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Short Note

ANGSTRÖM-SIZE PHASE CHANGE MEMORY

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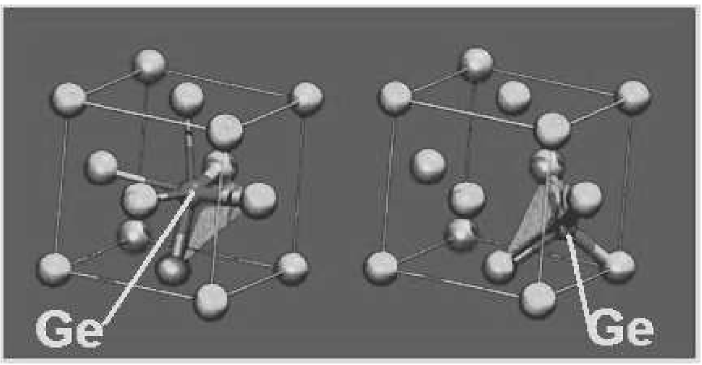
One of the most promising media for rewritable applications is phase-change materials. The idea to use an amorphous-crystalline phase transitions for information storage dates back to the 1960s when Stanford R. Ovshinsky suggested a memory switch based on changes in the properties of amorphous and crystalline phases of multi-component chalcogenides [1].

The initial amorphous as-deposited $Ge_2Sb_2Te_5$ layer is crystallized by exposure to a laser beam of intensity sufficient to heat the material to a temperature slightly above the T_g. A subsequent exposure to an intense and short laser pulse melts the material that is then converted into the amorphous state on quenching. A record bit is an amorphized mark against the crystalline background. The process is reversible and this is essential for a rewritable memory.

Strand et al. [2] have shown that Ge-Te alloys having non-stoichiometric atomic ratios phase separate during crystallization into a Te50Ge50 phase plus purre crystalline tellurium or germanium. The limitation of the crystallization rate is given by this slow process of phase segregation. Phase segregation during crystallization of non-stoichiometric Ge-Te can be avoided by adding antimony to samples having a tellurium concentration of from 45 to 55 at.% over a wide range of Ge:Sb ratios. These alloys\can have laser induced crystallization times of less than 50 ns.

Kolobov et al. [3] have shown the angström-scale mechanism of structural phase-change in materials, on the case of Ge-Sb-Te chalcogenide.

In Fig. 1 (after [3]), it 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 with 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.



a b

Fig. 1. Local structure of Ge-Sb-Te around germanium atoms in the crystalline (a) and amorphous (b) states [3].

The authors conclude that Ge-Sb-Te can be viewed as being built from well-defined rigid building blocks of composition $Ge_2Sb_2Te_5$. 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 results presented in [3] provide a clear explanation as to why switching in Ge-Sb-Te is fast and stable and point out the power of angström-science (angström-scale phenomena). This is because the crystallization – amorphization process does not require the rupture of strong covalent bonds and the transition is diffusionless.

The fact that the tellurium sublattice is partially preserved, as well as the conservation of the antimony atoms, account for why the transformation can be easily reversed. The material does not have to be transformed into a truly liquid state. Bond rupture is believed to be due, at least partially, to electronic excitation. It also should be noted that the amorphous structure, at least on a local level, is well defined, thus enhancing the reversibility of the transition.

Welnic et al. [4] have shown that a strong difference exists between a covalent semiconductor and the prototype compound of phase-change material, $Ge_2Sb_2Te_5$.

While the covalent semiconductors have, in general, similar local arrangements, not only in crystalline, but also in amorphous phase, Ge-Sb-Te, undergoes a profound change in local order on amorphization. The last class of materials (Ge-Sb-Te) is characterized by two competing structures with similar energy but different local order and different physical properties. Both local distortions found in the crystalline phase and the occurrence of octahedral and tetrahedral coordination in the amorphous state is explained. Although the atomic rearrangement is most pronounced for germanium atoms, the strongest change of the electronic states affects the tellurium states close to the Fermi energy, resulting in a pronounced change of electronic properties such as an increased energy gap.

For some phase-change memory materials, as e.g. Si-Ge-As-Te, an angström-scale mechanism was shown in [5].

The structure of the quaternary glass $Si_{12}Ge_{10}As_{30}Te_{48}$ seems to be given by a random network of atoms linked by covalent bonds. The atoms retain the covalence known from their crystalline compounds. Nevertheless, the As-Te bonds are favoured. 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 in 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 in-between the layers. The change of phase under heat consists in the separation of the layers by breaking the interlayer bonding and releasing of Ge and Si from the As_2Te_3 layers. Thus, the new phase becomes more ordered and more stable than the initial phase. A return back to the former glassy phase is possible only by strong excitation (melting and quenching).

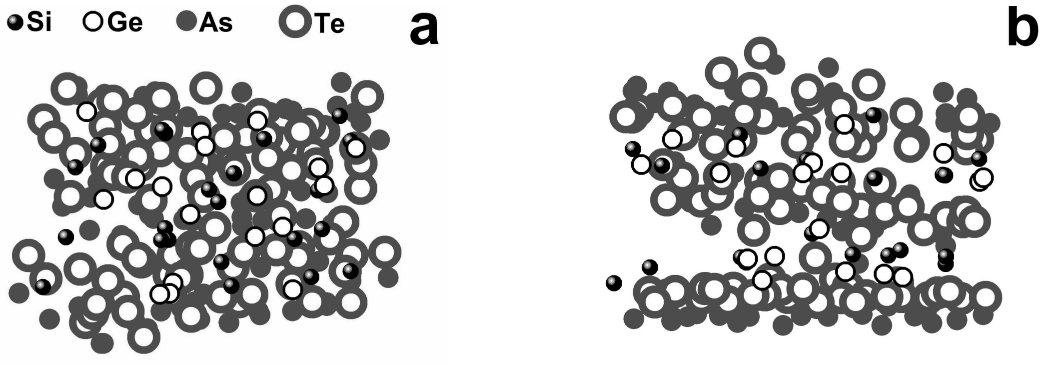


Fig. 2. Model of $Si_{12}Ge_{10}As_{30}Te_{48}$ glass (a) and the model of a new phase got by structural transformation (b).

The angström-scale model consists in an arrangement of three disordered layers of type As_2Te_3. These layers are doped randomly with Si and Ge. The physical model made of plastic units has 202 atoms. Silicon and germanium take the places of tellurium atoms. They bind two neighbouring layers though the intermediation of the tellurium atoms released from the bonds occupied by Ge or Si. Thus, two disordered As_2Te_3 type layers are linked by square bridges Si-Te-Si(Ge)-Te. The model was relaxed by computer using the standard Monte-Carlo – Metropolis procedure and appropriate force constants. The results are shown in Fig. 2a. In the following step we modeled the phase transformation induced by external factors acting on the glass. The excitation of the stressed bonds in the glass leads to the breaking and reforming of the bonds in a new configuration. The bond breaking between disordered layers is most probably due to stressed bonds Si-Te and Ge-Te. Tellurium takes the place of Ge (or Si) in the layers and forms strong As-Te bonds that fit the network of type As_2Te_3. The remaining Si and Ge atoms form separated dimmers or small clusters in-between the As_2Te_3 layers. The atomic scale model of the new phase, relaxed by computer is shown in Fig. 2b.

By melting and quenching, the phase obtained when the glass is annealed would induce the reverse transformation to a higher free energy state.

References

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