect and some factors affecting it . The electrical phenomena have, from the beginning, switching attracted considerable interest, and have been investigated by many authors. A lot of work has been done to establish the mechanism of switching process,^(11,12) 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. The aim of this work is to study the switching phenomenon in $Tl_2GalnTe_4$ single crystal in wide range of temperatures as well as light intensity and sample thickness. The absence of data on the characteristics switching about this compound makes it difficult to estimate potential application of this material in electronic technology.

2- Experimental procedures

2-1- Sample preparation

The modified Bridgman technique was used to grow $Tl_2GalnTe_4$ single crystal from astoichiometric melt of the initial materials sealed in evacuated (~10⁻⁶ Torr) quartz ampoules each with a tip at the bottom. All the initial materials used were extra pure elements (99.9999%). The appropriate amounts were first sealed in evacuated quartz ampoule. $Tl_2GalnTe_4$ single crystals were grown from $TlGaTe_2$ and $TlInTe_2$ polycrystalline by slight freezing of the charge in sealed evacuated quartz ampoule. The tipped silica tube was internally coated with aspecular layer of pyrocarbon before introducting the chemicals. In the first procedure the tube was placed in a three-stage tube furnace in which controlled temperature gradient was maintained. The ampoule is allowed to move with a constant rate of 1.5 mm/h through the stationary furnace. The details of the experimental apparatus and method of growth technique was described and reported elsewhere.⁽¹³⁾

The movement of the ampoule was very gently and slowly with the aid of the hydraulic mechanical system. At least two weeks growth are need to obtain $Tl_2GaInTe_4$ single crystal.⁽⁹⁾ The resulting ingots (grey-black in color) showed a good optical quality and had no cracks or voids on the surfaces. The single crystallinity of this material was verified by means of x-ray diffraction (XRD) technique. The samples for measurement were taken from the middle of ingots with a razor

blade. All samples of $Tl_2GaInTe_4$ used in the present study were freshly cleaved from a crystal grown in the same ampoule.

2-2-Switching –effect measurements

Specimens of Tl₂GaInTe₄ with plane-parallel mirror surfaces were prepared from a large ingot. Their typical dimensions are 4.2x3.2x1 mm³. The samples are symmetric sandwich type structure in which single crystals are placed between two metal electrodes. The sample holder was described early.⁽¹⁴⁾ The system was attached to a vacuum pump giving the possibility of measurements under vacuum. The environment temperature of the specimens under test was measured by means of a calibrated spot-welded chromel-alumel thermocouple. The investigation was carried in wide range of temperature to demonstrate the influence of the ambient temperature on the switching behavior of the crystal. The currentvoltage characteristic was measured using programmable power supply thermo EC-type. The current was measured by means of digital keithley 617 electrometer. The current passing through the sample can be easily reversed or cut-off by applying three-pole doule stage reversing switch. In order to investigate the effect of light intensity on the switching phenomena at 193 k, samples with appropriate thickness were mounted in a cryostat equipped with suitable windows and clamped in its holder provided with aperture to allow the passage of the radiation. Details of the apparatus and cryostat as well as the utilized circuit are described in reference.⁽¹⁵⁾ The sample was illuminated at normal incidence. Luxameter (Fisher Scientific mark) was used for measuring light intensity. The current and the potential drop across the sample as a function of intensity of illumination were registered directly. The effect of sample thickness on CVC was also studied. A specimen with an initial thickness equal to 1mm was first tested for its current-voltage characteristics, and its thickness was then successfully reduced. Samples with thickness varying from 1mm to 0.2 mm were used to investigate the influence of the sample thickness on the switching characteristics.

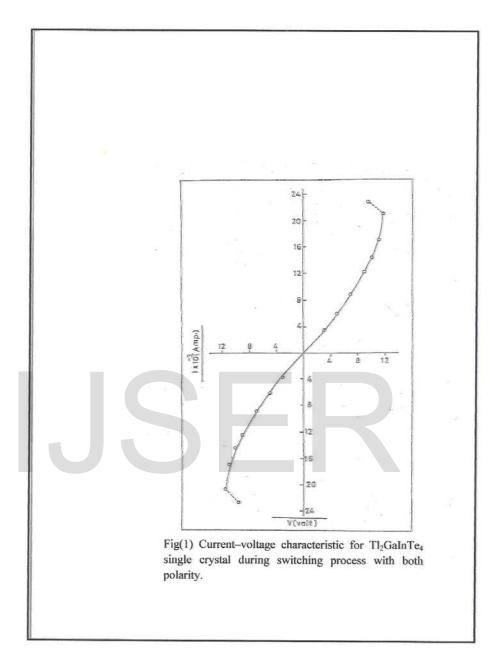
3- Results and discussion

In the present investigation, I studied the switching phenomenon of the quaternary thallium chalcogenide, in a sandwich type Ag- Tl₂GaInTe₄ structure. This phenomenon was observed when the current-voltage characteristics were measured as a function of the increasing applied electric field. The effects of the temperature, the light intensity, and the sample thickness on the switching behavior were observed.

3-1- CCNR (current-controlled negative resistance) with memory.

Fig.1 shows the I-V characteristic of Tl₂GaInTe₄ single crystal under DC condition at T =213°k. At low applied voltages the characteristic in ohmic and the sample has a high resistivity $\left[\,{\sim}10^2~\Omega~\text{cm}\,\right]$. It becomes linear with a slope of about 2 at higher values of the voltage until the current rises steeply .Afterwards the sample goes into a state of lower resistance. This state is maintained even without any energy being applied to the sample. A current pulse of about 2.1 mA amplitude can bring the sample to its original state of high resistance. The threshold voltages for the passage from the high to the low resistance state in this sample whose thickness is about 1mm, are of about 11.6V. The I-V characteristic reported in fig1 where it can be seen that the process takes place with both polarities on the crystal and has symmetrical shape with respect to the reversal of the applied voltage and current In the highly resistive state, the material is ohmic at field below 116 V/Cm.

When the applied voltage exceeds some critical values of potential V_{th} the unit switches along the load line to the conduction state. As the crystal goes into the conduction state it remains there, even if it is taken away from the circuit. A highly conducting state is retained in the absence of a voltage for an indefinite time, which is important in data storage. The process can be repeated several times. The memory switching phenomenon is an effect which follows a negative-resistance process. The form of the I-V characteristic suggests that the memory effect is composed of two processes.



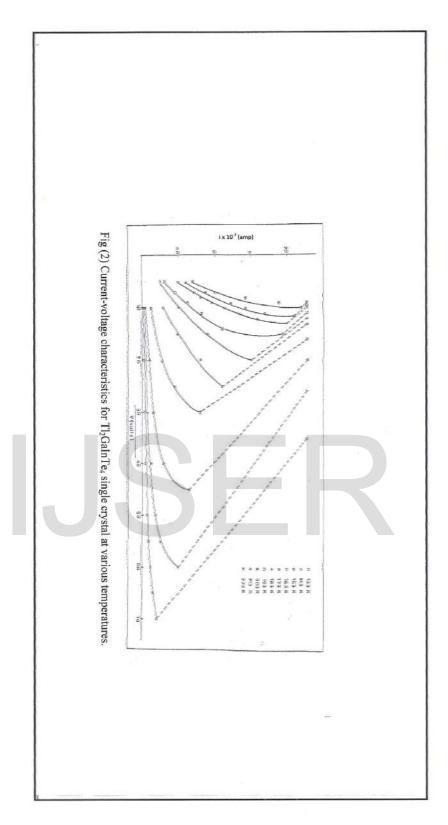
- (1) One is an electronic process which brings the sample into an S-type negative resistance zone. This process seems to be due to a double injection phenomenon.⁽¹⁶⁾
- (2) The other one could be a thermal effect which is caused by the current previously canalized in the filament. There well be a Joul heating effect in the filment due to the high current in the device and the temperature rise so produced is sufficient to form the mono-state ON-state. In order to explain the ON-state switching can be included by (a) a sharp increase in carriers concentration (b) a sharp increase in mobility, or (c) sharp increase in both.

It was found that the reversing of the voltage applied on the sample resulted to the same behavior, indicating that the silver paste formed an ohmic contact with the investigated sample.

The parameters of the high- resistivity, low-resistivity state depend to some extent on the quality of the sample (its thickness) and on the surrounding condition (temperature, illumination).

3-2-Temperature dependence of switching phenomena.

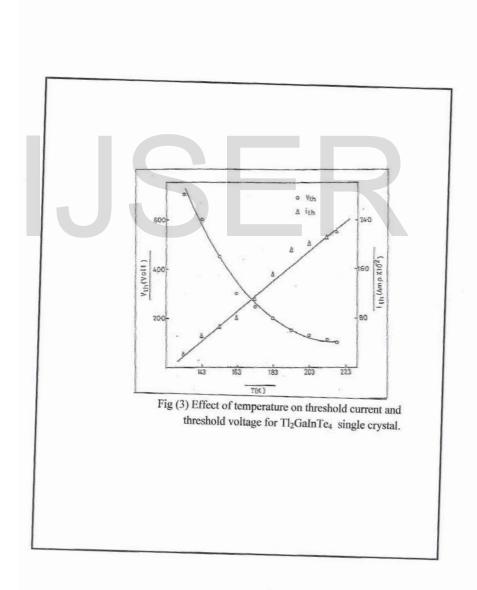
The I-V characteristics are strongly influenced by ambient temperature as shown in fig 2. In the temperature range of investigation (133-223)k, the characteristics shape is the same as in fig 1 with an increase in temperature the current-voltage characteristic as a whole is shifted toward the lower potentials. The temperature dependence of the I-V characteristic is an important for information storage applications. Usually, in memory switching materials different samples of the same thickness are used to study the effect of temperature on the switching behavior. As seen from these curves for the I-V behaviors there are two distinct regions, one is the OFF state region and the other negative differential resistance (NDR region). As is evident from the experimental curves as well as predicted by the electrothermal model.^(17,18) The ambient temperature greatly influences both the form of the CVC curves and the threshold voltage V_{th} , and holding voltage V_{h} .



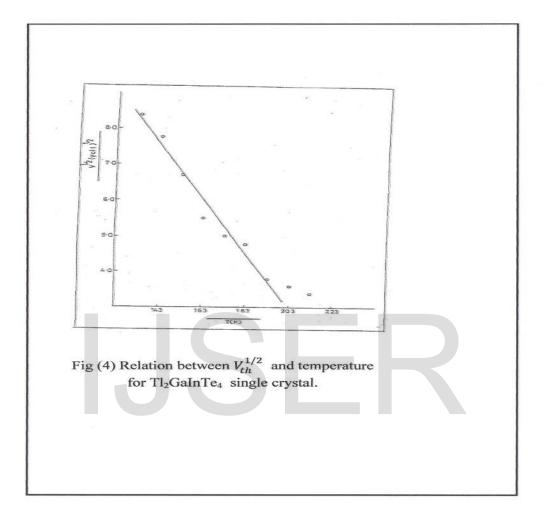
The NDR region of the curves is more pronounced at lower ambient temperature. The transition from the low to the high conductivity state of the curves is almost abrupt at lower temperature. The threshold voltage V_{th} after which the NDR region set in, become higher with decreasing temperature. There exist some fluctuations in the value of V_{th} when the first three or four switching cycles were measured. After three or four sets of measurements, the device become more stable and V_{th} sets to a constant value. Also we observe from the curves in fig 2 the conduction state can be kept at a certain holding current In and holding voltage V_h. The holding voltage V_h increase with temperature, while the holding current I_h is independent on temperature and has the same value at the whole temperature range of investigation. Also it is found that the threshold and memory switching stability increase with temperature increase. As the temperature increases one can observe three zones in the characteristics, ohmic zone, at low voltage, non-ohmic at higher voltages and thirdly the threshold voltage V_{th}. From the curves in fig.2 we notice the range of measurements begins from 133 to 223 k, since at temperature in excess of 223 k the OFF device with increasing field applied eventually exhibits filamentary breakdown and double injection, the enhanced conducting state being lost if a certain minimum voltage is not maintained. The effect of the ambient temperature on the switching parameters V_{th} and I_{th} is illustrated in fig.3. It is clear from the figure that cooling increases the threshold voltage where as the threshold current decreases, i.e as the temperature increases the threshold voltage decreases and the threshold current increases. This indicates that an electrothermal mechanism is involved in the switching process. The dependence of V_{th} on T was analyzed on the basic of the thermal- field Frenkel effect. Allowance for this effect in reference $^{\left(19\right) }$ yields the following expression relating V_{th} and T.

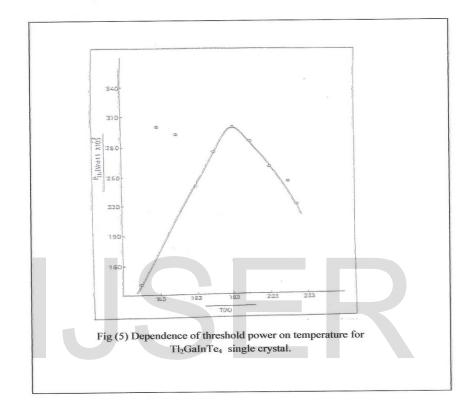
$$V_{th} = \left[\frac{\pi\epsilon_0\epsilon_\infty d}{e}\right](Q - cT)^2$$

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Where ϵ_0 is the permittivity of vacuum, ϵ_∞ is the electron component of the permittivity, d is the distance between the electrodes, c is a constant, e is the electron charge, Q is the depth of the potential well and T is the absolute temperature. Variation of V_{th} with temperature is plotted in fig.4. On the basis of the equation, using the coordinates $(V_{th})^{1/2}$ and T. Clearly, within the limits of the experimental error the results fit a single line. It is seen that in the whole temperature range of investigation, the threshold voltage decreases with temperature increases as expected from the above equation. This shows that the switching in Ag-Tl₂GaInTe₄-Ag structures from a high to a low resistivity state occurs under the simultaneous action an electric field and temperature.⁽²⁰⁾ This is of supported by the dependence of the threshold field on thickness of the active region. The power necessary to change the material from the high-resistance state to the low- resistance state called threshold power (P_{th}). The threshold power dependents also on the ambient temperature. The dependence of the threshold power on temperature was plotted in fig.5. It is found that the the relation between threshold power and temperature increases exponentially with temperature up to 183 k, after which the threshold power decreases exponentially with temperature. This led us to the assumption that as the temperature increases the rate of thermal generation of free charge carriers greater than the rate of recombination and the effect of trapping centers can be neglected, this led to increase of the threshold power as the temperature increase up

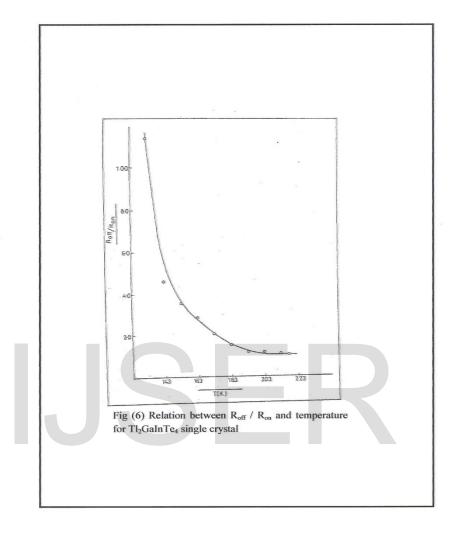


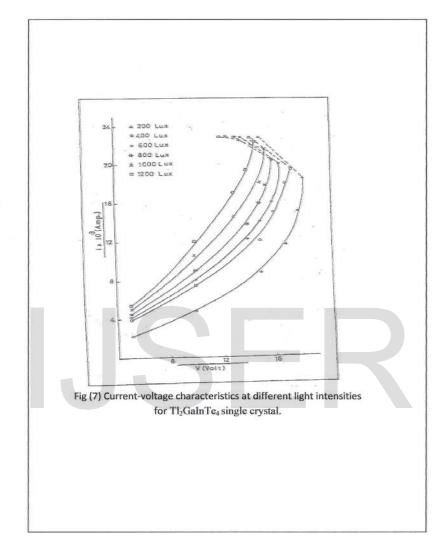


to 183 k. After which the effect of recombination become more than the generation also the effect of trapping centers increases, all these factors led to the decrease of the threshold power as the temperature increase, in the high temperature region (183-223k) this result is quite logical, since the power necessary to switching decreases initiate when temperature increases. The effect of surrounding temperature on the sample resistance ratio (R_{OFF}/R_{ON}) as seen in fig.6 depends on temperature which decreases exponentially with temperature. The resistance ratio R_{OFF}/R_{ON} varies from 11.4 to 1.036 in the range of temperature investigated.

3-3- Influence of light intensity on switching effect.

The VAC of Tl₂GaInTe₄, when the sample illuminated with different does of white light extended from 200 up to 1200 Lux, is illustrated in fig.7. The measurements were taken at low temperature and under vacuum, to prevent condensation around the cryostat which delays the incident light on the sample. The measurements were taken at T=193 k. As shown from the figure the curves of the CVC under illumination has the general form of switching with S-shape. It is evident from this figure that I-V characteristics as a whole are shifted toward lower potentials with an increase in the intensity of the incident light, also we can see that the form of CVC and the magnitude of the photocurrent depend strongly on the intensity of the incident light. This means that in case of weak illumination the threshold voltage is larger and the threshold current value smaller than the value obtained in case of intense light. The characteristic behavior can be described as follows (a) values of high resistance state decrease by increasing light intensity (b). The field necessary for switching to be performed is reached early on increasing the light





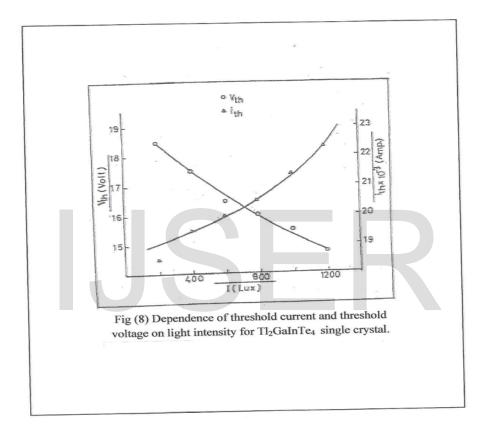
intensity dose (c). Near switching delicate control of the applied voltage is required since an increment of 0.1 volt is sufficient to move the sample from a stationary condition to a switching condition, d-The holding voltage V_h decreases as the intensity of illumination increases, while the holding current I_h does not vary with the intensity of illumination.

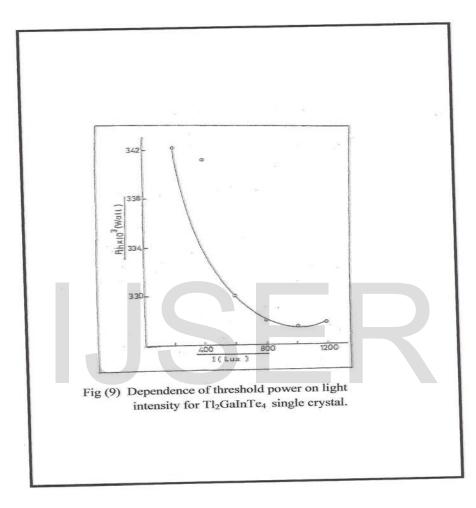
The variation of the threshold voltage and current with light intensity is represented in fig.8. As can be seen, threshold voltage decreases with light intensity, whereas the threshold current increase with light illumination, both of them vary with exponential relation. The main contribution comes from photo carriers generation through excitation states and is larger than recombination process. The relation between threshold power and light intensity is represented graphically in fig.9. As it is noticed P_{th} decreases exponentially with increasing incident light intensity.

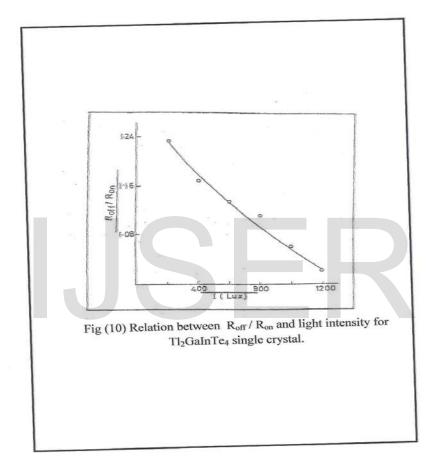
This may be photogeneration process for excited free charge carriers, which take place under illumination of the sample, leading to a small power required for switching as the illumination dose increase. The dependence of the ratio R_{OFF}/R_{ON} on the illumination intensity is shown in fig.10,where it is obvious that this ratio decreases continuously with illumation intensity increases. The ratio R_{OFF}/R_{ON} varies from 1.37 to 1.01 in the range of light intensity.

3-4- Effect of sample thickness

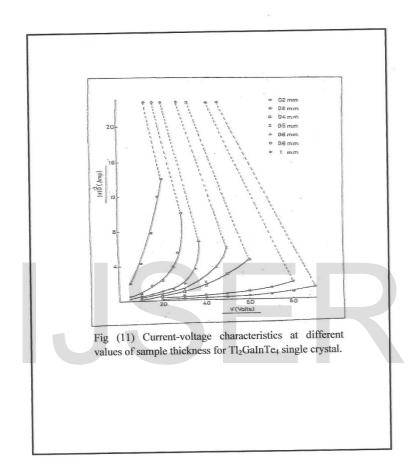
The overall feature of I-V characteristic of $TI_2GaInTe_4$ are altered by change in sample thickness. For switching process one has to choose a specimen whose resistance is changed from high value (OFF state) to a very low value (ON state) by the lowest switching power. This can be achieved through the study of the effect of the specimen thickness on switching. The measurements were taken in the dark, under vacuum at temperature T=183 k. Fig.11 represents the dependence of the switching behavior on the thickness of $TI_2GaInTe_4$ specimen.





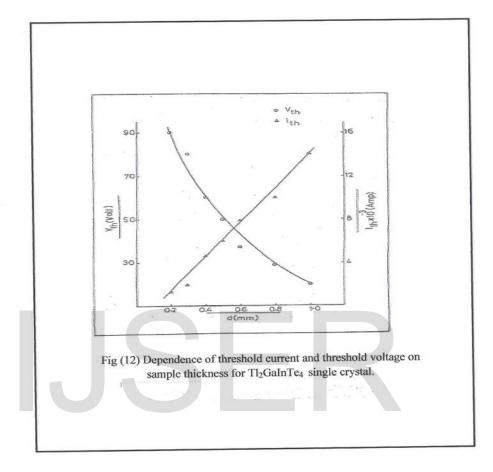


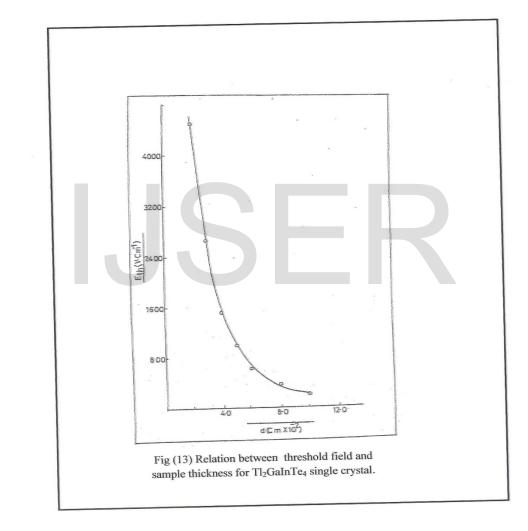
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The investigated range of the sample thickness varies from 1 mm to 0.2 mm. The figure indicates that the threshold potential and current change with the inter electrode gap and the width of the dashed lines which represents the variation from OFF to ON state decreases with thickness. This result indicates that the switching can be easily controlled with the sample thickness. The holding voltage also affected with the active thickness of the specimen (increases with the decrease of sample thickness) and its value lies between (12-32) volt,

whereas holding current I_h is independent on the sample thickness and has the value 22.8 mA. The variation of the threshold voltage and current with thickness is represented in fig.12. It shows that V_{th} decreases exponentially as the crystal thickness increases, whereas I_{th} decreases linearly as the active region between the electrodes decreases. This indicates that the switching behavior can be easily controlled with specimen thickness. The dependence of V_{th} on thickness shows that switching is a bulk effect. The previous assumption that switching occurs under the simultaneous action of the electric field and temperature is supported by the dependence of the threshold field on the thickness of the active region. Fig.13 shows the dependence of the threshold field on the thickness of the Tl₂GaInTe₄ samples. The experimental results indicate that the dependence exponentially decreases as the sample thickness increases as shown in fig.13. This is due to the appearance of Pool-Frenkel conductivity in the thinner samples, which occurs for fields greater than about 200 V/Cm⁽²⁰⁾. It is clear that E_{th} decrease as the sample thickness increase. This indicates that the electric field has a profound influence on the ability of the samples to undergo a transition from the OFF state to an effective region of NDR. This supports the suggestion that the mechanism of the switching in Tl₂GaInTe₄ sample may involve both electric and thermal processes.⁽²¹⁾ Investigation of the effect of the sample thickness on switching phenomena is useful for a chosen



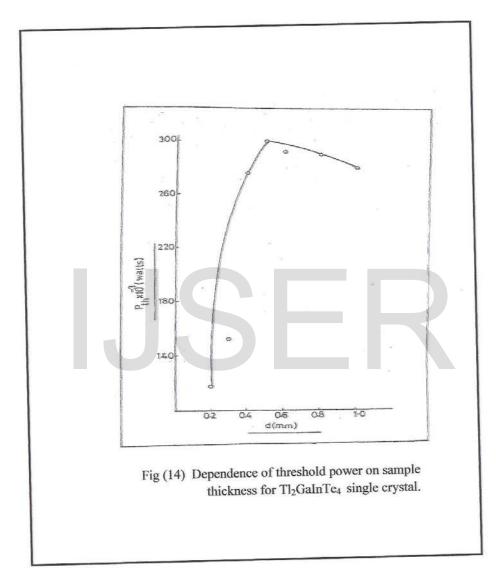


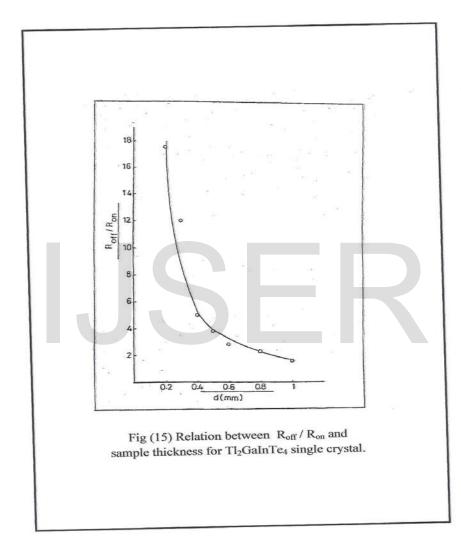
specimen whose resistance is changed from high value (OFF state) to a very low value (ON state) by lowest switching power. The variation of the threshold power P_{th} with sample thickness was plotted in fig.14. It is clear that the threshold power increases sharply with sample thickness increase and reaches its maximum value at d=0.5 mm, then it decreases with the increase of sample thickness. The relation between R_{OFF}/R_{ON} and sample thickness of $TI_2GaInTe_4$ single crystal is shown in fig.15. It is clear from the figure that the ratio is strongly dependent on sample thickness. Increasing ^{((d))} leads to larger value of R_{OFF}/R_{ON} . The resistance ratio R_{OFF}/R_{ON} varies from 1.62 to 17.54 in the range of sample thickness under investigation

4- Conclusion

The major features of the switching in Tl₂GaInTe₄ single crystal can be summarized as follows:

- From the I-V characteristic we can see that the process take place with both polarities on the crystal and has symmetrical shape.
- When the applied voltage exceeds threshold the unit switches along the load line to the conducted state. The critical field for switching in Tl₂GaInTe₄ is 116 V/Cm at 213k.
- * The specimen under test exhibit bistable or memory switching of the negative resistance process.
- * The VAC has S-shape type from the common form of the switching phenomena with CCNR effect.
- * The switching phenomenon in our sample is very sensitive to the temperature, intensity of light and sample thickness.
- * The switching parameters (V_{th} , I_{th} , P_{th} , E_{th} , V_h , I_h , R_{OFF}/R_{ON}) are checked under the influence of different factors of the ambient conditions.
- * The parameters of the high-resistivity, low-resistivity state depends to some extent on the quality of the sample and on the surrounding conditions.





In view of these interesting properties our sample can be used in the field of switching elements and memory elements in electronic devices.

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