

Role of Te lone-pair electrons in structure and properties of layered GeTe-Sb₂Te₃ phase-change memory materials

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ABSTRACT

Usually, discussions of the mechanism of phase-change are centered around the movement of Ge atoms, the role of Sb and Te is usually not discussed. At the same time, Ge-Sb-Te alloys possess properties that are different from those of the binary GeTe material clearly demonstrating that inclusion of Sb has an important effect on materials properties. In this work, the role of Sb and Te atoms in the phase-change process is discussed and an important role of Te lone-pair electrons is demonstrated.

Key words: GeTe, Sb₂Te₃, lone-pair electrons, DFT simulations

1. INTRODUCTION

Ultra-fast phase-transitions in so-called phase-change materials are currently widely used in optical memories such as digital versatile disc random-access memory (DVD-RAM) and also in recently commercialised electronic nonvolatile phase-change random access memory devices (PC-RAM). The basic idea behind phase-change recording is to utilize the optical and/or electronic property contrast between crystalline and amorphous states suggested by S.R. Ovshinsky back in the 1960s [1]. Years of intensive research have singled out GeTe-Sb₂Te₃ (GST) alloys. This class of compounds exhibits atypically large differences in optical/electronic properties between the crystalline (SET) and amorphous (RESET) phases, high thermal stability of both phases, a fast switching rate, and excellent scalability, making them ideal candidates for storage applications [2,3]. As only a small subset of possible compounds displays the required attributes for practical applications, further investigation of the switching mechanism on the atomistic scale in these materials - and hence a precise knowledge of the structure - is needed to enable prescient development.

The most significant achievements along the route to an atomistic understanding should be recalled. First was the observation that thin amorphous films of quasi-binary GeTe-Sb₂Te₃ compositions initially form a metastable cubic (rocksalt-like) structure at temperatures around 160 °C which subsequently transforms into the stable trigonal phase at higher temperatures [4]. The anion sublattice in the rocksalt-like structure was found to be fully occupied by Te atoms, whereas the cation sites were populated with a composition-dependent random mixture of Ge and Sb atoms and vacancies. This structure was characterised in early works by an unusually large isotropic thermal factor indicating a large degree of structural disorder [4]. It is this cubic phase of GST that reversibly switches into the amorphous phase during the phase-change process.

Subsequent extended X-ray absorption fine structure (EXAFS) studies demonstrated that the rock-salt structure is distorted, i.e. there are subsets of three shorter and three longer bonds. Even the shorter bonds were found to be significantly longer than the sum of the covalent radii of the participating atoms [5]. It should also be noted that, counterintuitively, the mean-square relative displacement (MSRD) that characterises disorder in the bond lengths, was found to be larger in the crystalline phase than in the corresponding amorphous phase.

The coordination numbers in the crystalline phase are usually described as $N_{\text{Ge}} = 6$, $N_{\text{Sb}} = 6$, and $N_{\text{Te}} = 4.8$ [6]; the lower Te coordination being due to the presence of nearby vacancies. A significant achievement was the proposal that, in order for Ge (and Sb) atoms to be six-fold coordinated, the bonding in the crystalline state of GeTe and GST should be resonant [7,8]. This proposal provided a natural explanation for the large optical/electrical contrast between the two phases. The ferroelectric-to-paraelectric (rhombohedral-to-cubic) displacive

transition in GeTe deduced from neutron diffraction studies [9] with the concomitant bond softening [10] were strongly supporting the resonance bonding idea.

Recent studies have demonstrated, however, that the apparent displacive nature of the rhombohedral-to-cubic phase transition in GeTe resulted from the averaging nature of the Bragg diffraction. Local structure studies by means of EXAFS [11] and total scattering [12] have revealed that the subsets of the shorter and longer Ge-Te bonds were preserved across the transition and the bond stiffness remained unchanged. It should be noted that in the case of total scattering the conclusion about the existence of the shorter and longer bonds within a rhombohedrally distorted structure was drawn from an analysis of the same type of dataset, for which a Bragg peak analysis led to the conclusion about the cubic rock-salt structure. The strong bonding energy hierarchy reported for the short and long bonds in GeTe [13] casts additional doubt about the possibility of resonance bonding in GeTe.

As regards the amorphous phase, EXAFS measurements found that amorphisation of the crystalline phase resulted in the shortening of both Ge-Te and Sb-Te bonds to a value corresponding to the sum of the covalent radii, with a concomitant decrease in MSRD [5]. These findings are inconsistent with a simple randomization of the structure where, due to the anharmonicity of the interatomic potential, bonds would be expected to get longer and weaker. X-ray absorption near-edge structure (XANES) studies suggested that the crystal-to-amorphous transition involved a switch of Ge atoms from octahedrally coordinated in the crystal to covalently bonded tetrahedrally or pyramidally coordinated sites in the amorphous phase [5,14].

Density functional theory (DFT) simulations performed on the melt-quenched amorphous phase of GST (used to model the laser- or electron pulse-amorphised phase) by different groups confirmed the existence of both tetrahedral and pyramidal Ge sites [6,15,16]. In DFT studies, the pyramidal sites are usually referred to as defective octahedral sites; the term being used to describe the structure with three equidistant Ge-Te bonds with the bond lengths characteristic of covalent bonding and angles close to 90° with an additional fourth (and occasionally fifth) atom located at a larger distance with a bonding angle of close to 90° . The coordination numbers for Sb and Te atoms (using 3.2 Å as an offset) were found to be close to four and three, respectively [6,15], i.e. over-coordinated with respect to their usual valency. It should also be noted that the results of DFT simulations are usually analyzed in terms of interatomic distances and bonding angles; the electron distribution is typically not analyzed, although it is the electrons that determine electronic properties of a material.

Finally, it is instructive to note that the properties of the binary GeTe end-point in many aspects are different from the quasibinary GST alloys. Thus while the dielectric function ϵ_1 becomes negative for GeTe at low energies (-10) at $E = 0$ eV, it saturates at positive values (close to +40) for various studied GST alloys [8]. Furthermore, whilst GST alloys exhibit Anderson localization of charge carriers, the binary GeTe does not [17]. These results clearly demonstrate the significance of the Sb_2Te_3 component in the GST alloys. At the same time, in existing studies, the role of Sb and Te atoms is typically not discussed. The only exception is a recent work [18] where it was suggested that in the amorphous phase Sb-Te formed a pseudo network co-existing with the Ge-Te core network.

2. SIMULATIONS

In the present work, by use of DFT simulations we investigate the local atomic and electronic structure of GeTe-based layered phase-change alloys. Density functional calculations were carried out using the plane-wave code CASTEP [19]. Ultrasoft pseudopotentials were used for Ge, Sb, and Te atoms. The Ge and Te pseudopotential included the Ge $4s^24p^2$ and the Te $5s^25p^4$, as valence electrons, respectively. The exchange term was evaluated using the local density approximation from the numerical results of Ceperley and Alder [20] as parameterized by Perdew and Zunger [21]. For the relaxation process, the Broyden, Fletcher, Goldfarb, and Shannon algorithm [22] was used to relax the atomic coordinates at 0 K within a supercell of fixed volume; the volume was fixed to reflect the experimental determined density as conventionally done in the literature [16].

3. RESULTS & DISCUSSION

First we show for the simplest case of a Ge_4Te_4 cluster that the origin of the $\text{Ge}(3):\text{Te}(3)$ local bonding geometry in crystalline GeTe arises from the presence of Te lone-pair electrons that can serve to form dative Ge--Te bonds utilising empty p-orbitals of Ge atoms (Fig. 1a). Despite a different source of electrons (one electron provided by each atom for a conventional covalent bond and two-electrons provided by the same atom for a dative bond) all bonds - once formed - are identical (Fig. 1b).

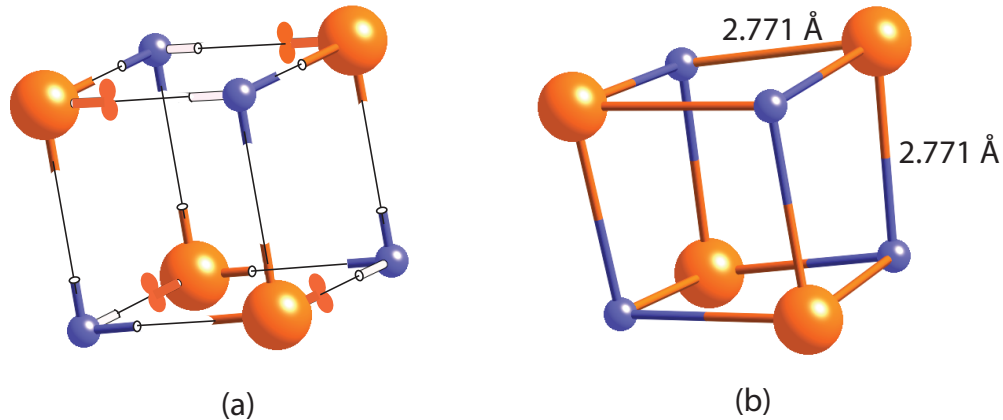


FIGURE 1: (a) A Ge_4Te_4 hypothetical cube. Large orange circles depict Te atoms and small blue circles correspond to Ge atoms. Solid coloured lines indicate p-orbitals with unpaired electrons, the colour being the same as the atomic source of electrons; unfilled lines depict empty p-orbitals of Ge and a coloured lines with an 8-shape edge represent Te lone-pair electrons. (b) The relaxed structure of the Ge_4Te_4 cluster. Two-coloured lines represent conventional covalent bonds (the colour being the same as the atomic source of electrons), single colour lines represent dative bonds formed using Te lone-pair electrons. Despite a different source of electrons, all bonds are identical.

We then demonstrate that incorporation of an Sb atom into the rhombohedral structure of GeTe serves to create Te atoms with unused lone-pair electrons. Interaction of the latter with neighbouring atoms serves to create a large variety of local configurations whose presence leads to local disorder and subsequent fluctuations in electrostatic potential that results in Anderson localisation of charge carriers. The inclusion of Sb atoms are shown to effect the interlayer interaction and consequently have an effect on performance of the layered GeTe-Sb₂Te₃- based structures.

A way to engineer materials with desired properties through an appropriate choice of composition is proposed.

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The presenting author's biography

Alexander Kolobov started his scientific career in 1979 at A.F. Ioffe Physico-Technical Institute in the laboratory headed by Professor B.T Kolomiets, the Father of amorphous semiconductors. He got his PhD and D.Sc. degrees in 1983 and 1992, respectively. In 1989-1993 he worked for various periods of time at Cambridge University (UK), Ecole superieure de physique et de chimie industrielles de la ville de Paris (France), and Katholieke Universiteit Leuven (Belgium). Since 1994 he has been working in Tsukuba (Japan) and now holds a position of prime senior researcher at Nanoelectronics Research Institute at National Institute of Advanced Industrial Science & Technology. In 2002 he received the Ovshinsky Award for excellence in amorphous chalcogenides.