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ANALYSIS OF ELECTRICAL SWITCHING EFFECTS IN THE CHALCOGENIDE GLASSY SEMICONDUCTOR $Cu_1(AsSe_{1.4}I_{0.2})_{99}$*

The current–voltage characteristics of the bulk metal chalcogenide glassy semiconductor $Cu_1(AsSe_{1.4}I_{0.2})_{99}$ are obtained by Tektronix 576 Curve Tracer. It was found that this glass has current-controlled negative resistance (CCNR) and switching characteristic with memory. Experimental results have shown a strong decrease in electrical resistivity and threshold voltage due to the presence of the metallic element copper and change of ambient temperature. Also, photomicrographs of the sample surface are presented and the impact of electrical switching on forming crystalline conductive channels on the surface of the investigated amorphous semiconductor is discussed.

In the group of non-crystalline semiconducting materials a special place is occupied by chalcogenide amorphous semiconductors, *i.e.* the materials that contain one or more chalcogen elements: sulphur, selenium and tellurium [1]. They can be obtained in the form of glasses either as bulk amorphous samples, or in the form of thin films.

The possibility of obtaining a large number of amorphous semiconductors of different composition, including also non-stoichiometric compounds and mixtures, has opened a wide perspective for the application of these materials. Scientists have discovered a lot of new chalcogenide materials, phenomena and applications. Following the development of the glassy chalcogenide field, new optoelectronic materials based on halides have been discovered. Complex oxide and non-oxide glasses have been prepared and investigated in the last several decades, thus widening the groups of materials used in various optical, electronic and optoelectronic semiconductor glasses. The great advantages of the disordered materials are: simple preparation procedures, low sensitivity to impurities, high stability to the action of ionizing radiation, chemical stability towards the majority of aggressive chemical substances, low cost, and the possibility to produce large area films of various thickness in classical systems for deposition: systems for evaporation in vacuum, magnetron systems, flash, spin-coating systems, sol–gel systems, etc. [2].

Chalcogenide glassy semiconductors have a number of properties important for device application. They show continuous change of physical properties with change in chemical composition. A lot of work has been done on impurity effect on conductivity and optical properties [3,4]. Electrical conductivity and switching of amorphous semiconductors depends on synthesis, melt cooling rate, purity of the starting components, thermal treatment and other factors [5–7].

Electrical switching in chalcogenide glasses has been discovered by Ovshinsky about four decades ago [8]. Though the promised applications in information storage or power control have not been fully realized, electrical switching has remained to be one of the fascinating properties of these materials.

The relation between switching parameters and other properties of chalcogenide glasses has been a topic of intense investigations for long time. Several investigations have been directed towards understanding the relation between the switching voltages and glass transition temperature [9,10], crystallization temperature [11], electrical resistivity [12], ambient temperature and conductivity activation energy [13], etc., of glassy chalcogenides. Recently, considerable attention has been given to the understanding of the influence of two network topological thresholds, namely the rigidity percolation threshold (RPT) and chemical threshold (CT) respectively, on the switching behavior of chalcogenide glasses [14].

SWITCHING EFFECT

Interesting electrical switching effects have been observed in a large variety of amorphous semiconductors when they had been placed as a thin layer between two electrodes [15]. Most of these switching effects have in common the fact that they are current-controlled so that the *I–V* characteristic is obtained with a protective load resistor R_L placed in series with the switching unit.

The appearance of the observed *I–V* characteristics suggests the fourfold classification shown in Fig. 1. The negative resistance device has an *I–V* characteristic which is retraceable and shows an extended negative differrential resistance region, see Fig. 1.1. With a proper choice of R_L this negative resistance device can be kept at any point of the *I–V* curve. Some hysteresis is observed when the current is changed too rapidly for maintaining thermal equilibrium. With a small value of R_L this device can be made to switch along the load line from a point at which $-(dV/dI) = R_L$ to the point of intersection of the load line and the *I–V* characteristic.

The switching device has no stable operating point between the original high resistance state and the con-

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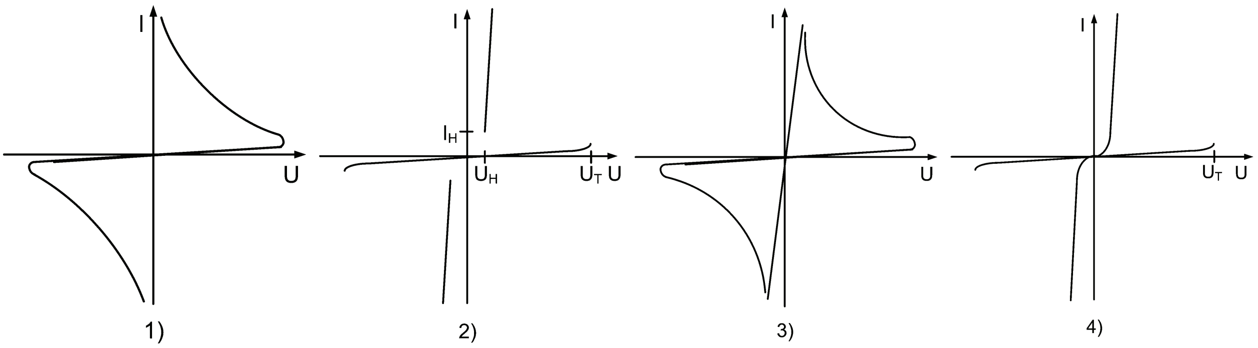

Fig. 1. Classification of current-controlled breakdown characteristics: 1) negative resistance device; 2) switching device;3) negative resistance device with memory; 4) switching device with memory.

ductive state to which the device switches at the threshold voltage U_T, see Fig. 1.2. The conductive state can be maintained only above a holding current I_H. When I is decreased below I_H, the device switches to its original high resistance state. The negative resistance device with memory has two states: high resistance and conductive, see Fig. 1.3.

Conductive states are established at higher currents and then remain without noticeable decay. The high-resistance state can be re-established by increasing the current above a certain value and switching it off rapidly. The switching device with memory also has two stable states, see Fig. 1.4. The initial high-resistance state and the mode of switching resemble those of the second device. The second state is conducting and persists without change. The high resistance state can be re-established by applying a short current pulse.

Almost all of these phenomena occur in the same manner for both polarities of the applied voltage. This phenomenological classification is, however, insufficient to separate the physical causes that give rise to the switching effects.

Although self-heating of a semiconducting material whose resistivity drops rapidly with increasing temperature can easily lead to thermal run-away, this need not be the only mechanism which yields to negative differrential resistance.

On the other hand, regardless of the physical mechanism and despite the obvious differences among the cases shown in Fig. 1, all of these have in common the transition from the high-resistive to the conductive state that occurs with a constriction or narrowing of the current path.

The memory action, *i.e.* the persistence of two states in which resistances differ by many orders of magnitude, is possible in the switching devices with memory (Fig. 1.4) only when a structural change can take place in the material. Simple binary or ternary glasses near eutectic or compound compositions are examples of suitable materials. Simpler structures like those of elemental semiconductors or stoichiometric compound materials were found impractical because of their excessive tendency to crystallize. In contrast to this, any structure change has to be inhibited in order to obtain the switching effect without memory (Fig. 1.2). Examples of these materials are multicomponent glasses of alloys of Group III, IV, V and VI elements. These can be cooled very slowly from the liquid without showing traces of crystallite growth. The switching devices without and with memory have in common that switching occurs very abruptly at a threshold voltage, U_T, when the applied voltage is increased slowly. When a square-wave voltage is applied, switching occurs after a delay time which decreases nearly exponentially with increasing square-wave voltage amplitude. No switching appears possible below a certain voltage which for practical purposes is equal to U_T. The switching time measured in several laboratories is less than 10^{-9} s [2]. This upper limit is determined by the response time of the measuring equipment. The conduction in the high-resistance state was found to be bulk limited rather than contact limited. All conductors tested were found to form low-resistance contacts with these amorphous semiconductors when precautions were taken to free the electrodes from oxide layers. Evidence for this was obtained by four-probe measurements and by testing the scaling of the resistance with the film thickness.

Before switching occurs, the conductance increases approximately exponentially with applied voltage. Pulse measurements show that the temperature of the semiconductor rises less than about 15 °C above ambient, due to self-heating before switching under static conditions.

The dimensions of the unit, the specific heat per unit volume of the amorphous layer, and the temperature dependence of its resistivity allow us to estimate whether self-heating is a possible mechanism for switching. We note that the apparently discontinuous change of slope from a positive differential resistance at the point of breakdown to a slope equal to that of the load line, already speaks against a thermal run-away.

EXPERIMENTAL AND RESULTS

The studied alloy was synthesized by the usual melt-quench method, using high-purity elementary components [1]. The non-crystalline nature of the ingot thus obtained was confirmed by X-ray diffraction and by differential scanning calorimetry (DSC) [6].

Samples used for electrical switching measurements were prepared in sandwich structure of electrodes [15]. The polished plate sample with thickness of 2.4 mm has contacts of Ag paste (ohmic contacts). This procedure ensures correct electrical contacts, as well as easy detection of any process which could take place on the material surface, such as the growth of a low-resistance channel between the electrodes [16]. Fig. 2 shows appearance of the final sample with silver electrodes.

Fig. 2. Sample's appearance.

For DC current–voltage characteristics measurements a Tektronix 576 Curve Tracer is used. It is a rugged high power measurement system for tests on 2- and 3-terminal discrete semiconductors. Display area readout of test results and setup parameters decreases the chances of operator error. Voltage step ranges are up to 1500 V and current step ranges are up to 20 A peak pulse. Switchable polarity and display magnification use for more accurate resolution. Due to better results of measurement and later analysis the Curve Traces with the Sony HC-23 video camera are used.

Measurements above room temperature were undertaken by placing the sample holder in a thermally controlled furnace. The ambient temperature was regulated with a temperature controller BECKMAN CTC 250 (PID type). The temperature was measured using a copper-constantan thermocouple with accuracy of ±0.5 K. All measurements were done in air and in dark.

Manual probe system PM5 - SUSS MicroTec Test Systems is used for failure analysis (FA) of the sample surface during electrical stimulation.

Figures 3–5 shows *I–V* characteristics of the sample during electrical stimulation on temperature of 150 °C. This temperature is chosen because the sample has high electrical resistance and threshold voltage (over the range of the Tracer) on lower temperatures. During measurements on the cathode Tracer, the video camera records characteristics appearance from the monitor. Analysis of captured pictures (30 frames per second) is performed by Adobe Premiere Pro 1.5 software. Maximal voltage and power supply was Vmax = 1500 V and Pmax=10 W, whereas the serial resistance was Rs = 65 kΩ. Fig. 3 depicts high resistance – "OFF" state, *i.e.* voltage on the sample is relatively high whereas current is low.

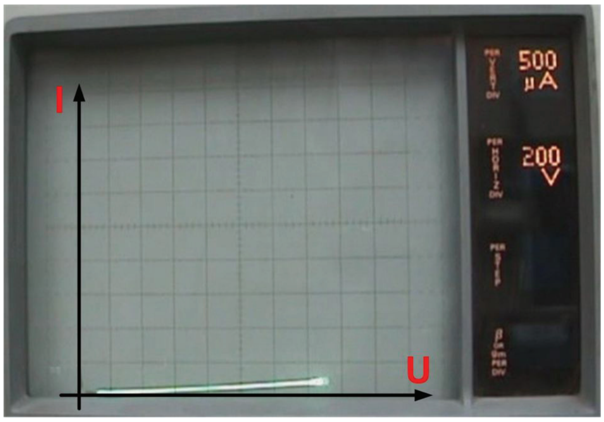

Fig. 3. High resistance state – "OFF".

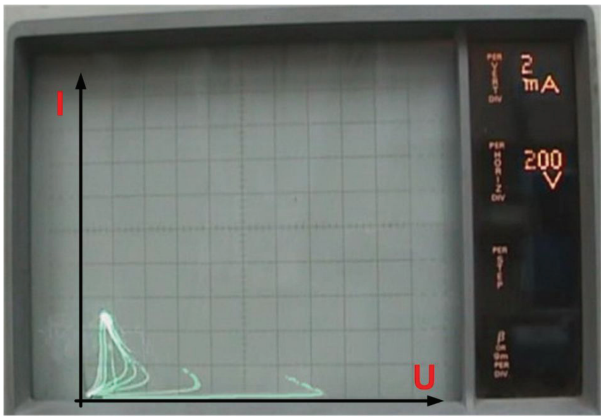

Fig. 4. Transient switching state.

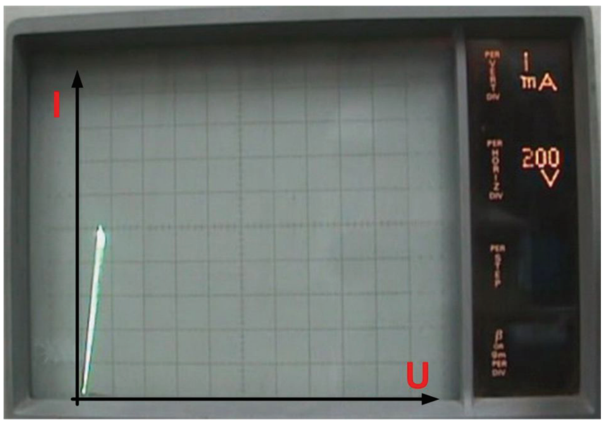

Fig. 5. Low resistance state – "ON".

Transient switching state is shown in Fig. 4. In this moment, the working point abruptly crosses from OFF to ON state (Fig. 5).

There is a negative resistance region (voltage drop, during current rises) between the OFF and ON state, the slope of which depends on the value of the serial resistance. Threshold voltage is 1500 V, whereas threshold current is 250 μA approximately.

Experimental results [17] have shown a strong decrease in electrical resistivity (which ranges from 10^{11} to 10^{12} Ω cm in AsSeI glassy alloys and its value for this alloy is 10^{10} Ω cm at room temperature), and in the semiconductor electron mobility gap (which ranges from 0.72 eV for AsSeI glassy semiconductors and is 0.67 eV for this alloy), due to the presence of the metallic element copper. Because of these facts, it is expected of the threshold voltage to decrease as well, with increasing Cu content [18]. Threshold voltage decreases whereas current increases with the increase of ambient temperature [19].

Fig. 6 shows the micrograph of the amorphous surface of the sample. Fig. 7 shows conductive channels

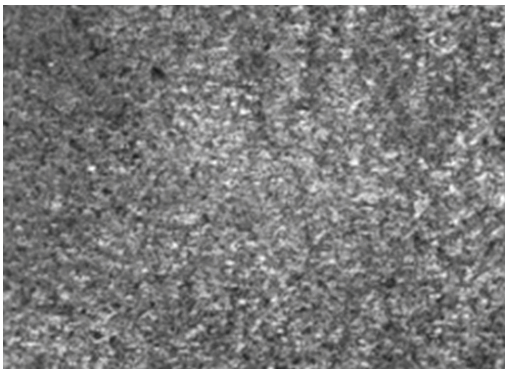

Fig. 6. Micrograph of the amorphous surface of the sample.

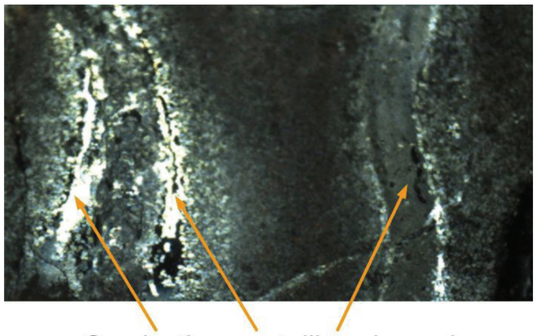

Fig. 7. Micrograph of crystalline channels on the surface.

that appeared on the surface of the sample, after the switching process had occurred in a CCNDR experiment, carried out with a contact electrode arrangement. The occurrence of these channels is additional evidence of current (and so, thermal) filamentation in the material, when the CCNDR effect appears. Several regions can be observed in these micrographs: first, the amorphous matrix, *i.e.* the zone of the material unchanged during electrical stimulation; secondly, between both electrodes, there is a region which melted during the electrical stimulation, and re-amorphized after this stimulation was suppressed; finally, inside this melt-quenched zone, a narrow channel can be seen, showing dendrite-like growth, characteristic of crystalline materials.

CONCLUSION

Switching effects in the bulk metal chalcogenide glassy semiconductor $Cu_1(AsSe_{1.4}I_{0.2})_{99}$ are confirmed during the electrical stimulation experiments. It was found that this glass has current-controlled negative resistance (CCNR) switching characteristic with memory. Experimental results have shown a strong decrease in electrical resistivity and threshold voltage, due to the presence of the metallic element copper and the increase of ambient temperature. Also, photomicrographs of the sample surface confirm that electrical switching causes crystalline conductive channels on the surface of the investigated amorphous semiconductor to appear. The next step in these investigations will be detailed examination of temperature impacts on switching parameters in various amorphous samples.

Acknowledgements

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IZVOD

ANALIZA ELEKTRIČNIH PREKIDAČKIH EFEKATA KOD AMORFNOG POLUPROVODNIKA $Cu_1(AsSe_{1.4}I_{0.2})_{99}$

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(Naučni rad)

U grupi nekristalnih poluprovodničkih materijala važno mesto zauzimaju amorfni halkogenidi. Oni se dobijaju u formi čvrstih uzoraka i filmova. Ovi materijali su našli široku primenu u elektronici i optoelektronici, pre svega za izradu memorijskih medijuma. Jedan od najzanimljivijih fenomena vezanih za ove materijale je prekidački efekat, tj. mogućnost nagle promene električne provodljivosti povećanjem električnog polja. Osnovna podela prekidačkog efekta je na one sa i bez memorijskog efekta. Materijali koji imaju memorijski efekat, mogu stanje visoke električne provodljivosti (ON stanje) da održavaju bez postojanja spoljašnjeg električnog polja. U cilju istraživanja postojanja i parametara prekidačkog efekta kod složenog sistema Cu–As–Se–I ispitan je uzorak $Cu_1(AsSe_{1.4}I_{0.2})_{99}$. Strujno–naponske karakteristike složenog amorfnog poluprovodničkog stakla $Cu_1(AsSe_{1.4}I_{0.2})_{99}$ dobijene su pomoću Tektronix 576 Curve Tracer-a. Utvrđeno je da taj materijal ima strujom kontrolisanu negativnu otpornost – – CCNR (current-controlled negative resistance) i prekidačku karakteristiku sa memorijom. Eksperimentalni rezultati pokazuju veliku zavisnost električne otpornosti i napona praga provođenja zbog prisustva bakra i promene temperature uzorka. Takođe, prikazani su i snimci površine uzorka dobijenih pomoću mikroskopa pre i posle dovođenja visokog električnog polja na elektrode uzorka. Razmotren je i uticaj električnog prekidačkog efekta na formiranje kristalnih provodnih kanala na površini ispitivanog amorfnog poluprovodnika. Dobijeni rezultati ukazuju da nakon povećanja električnog polja preko određene kritične vrednosti usled elektrotermalnog efekta dolazi do prelaska materijala iz amorfnog u kristalno stanje duž uskih kristalnih kanala male električne otpornosti.

Ključne reči: Prekidački efekat • Halkogenidi • Amorfni poluprovodnici
Key words: Switching effect • Chalcogenides • Amorphous semiconductors