

PECULIARITIES OF SWITCHING IN PROGRAMMABLE METALLIZATION CELLS BASED ON GLASSY As_2S_3 AND GeS_4

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INTRODUCTION

The Programmable Metallization Cell (PMC) that consists of a thin film of solid electrolyte sandwiched between an oxidizable silver anode and a cathode can act as memory elements [1]. Key attributes are low voltage and current operation, rapid write and erase operations, 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 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]. In our previous works [8-10] the switching properties of a large area (150 mm^2) PMC structure based on the Ag- As_2S_3 as a solid electrolyte were investigated. The purpose of present work is to investigate the switching behavior of two analogues PMC structures based on Ag- As_2S_3 and Ag- GeS_4 solid electrolytes with relative small effective area. The interest in a common investigation of As_2S_3 and GeS_4 glasses arise from the fact, that these materials have the same mean coordination number $r = 2.4$ and, according to constraint counting theory [11, 12], this results in a very stable glass as the number of constraints per atom equals the degree of freedom per atom.

1. BACKGROUND

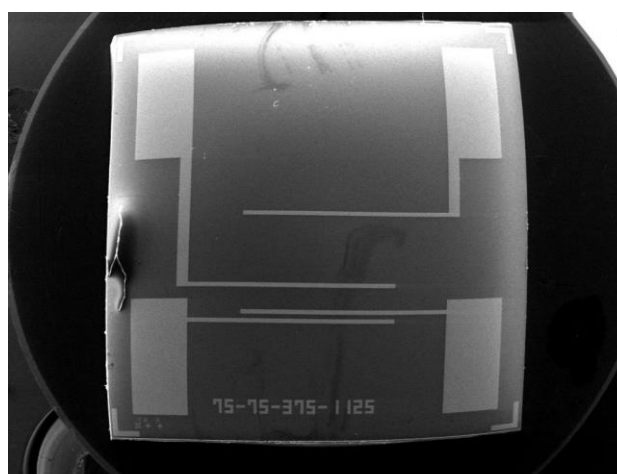
The principle of operation of the PMC structures as memory elements is based on electrochemical control of nanoscale quantities of metal (usually silver) in a solid electrolyte thin film. They consist in a chemically indifferent cathode and an oxidizable silver-containing anode formed in contact with a solid electrolyte.

A good solid electrolyte, which conducts ions over a wide range of temperatures, can be obtained by thermal or/and photodissolution of silver from a metallic surface source into a thin film of chalcogenide glassy semiconductor, until the resulting material becomes chemically saturated with metal. The resulting material takes the form of a continuous glassy chalcogenide backbone in which nanoscale silver rich (superionic) regions

are dispersed. The metal rich phase is both an ion and an electron conductor, but the backbone material that separates each of these conducting regions is a good dielectric, so the overall resistance of the material initially is high. Under the influence of an electric field the electron current from the cathode reduces an equivalent number of Ag ions as injected from the anode and a metal-rich electrodeposit is thereby formed in electrolyte. By applying a bias with opposite polarity the formation process can be reversed. The reverse ion current flows until the previously injected Ag has been oxidized and deposited back to the electrode, which supplied the metal. Thus, the Ag atoms can be electrodeposited or removed from the chalcogenide based thin film, switching the structure between two resistance states that differ with several orders of magnitude. The state of the structure is retained even the power supply is disconnected making PMC structures to work as non-volatile memory elements.

2. EXPERIMENTAL

Figure 1 shows the SEM image of silicon substrates with preliminary deposited Pt cathodes used to manufacture PMC structures.



SEM MAG: — DET: SE Detector
HV: 20.0 kV DATE: 03/01/07
Vega ©Tescan
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Figure 1. SEM image of the silicon substrate with Pt cathodes

The complete process is described in Figure 2.

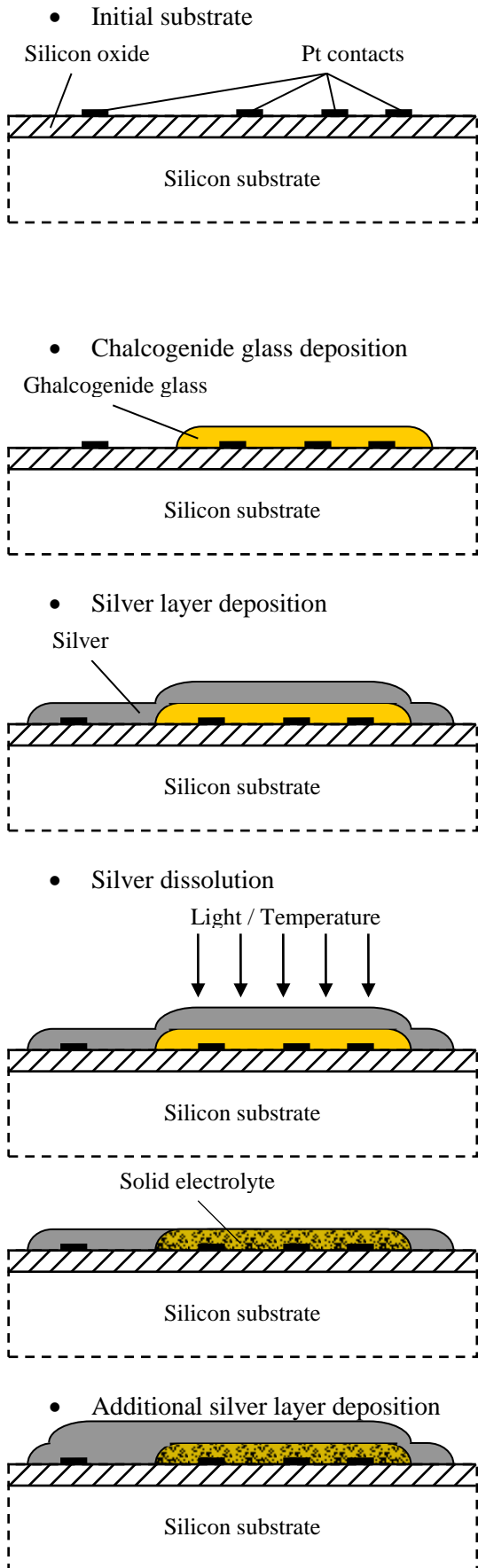


Figure 2. The complete process of the PMC fabrication.

Glassy As_2S_3 (or GeS_4) thin films were deposited by vacuum evaporation at 10^{-5} Torr. To transform the chalcogenide glassy material into a solid electrolyte, a silver layer was deposited by the same method of deposition and then dissolved in the chalcogenide thin film through thermal and light induced dissolution. An additional layer of Ag was then added to ensure a source of silver atoms for the electrodeposition. This last layer acts also as oxidizable anode. The effective functional area of the structures was 0.3 mm^2 .

The switching and memory properties of structures have been studied in the quasi-static electrical conditions. 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 measurements were performed using an AT-MIO-16X data acquisition board manufactured by National Instruments Inc and a LabView based Virtual Instrument. The measured signal was the current trough the sample measured using Y5-11 electrometer. The data was saved in digital format for subsequent plotting and analyzing.

All measurements were performed at room temperature.

3. RESULTS AND DISCUSSIONS

Figure 3 shows the typical current-voltage plots for $Pt-Ag_x(As_2S_3)_{1-x}-Ag$ and $Pt-Ag_x(GeS_4)_{1-x}-Ag$ structures. The voltage sweeps were $-1.0V$ to $+0.55V$ and back to $-1.0V$. The applied voltage varied in steps of 5 mV while the respective values of the current were measured. The delay time between subsequent measurements was 0.1 sec .

It is seen, that the plots have the same aspect, showing that both structures operate as PMC devices, however there are some differences in parameters of switching process. The last, calculated from the current voltage plots, are summarized in the Table 1.

From this table it is seen that the solid electrolyte composition affects mostly the off state resistance. As in the off state current flows homogeneously through entire area of the active layer, consisting in chalcogenide glass doped with Ag until the saturation, the off state is firstly

determined by the effective area of the structure and the resistance of the solid electrolyte. The solid

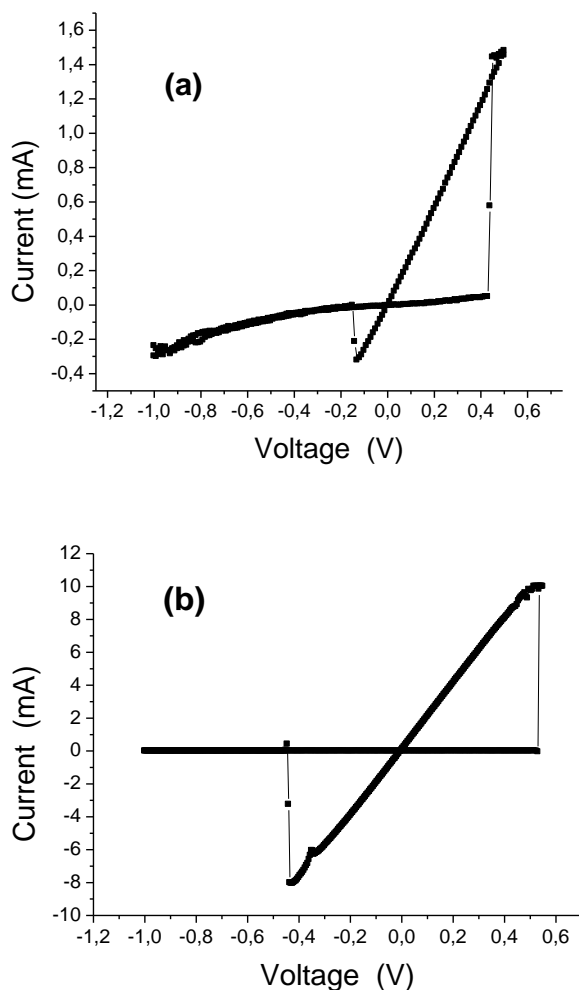


Figure 3. Current-voltage plot PMC structures:
 a) $Pt-Ag_x(As_2S_3)_{1-x}-Ag$;
 b) $Pt-Ag_x(GeS_4)_{1-x}-Ag$.

electrolyte resistance depends on its chemical composition and the concentration of Ag atoms resulted from saturation of the chalcogenide-based glass with silver by photo or thermal dissolution.

On the other hand, the on state resistance of the $Pt-Ag_x(As_2S_3)_{1-x}-Ag$ and $Pt-Ag_x(GeS_4)_{1-x}-Ag$ structures does not differ so much, because in the on state, the current flows through the metal rich electrodeposit, which is extended from the cathode to anode. Obviously, the on state resistance of the device depends mainly on the geometry and dimensions of the electrodeposit, formed in the solid electrolyte.

Multiple sweeps under the same conditions show small variations of threshold voltage, however the As_2S_3 based PMC device require a lower

positive bias to be switched in on state than its GeS_4 counterpart.

Table 1. Switching parameters of PMC structures with different compositions of the used solid electrolyte.

Switching parameter	Used solid electrolyte	
	$Ag_x(As_2S_3)_{1-x}$	$Ag_x(GeS_4)_{1-x}$
Off-On switching voltage	430 mV	530 mV
On-Off switching voltage	-150 mV	-445 mV
Off state resistance	$4 \cdot 10^3$ Ohms	$3 \cdot 10^8$ Ohms
On state resistance	300 Ohms	50 Ohms

The switching at threshold voltage from a high-resistive off state to a low-resistive on state of the structures with relative small effective area (investigated in present work) occurs faster than in structures with large area (1.5 cm^2), investigated in previous works [8-10], but the final on state resistance is of the same order of magnitude. This fact in one hand and the dependence of the off state resistance on the effective area of the structure on the other hand, reveal that reduction of the structure dimensions leads to improvement of the switching properties of the device in context of practical applications.

The electrodeposition of silver atoms in solid electrolyte starts when the positive threshold voltage is applied. The reduction of silver ions will persist as long as sufficient potential difference is maintained. That is why the resistance of the conducting bridge between electrodes will continue to fall even after it has formed. On the other hand, the removing of a strong electrodeposit through the erasing operation requires relative high reverse current and voltage (see Figure 3b). Because of high power consumption this is not desirable and can be avoided by limiting the current using its external stabilization. Figure 4 illustrates the I-V plot for $Pt-Ag_x(GeS_4)_{1-x}-Ag$ structure, when external current source is limited to $4 \mu\text{A}$. In such a case, during write operation the resistance falls to a point where the voltage drop on the structure is no longer sufficient to support reduction of silver ions, hence the electrodeposition process ceases and the resistance between electrodes remains constant. Even in such a case the final on state resistance of the device ($\sim 4 \cdot 10^4$ Ohms) is still lower than the off state resistance by four-orders of magnitude. However only 30 mV (instead of 445 mV) of reverse bias is sufficient to bring the structure back to state with high resistance.

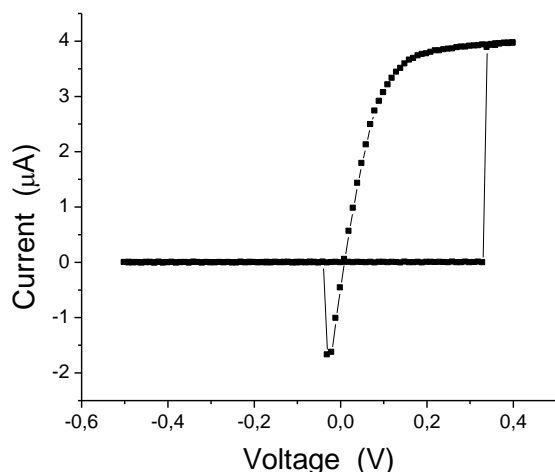


Figure 4. I-V plot of Pt-Ag_x(GeS₄)_{1-x}-Ag structure with an external current source limit

4. CONCLUSIONS

The switching behavior of PMC structures based on Ag-GeS₄ and Ag-As₂S₃ solid electrolyte manufactured by thermal and photo-dissolution of silver in chalcogenide semiconductor layer was investigated. It is shown that the composition of used solid electrolyte strongly influences the off state resistance of the PMC structure, but the on state resistance is relatively not affected. This result is owing to the peculiarities of conducting mechanism in PMC devices.

The erasing reverse biases can be essentially lowered using the external limitation of the current trough PMC.

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