

Preparation, properties and electrical switching effects in GeSb_2Te_4 and $(\text{GeSb}_2\text{Te}_4)_{90}(\text{SnSe}_2)_{10}$ amorphous films

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Thin films of composition GeSb_2Te_4 and $(\text{GeSb}_2\text{Te}_4)_{90}(\text{SnSe}_2)_{10}$ have been prepared by pulsed laser deposition and characterized by X-ray diffraction and scanning electron microscopy. The electrical switching was revealed in both compositions.

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The switching in chalcogenide glasses has been discovered by Ovshinsky [1]. Later many scientists investigated a high number of materials with switching properties. Strand [2] discussed the last achievement in this field, while Lucovsky [3] evidenced that self-organization in amorphous and crystalline states are characteristic for typical memory glasses, like Ge-Sb-Te. Many papers have been published recently on switching mechanism and phase change materials [4] including modeling [5].

The Ge-Sb-Te alloys have been recently proposed for random access memories [6-10]. The memory effect is based on the rapid phase change produced under the action of electrical current pulses. Two conduction states are typical for such materials. The high conductivity state that corresponds to the crystalline state and the low conductivity state that corresponds to the amorphous state of the material.

In the same time these alloys are characterized by strong change of reflectance when the amorphous phase transforms into crystalline one.

The recent progresses in multimedia, would not have been possible without the increased performances of various memory media, that become more and more rapid with a huge density of memory cells. The possibility to repeat the recording-erasure cycle is very important for long life memory devices. At the end of the '80s Matsushita-Panasonic developed the technology of the optical disc, stable for over one million cycles. In the process of developing new memory materials, many chalcogenide materials have been investigated, with the aim to find high rate switching and stable (slow aging) materials. There was found that performant materials up-to-day are the amorphous ternary alloys of Ge-Sb-Te used in DVD-RAM memories and amorphous Ag-In-Sb-Te, of interest for DVD-RW devices [1-10].

In a rewritable optical disc the information is recorded by the difference of the optical characteristics produced by

phase modification in the material, during the amorphous-crystalline transition. One of the best phase-change material seems to be $\text{GeTe-Sb}_2\text{Te}_3$, a pseudo-binary compound.

In this material the structural change between the amorphous phase and the crystalline phase is triggered by short laser pulse irradiation (tenth of nanoseconds). The irradiation alters the reflectivity and/or transmittivity of the recording layer of the memory disc. During irradiation the recording area is heated at a temperature situated above the melting point of the material (~ 900 K) with a high power laser beam. When the irradiation is stopped the material cools instantaneously and thus creates a "registration mark". For erasing the mark a local heat treatment is achieved at ~ 700 K, with a laser of moderate power that leads to crystallization of the material.

To read the recorded mark a low power laser is used. The laser beam does not modify the material. It only detects the reflectivity difference between the amorphous and crystalline phase.

GeSb_2Te_4 is a complex close-packed structure with the period of 21 crystalline layers. When the material is heated by a laser radiation pulse, and thereafter rapidly cooled (quenched), the crystallization in a NaCl structure occurs, as a metastable phase.

We have prepared and investigated two bulk chalcogenide alloys and thin amorphous films based on the ternary composition Ge-Sb-Te: GeSb_2Te_4 and $(\text{GeSb}_2\text{Te}_4)_{90}(\text{SnSe}_2)_{10}$.

The first composition (L1) is GeSb_2Te_4 . The second one (L2) is $(\text{GeSb}_2\text{Te}_4)_{90}(\text{SnSe}_2)_{10}$. The raw materials have been introduced in a quartz ampoule after careful weighting of the p.a. purity elements, to correspond to the stoichiometry of the compound. The ampoules were evacuated at 10^{-3} Torr, sealed and heated in a tubular furnace at around 1050°C (a temperature above the melting temperature of germanium) for 24 hours. The ampoules were periodically shaken during heating, and

quenched in air. Sn and Se were introduced into the second composition, as SnSe_2 from a previous element-based synthesis. The final ingots were sliced as thick discs (2–3 mm in thickness) that served as targets for thin film deposition. The films were deposited on silicon wafers cut along the (400) planes by PLD for which a KrF* excimer laser, operating at 248 nm wavelength with pulse duration of ~ 7 ns, and repetition rate of 2 Hz was used. A number of 35000 laser pulses were applied during the deposition process. The thickness of the films reached about one micrometer. The films are homogeneous, smooth and bright, without defects or microcracks.

The X-ray diffraction measurements evidenced the amorphous state of the films. The surface of the films has been investigated by scanning electron microscopy (SEM). A Hitachi S-2600 N apparatus provided with an energy dispersive spectrometer (EDS) has been used. The scanning electron microscope images are shown in Figs. 1 and 2. It is remarkable the surface roughness of both films.

In sample L1 craters with diameters in range of 5–50 micrometers are revealed. The surface of L1 shows a high density of small pores that probably correspond to the rapid process of reevaporation of the small droplets that are thrown on the film. A non-equilibrium process of evaporation-deposition may lead to a reorganization of the surface with small pores surrounded by thin walls.

The sample L2 shows much fewer small diameter pores and this could be explained by a better homogeneity of the films due to a higher number of constituent elements (5 elements) that build-up the material.

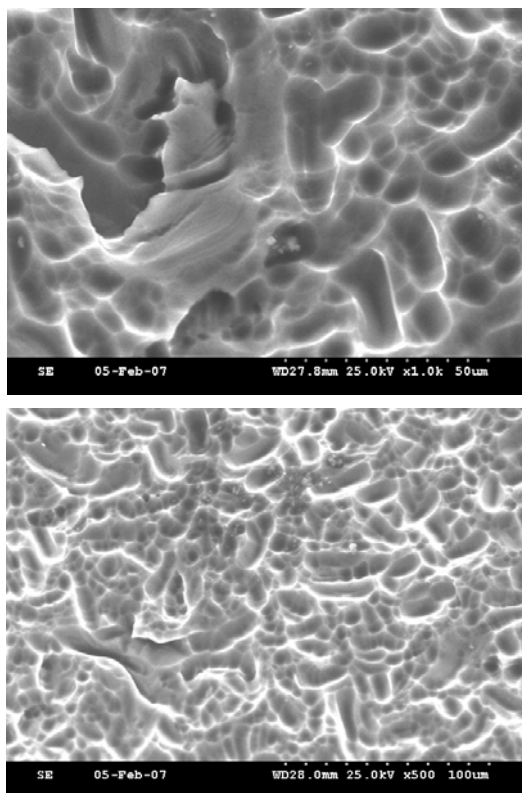


Fig. 1. The SEM image of the surface of the GeSb_2Te_4 amorphous film: a) X 1000, b) X 500.

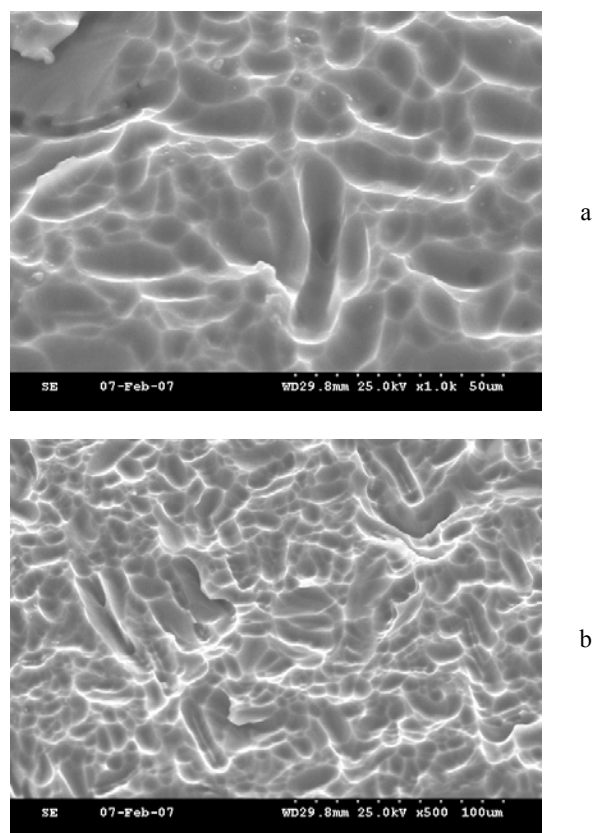


Fig. 2. The SEM image of the surface of the amorphous film $(\text{GeSb}_2\text{Te}_4)_{90}(\text{SnSe}_2)_{10}$.

The electrical switching in the films has been obtained in a sandwich configuration and the local switching was triggered through a thin metallic wire. An aluminium electrode was deposited on the Si wafer before the deposition of the memory film. An increasing voltage of several volts was applied and the current through the film was monitored. The switching effect in GeSb_2Te_4 is shown in Fig. 3.

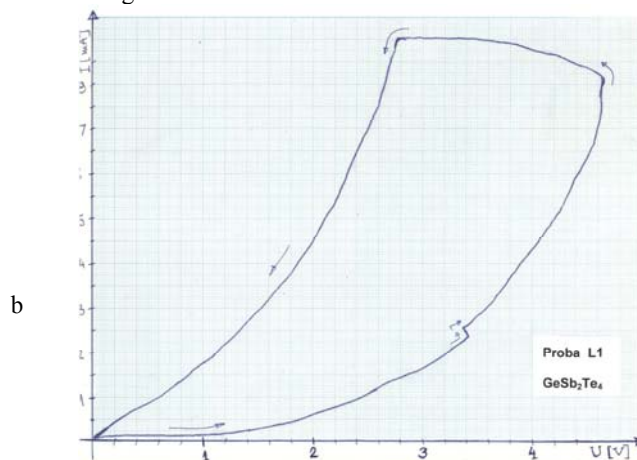


Fig. 3. Electrical switching in the amorphous film L1.

By applying an increasing voltage a threshold value is obtained, from which the film resistivity basculates in a low resistivity state. Thus the amorphous $\rightarrow$ crystalline transition takes place.

In the case of the complex composition $(\text{GeSb}_2\text{Te}_4)_{90}(\text{SnSe}_2)_{10}$ the switching from amorphous to crystalline state is not linear. A complicated evolution of the electrical curve, with resistivity and current fluctuations, demonstrates the development of crystallites that are probably different from those from L1. It is also possible that the inhomogeneity on small scale influences the switching.

In conclusion we have prepared new amorphous switching films based on the Ge-Sb-Te in pure and in SnSe_2 -alloyed form. The films were prepared by pulsed laser deposition. The switching cycles have been identified in the films. The films with SnSe_2 exhibit a more complex switching curve that point out to the inhomogeneity and the specific crystallization processes in that film.

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