Chalcogenide Letters Vol. 13, No. 4, April 2016, p. 139 - 144

ELECTROCHEMICAL METALLIZATION CELLS BASED ON Ag-Ge-S AND Ag-Ge-Ga-S ELECTROLYTES

S. VALKOVA[a], T. WAGNER[a,b*], J. PRIKRYL[b]

[a]*Department of General and Inorganic Chemistry, Faculty of Chemical Technology, University of Pardubice, Cs. Legii 565 Square, 530 02 Pardubice, Czech Republic*

[b]*Centre of Materials and Nanotechnologies, Faculty of Chemical Technology, University of Pardubice, Cs. Legii 565 Square, 530 02 Pardubice, Czech Republic*

Electrochemical metallization cells (EMC) are based on the electrochemical growth and removal of nanoscale metallic filaments in thin films of solid elektrolyte. EMC shows a great promise to replace conventional data storage technologies. It has low programming current and voltage and smaller sizes that can be seen as a way to store more data in small space. In this work ITO/Ag-GeS/Ag and ITO/Ag-GeGaS/Ag memory cells were prepared to study an influence of incorporation of Ga into glassy backbone matrix of Ge-S electrolyte and it's switching characteristics. The transparency of ITO films was used for application of OIDD process that can be seen as a method to stabilize cells switching.

(Received February 25, 2016; Accepted April 7, 2016)

Keywords: EMC memories, thin films, amorphous chalcogenides

1. Introduction

Nowadays conventional data storage technologies, such as SRAM or SDRAM are close to their limits. Due to the trend of miniaturization in electronic systems there is a high interest in developing new memory devices. Many new concepts of usable memory devices such as CBRAM (*Conductive bridging Random Access Memory*), also called EMCs (*Electrochemical Metallization Cells*) are in the way of development [1,2].

CBRAM memory is based on the electrochemical growth and removal of nanoscale metallic filaments in thin films of solid electrolyte. The memories exhibit bipolar switching that depends on the DC voltage polarity. In „ON“ state conductive filament forms from electrochemically active electrode, typically made from Ag or Cu through ionically conductive film to inert electrode, such as Pt or W. The conductive filaments enriched by Ag or Cu metal formation bring several orders decrease of resistivity. After that application of reverse polarity of DC electric field causes a dissolution of the metal filaments and resistivity of the system grows, which is called „OFF“ state [2,3]. Key attributes of the ideal non-volatile memory (*NVM*) are low current operation, high speed, high density, low cost, good retention and endurance [3,4]. This requirement is mostly satisfied for ionic conductive chalcogenide films.

It was discovered by Kozicki et al. [4], that Ag-GeS devices have excellent switching characteristics even after processing at 300°C and more. They exhibit a high OFF resistance but can be switched to a lower ON resistance, from 10^{11} Ω at OFF state to 10^4 Ω at ON state that is highly stable with good non-volatility. In 2007 Gilbert and Kozicki presented 2kbit memory block using solid electrolyte cells [5]. A few years later Gopalan et al. [6] presented 384 kbit and 1 Mbit EMCs of Ag/Ge_xS_y/W with SET conditions of 1.5V/250ns/30μA, RESET conditions of 0.6V/12ms/20μA and endurance of 10^5 cycles.

---

[*] Corresponding author: tomas.wagner@upce.cz

In this work ITO/Ge-S-Ag/Ag and ITO/Ge-Ga-S-Ag/Ag memory cells were prepared to study an influence of incorporation of Ga into glassy backbone matrix of Ge-S electrolyte and to study their memory switching characteristics. It was suggested to prove experimentally that with introduction of Ga into Ge-S glassy matrix, concetration of Ag that can be doped into electrolyte through optically-induced diffusion and dissolution (OIDD) proces will increase [7,8].

2. Experimental

The chalcogenide thin films were prepared by the pulsed laser deposition (PLD) technique. For that, it is important to note that a sulfur depletion for about 7 at.% in S-based systems was observed during pulsed laser deposition [9,10,11], therefore it was necessary to use sulfur enriched targets to meet the required compositions of prepared thin films, namely in our case GeS_2 and $Ge_{28}Ga_6S_{67}$ films from $Ge_{28}S_{72}$ and $Ge_{22}Ga_6S_{72}$ bulk samples, respectively.

Amorphous bulk samples with compositions of $Ge_{28}S_{72}$ and $Ge_{22}Ga_6S_{72}$ were prepared by direct synthesis (980°C, 24 hrs) from very pure elements in evacuated quartz ampoules.

Consequently, the chalcogenide films with compositions of $Ge_{34,5}S_{65,5}$ and $Ge_{28}Ga_{6,5}S_{65,5}$ were deposited from these glasses on top of the ITO substrates by PLD with energy of pulses 7 J/cm^2, frequency 20Hz and wavelength of laser beam 248nm. The thickness of the chalcogenide layers were 150nm. Pilkington ITO substrates with square resistivity of 12-14 $\Omega.cm^2$ were used as inert electrodes due to their high transparency that allows to provide OIDD process on as prepared chalcogenide films. In the next step Ag electrodes with thickness of 160nm and 2mm diameter were deposited on the chalkogenide surface by thermal evaporation through appropriate mask. As it is shown in Fig. 1. a simple structure of memory cells was used for comparison of switching characteristics of two different Ag-Ge(Ga)S electrolytes.

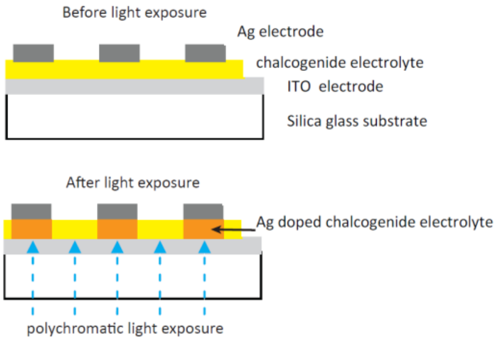

Fig. 1. Schematic drawing of thin films profile for the memory cells study

The OIDD of silver was applied by Xe lamp (1000W) exposure for 1(3) hours in inert atmosphere of N_2 to obtain Ag doped electrolyte for conductive bridge memory switching. It was calculated from our experimental data that 150nm thick film of composition $Ge_{34.5}S_{65.5}$ can dissolve up to 8.5 at.% of Ag and 150 nm thin film of $Ge_{28}Ga_{6,5}S_{65,5}$ can dissolve up to 10.3 at% of Ag [12]. This amount of Ag was enough for the formation of Ag-rich conductive filaments that are necessary for the memory switching.

Memory switching experiments were tested with maxima number of cycles in one measurement from 10 to 1000 with different starting voltages and differet times for both states.

3. Results

In this work the main target was to investigate the effect of Ga in the amorphous GeS_2 electrolyte on switching characteristics of memory cells. I-V curves for switching from 1 to 1000 cycles are basically similar for both tested electrolytes in ITO/Ag-Ge(Ga)S/Ag cells, as it can be seen from Fig. 2. However some differences in shapes of individual switching loops (I-V curves) were observed in ITO/Ag-GeS/Ag cells.

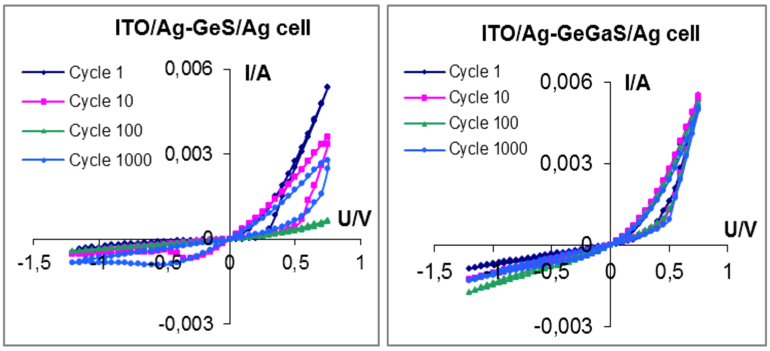

Fig. 2. Cyclic I-V curves of ITO/Ag-$Ge_{34.5}S_{65.5}$/Ag cell and ITO/Ag-$Ge_{28}Ga_{6.5}S_{65.5}$/Ag cell

The same experimental data can be also plotted as the resistence (R) vs. voltage (U) curves that are shown in Fig. 3. It is apparent from Fig. 2 and 3 that the reproducibilty of I-V or R-V switching characteristics between cycles 1 and 1000 is significantely better for cells with electrolytes containing Ga.

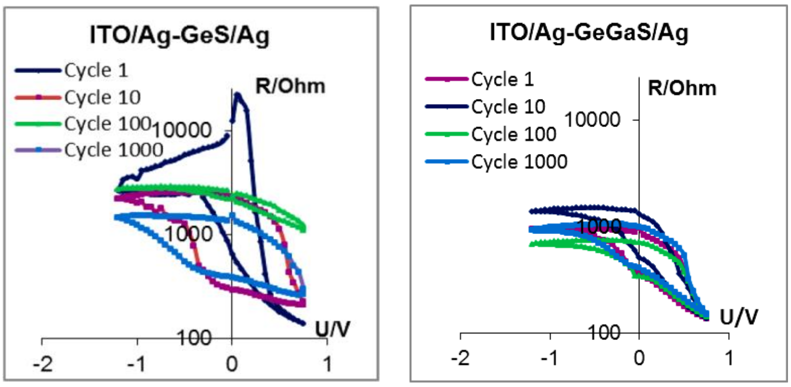

Fig. 3. Resistance vs. voltage curves of ITO/Ag-$Ge_{34.5}S_{65.5}$/Ag cell and ITO/Ag-$Ge_{28}Ga_{6.5}S_{65.5}$/Ag cell

Fig. 4. demonstrates dependences of ON and OFF resistance states on switching cycles (N) for both ITO/Ag-$Ge_{34.5}S_{65.5}$/Ag cells and ITO/Ag-$Ge_{28}Ga_{6.5}S_{65.5}$/Ag cells, where (in)stabilty of resistance of both states can be transparently compared. It can be seen that even if both types of cells have relatively small differences between resistence in OFF and ON states due to the cell dimensions [13] switching of ITO/Ag-GeGaS/Ag cell seems to be more stable than switching of ITO/Ag-GeS/Ag cell.

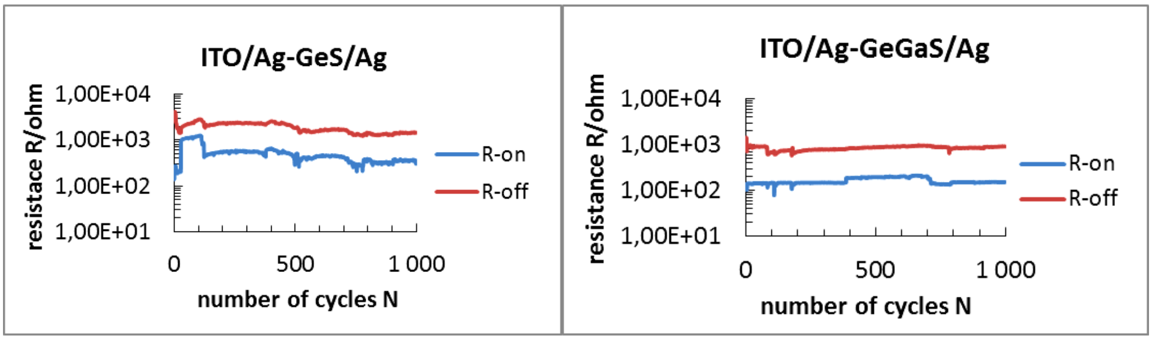

Fig. 4. Comparison of R_{on} and R_{off} states for ITO/Ag-$Ge_{34.5}S_{65.5}$/Ag cell and ITO/Ag-$Ge_{28}Ga_{6.5}S_{65.5}$/Ag cell, when OIDD process was applied.

We also address in this paper the question whether OIDD process is really necessary for switching functionality of the memory cells. An interesting results are shown in Fig. 5.

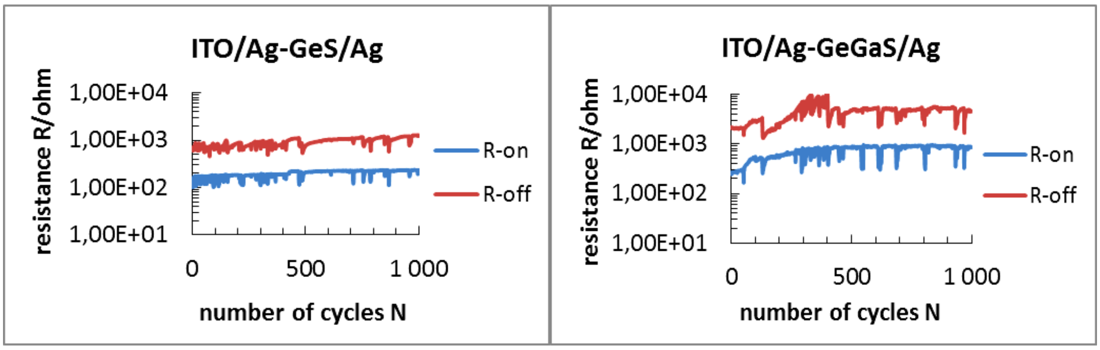

Fig. 5. Comparison of R_{on} and R_{off} states for ITO/Ag-$Ge_{34.5}S_{65.5}$/Ag cell and ITO/Ag-$Ge_{28}Ga_{6.5}S_{65.5}$/Ag cell without application of OIDD process.

It can be clearly seen that even without applying of OIDD process cells show switching characteristics. However it seems that application of the OIDD process brings larger stability of R_{on} *and* R_{off} states resulting in their smoother courses. Results in Fig. 5. show that without OIDD process ITO/Ag-GeS/Ag cells stabilizes it's switching after 100 cycles and ITO/Ag-GeGaS/Ag cells needs approximatelly 400 switching cycles to reach stable behaviour of it's switching. This stabilization of the switching cycles (approx. 100 cycles) is also observed for ITO/Ag-GeS/Ag cells even if we apply OIDD process before switching starts. Moreover it can be seen that applying of OIDD process leads to decreasing of stability of switching which is in contrast with previous results in Fig. 3. On the other hand ITO/Ag-GeGaS/Ag cells switch seems to be stable in switching behaviour right from the begining of switching process, i.e. OIDD process seems to be crucial for stable switching of this type of cells.

4. Discussion

One of the possible keys to larger stability of ITO/Ag-GeGaS/Ag cells in comparison to ITO/Ag-GeS/Ag cells can be seen in formation of donor-acceptor bonds between Ga and S in GaS_4^- tetrahedra as shown in Fig.6. Since higher Ag content can be dissolved in the Ge-Ga-S thin films in comparison with pure Ge-S [12], one may speculate that the additional silver atoms can be locallized nearby these GaS_4 tetrahedra in the similar manner as lanthanides [14]. A higher silver concentration in chlacogenides leads to a higher ionic conductivity [15]..

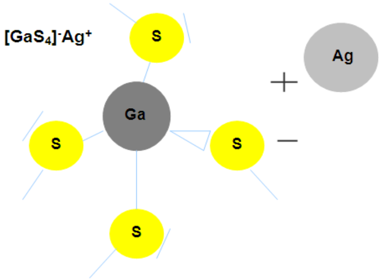

Fig. 6. Scheme of $[GaS_4]^-$ *tetrahedra and* Ag^+ *ionic bond.*

As it is known from the literature [16] introduction of Ag into glass backbone of Ge-S causes increase of Ge-Ge bonds as the silver bonds itself with S. In this case Ag behaves as glass modifier that steadily incorporates itself in glass matrix and more conductive electrolyte is formed [17]. However, bonded Ag and mobile Ag^+ ions are necessary for conducting bridge switching. One of our previous experimental works [12] showed that incorporation of Ga into Ge-S glass backbone increase amount of Ag atoms that can be dissolved into glass matrix of chalcogenide thin films. If Ga atoms partly replace Ge ones in the backbone structure of glass it brings possibility of formation of the donor - acceptor bond with one of the atoms of S. The charging of $Ag^+[GaS_4]^-$ tetrahedra in comparison to tetrahedra of „neutral“ GeS_4 that are more structurally stable can cause an increase of amount of silver atoms dissolved in the structure and also increase of Ag^+ ions/Ag ratio in glass matrix.

We also proved that since the overall amount of dissolved Ag atoms is lower for ITO/Ag-$Ge_{34.5}S_{65.5}$/Ag cells, it has higher resistance for both ON and OFF states than ITO/Ag-$Ge_{28}Ga_{6.5}S_{65.5}$/Ag cells.

We tested I-V characteristics of our memory cells. We found that the absolute difference between both ON and OFF states during switching however seems almost the same. As it is reffered in works by Mitkova and Kozicky [4, 16, 18] the difference between R_{on} and R_{off} should be at least in range of 4 orders. In the case of our memories the difference in values of resistivity is around only 1 or 2 orders. The small difference between R_{on} and R_{off} can be seen in Fig. 4 and Fig. 5.

Similar issue was also addressed by Kolar [12], who studied switching characteristics in Ag-AsS_2 system and compared resistivity difference of nanostructured switching cells and switching in simple planparalel cells. The resistivity switching is definitely influenced by the 3D cells dimensions [19, 20]. Generally planparallel cells has smaller difference between ON and OFF states compared to nanostructured.

We assume that also in case of cells studied in this paper the thickness of electrolyte has large influence in switching and partly causes small difference in resistivity of ON and OFF states. Since the surface of commercial ITO thin films was not fully uniform we needed 150nm of chalcogenide thin films to cover cracks and holes in it and to have enough space for Ag filament creation.

The other issue in our case is if the OIDD process is necessary for overal perfomace during switching proces. It is clear that in both types of cells even if OIDD process is not applied switching is still possible. However our results prove that OIDD process brings more stability of resistence between ON and OFF states in long switching cycles.

5. Conclusions

ITO/Ag-$Ge_{34.5}S_{65.5}$/Ag and ITO/Ag-$Ge_{28}Ga_{6.5}S_{65.5}$/Ag memory cells were prepared to study an influence of incorporation of Ga into glassy backbone matrix of Ge-S electrolyte and it’s switching characteristics. For easier introduction of Ag into the chalcogenide electrolyte OIDD process was chosen. It was discovered that memory cells with the electrolyte containing Ga have more stable switching characteristics than those cells with the Ga-free electrolyte. Both types of the cells showed that they can be switched at even longer regimes than 1000 cycles that is with agreement of Kozicki and Mitkova´s works. However in contrary to their works the differences between R_{on} and R_{off} were only around one order of magnitude, which is mainly issue of the cell dimensions.

Acknowledgment

The authors thank to the project of the Ministry of Education, Youth and Sports, CR, KONTAKTII (CR-USA) LH14059 and grant LM2015082 Center of Materials and Nanotechnologies for financial support.

References

[1] I. Valov, M.N. Kozicki; J. Phys. D: Appl. Phys., **46**, 074005 (2013).
[2] R. Waser, M. Aono; Nat. Mater., **6**, 833 (2007).
[3] W. Lu, D.S. Jeong, M.N. Kozicki, R. Waser; MRS Bulletin, **37**, 124 (2012).
[4] M.N. Kozicki, M. Balakrishnan, C. Gopalan, C. Ratnakumar, M. Mitkova; IEEE Non-Volatile Memory Technology Symposium, Proceedings (2005) 86-89.
[5] N.E. Gilbert, M.N.Kozicki; IEEE J. Solid-State Circuits, **42**, 1383 (2007).
[6] C. Gopalan, Y. Ma, T. Gallo, J. Wang, E. Runnion, J. Saenz, F. Koushan, P. Blanchard, S. Hollmer; Solid-State Electronics **58**, 54 (2011).
[7] T. Kawaguchi, K. Masui; Jpn. J. Appl. Phys., **26**, 15 (1987).
[8] J. M. Oldale, S.R.Elliott; J. Non-Cryst. Solids, **128**, 255 (1991).
[9] M. Krbal. T. Wagner, T. Kohoutek, P. Nemec, J. Orava, M. Frumar; J. Phys. Chem. Solids, **68**, 953 (2007).
[10] T. Wagner, M. Krbal, J. Jedelsky, M. Vlcek, B. Frumarova, M. Frumar; J. Optoelectron. Adv. Mater., **7**(1), 153 (2005).
[11] T. Wagner, M. Krbal, P. Nemec, M. Frumar, Th Wagner, M. Vlcek, V. Perina, A. Mackova, V. Hnatovitz, S.O. Kasap; Appl. Phys., **79,** 1563 (2004).
[12] M.Bartos, T.Wagner, S.Valkova, M.Pavlista, M.Vlcek, L.Benes, M. Frumar; J. Optoel. Adv. Mater., **13** (2011)
[13] K.-Ch. Kwon, M.-J. Song, K.-H. Kwon, H.-V. Jeoung, D.-W. Kim, G.-S. Lee, J.-P. Hong J.-G. Park; J. Mater. Chem. C, **3**, 9540 (2015).
[14] T. H. Lee, S. I. Simdyankin, J. Hegedus, J. Heo and S. R. Elliott, Phys. Rev.B, **81** (2010), p. 104204.
[15] M. Krbal, T. Wagner, T. Srba, J. Schwarz, J. Orava, T. Kohoutek, V. Zima, L. Benes, S.O. Kasap, M. Frumar, J. of J. Non-Cryst. Solids, **353**, 1232 (2007).
[16] M. Mitkova, M.N. Kozicki; J. Phys. Chem. Solids, **68**, 567 (2007).
[17] E. Bychkov, V. Tsegelnik, Yu. Vlasov, A. Pradel, M. Ribes; J. Non-Cryst. Solids, **208,** 1 (1996).
[18] M.N. Kozicki, M. Mitkova, M. Park, M. Balakrishnan, C. Gopalan; Superlatt. Microstruct., **34,** 459 (2003).
[19] J. Kolar, J.M. Macak, K. Terabe, T. Wagner; J. Mater. Chem. C, **2**, 349 (2014).
[20] C. Liang, K. Terabe, T. Hasegawa, R. Negishi, T. Tamura, M.Aono; Small, **10**, 971 (2005).