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A programmable metallization cell based on Ag-As_2S_3

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The switching properties of a Programmable Metallization Cell (PMC) structure based on the Ag-As_2S_3 solid electrolyte were investigated. It was found that at 120 mV of forward bias voltage the device switches from an off state resistance to an on resistance state which is more than two orders of magnitude lower. To bring the structure back in an off state, a reverse bias of several volts is required. The frequency dependence of the switching threshold was carried out. Also is found that time required to switch the structure in a stabile on state is less than 10 µsec and around 60 µsec of reverse bias is required to put the structure back in an off state. The threshold voltage is shown to be nearly independent on temperature, but a linear increase of the on state resistance is observed within 20-80 ^oC. The results are interpreted in terms of an electronic – superionic transition in chalcogenide glassy semiconductors due to a high concentration of dissolved metal.

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1. Introduction

The Programmable Metallization Cells belongs to structures, which are often used in electronic systems to store information in form of binary data. Their principle of operation is based on electrochemical control of quantity of metal in a thin film of solid electrolyte. Key attributes are low voltage and current operation, rapid write and erase, good retention and endurance, the ability for the storage cells to be physically scaled to a few tens of nm, and a simple fabrication sequence. The memory elements consist from an electrochemically indifferent cathode, a solid electrolyte layer and a source of oxidizable metal atoms which can also act as anode. The solid electrolyte is usually manufactured by dissolving in chalcogenide glassy semiconductors metals, such silver or copper, via thermal or/and photo-dissolution. A review of basic electrochemistry that enables PMC memory operation is reported in [1]. The mostly investigated materials for solid electrolyte are silver doped Ge–S and Ge–Se ternaries [2-5], as well as germanium telluride glasses doped with Cu or Ag [6,7]. However, the As–S chalcogenide glasses were not studied thoroughly yet. The purpose of present work is to investigate the switching properties of a PMC structure based on the Ag-As_2S_3 as a solid electrolyte manufactured by an analogue technique. The Au–$Ag_x(As_2S_3)_{1-x}$–Ag structures are characterized with electrical properties of current-voltage, switch time, and the evolution of I–V characteristics with frequency and temperature.

2. Experimental

To manufacture PMC structures, the thin films of solid electrolyte have been prepared by vacuum evaporation of glassy arsenic trisulphide from a crucible onto Pyrex glass substrate with a priory deposited gold cathode. The upper electrode i.e. the anode was manufactured from pure silver using the same method of deposition. The transformation of chalcogenide glassy material into a solid electrolyte was performed by dissolution of silver in it, through the light and thermal induced doping.

The switching and memory properties of structures have been studied in the quasi-static electrical conditions. The processing of the data was performed with PC and a data acquisition board manufactured by National Instruments Inc. Voltage double-sweeps were carried out starting at maximum reverse bias, sweeping through zero to an appropriate forward voltage, and sweeping back again through zero to the reverse bias starting point. The acquired signal was the voltage drop across a 10 Ohms series resistor. No programming current was used. The same measurement was performed using different delay times between two consecutive data acquisitions. The data saved in a digital format were analyzed and plotted.

The transient characteristics have been measured using a single or trains of squared voltage pulses with different amplitudes and polarities, obtained from a programmable pulse generator PG8021 (AD Electronic GmbH, Germany).

The effect of temperature was studied by placing the memory devices inside of an electrical furnace. A platinum resistance temperature detector Pt-100 close to the sample served as a temperature controller.

3. Results and discussion

Fig. 1 shows a typical current-voltage plot for Au–$Ag_x(As_2S_3)_{1-x}$–Ag structures for two different frequencies of applied voltage. Initially the current through the sample is low i.e. the structure resistance is high. At an applied forward bias of around 120 mV in stacked thin-film structures, the silver ions are reduced at the cathode and the silver in the anode oxidized. The result of this electrochemical reaction is the rapid formation of a stable conducting electrodeposit extending from cathode to anode. Once the electrodeposit reaches the anode the resistance of the structure drops from the off state value of around 10^3 Ohms to the on state value, which is less than 10 Ohms. The on state is retained even after the applied field is reduced to zero i.e. the power supply is disconnected. To return the structure to the high resistance a reverse bias is required, which will cause dispersion of the link. The R_{off} / R_{on} ratio for the 1.5 cm^2 structures is around 10^2.

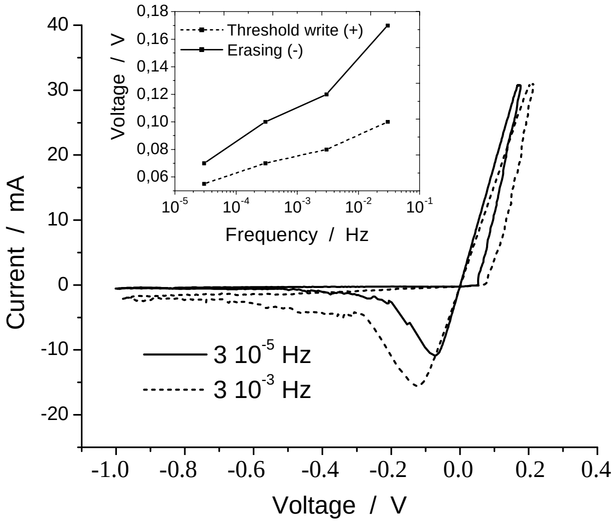

Fig. 1. Typical current-voltage plot for Au–Ag$_x$(As$_2$S$_3$)$_{1-x}$–Ag structures at different frequencies of applied signal. Inset shows the threshold writing voltage and erasing oltage versus frequency of applied voltage.

Analyzing the plots of Fig. 1 one can see that both switching on (storage) and switching off (erasing) occur at a lower biases in case of low frequency and vice versa, at a higher voltage – in case of high frequency. Inset of Fig. 1 shows the threshold writing voltage and erasing voltage versus frequency of applied voltage. These dependences indicate that the reduction and oxidation processes take place at either applied bias but they are more intensive at higher voltage. Hence, at a higher bias the switching phenomenon will occur earlier than in case of a lower voltage and one can expect an adequate relation between the voltage amplitude and duration of its application to switch on the device.

Fig. 2 illustrates the relation between the maximal value of a linear increasing voltage signal and its duration required to bring the structure from an off state into an on state, with resistance of 10 Ohms.

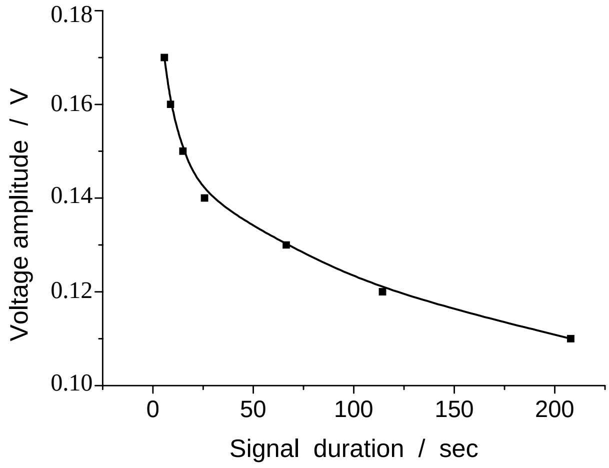

Fig. 2. The relation between applied voltage and its duration to switch on the device.

Further, either the on or the off state resistances appear to depend on frequency of applied voltage. This statement is illustrated in Fig. 3, where the device resistance in "on" and in "off" state are plotted as a function of frequency. The increasing of frequency results in decreasing of "off" state resistance and in enhancing of the "on" state resistance. Such a behavior is in agreement with electrochemical model of operation of PMC devices [1].

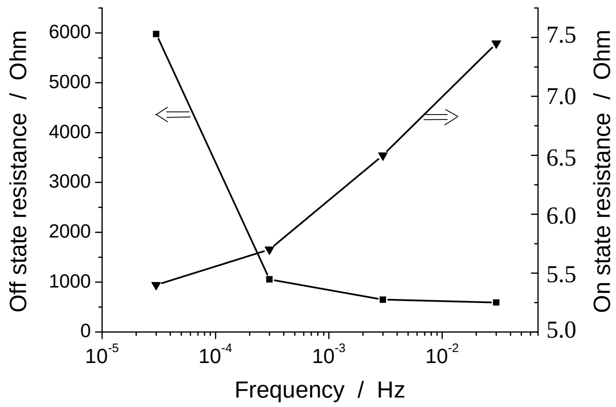

Fig. 3. "On" and "off" state resistance versus frequency of applied bias.

Using trains of positive (write) pulses of 2V in magnitude followed by –2V negative (erase) pulses, both with different duration, was found that the minimum time required to put the structure in a stabile on state is around 10 µsec. To bring the structure back to initial off state around 60 µsec of reverse bias is required. The storage oscilloscope output for the response of the structure to one cycle is presented in Fig. 4.

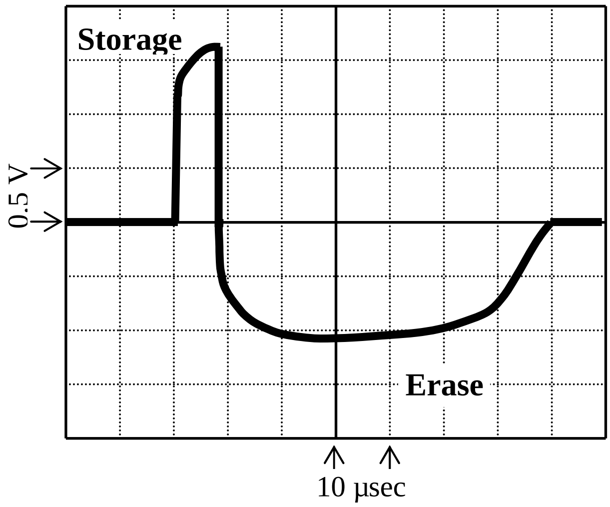

Fig. 4. The storage oscilloscope output for the response of the Au-$Ag_x(As_2S_3)_{1-x}$-Ag to an input signal which goes from –2V to +2V and 8 µsec later drops back to –2V. The horizontal scale is 10 µsec per division and the vertical scale is 500 mV per division.

The temperature dependence of I – V characteristic is an important factor in considering a switching material for information storage applications. In the present study the effect of temperature on the current-voltage characteristic has been investigated. The same sample after resetting has been used for investigations at different temperatures in range of 20-80 ^{o}C. Within this temperature range a significant threshold voltage variation was not observed. On the other hand, the on state resistance essentially depends on operation temperature. The temperature dependent electrical resistance in the on state is reported on Fig. 5.

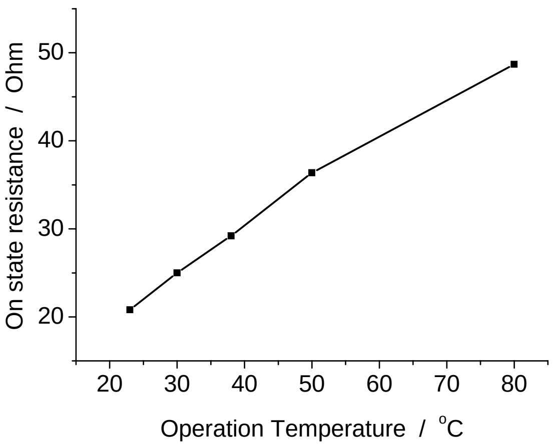

Fig. 5. The on state resistance versus operating temperature.

The increasing of operation temperature leads to a nearly linear increase of the on state resistance, with around 2.4 %/^{o}C. This behavior is justified by the metallic nature of the electrodeposit – the basic conductive material in this state. After the sample is cooled down to the room temperature I–V characteristic come back to its initial shape.

5. Conclusions

The Au-$Ag_x(As_2S_3)_{1-x}$-Ag structure made by usual technique of manufacturing of PMC devices are found to exhibit memory switching. Basic properties of operation were investigated. It was found an adequate nonlinear dependence between the level of applied voltage and its duration to write or to erase information.

For writing / erasing amplitudes of +2V / –2V the on / off states are realized in 10 / 60 µsec. The heating until temperature of 80 ^{o}C does not influence noticeable the threshold voltage but linearly enhances the on state resistance of the device.

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