Re-writable DVDs: what makes phase-change materials work the way they do

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INTRODUCTION

In the 1960s S.R. Ovshinsky suggested [1] to use differences in the electrical and optical properties between the crystalline and amorphous states of multicomponent chalcogenides for data storage. This idea gave rise to numerous memory applications of multicomponent chalcogenides. One of the latest industrial applications of phase-change recording is the re-writable digital versatile disc (DVD) first commercialized by Matsushita in the mid 1990s. The basic principle of phase-change optical recording is very simple: intense laser pulses melt the recording material that is subsequently quenched into the amorphous state. The recorded bits are thus amorphous areas amidst a crystalline background. To erase the recorded information, areas recorded upon are heated by laser light to a temperature that is sufficient to induce crystallization. Various materials have been tested but only two have been found suitable for industrial applications, namely, Ge-Sb-Te (GST) alloys as exemplified by $Ge_2Sb_2Te_5$ used in DVD-RAM and Ag-In-Sb-Te (AIST) alloys used in DVD-RW [2]. These materials allow for very fast switching to the amorphous state (transition times as short as hundreds picoseconds have been measured), fast recrystallization (on the order of 30 ns), and high cyclability (over 1,000,000 cycles) [2].

It is very difficult to believe that an arbitrary material would reversibly and reproducibly melt and recrystallize so many times and one has to search for a more specific mechanism of the reversible amorphous-to-crystal phase transition.

An important step forward was the observation that GST/AIST thin films crystallize into a "cubic" structure - rocksalt-like for GST [3] and A7 for AIST [4]. It was suggested that the high symmetry of the structure was the reason for the transition being fast [5].

RESULTS AND DISUSSION

Crystal structure – shorter and longer bonds

Based upon extensive x-ray absorption measurements, we recently demonstrated that the local arrangement of atoms in $Ge_2Sb_2Te_5$ is best viewed as a distorted rocksalt structure. While the Te atoms do indeed form a well ordered face-centered cubic (fcc) lattice, the Ge and Sb atoms are located off center and there are two types of Ge(Sb) - Te bonds, namely shorter bonds and longer bonds [6]. The off-center location of Ge was also confirmed in [7,8].

The differences between the shorter and longer bond lengths (2.83 Å and 3.15 Å for the Ge-Te pair) are quite large and suggest that the nature of the bonding is different in the two cases. While the short bonds are covalent (this issue is discussed in detail below), the long bonds are a consequence of long-range order in the material [9]. The situation is similar to molecular crystals such as Selenium or Tellurium. In the latter, covalently bonded helical chains are held together by weaker van der Waals forces. We would like to stress here that Selenium also exhibits photo-induced phase transition, namely it can be rendered either crystalline or amorphous upon exposure to light. Photo-crystallization is a better known phenomenon and consists in enhanced crystallization of Selenium upon photoexcitation. In earlier papers it was suggested that the process was mostly thermal in origin and exposure to light resulted in heating Selenium above its nearly room-temperature glass-transition. Recently, several groups have independently demonstrated that exposure to linearly polarised light results in *anisotropic* crystallization [10-12] from which it was concluded that photo-crystallization has its origins in electronic excitation rather then in purely thermal effects.
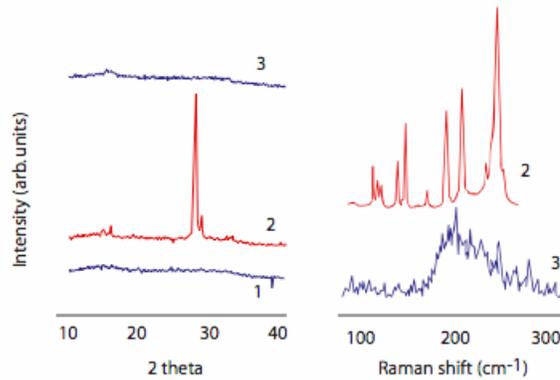

Figure 1: XRD pattern (left) and Raman scattering spectra (right) of as-deposited (1), crystallized (2) and photo-amorphized (3) As50Se50 films

The reverse phenomenon also exists although is less well known. In particular, exposure to light results in *athermal* amorphization of certain chalcogenides, such as As_2S_3 [13], Se [14], and AsSe [15], the latter two being well known molecular crystals. It was argued that photoexcitation breaks the (weaker) bonds between the molecular building blocks (chains in Se and As4Se4 molecules in AsSe), resulting in relaxation of the building blocks and eventual loss of long-range order. Fig. 1 shows x-ray diffraction and Raman spectra of crystallized and photo-amorphized AsSe.

The existence of the bond energy hierarchy in GST on the one hand and in molecular Se and AsSe on the other hand, suggests that a similar mechanism may be operative in both cases, namely, photo-excitation breaks the weaker bonds after which lattice relaxation takes place. Indeed, we have demonstrated that the amorphization of $Ge_2Sb_2Te_5$ primarily consisted of the rupture of the longer Ge-Te bonds followed by Ge atoms switch from a (distorted) octahedral to a tetrahedral configuration within the Te fcc sub-lattice (Fig.1b). Our later studies have shown that rather similar structural changes take place in other GST alloys (GeSb_2Te_4 and binary GeTe having been studied) [16].

On the other hand, AIST alloys do not contain Germanium. Should one then expect a totally different switching mechanism in the AIST alloys? As already mentioned, GST possesses a distorted rocksalt structure with subsystems of longer and shorter bonds. It turns out that AIST has many of the same features. The structure of AIST is A7 that is a rhombohedral (distorted cubic) structure with subsystems of shorter and longer bonds. The numerical values for GST, AIST, and Se bond lengths are summarized in Table 1. *The longer bonds are weaker and are easier to break.* We argue that (photo-induced) rupture of the weaker bonds is a necessary pre-requisite for structural change to take place.

Soft potentials

It is informative to compare the bond lengths in the crystalline state with the sum of the corresponding covalent radii. The values for $Ge_2Sb_2Te_5$ are: R_{Ge}=1.22 Å, R_{Te}=1.35 Å and R_{Sb} = 1.38 Å. Ag and In are present in AIST in very small concentrations are we do not consider them here. The (short) Ge-Te bond length in GST is 2.83 Å, i.e. significantly longer than the sum of the two radii. The same observation can be made for AIST. This allows one to draw a conclusion that bonds - provided they are covalent - are strained. It should be stressed here that referring to the bonds as strained we only mean that the bond lengths are larger than the sum of the corresponding covalent radii. The definition used here does not imply that there are net forces acting on any atoms in the ground-state configuration.

To further address this issue, we have measured bulk XPS spectra of laser crystallized $Ge_2Sb_2Te_5$ using high-energy synchrotron radiation as the excitation source. Our measurements yielded the following values for the bonding energies: Ge 3d - 30.8 eV, Sb $3d_{5/2}$ - 529.6 eV, Te $3d_{5/2}$ - 573.2 eV. These values are similar to those in covalently bonded solids. The absence of charge transfer has been independently deduced from *ab initio* simulations [7]. We thus conclude that (even the shorter bonds) in the crystalline state are stretched and thus strained.
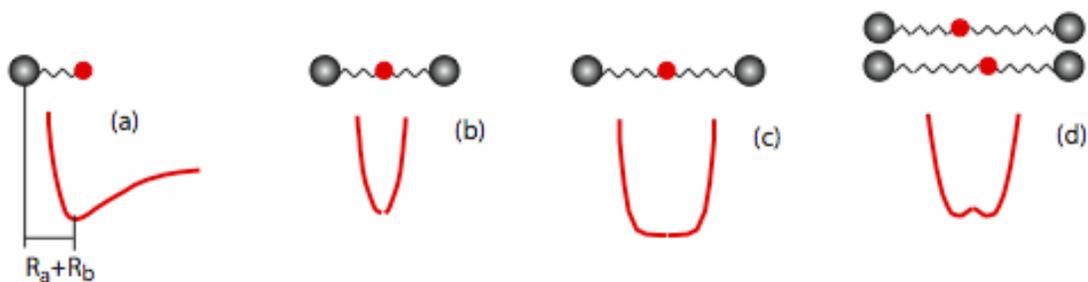

Figure 2: Interatomic potential for a biatomic molecule (a), and three atoms with interatomic distances between the first-nearest neighbours equal to the sum of covalent radii (b), somewhat larger (c) and larger (d) that the corresponding sum. In cases c,d the interactomic potential is flat (or a double-well potential exists) which allows for large atomic displacements with very low energy cost.

The interatomic potential for two atoms forming a bond is shown in Fig. 2a. The interatomic distance is equal to the sum of the corresponding covalent radii. For a more complex structure the situation varies. Depending on the distances between the second-nearest neighbours and their spatial location, the energy dependence of an atom at the center of the cell (Ge atom in this case) can be different. This is schematically demonstrated for a three-atom linear system with the distance between the end atoms being fixed to a certain value (Fig. 2b-d). The central atom can find itself either in a very stable minimum and strong bonds exist if the distance to each neighbour is equal to the sum of covalent radii (slightly larger for increased coordination number) (Fig. 2b), or in a very flat minimum if the distances are just somewhat larger than the sum of the radii (Fig. 2c), or in a double-well potential if the distance is larger than the sum of the covalent radii but not too large to allow for bonding with both neighbours. The latter two cases are often referred to as "soft potentials". The soft-potential approach for chalcogenide glasses was first suggested in the 1970s and was subsequently used to explain a variety of glass properties [17].

In order for such soft potentials to exist, the distance between the end atoms should be determined by forces other than first-nearest neighbour interactions. We believe that this is the case for phase-change materials. To justify this, we present two different arguments. First, we would like to note that the mean-square relative displacement (MSRD) which is a measure of the bond strength (spring constant) is significantly smaller for the second-nearest Te-Te interaction than for the first-nearest Ge(Sb)-Te interaction suggesting that the long-range order of GST is determined by the Te subsystem. Secondly, we would like to note that in Si_2Te_3 where Si can occupy either octahedral or tetrahedral symmetry positions, the Si-Te bond lengths for the two geometries are 2.84 Å and 2.62 Å, respectively [18], which is the same as those for the Ge-Te bonds for the octahedral and tetrahedral geometries in GST (2.83 ± 0.01 Å and 2.61 ± 0.01 Å), although the covalent radius of Si is 0.11 Å smaller than that of Ge. Should it be the first-nearest neighbour interaction that determined the interatomic distances, the Si-Te bond lengths would have been about 0.1 Å shorter. These two arguments provide grounds to conclude that the conditions for the soft-potential structure to exist are indeed satisfied.
The very large isotropic thermal factors observed for both GST and AIST [3,4] further suggests that in the case of phase-change materials the atomic potentials shown in Figs. 2c,d is an appropriate approximation.

While in the ground state, the system is in the minimum energy position and there is no net force acting on any of the constituent atoms/ions. However, photo-induced rupture of any one bond results in inbalance of the forces acting on the central atom and significant atomic displacements may occur in order for the central atom to assume the new equilibrium position. The structure is thus potentially locally unstable and excitation may easily induce forces resulting in significant lattice relaxation and structural modification. We suggest that this *potential local instability* is crucial for the fast phase-change transition.

Bond shortening in the amorphous state

Of special interest is the fact that bonds get shorter in the amorphous state. Thus in GST Ge-Te bond length is 2.83 Å in the crystalline state and 2.61 Å in the amorphous state. There are no published data available on the bond lengths in the amorphous phase of AIST However, our recent XAFS measurements (Fig. 3) clearly indicate that the peak corresponding to the first nearest neighbor interaction shifts to shorter distances in the amorphous state. A detailed data analysis is underway.

The bond shortening in the amorphous state is unusual. Typically, in covalently bonded solids bonds get longer in the amorphous state because of anharmonicity of the interatomic potential.
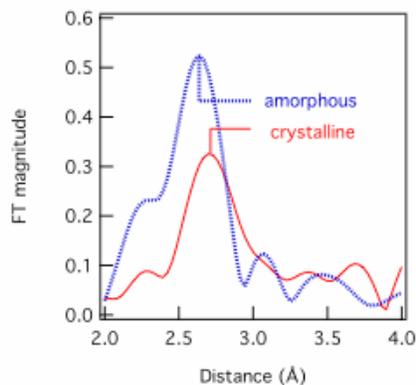

Figure 3: Fourier-transformed EXAFS spectra of crystalline and re-amorphized AIST. It is seen that the bond length becomes shorter in the amorphous state.

Of interest is also the fact that despite the observed bond shortening in the amorphous state, the density of the amorphous phase is lower than that of the crystal. From this it immediately follows that although the distances between the first-nearest neighbors get shorter, the *average* interatomic distances increase in the amorphous phase (due to an increase of distances between pairs of atoms previously bonded by the weaker bonds.)

CONCLUSIONS

We can summarize the unusual properties of GST/AIST that are crucial for phase-change applications as follows.
1. There are two kinds of bonds between similar pairs of atoms in the crystalline state. This has a consequence that there are a more stable and less stable subsystem of bonds. The weaker bonds derive from long-range forces. They are easier to break and upon

amorphization the short bonds get even shorter and stronger at the expense of the broken weaker (resonant) bonds.

2. Bonds in the crystalline state are strained (although there is no net force acting on any atom/ion in the ground state). As a result, the structure is potentially locally unstable and rupture of the weak bonds results in substantial and very fast lattice relaxation changing the local structure.

3. Bonds in the amorphous state are shorter than in the crystalline state. The strengthening of first-nearest neighbor interactions at the expense of the longer-range interactions in the amorphous state is the reason why the amorphous state has a free energy not much different from that of the crystalline state.

We suggest that any search for new phase-change materials should be based on the above structural criteria.

ACKNOWLEDGEMENT

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