

STRUCTURAL MODELING OF OVONIC MATERIALS

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The problem of phase-change mechanism at the atomic scale in ovonic materials is still challenging. Various models have been developed, but no definite conclusions have been drawn up to day. The old and new points of view on the phase change mechanism are reviewed. The structural modeling achieved recently in the group of research of the author is presented and compared to the results from literature. A general mechanism of transition from amorphous to crystalline state and back, on the case of typical phase-change material GeSb_2Te_4 is advanced.

Keywords: Ovonic, Phase-change, Ge-Sb-Te, Modeling, Crystal-amorphous transition

1. Introduction

One of the most promising media for rewritable applications is represented by phase-change, ovonic materials. The idea to use an amorphous→crystalline phase transition for information storage dates back to the 1960's when Stanford R. Ovshinsky suggested a memory switch based on changes in the properties of amorphous and crystalline phases of multi-component chalcogenides [1] after registering an US patent on "Symmetrical Current Controlling Device" in 1966 [2].

The chalcogenide non-crystalline films exhibit important phenomena such as electrical switching and sharp contrast in optical reflection when phase change is triggered [3]. In rewritable optical DVD-RAM disks the information is registered using the contrast in optical characteristics induced by the phase change in the material.

The typical phase-change material is the pseudo-binary system $\text{GeTe-Sb}_2\text{Te}_3$. In this system a reversible structural change between the crystalline and amorphous phases is caused by the application of short laser irradiation pulse. As a consequence the reflectivity and transmissivity of the material are strongly modified.

Ge-Sb-Te alloys, have been proposed for phase change nonvolatile random access memories (PCRAM) based on the rapid phase change which occurs in them under fast electrical current pulses. The storage mechanism consists in the structural reversible phase change and the two logical states are represented by the crystalline phase (low resistivity) and the amorphous phase (high resistivity). The advantage of these memories consists in the possibility to be programmed to intermediate resistance values (important for multi-state data storage) and high scalability, since the energy required for phase transition decreases with cell size, allowing the scaling of the write/erase current with cell size. The shortcoming of the phase change recording with these materials is the low crystallization temperature (~ 150 °C) that adversely affects the stability of the amorphous phase, making PCRAMs not suitable for applications when high temperature regime is required.

When in thermal equilibrium the pseudo-binary system $\text{GeTe-Sb}_2\text{Te}_3$ forms three intermetallic compounds: $\text{Ge}_2\text{Sb}_2\text{Te}_5$, GeSb_2Te_4 and GeSb_4Te_7 . The crystalline structures of these compounds are well known [4, 5]. Despite the considerable experimental efforts [6-11] the structure of the corresponding non-crystalline phases is not completely known.

Without knowing the main characteristics of the amorphous structure of the phase-change material it is difficult to understand the change from crystalline to amorphous phase. On the other hand, the reversible transformation crystal – amorphous phase can be understood better in the frame of a modeling procedure, if one takes into account the crystallo-chemical difference between the ordered and disordered phases.

2. Old models for phase-change mechanism

Roy and Caslavská [12] have shown by X-ray, electron and scanning electron microscope study of some chalcogenide materials, that they show diphasic (or even more complicated) structure. Some are mainly crystalline, many contain well dispersed small crystals, but even those which are really glasses, consist of two non-crystalline phases. The authors stated that, since their compositions correspond to various glasses used as the source material for electrical devices, investigated for their “switching” and “memory” properties, the observed finely dispersed two (glass)-phase character of these materials is important for any theoretical consideration of their physical models.

The authors conclude that any model of the action of “amorphous” chalcogenide switching glasses must deal with the fact that even in the most favorable cases, which are essentially non-crystalline, the glasses have a pronounced finely dispersed diphasic (or polyphasic) structure. This is true of the bulk materials and even if it turns out not to be true of freshly prepared evaporated films, the possibility of such phase separation and or partial crystallization during the thermal history accompanying switching cycles and the resultant heating, it is probable to occur. A diphasic, finely interpenetrating structure, has been shown to be characteristic of many electrically important glasses [13]. The phase separation is important especially in interpreting the breakdown properties of the chalcogenide glasses.

Takamori et al. [14] have studied the structure of memory glasses with special emphasis on Ge-Te glasses. In such glasses the switching mechanism is almost unanimously considered as thermal. The glass switches “on” by crystallization through Joule heating and switches “off” by rapid quenching back to a glass after pulse melting [15]

The existence of diphasic glasses near the borders of the glass-forming region was shown to be a general phenomenon by Phillips and Roy [16] and is consistent with the discussion on the possible existence of a metastable free-energy line for two-phase glasses between homogeneous glasses and crystals on the free energy – temperature diagram [17]. The existence of diphasic glasses near the borders of a chalcogenide glass-forming region has also been evidenced by Fritzsche and Ovshinsky [15]. Later, in 1972, Moss and deNeufville [18] have shown that in thin films of Te-based memory glasses $\text{Ge}_{15}\text{Te}_{85}$ and Sb, S -doped Ge-Te material: $\text{Ge}_{15}\text{Te}_{81}\text{Sb}_2\text{S}_2$, fine changes are produced during crystallization, that depend on the presence of doping elements. The authors choose to compare the behavior of the above shown materials in order to unravel the role played by the additives S and Sb in enhancing the reversibility in memory switches. They concluded that the thermal crystallization of these two alloys show many common features. In particular, neither alloy displays direct evidence for fine scale composition fluctuations, or spinodal decomposition, and neither exhibits internal nucleation as might be anticipated from such fluctuations if they existed (i.e., phase-separation). The thin films (~50 nm) of $\text{Ge}_{15}\text{Te}_{81}\text{Sb}_2\text{S}_2$ appear to have a higher volume fraction of crystalline tellurium at 140 °C than at 275 °C (~50%) and this is tentatively associated with temperature dependent metastable equilibrium between glass (or liquid) and crystalline tellurium, as deduced from the phase diagrams Te-GeTe [18]. Antimony seems to be concentrated in GeTe crystals because the structures of Sb-Te and Ge-Te are similar. The role of the Sb segregation on the inhibition of the telluride formation has been not demonstrated. However, the telluride inhibition may be a key aspect of reversible electrical memory action. To revitrify a network of percolating dendrites of tellurium requires that they be heated above their dissolution temperature without allowing to coarsen. If the influence of Sb and S on the inhibition of GeTe formation is accepted, then the return of the switch back to the initial amorphous state could be explained by

redissolving, without growth, of the tellurium dendrite network, which leaves few, if any, tellurium crystallites behind. We must note that crystalline tellurium exhibits higher reflection and lower resistivity if compared e.g. to GeSb_2Te_4 stoichiometric phase.

Crystallization studies of Ge-Sb-Te optical memory materials have been carried out by Gonzalez-Hernandez et al. [19]. They have shown by X-ray diffraction the presence of the nucleation sites, which transform into the cubic $\text{Ge}_2\text{Sb}_2\text{Te}_5$ cubic phase for longer annealing times. The crystallization process may be dominated by grain growth or by nucleation rate. The initial nuclei are induced by defects, impurities or the film-substrate interface at the early stage of crystallization. If nucleation is the dominant mechanism at large temperatures, then the particle size will be larger for samples annealed at low temperatures. For films of ternary Ge-Sb-Te phases with the compositions near to those five crystalline compounds that exist in the pseudo-binary system Ge-Sb₂Te₃ crystallize at high speeds at the temperatures experienced during laser pulse recording, yet have a very slow crystallization rate at temperatures in the storage range for optical memory media. The authors conclude that the crystallization kinetics of films whose composition corresponds to any of the five ternary phases on the pseudo-binary line is dominated by crystal growth, not nucleation.

Strand et al. [20] have shown that Ge-Te alloys that deviate slightly from GeTe stoichiometry show drastically slower crystallization kinetics. They demonstrated that during crystallization the non-stoichiometric compositions separate into GeTe and tellurium or germanium pure phase, as a function of the excess of Te or Ge. Phase segregation can be eliminated by adding antimony. Thus, the crystallization time is strongly reduced, because the slow process of phase segregation (Te or Ge) limits drastically the crystallization rate. The crystallization process in composition with 11 at.% Sb seems to be controlled more by crystallite growth than by nucleation rate. For other compositions the situation could be essentially different.

Ovshinsky has shown [21] that, in order to achieve long cycle life, alloys are chosen that produce crystalline and amorphous phase of the same elemental composition. These congruently crystallizing materials occur along the pseudo-binary line between GeTe and Sb₂Te₃. Since in such a case no diffusion or phase segregation is involved in the structural phase-change process, it occurs quickly and rewrite life is limited only by the integrity of the substrate. The speed of the structural transition must be very fast. It is desirable that the energy delivered by the laser beam at both amorphizing and crystallizing power levels be equally absorbed by the phase-change material when it is in either structural state. The indices of refraction and the absorption coefficients of the phase-change material in its two structural states inherently provide this capability.

3. New models for phase-change mechanism

Kolobov et al. [9, 22] have suggested an attractive atomic-scale mechanism of structural phase-change in materials, on the case of Ge-Sb-Te chalcogenide. In Fig. 1 is shown the germanium atom in the f.c.c. structure formed by tellurium atoms. The germanium atoms occupy the octahedral and tetrahedral symmetry positions in the crystalline and amorphous state, respectively. The stronger covalent bonds are shown by thicker lines than the weaker bonds (Fig. 1a). An intense laser pulse induces the rupture of the weak bonds and the germanium atom flips into the tetrahedral position (Fig. 1b). An alternative description of the structural transformation on melting is an umbrella flip distortion resulting in the disordering of the germanium sub-lattice. It is remarkable that the covalent bonds remain intact.

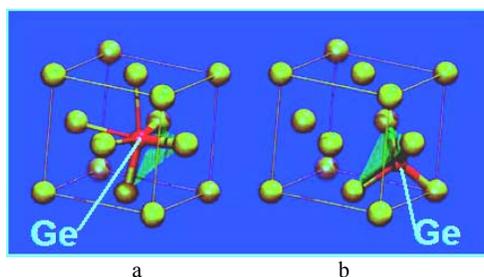


Fig. 1. Fragments of the local structure of GeTe/GST around Ge atoms in the crystalline (a) and amorphous (b) states. Upon heating the sample by a short intense pulse (above the melting point, T_m) and subsequent quenching, the Ge atom flips from the octahedral to tetrahedral-symmetry position. Notice that the stronger covalent bonds remain intact upon the umbrella-flip structural transformation rendering the Ge sublattice random. Exposure to light that heats the sample above the glass-transition temperature (T_g) – but below T_m – reverses the structure.

The authors conclude that Ge-Sb-Te can be viewed as being built from well-defined rigid building blocks of composition $\text{Ge}_2\text{Sb}_2\text{Te}_5$. In the crystalline state, the constraint of the mutual arrangement of the building blocks in space is such that tellurium atoms form a f.c.c. lattice. Inter-block interaction and long-range ordering cause the resulting structure to resemble the rock-salt structure. In the amorphous state, inter-block interaction is weakened, which allows the block structure to relax so that the bonds shrink and germanium umbrella flips into its preferred tetrahedral coordination. The model presented by Kolobov et al. provides a clear explanation as to why switching in Ge-Sb-Te is fast and stable. This is because the crystallization→amorphization process does not require the rupture of strong covalent bonds and the transition is diffusionless.

The mechanism of the phase-change in Si-Ge-As-Te switching material has been devised by Popescu et al. [23]. The structure of the quaternary glass $\text{Si}_{12}\text{Ge}_{10}\text{As}_{30}\text{Te}_{48}$ seems to be given by a random network of atoms linked by covalent bonds. The atoms retain the covalence known from their crystalline counterparts. Nevertheless, the As-Te bonds are favored. The composition with 30 As and 48 Te, approaching As_2Te_3 composition, supports the idea that the main configuration in this glass is based on As_2Te_3 layers. Therefore, the idea to embed Si and Ge into As_2Te_3 layers is attractive. Interconnection of the As_2Te_3 layers containing Si and Ge atoms is possible if Si(Ge)-Te-Si(Ge) bonds are considered between the layers. The phase change under heat consists in the separation of the layers by breaking the interlayer bonding and releasing the Ge and Si from the As_2Te_3 layers (Fig. 2).

Thus, the new phase becomes more ordered and more stable than the initial phase. The return to the initial glassy phase is possible by strong excitation (melting and quenching) of the quasi-ordered phase.

It is interesting to remark that, while the model devised by Kolobov et al. for Ge-Sb-Te is a model with short range transformation of the crystalline lattice of the material, the model developed by Popescu et al. is based on short-range transformation in the amorphous network of the material.

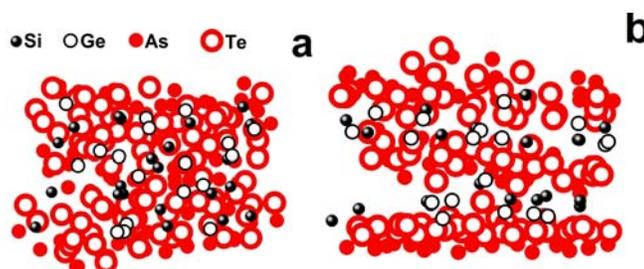


Fig. 2. Model of the $Si_{12}Ge_{10}As_{30}Te_{48}$ glass (a) and the model of a new phase got by structural transformation.

4. The modeling of phase-change mechanism in $GeSb_2Te_4$

The $GeTe-Sb_2Te_3$ pseudo-binary system, when in thermal equilibrium, forms three intermetallic compounds: $Ge_2Sb_2Te_5$, $GeSb_2Te_4$ and GeS_4Te_7 . The most interesting compound is $GeSb_2Te_4$ because it exhibits two possible structures: the stable phase with a complex structure refined by Matsunaga and Yamada [5] and the metastable phase which crystallizes into a NaCl-type simple structure. One important remark is that Matsunaga and Yamada obtained the metastable phase starting from the sputtering deposition of thin amorphous film of $GeSb_2Te_4$. The film was later crystallized in the metastable crystalline phase by means of laser irradiation. This is exactly what happens during switching process in the phase-change memory films. The crystalline structure of the metastable phase is shown in Fig. 3. It shows a rock-salt structure with Te atoms on one sublattice and Ge as well as Sb atoms and 25 % vacancies on the other. In this case all the atoms, therefore, have an octahedral coordination. In this structure the lone pair electrons take part to the bonding. The inter-atomic distances are longer than in normal covalent structure.

The lattice parameter of the cubical phase is $a = 0.604$ nm [6]. As shown by different authors [6] the local order in crystalline and amorphous phase of Ge-Sb-Te compounds is very different. The germanium atoms that occupy octahedral positions in the crystalline phase switch to a tetrahedral coordination in the amorphous phase. The tellurium atoms that has one Ge atom and three Sb atoms in the first coordination shell, is transferred into a configuration nearer to the double coordination when the material becomes amorphous. Sb atoms transforms from octahedral atoms into three-fold configuration atoms in the amorphous state of the Ge-Sb-Te. Thus we have a chemical basis for the model of crystal-amorphous reversible transition during switching.

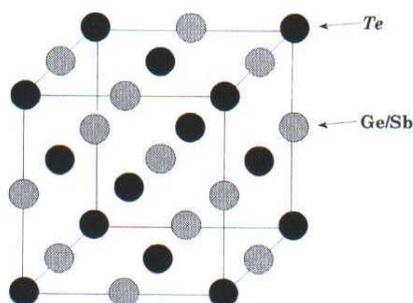


Fig. 3. Crystal structure of metastable $GeSb_2Te_4$. The Ge and Sb atoms are distributed at random a distorted rock-salt lattice. Gray-painted circles show the Ge or Sb atoms. Black circles are tellurium.

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The transition from crystalline phase GeSb_2Te_4 to the amorphous one has been modeled by using models built from units that simulate the octahedrally coordinated atoms, the tetrahedral coordination (Ge), the three-fold coordination (Sb) and two-fold coordination (Te).

Firstly, an octahedral coordinated lattice with 27 atoms was built and relaxed by computer, in order to get the coordinates of the atoms in the metastable phase of GeSb_2Te_4 . The model corresponds to 4 formula units, without one atom (a vacancy in the lattice is compulsory for this compound, at this small size of the crystalline nucleus). Fig. 4 shows the modeling of transition from the metastable crystalline state of GeSb_2Te_4 to the amorphous state. The initial crystalline state is shown in Fig. 4a. In the first stage we have partially substituted the octahedrally coordinated atoms of Sb and Ge. The new atoms enter into the structure with a three-fold and respective four-fold coordination.

Fig. 4b shows the model after the first stage of transformation from metastable towards the amorphous phase. It is remarkable the remnant of the crystalline structure evidenced by a plane of atoms that still maintain the octahedral configuration. In the following stage of transformation the last crystalline plane is destroyed. What still remains is the central atom, which is octahedrally coordinated (Fig. 4c). This is a tellurium atom. Meantime, after every simulation stage the covalent bonds are formed with the neighboring atoms immediately after the atoms take the covalent properties (4 for Ge, 3 for Sb and 2 for Te). In the last phase of simulation the central octahedral atom is substituted by a normal divalent Te atom, which is connected to the most approached atom. Finally, one gets a cluster configuration (Fig. 4d). In this cluster the atoms are situated not very far from the old positions, but the structure is new and not ordered. This way we realized a true fragment of amorphous network. It is possible to go back in this simulation chain by reforming the initial lattice. The final amorphous cluster was also relaxed by computer and the pair distribution function proved to be compatible with the crystallo-chemistry of the component atoms: correct distances, narrow bond angle distribution, well separated coordination spheres that speak in favor of the stability of the closed cluster of GeSb_2Te_4 . Such transformation is realistic in the material during switching.

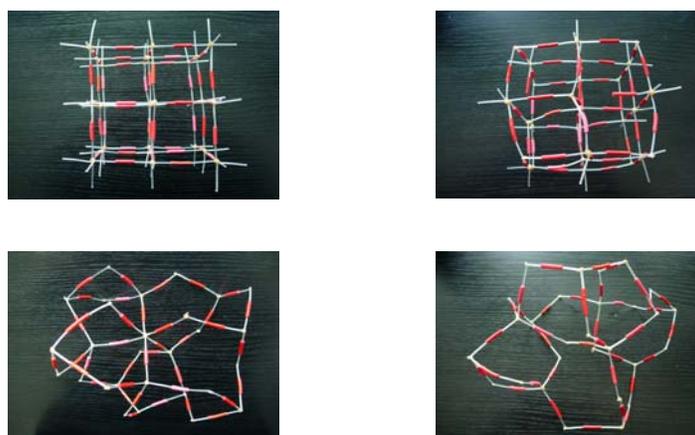


Fig. 4. The main stages of amorphization of the simulated cluster of metastable phase GeSb_2Te_4 . a. rock-salt structure crystallite (27 atoms) (state "on"); b. first stage (only one crystalline plane remains); c. second stage (only one octahedral atom remains in the center of the crystallite); d. last stage: the amorphous closed cluster (state "off").

The transition from the closed cluster to the piece of crystalline lattice and back under the action of the laser light of different power can be understood in the frame of this mechanism. No diffusion is needed. The covalence is not eliminated but the hybridization of the bonds is gradually lost or transferred to sp^3d^2 hybridization followed by the activation of the lone-pair electrons during transition. We must point out that due to shrinking of the bonds when the crystallites (characterized by long bonds between the octahedrally surrounded atoms) are transformed into amorphites (amorphous clusters) with typically covalent bonds, a significant growth in density must appear. This difference is absorbed by the more open structure of the disordered material compared to the crystal. Thus, the internal stresses in the material during switching cycles, which could be harmful to the memory cell, will be minimized.

5. Conclusions

The structural transition amorphous→crystalline and back in phase-change materials based on $GeSb_2Te_4$ composition has been modeled. It is possible to understand the particularities of the transition and the characteristics of high speed, reversibility and long cycle life, by local modification of the short range order around the atoms. While in crystalline phase octahedral configuration is dominant, with Ge and Sb exhibiting three short bonding and three longer ones, while tellurium makes six long bonds, in amorphous phase the elements takes the covalence normally observed in their compounds. As a consequence, during amorphization, closed clusters are formed, without long path diffusion. These clusters are distributed in the amorphous matrix and their size and density, control the change of resistance during switching and multi-step variation of the resistivity. The amorphous → crystalline transformation is achieved by switching to the ordered rock-salt-like assembly under the influence of a laser pulse of high power. It seems that the closed clusters are formed in the first cycles of the memory cell. Thereafter, the transition from amorphous to crystalline cluster and back is produced without difficulty, both phases being (meta)stable. This means that during the first working cycles the amorphous material suffers a fine transformation towards a disordered Ge-Sb-Te phase characterized by more or less extended closed clusters of atoms. We suggest, according to the above-described modeling, that the freshly deposited film of phase-change material is gradually changed in the first cycles of laser or electrical pulse action, towards a homogeneous structure with closed clusters, thus stabilizing the material for long-life working.

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