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MEMORY-SWITCHING EFFECT IN SINGLE CRYSTALS OF INDIUM SELENIDE (InSe)

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Abstract: It has been found that layered single crystals of indium selenide with a hexagonal crystal structure exhibit bistable or memory switching with the current along their c-axis when the applied electric field exceeds about $1 \cdot 10^4$ V/cm. Current-voltage d. c. characteristics measured with a constant current power supply reveal the negative differential resistance region followed by a rapid increase of current and a strong rise in temperature which precede the transition from the high resistivity or OFF state to the low resistivity or ON state of the sample. The resistance ratio (R_{OFF}/R_{ON}) for this transition is of the order of 10^3. The OFF state can be restored by applying a sufficiently high current pulse or by a sudden decrease of the ON-state current from a sufficiently high value (10 mA or higher) to the zero value. It is assumed that the applied high electric field leads to local reordering of atoms along a path between the electrodes and parallel to the c-axis, and to the creation of a high-conductive »bridge«, responsible for the ON state. The rupture of the conductive »bridge« as a result of Joule heating at sufficiently high temperature followed by rapid cooling brings the sample again to the high-resistivity state.

1. *Introduction*

Since the appearance of Ovshinsky's[1] paper on threshold switching a great deal of work, mostly on amorphous materials, has been done in order to clear up the question concerning the mechanism involved in this phenomenon. However, only a small number of papers have been devoted to the switching effect in single crystal materials. This effect has been observed almost solely in crystals possessing a layer structure, such as GaSe[2], GaS[3], GaTe[4], or SnS_2 and ZrS_2[5], mica[6] and Sb_2S_3[7]. Recently, the switching effect has also been observed in ZnS single crystals[8]. However, the nature and the mechanism of this phenomenon has not yet been completely cleared up in many cases, and different mechanisms may be responsible for switching in these crystals.

In the present work some results on conductivity memory switching in cleaved single crystals of indium selenide (InSe) are presented; the existence of switching effect in InSe, to the authors knowledge, has not been reported previously.

2. *Experimental procedure*

A single crystal ingot of InSe was obtained by direct synthesis of indium and selenium in a fused silica tube at 900°C. The melt was cooled, keeping a constant temperature gradient along the tube, and a layer single crystal with a hexagonal crystal lattice was grown[9]. Samples 10 — 100 μm thick were cleaved from the ingot and provided with indium contacts onto two c-faces. The contact area was about 1 mm^2. Bulk electrical resistivities of the samples in the direction of the c-axis were of the order of 10^2 to 10^3 Ω cm, being about 150 times larger than in

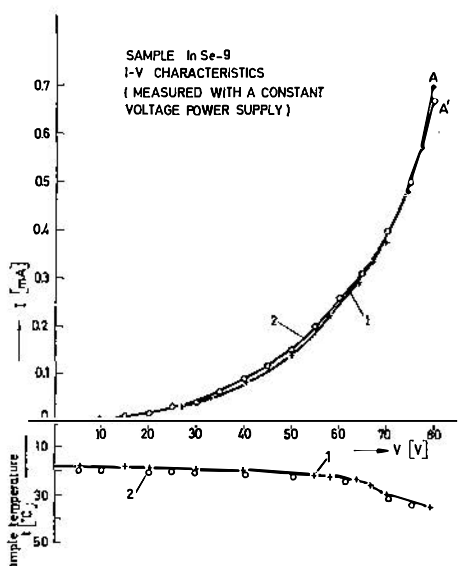

Fig. 1. I—V characteristics measured with a constant voltage power supply (regime A) and the corresponding average sample temperature vs voltage dependences: curve 1 — taken on the original sample, curve 2 — taken on the same sample after several switching cycles.

the direction perpendicular to the c-axis. The samples were homogeneous, as indicated by the measurements of their electrical and optical properties; they all show n-type conductivity. The impurity content was low, because the elements used for synthesis were of high purity (In — 6N, Se — 5N 8).

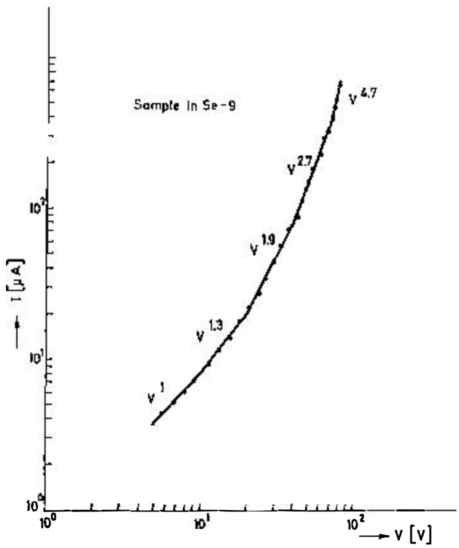

Fig. 1a. Curve 1 of Fig. 1 in the log I-log V representation.

The current-voltage characteristics of the crystals along the c-axis were measured by electrometers using a constant current power supply or a constant voltage power supply as a source.

A cryostat with a temperature region between 80 and 400 K was used to measure the temperature dependence of electrical conductivity in both the high- and the low-resistivity state of the sample.

3. *Experimental results and discussion*

It has been found that InSe single-crystal samples which are initially in a highly resistive state, change suddenly, in a time less than 1 μsec, to a low-resistance or ON state when the applied voltage exceeds some threshold voltage. The ON state is stable after the complete removal of the bias voltage while the high-resistivity or OFF state can be restored by applying a sufficiently high current pulse through the sample or by a sudden decrease of the current passing through the sample in the ON state, from a sufficiently high value (of about 10 mA or more) to zero. (This can be performed, for example, simply by turning the current--switch position of the constant current power supply from the »10 mA« to the »1 mA« switch position.)

The phenomenon observed in InSe is, therefore, bistable or memory switching. The electrical fields necessary to produce the OFF- → ON transition are of the order of $1 \cdot 10^4$ V/cm.

Typical I—V characteristics of the OFF state as measured by a constant voltage power supply (hereafter referred to as regime A) are shown in Fig. 1. Curve 1 was taken on an original sample, while curve 2 represents such a characteristics after several switching cycles performed with a constant current power supply. The average temperature of the sample was measured simultaneously with V and I by means of a Cu-Constantan thermocouple. In the low-voltage region (below 10 V) the I—V curve is linear, and in high-voltage region (above 70 V) it is characterized by a steep power-law form, $I \propto V^n$, where $n = 4.7$. In the intermediate region, the powers n obtained were 1.29, 1.94, and 2.69 as the voltage increased from 10 to 70 V (see Fig. 1a). The corresponding increase of the average sample temperature in this region is small. In point A or A′ the resistance decreased suddenly almost by three orders of magnitude, the sample being converted to the ON state.

A set of I—V curves taken on the same sample, measured with a constant current power supply (regime B), is shown in Fig. 2. As expected, the shape of the curves is different from that when measured in regime A. Although the data of Fig. 2 are scattered, all the curves measured in regime B show similar behaviour. Instead of the abrupt transition to the ON state, there are two intermediate regions in regime B. Region I includes part of the I—V characteristics with negative differential resistance, while region II corresponds to the voltage collapse (Fig. 2, curve 1). The voltage collapse can also occur at two stages (Fig. 2, curve 2). The negative differential resistance region is characterized by a strong increase in temperature (see Fig. 2).

The OFF state curves of Fig. 2 are presented again in Figs. 3 and 4 together with their corresponding ON state characteristics. The ON-state curve belonging to the OFF-state curve 2 of Fig. 2 is Ohmic (Fig. 3). When the ON-state current is increased to 10 mA and then s l o w l y decreased towards zero (curve 1 in Figs 2 and 4), the high-resistivity state is always partially restored. If the current in the ON state is a b r u p t l y decreased from 10 mA or more to 1 mA, the OFF state is always completely restored. However, if the ON-state current is of only few mA, the OFF state can be restored neither by rapid nor by slowly decrease of the ON-state current. The ON state can be maintained at constant current over prolonged periods unless the current exceeds several mA.

The I—V characteristics became »degenerate« after 30—40 switching cycles; their shape is shown in Fig. 5, and one can see that the OFF → ON transition was no longer possible.

The OFF state was examined by measuring the temperature dependence of the electrical resistivity in the original sample as well as after successive switching cycles. In Fig. 6 the original high resistivity sample (curve I) exhibits a typical behaviour as obtained for InSe single crystals with the current conduction in the direction of the c-axis[10]. After the first two switching cycles (curve II) as well as in the course of first twenty switching cycles (curves III—V, Fig. 6), the resistivity vs temperature dependence of the sample in the OFF state was more or less reproducible, and the room temperature value of R_{OFF} varied within a

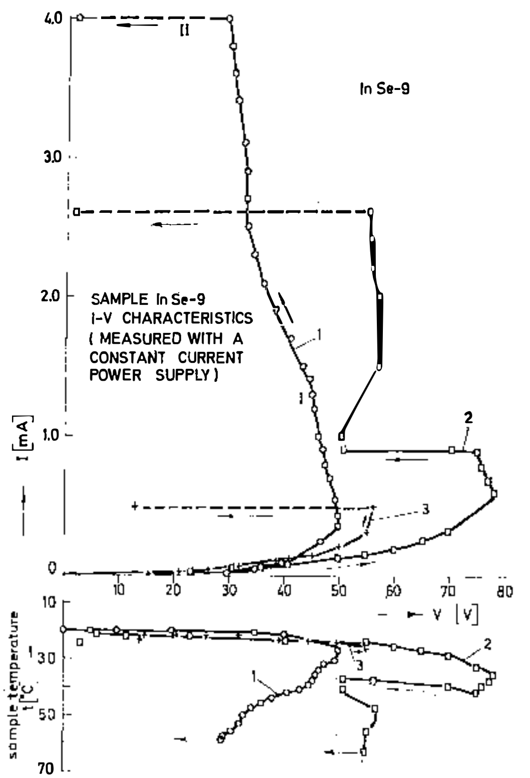

Fig. 2. I—V characteristics measured with a constant current power supply (regime B) and the corresponding average sample temperature curves.

factor of three. With further cycling, the value of R_{OFF} decreased by an order of magnitude or more (curve VI, Fig. 6), and, although the sample was still able to perform ten to twenty transitions between the OFF and ON states its electrical resistance in the OFF state was then almost completely independent of temperature in the entire region from 80 K to well above room temperature.

Studying the samples in the ON state it was found that the low resistance of the ON state, R_{ON}, is independent of temperature in the whole region between 80 and 400 K.

If for OFF → ON transitions overthreshold rectangular single voltage pulses are applied instead of the slowly increasing applied voltage, the destruction of the sample is much more pronounced, since the number of possible switching cycles is considerably reduced. The OFF → ON transitions were performed by 1 μsec pulses of 100 V, while for the ON → OFF transitions discharges of a 2 μF capacitor were used; at the beginning R_{OFF} decreased rapidly and then at a much slower rate, while R_{ON} showed only oscillations with increasing number of switching cycles.

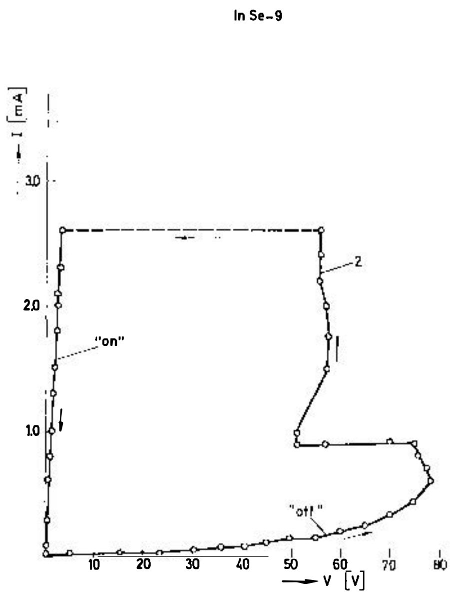

Fig. 3. The OFF-state and the corresponding ON-state characteristics (the OFF-state curve is also presented in Fig. 2, curve 2).

It is already known that hexagonal indium selenide possesses a disordered structure as seen in the direction of the c-axis[11]. However, it is not possible to associate the OFF → ON transition with the volume »healing« of such structural defects, since the R_{OFF}/R_{ON} ratio is too high and the semiconductor properties are lost in the ON state (R_{ON} is independent of temperature in the whole region between 80 and 400 K).

Our experimental results support the assumption that the high electric field applied to the sample and the accompanying Joule heating lead to a structural and electronic rearrangement of atoms between the electrodes and to establishment of the high-conductive state, which is maintained without external bias. Let us accept the assumption of current constriction phenomenon, i. e., the formation of a conductive current filament, which was observed by many authors[12)*]. By analogy with memory switching in gallium telluride single crystals[13)], where the filament was found to be built from gallium crystallites, one can expect the formation of an indium or at least indium-rich filament in the case of InSe single crystals;

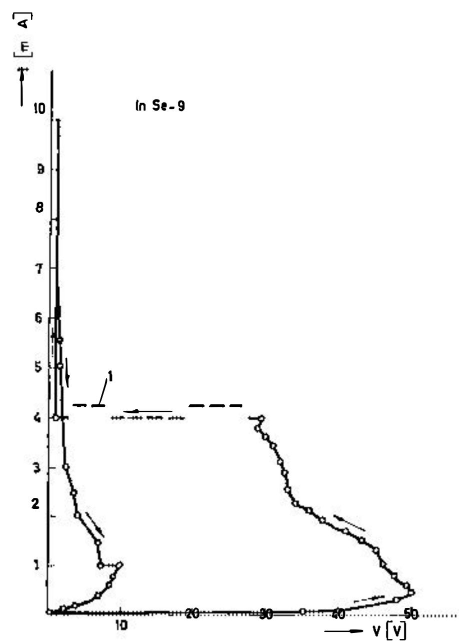

Fig. 4. The OFF-state and the corresponding ON-state I—V characteristics (the OFF-state curve is presented in Fig. 2, curve 1).

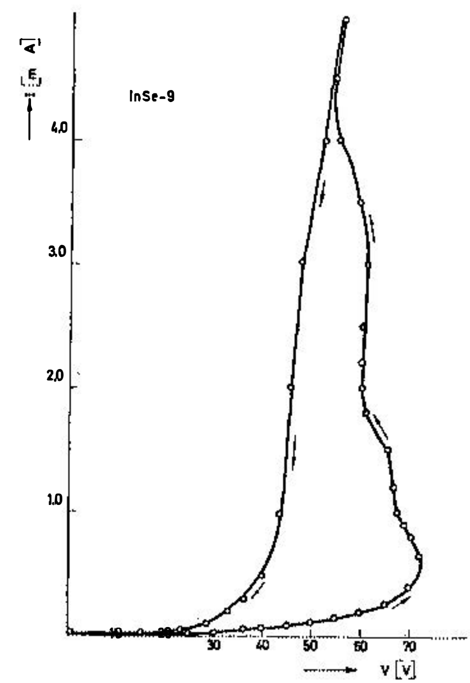

Fig. 5. »Degenerate« I—V characteristics of the sample presented in Figs. 1—4, after its destruction by switching cycling.

the R_{OFF}/R_{ON} ratio of $\sim 10^3$, observed in our case, could support this assumption. It should be pointed out that the change of contact material (e. g. silver dispersion instead of indium) does not influence switching phenomena in InSe. Application of a sufficiently high current pulse or the observed rapid decrease of the sufficiently high ON-state current which both lead to the restoration of the OFF state, show that heating to sufficiently high temperatures followed by rapid cooling is necessary for the re-establishment of the high-resistivity state, presumably through the rupture of the indium or indium-rich filament. It is also an open question what is the nature of processes leading to the reorganization of atoms during the transitions between the OFF and the ON states in indium selenide single crystals.

* See Ref.[4)] or Ref. [8)].

Both electronic and thermal processes might be included in this phenomenon. Phase transformation studies, the search for polar effects, role of the electrode material, must be done in order to explain these problems.

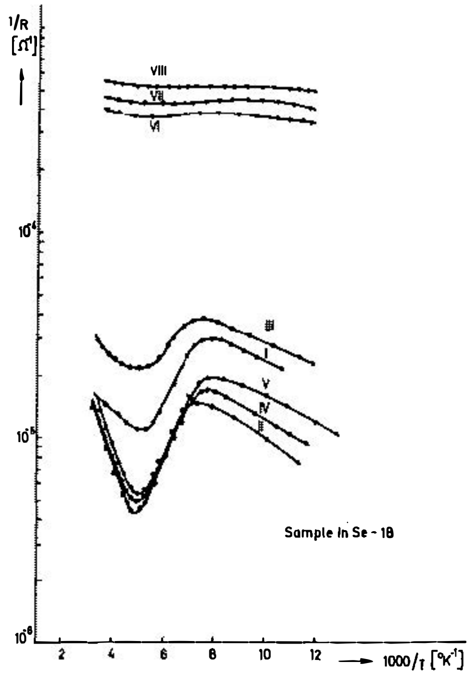

Fig. 6. The OFF-state electrical conductance vs reciprocal temperature dependences of the original sample (curve I), and of the same sample after switching cycling: curve II — after two switching cycles, curve III — after four switching cycles, curve IV — after eight switching cycles, curve V — after sixteen switching cycles, curve VI — after twenty switching cycles, curve VII — after twenty seven switching cycles, curve VIII — after thirty two switching cycles.

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EFEKT MEMORIJSKOG PREKAPČANJA U MONOKRISTALIMA INDIJ SELENIDA (InSe)

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Sadržaj

Ustanovljeno je postojanje efekta memorijskog prekapčanja u slojevitim monokristalima indij selenida sa heksagonalnom strukturom u smjeru paralelnom s osi c kristala kada priključeno vanjsko električno polje ima vrijednost veću od $\sim 1 \cdot 10^4$ V/cm.

I—V karakteristike dobivene uz upotrebu izvora napajanja stalne struje pokazuju područje negativnog diferencijalnog električnog otpora iza kojeg slijedi nagli porast struje i temperature uzorka, koji prethode naglom prijelazu iz visokootpornog ili OFF stanja u niskootporno ili ON stanje uzorka. Omjer električkih otpora u OFF i ON stanju (R_{OFF}/R_{ON}) je reda veličine 10^3.

OFF stanje može se ponovno uspostaviti primjenom dovoljno jakog strujnog pulsa kroz uzorak ili pak naglim smanjenjem dovoljno jake struje koja teče uzorkom u ON stanju (oko 10 mA ili više). Pretpostavljeno je da primjenjeno električno polje vodi do lokalne preraspodjele atoma između elektroda duž nekog puta paralelnog s osi c uzorka, te do stvaranja visokovodljivog »mosta« odgovornog za niski otpor uzorka u ON stanju.

Pucanje vodljivog »mosta« zagrijavanjem Jouleovom toplinom i naglim hlađenjem vraća uzorak ponovno u visokootporno stanje.