Electrical and Switching Parameters of Amorphous Chalcogenide Glassy Semiconductors Cu₅(AsSe_{1.4}I_{0.2})₉₅

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Abstract — The subject of this paper is experimentally determination of electrical and switching parameters at different temperatures of amorphous chalcogenide glassy semiconductors Cu₅(AsSe_{1.4}I_{0.2})₉₅. It was shown that amorphous semiconductors from the system Cu_x(AsSe_{1.4}I_{0.2})_{100-x} have relatively high electrical resistance and expressed memory and threshold switching nonlinear effect, so that they have great potential for applications in electronics and optoelectronics. On switching parameters of the realized switching component a great impact have next properties of the active amorphous semiconductor: values of the activation energy, electrical conductivity, softening and working temperature. It has been found that this glass has currentcontrolled negative resistance (CCNR) switching characteristic with memory and high values of switching threshold fields.

Index Terms — electronic switching systems, amorphous semiconductors, nonlinear systems, semiconductor device doping, semiconductor device measurements.

I. INTRODUCTION

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. 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, spincoating systems, sol-gel systems, etc. [2].

Chalcogenide glasses have received a lot of attention because of their potential and current use in various solidstate optical and electrical devices [2-4]. A most fascinating property of these materials is probably their electrical switching, discovered by Ovshinsky in 1968 [5], which has found applications in the areas such as information storage [6], power control devices, thermistors, oscillators, etc. [7].

There are two types of electrical switching observed in chalcogenide glasses, namely, threshold and memory type. In threshold type switching, the ON state persists only while a current flows down to a certain holding voltage, whereas in memory type switching, the ON state is permanent until a suitable reset current pulse is applied across the sample. Different mechanisms have been proposed to explain the phenomenon of electrical switching in chalcogenide glasses. These include pure electronic [8], electrothermal [9] and thermal [10] mechanisms. It is more or less accepted that threshold switching is generally electronic in origin, whereas memory switching is of thermal origin [11]. The formation of highly conducting crystalline channels or filaments is considered as a possible cause of memory switching in the chalcogenide glasses [12-14].

The doping of chalcogenide glassy semiconductors with d-elements such as Ag and Cu is an effective way of changing the electrical and switching properties of glasses in a definite direction. By means of this doping it is possible to overcome the difficulty of high electrical resistivity, which is characteristic of most chalcogenide glasses. Copper has been used as a chemical modifier in arsenic selenides, showing a marked influence on increasing electrical conductivity [15].

It was shown that amorphous semiconductors from the system $Cu_x(AsSe_{1,4}I_{0,2})_{100-x}$ have relatively high electrical resistance and expressed memory and threshold switching nonlinear effect [16-18], so that they have great potential for applications in electronics and optoelectronics.

II. SWITCHING EFFECT

Interesting electrical switching effects have been observed in a large variety of amorphous semiconductors when they are placed as a thin layer between two electrodes [12]. Most of these switching effects have in common the fact that they are current-controlled so that the I-U characteristic is obtained with a protective load resistor RS placed in series with the switching unit (Fig. 1). The switching device has no stable operating point between the original high resistance state and the conductive state to which the device switches at the threshold voltage UT, see Fig. 2.



Figure. 1. Measurement setup for obtained I-U characteristics.

The negative resistance device with memory has two states: high resistance and conductive. Conductive states is established at higher currents and then remains without noticeable decay. The high resistance state can be reestablished by increasing the current above a certain value and switching it off rapidly. The high resistance state can be reestablished by applying a short current pulse.



Figure 2. Characteristic of a switching device with memory.

III. EXPERIMENTAL

The studied bulk alloy was synthesized by the meltquench method, using high-purity elementary components, and amorphous character of the samples was checked by Xray diffraction as described in detail in [19]. Surface morphology and atomic composition of the samples were investigated using a JEOL JSM-6460LV scanning electron microscope (SEM) equipped with an EDAX energy dispersive spectroscopy (EDS) system.

The investigated samples were polished with alumina powder of 0.3 and 0.05 μ m grain size until a mirror-like surface was obtained. This procedure ensures correct electrical contacts. The rectangular-shaped samples had cross-section of 3.5x3 mm² and thickness of 0.2 mm. Silver paste was applied on the opposite parallel surfaces of the samples.

Both dynamic and static *I-U* characteristic curves were investigated by the usual two-probe method. Measurements were carried out in a specially constructed measuring cell of two electrodes, which is similar to the cells described previously [20, 21]. The samples were spiral springs loaded between two brass electrodes to ensure good electrical connections and constant pressure contact during the measurements. The measurement system for determining static I-U characteristics of the samples consisted of a stabilized DC power supply with a current meter (SourceMeter Keithley 2410), a series load resistor, and a Keithley 2000 multimetre (for measuring the voltage drop across the sample). These instruments were connected to a PC to provide effective acquisition of the measured data.

Measurements above room temperature, in the range 300– 373 K, were performed by placing the measuring cell 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 \pm 0.5 K. All measurements were done in air and in dark.

IV. RESULTS AND DISCUSSION

IV.1. Structural studies

The bulk composition was investigated by EDS analyses carried out at different points of the sample surface. The results given in table 1 show that the composition at each particular point is almost the same, and atomic percentages of the elements are very close to those of the starting materials. The estimated average deviation did not exceed 2% in atomic fraction of each element in all the cases.

Table 1. EDS measurements (atomic %) for the bulk $Cu_5(AsSe_{1.4}I_{0.2})_{95}$ glass.

Spectrum	Cu	As	Se	Ι	Total
1	4.92	37.05	51.01	7.02	100.00
2	4.94	36.85	51.18	7.03	100.00
3	4.93	36.92	51.10	7.05	100.00
Ideal	5.00	36.58	51.30	7.12	100.00

The morphology of the investigated glass was examined by SEM. Figure 3 shows the SEM micrograph of a fractured surface of the sample. As can be seen, the contrast is uniform, as might be expected for an amorphous glassy structure.



Figure 3. SEM of fractured surface of the bulk $Cu_5(AsSe_{1.4}I_{0.2})_{95}$ glass. IV.2. Switching properties of the bulk glass $Cu_5(AsSe_{1.4}I_{0.2})_{95}$

The static I-U characteristic curve for the sample of 0.2 mm thickness is shown in figure 4 as a representative example. As can be seen, an increase in the applied voltage produces a very low current (the first branch oa), representing the OFF state with high resistance of the switch. At point a, an

abrupt increase in current and drop in voltage to point b takes place in a very short time of the order 10-9 s [4], i.e. the switching occurs through the load line ab (a negative resistance region). Therefore, no data points were recorded in this range. A further increase in the applied voltage produces an increase in the current without any significant increase in the potential drop across the sample (part bc). This part of the curve represents the ON state with low resistance. On decreasing the applied voltage in this state, the current decreases until finally both values become zero (part co). The observed curves have a typical CCNR (current-controlled negative resistance) switching characteristic with memory, similar to that of many of chalcogenide glasses [9, 10, 15, 22, 23]. The sudden drop in voltage along the AB segment in figure 4 may be related to the formation of localized highly conductive filaments across the sample [12].



Figure 4. Static *I-U* characteristic for the bulk $Cu_5(AsSe_{1.4}I_{0.2})_{95}$ glass at room temperature. Full-line arrow represents the region of current increase, the broken-line arrow shows the region of current decay.

IV.3. Effect of temperature on the I–U characteristics

The effect of the ambient temperature on the I–U characteristics is illustrated in figure 5. During the measurements, the temperature of the specimen was maintained constant at eight different points in the 300–373K temperature range. It was found that the threshold voltage Uth decreased exponentially, whereas threshold current Ith increased exponentially with increase in temperature, as shown in figure 6.

The observed variation of these parameters is similar to those reported in the literature for bulk [14] and thin-film [10] amorphous chalcogenide semiconductors. If the ambient temperature increases, the thermal energy required for the transformation of the channel material (filament) from the amorphous to crystalline state will be lower. Therefore, the magnitude of the threshold voltage Uth decreases with the increase of the ambient temperature.



Figure 5. I-U *characteristics* characteristic for the bulk $Cu_5(AsSe_{1.4}I_{0.2})_{95}$ glass at different temperatures: a) 303-333 K i b) 343-373 K.

A plot of $\ln U_{\text{th}}$ versus 1000/T for the investigated sample of 0.2 mm thickness is presented in figure 7. The straight line obtained by least squares fitting satisfies the following Arrhenius formula:

$$U_{\rm th}(T) = U_0 \exp(\Delta E_{\rm th} / k_{\rm B}T), \qquad (1)$$

where U_0 is a constant and ΔE_{th} is the threshold voltage activation energy. The value of the ΔE_{th} was calculated from the slope of the linear relation and it is equal to 0.43 ± 0.02 eV. The ratio $\Delta E_{\text{th}}/\Delta E_{\sigma} = 0.60$ was calculated using the value of $\Delta E_{\sigma}=0.72 \pm 0.02$ eV obtained in [24]. This ratio is higher then theoretical value of 0.5, derived on the basis of an electrothermal model for the switching process [20]. Based on this fact it can be concluded that thermal model is dominant in switching process.

It is suggested that the memory switching phenomenon is caused by a phase transition of the material from glassy to the crystalline state due to Joule heating, and can be understood in terms of thermal process. The application of a high electric field causes Joule heating of the medium, which results in an increased carrier concentration in the current path. This leads to a larger electronic contribution to thermal conductivity, which enhances Joule heating in this region. Finally, the temperature rise will become adequate to initiate a thermal breakdown and formation of narrow crystalline filaments in the material between the electrodes.



Figure 6. Plots of: a) U_{th} and b) I_{th} in the investigated range of temperatures.



Figure 7. Plot of lnU_{th} versus 1000/T for the chalcogenide $Cu_5(AsSe_{1.4}I_{0.2})_{95}$ glass.

V. CONCLUSION

The switching characteristics of the chalcogenide glassy semiconductor Cu5(AsSe1.4I0.2)95 have been discussed on

the basis of the thermal model. The obtained static currentvoltage characteristics show a typical memory type switching. Crystalline filaments, which may be formed between the electrodes in ON state, cause the electrical conductivity to increase by more than four orders of magnitude at room temperature. The value of threshold voltage Uth decreases exponentially with increasing the ambient temperature of the investigated glass. The obtained value of $\Box Eth / \Box E \Box = 0.60$ has confirmed the existence of thermal process based on Joule heating. The exponential current increase with increasing voltage indicates non-ohmic behaviour at high electric field. According to the presented experimental results, this investigated amorphous semiconductor has possible application in memory elements which demand high threshold voltage.

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REFERENCES

- S. R. Lukić and D. M. Petrović, "Complex amorphous chalcogenides: Thermal stability and crystallization tendency, Physics applications of disordered materials," edited by M. Popescu, Romania, pp. 259-276, 2002.
- [2] M. Popescu, "Disordered chalcogenide optoelectronic materials: Phenomena and applications," Journal of Optoelectronics and Advanced Materials, vol. 7, pp. 2189-2210, Aug 2005.
- [3] D. Strand, "Ovonics: From science to products," Journal of Optoelectronics and Advanced Materials, vol. 7, pp. 1679-1690, Aug 2005.
- [4] H. Fritzsche, "Why are chalcogenide glasses the materials of choice for Ovonic switching devices?," Journal of Physics and Chemistry of Solids, vol. 68, pp. 878-882, May-Jun 2007.
- [5] S. R. Ovshinsky, "Reversible electrical switching phenomena in disordered structures," Phys. Rev. Lett., vol. 21, pp. 1450-1453, 1968.
- [6] S. J. Park, I. S. Kim, S. K. Kim, S. M. Yoon, B. G. Yu, and S. Y. Choi, "Phase transition characteristics and device performance of Sidoped Ge2Sb2Te5," Semiconductor Science and Technology, vol. 23, p. 105006, Oct 2008.
- [7] A. S. Glebov, "Semiconducting Chalcogenide Glass III: Applications of Chalcogenide Glasses, ed R Fairman and B Ushkov," London: Elsevier Academic Press, vol. 80, 2004.
- [8] N. Kalkan, S. Yildirim, K. Ulutas, and D. Deger, "Electrical switching in TISbSe2 chalcogenide semiconductors," Journal of Electronic Materials, vol. 37, pp. 157-160, Feb 2008.
- [9] M. A. Afifi, N. A. Hegab, H. E. Atyia, and A. S. Farid, "Investigation of DC conductivity and switching phenomenon of Se80Te20-xGex amorphous system," Journal of Alloys and Compounds, vol. 463, pp. 10-17, Sep 8 2008.
- [10] M. M. Abdel-Aziz, "Memory switching of germanium tellurium amorphous semiconductor," Applied Surface Science, vol. 253, pp. 2059-2065, 2006.
- [11] R. Rajesh and J. Philip, "Memory switching in In-Te glasses: results of heat-transport measurements," Semiconductor Science and Technology, vol. 18, pp. 133-138, Feb 2003.
- [12] H. Fritzsche, "Physics of Instabilities in Amorphous Semiconductors," IBM J. Res. Develop., vol. 13, pp. 515-521, 1969.
- [13] [M. Dominguez, E. Marquez, P. Villares, and R. Jimenez-Garay, "On the electrical conduction and current-controlled negative differential resistance with memory in bulk samples of glassy semiconductor Cu0.05As0.50te0.45: NTC thermistor-type behaviour," Semiconductor Science and Technology, vol. 3, pp. 1106-1111, 1988.

- [14] A. S. Soltan and A. H. Moharram, "Electrical switching in the chalcogenide AS(60-x)Te(40)Cu(x) glasses," Physica B-Condensed Matter, vol. 349, pp. 92-99, 2004.
- [15] M. Haifz, M. Ibrahim, M. Dongol, and F. Hammad, "Effect of composition on the structure and electrical properties of As-Se-Cu glasses," Journal of Applied Physics, vol. 54 pp. 1950-1954, 1983.
- [16] M. P. Slankamenac, S. R. Lukić, and M. B. Živanov, "Electrical switching effects in the chalcogenide glassy semiconductor Cu5(AsSe1.410.2)95," ReCIMiCo Workshop, Novi Sad, 2008.
- [17] M. P. Slankamenac, S. R. Lukić, and M. B. Živanov, "Analysis of Electrical Switching Effects in the Chalcogenide Glassy Semiconductor Cu1(AsSe1.4I0.2)99," Hemijska industrija, vol. 63, pp. 183-187, 2009.
- [18] M. P. Slankamenac, S. R. Lukić, and M. B. Živanov, "Electrical switching in the bulk metal chalcogenide glassy semiconductor Cu10(AsSe1.4I0.2)90," Semiconductor Science and Technology, vol. 24, pp. 29-36, 2009.
- [19] S. R. Lukić, D. M. Petrović, I. O. Guth, and M. I. Avramov, "Complex Non-crystalline Chalcogenides: Technology of Preparation

and Spectral Characteristics," Journal of Research in Physics, vol. 30, pp. 111-130, 2006.

- [20] M. A. Afifi and N. A. Hegab, "Threshold switching in Te46xAs32+xGe10Si12 chalcogenide glass system," Vacuum, vol. 48, pp. 135-141, 1997.
- [21] I. A. Gohar, Y. M. Moustafa, A. A. Megahed, and E. Mansour, "Switching characteristic of barium vanadate glasses doped with iron oxide," Physics and Chemistry of Glasses, vol. 38, pp. 37-41, 1997.
- [22] K. Ramesh, S. Asokan, K. S. Sangunni, and E. S. R. Gopal, "Electrical switching in germanium telluride glasses doped with Cu and Ag," Applied Physics a-Materials Science & Processing, vol. 69, pp. 421-425, Oct 1999.
- [23] A. E. Bekheet, "Memory switching characteristics in amorphous Ga2Se3 films," Journal of Electronic Materials, vol. 37, pp. 540-544, Apr 2008.
- [24] S. R. Lukić, D. M. Petrović, and A. F. Petrović, "Effect of copper on conductivity of amorphous AsSeyIz," Journal of Non-Crystalline Solids, vol. 241, pp. 74-77, Nov 1 1998.