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Phase-change electrical memory elements and devices

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Electrical memory elements based on Ge-Sb-Te pure and doped by Sn-Se have been obtained by pulsed laser deposition on special substrates covered by gold as well as on common glass. A set of electrical memory elements in a 4x4 matrix structure on the glass substrate has been produced. Devices with 3 and 10 memory elements have been constructed and tested for their memory properties. The special features of the voltage-current characteristics have been revealed.

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Keywords: Phase-change material; Chalcogenide; Ge-Sb-Te; Memory element; Memory device; Voltage-current characteristics

1. Introduction

The conventional computer and semiconductor industries today face both economical/technical problems and have become cyclical industries. The prospects for future growth and higher margins need fundamental scientific and technological advancements.

Soon after starting in the mid – 1950s of an unexpected field of amorphous and disordered materials, wherein the constraints of the crystalline lattice were lifted so that new degrees of freedom for the atomic design of synthetic materials were made possible. Ovshinsky announced amorphous semiconductor switching and memory effect “Ovonic” in 1968 [1]. This opened a new research area in so-called recording of information by phase change effect.

Now phase change rewritable optical disc technology has become the main stream of the optical disc world as demonstrated by rewritable compact discs (CD) and digital versatile discs (DVD), which are based upon it [2].

Flash memory cards are popular for mobile electronic products, such as digital cards, mobile computers and mobile phones. The ovonic phase-change materials are leading candidates for mobile electronic products, such as digital cameras, mobile computers and mobile phones. The Ovshinsky Unified Memory (OUM) is a good candidate of replacing all the electrical memories such as the volatile memories of DRAM and SRAM.

Phase-change chalcogenide materials have been reported by Feinleib et al. in 1971 [3]. Many chalcogenide systems have been studied [4] and recent papers published in many journals including Journal of Non-Crystalline Solids, Chalcogenide Letters, Journal of Ovonic Research and J. Optoelectron. Adv. Mater. show the many-sided investigation of these materials of large importance from the theoretical and practical points of view [5-45]. Papers on phase change materials with special emphasis on Ge-Sb-Te system have been published in huge amount [46-59]. A review on the evolution of the chalcogenide field of research can be found in [45].

In this paper we report the results on thin film phase change memory elements and memory systems based on pure Ge-Sb-Te amorphous material, as well as on Sn-Se doped Ge-Sb-Te. Compact devices of three and ten elements have been built and characterized for its memory properties.

2. Experimental

Materials

Chalcogenide materials are distinguished from other alloys by their electronic structure wherein the structural integrity of the material is provided by the strong p-electron bonding orbitals, but the remaining lone-pair p-orbitals are either spin-up and spin-down configurations or have some weakly-bonded configurations based upon p-orbital interactions. Most chalcogenide alloys behave as intrinsic semiconductors with the Fermi level pinned at midgap. These materials can sustain a high electric field, exciting the lone-pairs which, then, because the material exhibits differential negative conductivity, permit a conduction plasma filament of electrons and holes to be formed. This filament expands and contracts in diameter in order to maintain a constant current density. The contacts to these chalcogenide devices are ohmic and the presence of a high electric field initiates current injection from the contacts. The electron-hole “plasma” which results from current injection in the two-terminal device, electrically short-circuits its contacts, resulting in very little voltage drops across them. The switching of the ovonic threshold switch goes from a highly resistive (amorphous) state to a metallic-like conducting (crystalline) state, at room temperature and is very fast.

Adding Sb to the GeTe binary system will transform it into a nonstoichiometric material and this greatly increases the compositional range over which rapid crystallization can be achieved [60].

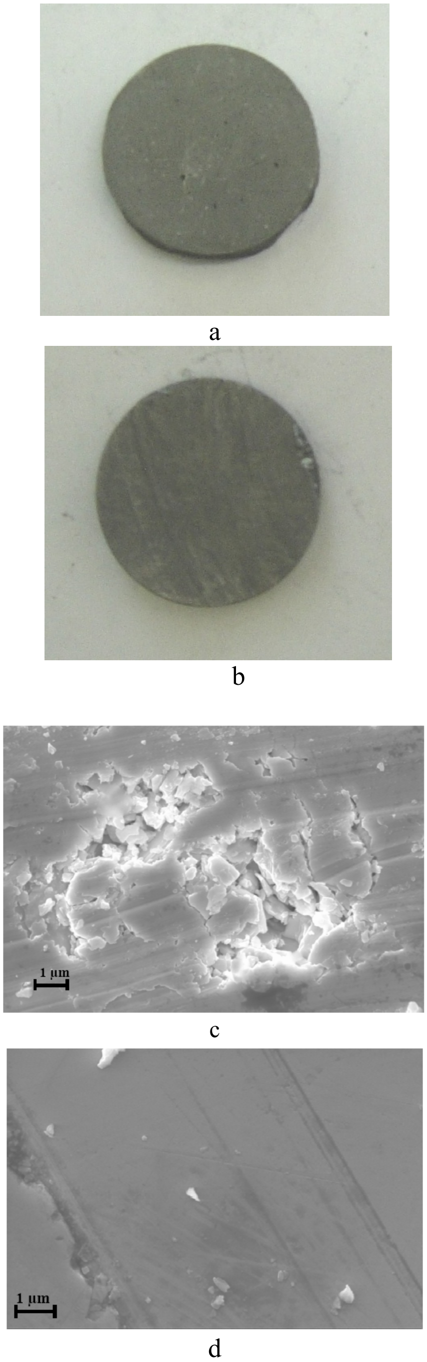


Fig. 1 Disc-shaped samples used as targets for pulsed laser deposition (a,b) and electron micrograph of the surface of the bulk samples (c. d).
a – L1; b – L2; c – L1; d – L2

We have prepared two bulk compositions $GeSb_2Te_2Bi_{1.3}$ (L1) and $GeSb_2Te_4Sn_{0.1}Se_{0.2}$ (L2). The contribution of each element was calculated in mass percents and the corresponding quantities of high purity elements were introduced in glass ampoules. The ampoules were evacuated and sealed. Finally the ampoules were heated at the temperature of 1050°C. The cooling of the ampoules was made in air. The ingots were cut by a wire-saw method as disc-shaped pieces with 1 cm diameter and 2-3 mm width (Fig. 1a, b).

The obtained discs were used as targets for pulsed laser deposition in the system shown in Fig. 2.

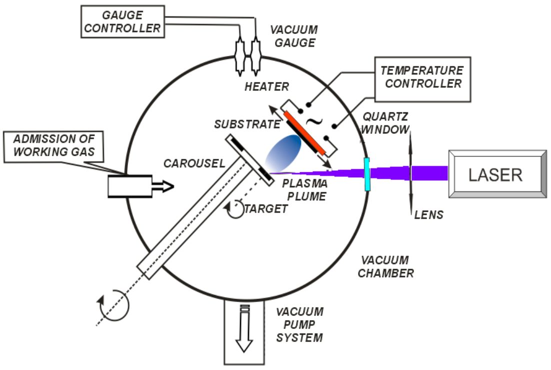


Fig. 2 System for pulsed laser deposition of memory films. (excimer laserKrF λ= 248 nm, and τ_{FWHM}~7-9 ns)*

Thin films of L1 and L2 composition have been prepared by pulsed laser deposition. The deposition chamber was evacuated down to a residual gas pressure below 10^{-4} Pa.

Devices

Special devices made either of ten electrodes or three electrodes embedded in insulating ceramics and mounted on a gold covered substrate (see fig. 3 a,b) have been built.

In these cases the thin films memory cells defined by electrode wires and metallic support operated between the contacts on a rather large distance (0.6 mm).

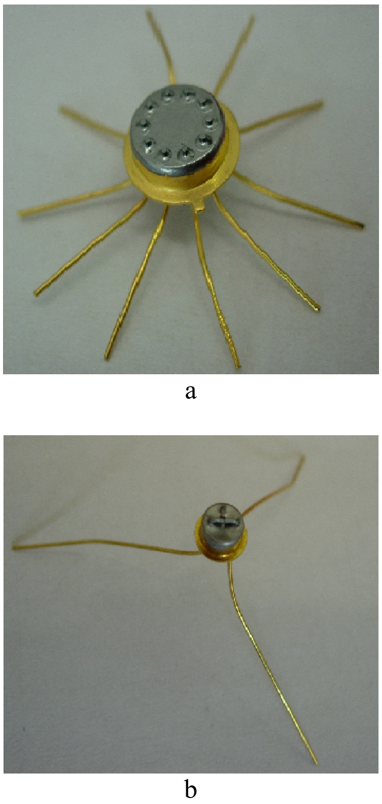


Fig. 3 Memory chip with a) ten cells and b) three cells integrated on special supports covered by gold.

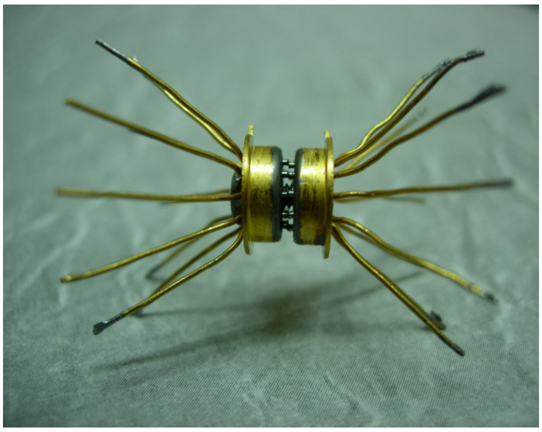


Fig. 4 Complex memory device with 10 cells and possibility to trigger simultaneous all the cells or to achieve steps of memory.

A second version of the device consisted in substrates as in Fig. 3a covered by thin films of phase-change material (L1). Two such identical configurations have been mounted one over the other, so as the electrode contacts be in touch. This device operates between electrodes through the double film of phase-change materials deposited on the top of the electrodes. In this case the thickness of the active phase-change layer between electrodes was ~ 2 micrometers (Fig. 4).

One important advantage of the configurations with several memory cells is the possibility to use the switching between two electrodes triggered by any other electrode in neighbouring cells. As a function of the cell properties and voltage strength one can trigger one or another cell, thus making possible a complex device with special functionalities.

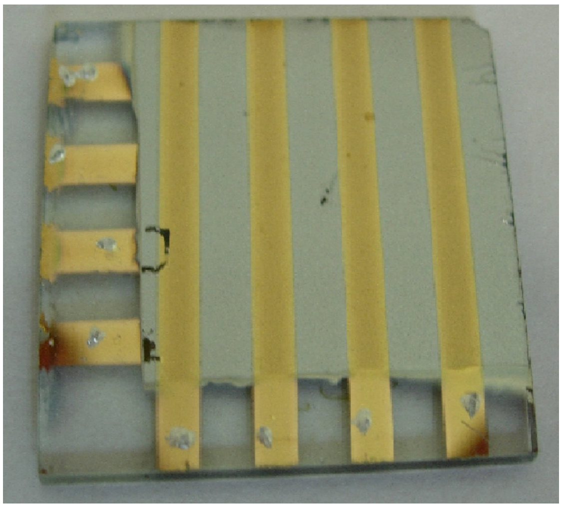


Fig. 5. A device that defines a lattice of 16 memory cells.

Another configuration was made from the chalcogenide material sandwiched between two groups of gold electrodes oriented perpendicularly one to another (Fig. 5).

2. Results

The X-ray diffraction pattern of chalcogenide films deposited on a silicon wafer shows an amorphous structure (Fig. 6). The diffraction lines are due to crystalline silicon.

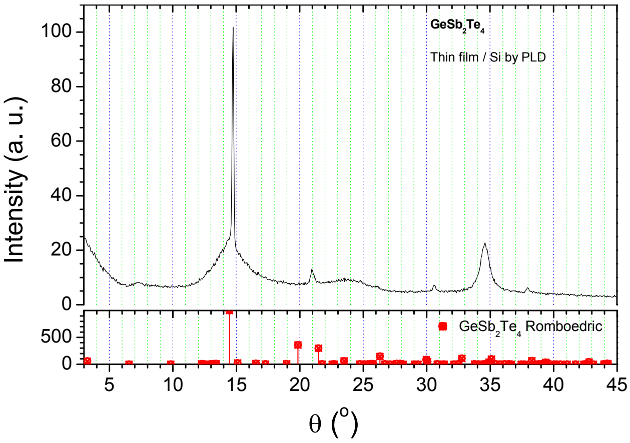


Fig. 6 X-ray diffraction pattern of the as deposited film.

The electron micrographs of the surface of pulsed laser deposited amorphous chalcogenide film are presented in Fig. 7, 8. Special droplets, characteristic to PLD method, of diameter 1-10 μm, do appear. No significant differences between the undoped and doped material might be seen on the micrographs (Fig 8 a, b).

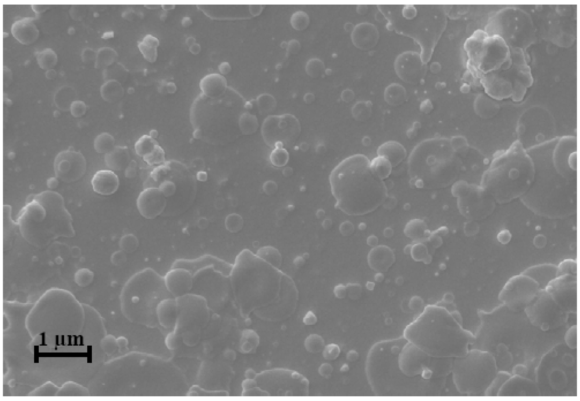
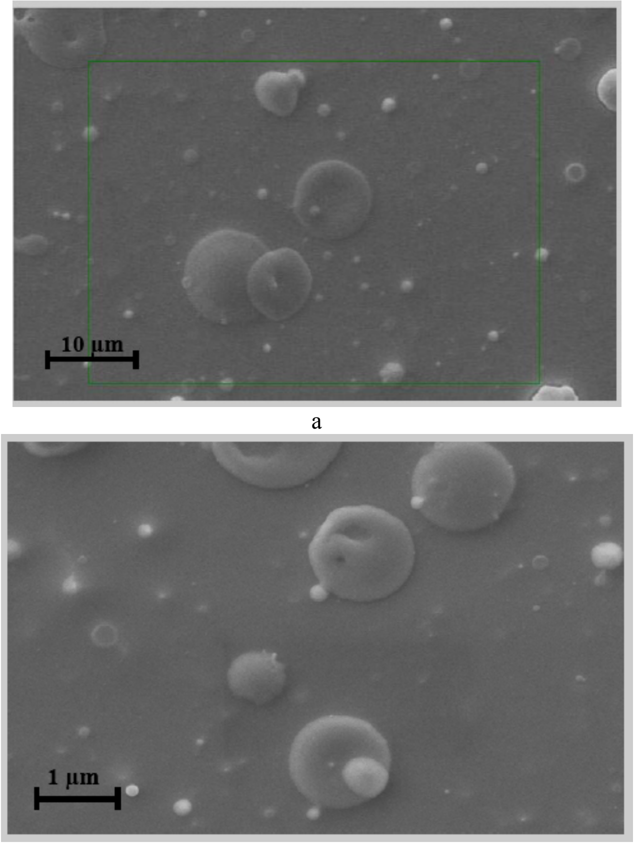


Fig. 7 SEM picture of the as deposited film (l1).

Both types of devices made with three memory cells and, respectively, ten memory cells have been tested for the switching properties.

The results are shown in Figs. 9 and 10 for two typical memory cells (three electrode cell). The threshold voltage is 3.3-4 V for the ten electrode cell. The current raises up to 12 mA. The threshold voltage is 22 V for the 3 electrode device (Fig. 3b) and the current raises up to 11.5 mA.



a

b

Fig. 8. Surface morphology of pulsed laser deposited films of L1 (a) and L2 (b) memory material.

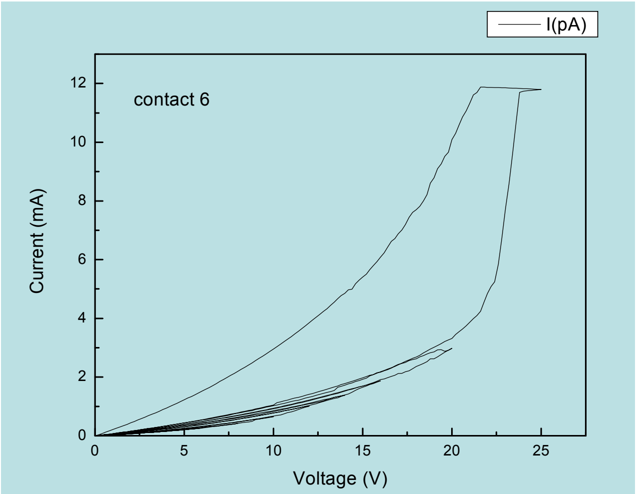


Fig. 9. The I-V characteristics of a memory cell (L1) in three memory cells device shown in Fig. 3b.

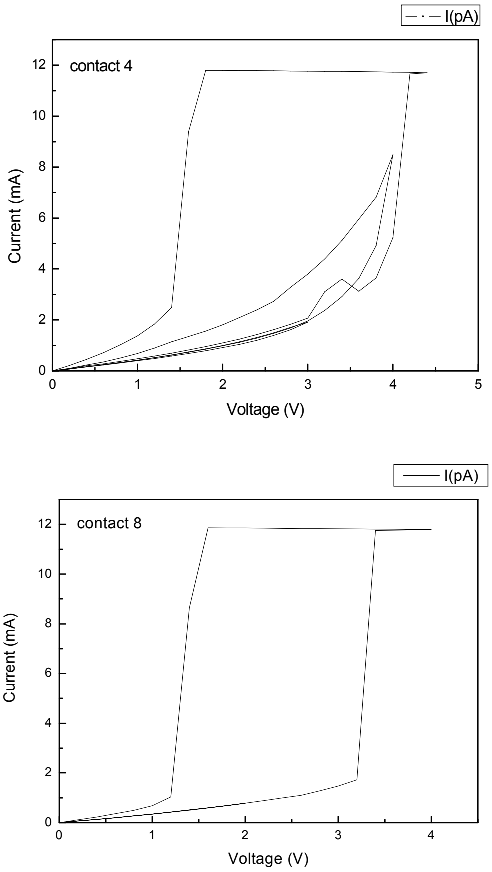


Fig. 10. The cycles that describes the switching of two different memory cell (L1) defined by the device shown in Fig. 4.

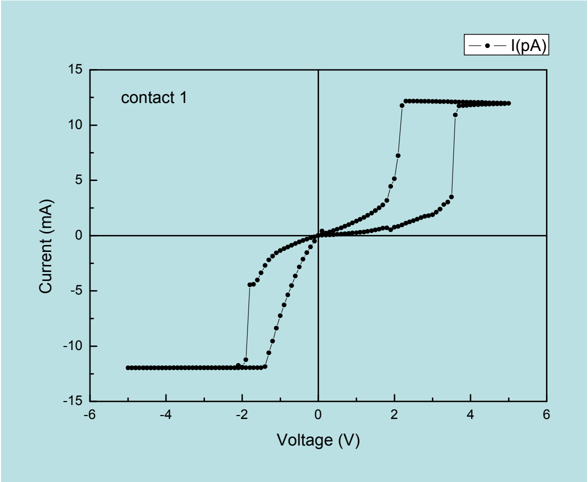


Fig. 11. Shape of the characteristic cycle of the memory device (based on L2 composition) built as in Fig. 4.

The special configuration shown in Fig. 4 with double memory layer sandwiched between metallic contacts gives rise to different switching characteristics with asymmetric loops (Fig. 11).

3. Conclusions

We have successfully prepared and operated phase change materials based on Ge-Sb-Te and Ge-Sb-Te-Sn-Se compositions. Devices based on a system of three and ten memory cells have been built. A special planar configuration with 4 × 4 cells has been achieved. The cycling of every memory cell demonstrates the possibility to get good memory devices by simply deposition by pulsed laser of phase-change chalcogenide material. Further research to use these memories in electronic systems is planned.

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References

[1] S. R. Ovshinsky, Phys. Rev. Lett. **21**, 1450 (1968).
[2] Panasonic Catalog, Rewritable optical discs DVD-RAM 4.7 GbLF-D100J, DY –HB47 (2000).
[3] J. Feinlieb, J. de Neufville, S. C. Moss, S. R. Ovshinsky, Appl. Phys. Lett. **18**, 254 (1971).
[4] M. Popescu, Non-Crystalline Chalcogenides, Kluwer Academic Publishers (Solid State Science and Technology Library, Volume 8, 2000), The Netherlands.
[5] A. Kolobov, J. Haines, A. Pradel, M. Ribes, P. Fons, J. Tominaga, J. Optoelectron. Adv. Mater. **8**(6), 2161 (2006).
[6] I. Stratan, D. Tsiulyanu, I. Eisele, J. Optoelectron. Adv. Mater. **8**(6)2117 (2006).
[7] M. Popescu, J. Optoelectron. Adv. Mater. **8**(2), 755 (2006).
[8] Ke. Tanaka, A. Saitoh, N. Terekado, J. Optoelectron. Adv. Mater. **8**(6), 2058 (2006).
[9] M. Popescu, J. Optoelectron. Adv. Mater. **8**(6), 2164 (2006).
[10] M. A. Paessler, D. A. Baker, G. Lucovsky, A. E. Edwards, P. C. Taylor, J. Optoelectron. Adv. Mater. **8**(6), 2039 (2006).
[11] C. Steiner, W. Welnic, J. Kalb, M. Wuttig, J. Optoelectron. Adv. Mater. **8**(4), 2044 (2006).
[12] F. Sava, A. Lőrinczi, Journal of Ovonic Research **2**(2), 4 (2006).
[13] L. Heireche, M. Belhadji, J. Ovonic Research, J. Ovonic Research **2**(6), 125 (2006).
[14] F. Sava, A. Lőrinczi, M. Popescu, G. Socol, E. Axente, I. N. Mihailescu, M. Nistor, J. Optoelectron. Adv. Mater. **8**(4), 1367 (2006).
[15] M. Kubliha, J. Kaluzny, J. Pedlikova, J. Zavadil, V. Labas, J. Optoelectron. Adv. Mater. **9**(10), 3082 (2006).
[16] E. Prokhorov, G. Trapaga, Yu. Kovalenko, J. Optoelectron. Adv. Mater. **8**(6), 2066 (2006).
[17] S. O. Kasap, G. Belev, J. Optoelectron. Adv. Mater. **9**(1), 1 (2007).
[18] J. Singh, J. Optoelectron. Adv. Mater. **9**(1), 50 (2007).
[19] S. Kugler, J. Hegedüs, R. Lukács, J. Optoelectron. Adv. Mater. **9**(1), 37 (2007).
[20] Tz. Babeva, J. Dikova, V. Rashkova, J. Optoelectron. Adv. Mater. **9**(1), 170 (2006).
[21] V. B. Petrovic, S. R. Lukic, M. V. Siljegovic, F. Skuban, J. Optoelectron. Adv. Mater. **9**(4), 825 (2007).
[22] M. Sakurai, F. Kakinuma, E. Matsubara and K. Suzuki, J. Non-Cryst. Solids, 312-314, 585 (2002).
[23] G. R. Strbac, F. Skuban, S. R. Lukic, D. D. Strbac, J. Optoelectron. Adv. Mater. **9**(6), 1690 (2007).
[24] J. Pedlikova, J. Zavadil, O. Prochazkova, D. Lezal, J. Optoelectron. Adv. Mater. **9**(6), 1679 (2007).
[25] V. M. Kryshenik, M. L. Trunov, V. P. Ivanitsky, J. Optoelectron. Adv. Mater. **9**(7), 1949 (2007).
[26] E. Vateva, B. Terziyska, D. Arsova, J. Optoelectron. Adv. Mater. **9**(7), 1965 (2007).
[27] R. Singh, S. K. Tripathi, S. Kumar, J. Optoelectron. Adv. Mater. **9**(7), 1974 (2007).
[28] J. Holubova, Z. Cernosek, E. Cernoskova, J. Optoelectron. Adv. Mater. **9**(7), 1979 (2007).
[29] G. Achamma, D. Sushama, P. Predeep, J. Optoelectron. Adv. Mater. **9**(7), 1985 (2007).
[30] P. Sharma, J. Optoelectron. Adv. Mater. **9**(7), 1988 (2007).
[31] P. Sharma, S. C. Katyal, J. Optoelectron. Adv. Mater. **9**(7), 1944) (2007).
[32] P. Sharma, V. Sharma, S. C. Katyal, J. Optoelectron. Adv. Mater. **9**(7), 2000 (2007).
[33] D. Sushama, G. Achamma, P. Predeep, V. G. Sathe, A. Dubey, J. Optoelectron. Adv. Mater. **9**(7), 2005 (2007).
[34] K. Wang, C. Steimer, M. Wuttig, J. Optoelectron. Adv. Mater. **9**(7), 2008 (2007).
[35] V. Pandey, S. K. Tripathi, A. Kumar, J. Optoelectron. Adv. Mater. **9**(7), 2010 (2007).
[36] I. Kaban, W. Hoyer, T. Petkova, P. Petkov, B. Beuneu, A. Schops, M. A. Webb, J. Optoelectron. Adv. Mater. **9**(9), 2750 (2007).
[37] Y. Ledemi, L. Calvez, M. Roze, X. H. Zhang, B. Bureau, M. Poulain, Y. Messaddeq, J. Optoelectron. Adv. Mater. **9**(12), 3751 (2007).
[38] A. Kumar Singh, Kedar Singh, J. Optoelectron. Adv. Mater. **9**(12), 3736 (2007).
[38] R. S. Sharma, R. K. Shukla, A. Kumar, J. Optoelectron. Adv. Mater. **9**(12), 3760 (2007).

[39] K. Shimakawa, J. Optoelectron. Adv. Mater. **9**(10), 2973 (2007).
[40] Jai Singh, J. Optoelectron. Adv. Mater. **9**(10), 3013 (2007).
[41] K. D. Tsendin, J. Optoelectron. Adv. Mater. **9**(10), 3035 (2007).
[42] M. S. Iovu, I. A. Cojocaru, E. P. Colomeico, J. Optoelectron. Adv. Mater. **9**(10), 3134 (2007).
[43] A. Gerbreders, J. Teteris, J. Optoelectron. Adv. Mater. **9**(10), 3164 (2007).
[44] Z. G. Ivanova, J. Optoelectron. Adv. Mater. **9**(10), 3149 (2007).
[45] M. Popescu, J. Non-Crystalline Solids, **352**, 887 (2006).
[46] N. Yamada, T. Matsunaga, J. Appl. Phys. **88**, 7020 (2000).
[47] T. Matsunaga, N. Yamada, "Structural investigation of $GeSb_2Te_4$: A high-speed phase-change material", Phys. Rev. **B69**, 104111 (2004).
[48] R. Roy, V. Caslavska: "Di-phasic structure of switching and memory device 'glasses'", Solid State Comm. **7**, 1467 (1969).
[49] V. Caslavska, D. Strickler, D. Gibbon, R. Roy, J. Mater. Sci. **3**, 440 (1968).
[50] M. Popescu, M. Kubliha, J. Kaluzny, A. Velea, A. Lőrinczi, J. Optoelectron. Adv. Mater. **9**(12), 3951 (2007).
[51] A. Lőrinczi, J. Optoelectron. Adv. Mater. **9**(9), 2970 (2007).
[52] A. Kolobov, P. Fons, A. I. Frenkel, A. L. Ankundinov, J. Tominaga and T. Uruga: "Understanding the phase-change mechanism of rewritable optical media", Nature Materials **3**, 703 (2004).
[53] S. R. Ovshinsky, Applications of Non-Crystalline Materials, p. 729-779, Chapter 12 in Insulating and Semiconducting Glasses, Kluwer, 1999.
[54] T. Ohta, S. R. Ovshinsky in Photo-induced metastability in amorphous semiconductors, Chapter 18, Wiley VCH, 2003.
[55] W. Welnic, A. Pamungkas, R. Detemple, C. Steimer, S. Bluegel, M. Wuttig, Nature Materials 2005, p.1.
[56] A.L. Lacaita, Solid State Electronics **50**, 24-31 (2006).
[57] J. Gonzalez-Hernandez: "Crystallization studies of Ge:Sb:Te optical memory materials", Applied Phys. Comm. **11**(4), 557-581 (1992).
[58] D. Strand, J. Gonzalez-Hernandez, B. S. Chao, S. R. Ovshinsky, P. Gasiorowski and D. A. Pawlik: "The relationship between crystal structure and performance as optical recording media in Te-Ge-Sb thin films", Mat. Res. Soc. Symp. Proc., **230**, 251 (1992).
[59] T. Takamori, R. Roy, G. J. McCarthy: "Structure of memory-switching glasses", Mat. Res. Bull. **5**, 529 (1970).
[60] M. Chen, K. A. Rubin, R. W. Barton, Appl. Phys. Lett. **49**, 502 (1986).

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