

Cluster approach for the structure of amorphous phase in Ge-Sb-Te switching materials.

F. Sava, A. Lőrinczi

Laboratory of Low Dimensional Physics, National Institute R&D of Materials Physics
077125, Atomistilor Str. 105 bis, Bucharest-Magurele, Romania

Modeling of the structure of GeTe – Sb₂Te₃, pseudo-binary system, a typical material for switching applications, has been carried out. We have demonstrated that closed clusters can be constructed with minimum distortions of the covalent bonds. The clusters could be assembled in big amorphous units that simulate the structure of the amorphous phase in thin films of the memory switches.

(Received April 1, 2006; accepted April 28, 2006)

Keywords: Ge-Sb-Te, modeling, cluster approach, phase-change material, switching

1. Introduction

Amorphous materials based on GeTe-Sb₂Te₃ pseudo-binary system were found to have characteristics of an optical memory material, presenting a large optical change and enabling high-speed data recording and rewriting. The materials are used today in the phase-change optical disks such as DVD-RAMs. The materials can be crystallized by laser (for low power irradiation) or reamorphized (high power irradiation). The pulses of very short duration (< 50 ns) are used for writing or, respectively, erasing of information in the film. The cooling speed of the film irradiated by high power pulse is extremely high (10¹⁰ deg/s) and this gives the possibility to the molten material to pass into the amorphous state, instantaneously. Low power pulse irradiation of the same duration brings the exposed part to the crystalline state. The optical constant contrast between the amorphous and crystalline phases is large [1]. The crystallized part exhibits a GeTe-like f.c.c. structure. The high crystallization rate is ascribed to the process of formation of crystallites without any phase separation, to the specific high symmetry (f.c.c.) related to the spherical fuzzy symmetry of amorphous material, and, finally, to the large energy difference between the amorphous state and fcc crystalline state.

Rivera-Rodriguez et al. [2] have shown that the transformation kinetics of the nonstoichiometric Ge-Sb-Te films is significantly different from that of stoichiometric compositions. Samples with low tellurium and high Sb content exhibit three steps of transformations at the temperatures of 130, 180 and 200 °C. The first step is related with the crystallization into the f.c.c. GeSb₂Te₄ stoichiometric phase, the second step appears due to the formation of an additional crystalline Te phase and the third step occurs when the f.c.c. phase transforms into the hexagonal GeSb₂Te₄ stoichiometric phase, preserving the crystalline tellurium. Crystalline tellurium has higher reflection coefficient and lower resistivity than f.c.c. GeSb₂Te₄ crystalline phase. Large deviation from the stoichiometric compositions increases the onset temperature for crystallization.

The complicated phenomena occurring during the writing/erasure procedures in the phase-change materials make the understanding of the structure of the amorphous phase in the Ge-Sb-Te of high impact for the control and improvement of the recording possibilities in these materials.

In this paper we report our results on modeling of the amorphous structure of several Ge-Sb-Te stoichiometric compositions in the frame of a cluster approach, which proved to be useful for the case of arsenic chalcogenides [3, 4].

2. Modeling of the Ge-Sb-Te amorphous phase structure.

The pseudo-binary system, in thermal equilibrium, form three intermetallic compounds: $2\text{GeTe-Sb}_2\text{Te}_3$, $\text{GeTe-Sb}_2\text{Te}_3$, $\text{GeTe-2Sb}_2\text{Te}_3$. These compounds are described as cubic close-packed structures in which the Ge, Te and Sb layers are stacked differently.

The $\text{Ge}_2\text{Sb}_2\text{Te}_5$ exhibits 9-layer stacking, GeSb_2Te_4 exhibits 21-layer stacking and GeSb_4Te_7 exhibits 12-layer stacking structure [5]. In order to understand the structure of the amorphous phases that are produced by high power laser irradiation of these materials, we started from a typical ordered (crystalline) cluster with f.c.c. structure, having 27 atoms. This structure corresponds to a number of formula units for every compound, as shown below:

$\text{Ge}_2\text{Sb}_2\text{Te}_5$	3 formula units = 27 atoms;
GeSb_2Te_4	4 formula units = 28 atoms;
GeSb_4Te_7	2 formula units = 24 atoms.

Firstly we have prepared special plastic units that simulated the Germanium, Stibium and Tellurium atoms with their specific covalent bonds. The tetrahedral germanium atoms were simulated by tetrapods, the antimony atoms were simulated by tripods and tellurium atoms were simulated by dipods.

We have thereafter constructed, using the trial and error methods, an optimized cluster for every compound. The most important results consist in succeeding to build closed clusters for these compositions. In order to find the structure of minimum free energy for every cluster we have relaxed the cluster in the frame of valence force field theory with the interaction potential between the linked atoms, given by Keating [6].

The results of the simulation procedure and the characteristic data are given in this communication. The cluster that simulates the structure of amorphous $\text{Ge}_2\text{Sb}_2\text{Te}_5$ is given in the figure 1.

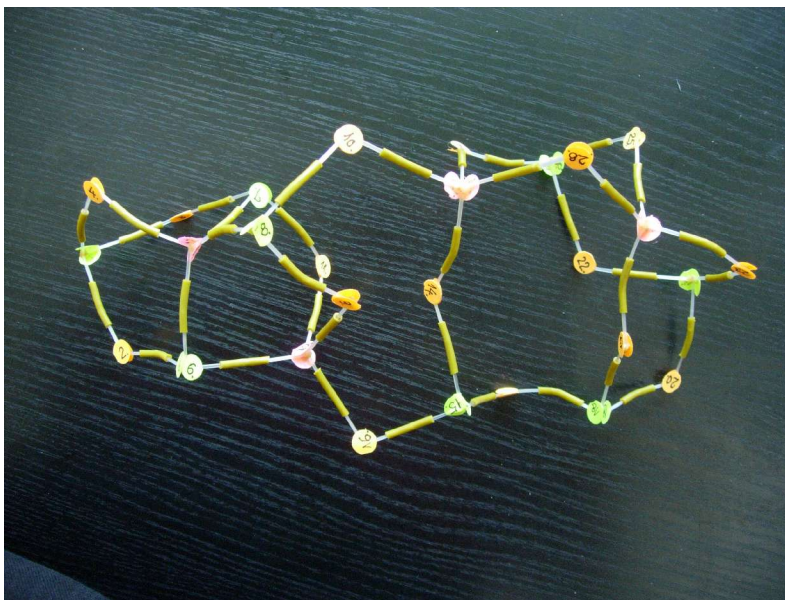


Fig. 1. The amorphous cluster $\text{Ge}_2\text{Sb}_2\text{Te}_5$

Figure 2 shows the cluster that simulates the structure of GeSb_2Te_4 , while Figure 3 shows the amorphous cluster that simulates the GeSb_4Te_7 material.

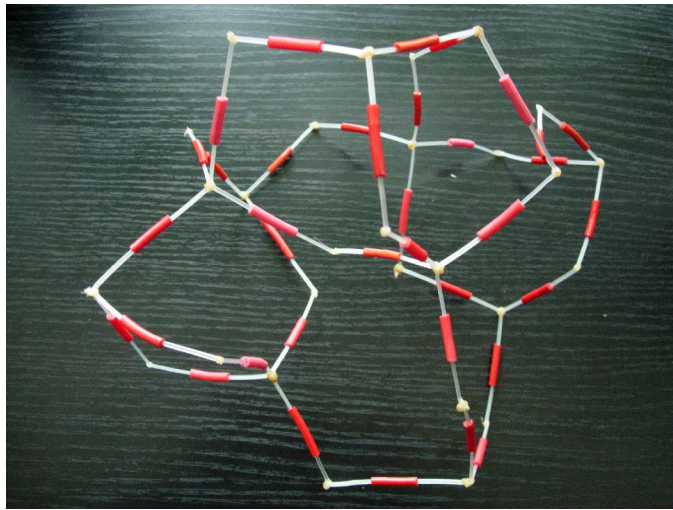


Fig. 2. The amorphous cluster GeSb_2Te_4

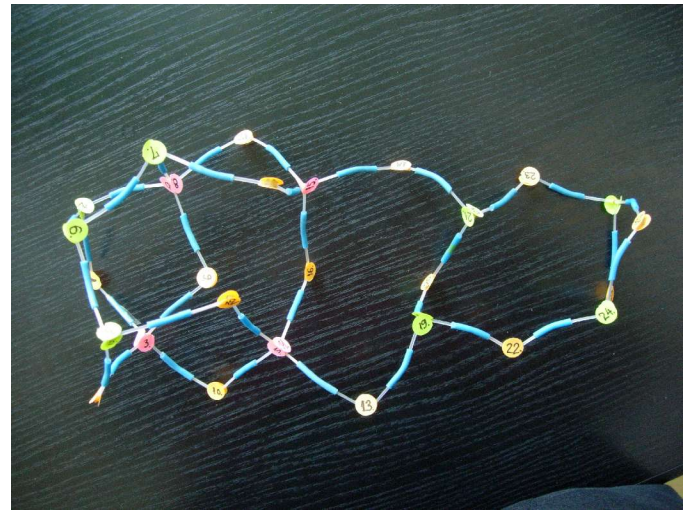


Fig. 3. The amorphous cluster GeSb_4Te_7

3. Discussion

The amorphous clusters show peculiarities as a function of composition. For example, the GeSb_2Te_4 cluster is rather a round cluster with a round shape approaching the shape of the crystalline rock-salt crystallite wherefrom it originates. The other two clusters are rather oblong. Taking into account the variation of the bond lengths when a crystallite transforms into an amorphous cluster, the density of the amorphous phase is higher. During the writing pulse the amorphous film is locally transformed into crystalline. Although initially the glassy matrix is not necessarily made of closed clusters as those simulated by us, it is possible that during repeated write/erase cycles, the material to be transformed into a complex configuration of clusters. Thus, the speed of amorphous→crystalline and back transition will be improved due to simple transformations of the clusters without diffusion or bonding changes on long distances into the material.

4. Conclusions

We have simulated the amorphous phase in the three stoichiometric compositions from the $\text{GeTe-Sb}_2\text{Te}_3$ pseudo-binary system. The closed clusters have been successfully built and relaxed by computer. We have demonstrated that the amorphous structures in the system could have as main ingredient small closed clusters. Based on the simulation results we have suggested that, while the initial structure of the amorphous film could be more or less homogeneous and containing a significant amount of defects, after several working cycles closed clusters start to be formed. Thus the material becomes gradually transformed in a stabilized molecular materials that ensures a long life to the memory device.

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