

X-ray Absorption Spectroscopy study of the complex structure of Phase-Change Materials

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ABSTRACT

Phase-change materials (PCMs) are a promising and widely studied class of materials for a broad range of applications in different fields like microelectronics, photonics, thermo-electricity to cite a few. This is the result of their unique contrast of electronic and optical properties between their amorphous and crystalline phases. Their fast crystallization time of few ns joined to a high durability upon amorphous/crystalline cycles as well as high integration yield make PCMs ideal for the production of non-volatile Phase-Change Memories and innovative Storage Class memories [1]. PCMs are mainly based on chalcogenide alloys located on the GeTe-Sb₂Te₃ (GST) pseudo-binary tie-line.

In the GST family, GeTe is considered as a prototypical PCM. As a result, GeTe has been the subject of a huge number of studies aiming at describing its structure in order to unveil origin of the unique properties of PCMs. More recently, GeTe is also a building block of the so called Interfacial Phase-Change Memory (IPCM) where very thin layers of (GeTe)₂ are deposited by van der Waals epitaxy alternatively with Sb₂Te₃ ones forming in average a GeSbTe atomic ratio located also along the tie-line [2].

The crystalline structure of room-temperature rhombohedral GeTe phase has been investigated thoroughly in bulk form revealing a distorted NaCl phase with the distortion vanishing at high temperature [3]. The thin film form is reported to exhibit different features in particular an excess of Ge-Ge homopolar bonds [4]. Ge-Ge bonds are also reported to play a major role in the amorphous phase of related systems like in GST alloys where the presence of this anomaly has been related to be at origin of an increased crystallisation time [5, 6]. For this kind of studies, X-ray Absorption Spectroscopy (XAS) is an ideal experimental technique as it permits the analysis of the local environment of selected components of the alloy.

In this contribution, we will report about our findings from several XAS experiments on GST and related systems. In these cases we show how, a detailed analysis of the local structure of the material, permits to explain some macroscopic features. First, this is illustrated in the case of GST for which we have evidenced an excess of GeGe bonds in as-deposited films when compared with melt-quenched or irradiated films explaining their different crystallization rates [5]. In the case of GeTe films, the role of Ge-Ge bonds was related to the resistance drift phenomenon that represents a major hurdle for the development of multi-level storage with PCMs [7]. Besides, we have recently found that, by using an appropriate film deposition method, the unwanted Ge-Ge bonds observed in crystalline GeTe films in [4] can be suppressed and the ideal rhombohedral structure as well-described

in [3] can be effectively obtained from XAS with the finest details [8]. In the case of IPCMs, we have also evidenced by XAS that around Ge a marked local structural exhibiting a difference from the previously proposed [2] GeTe structures in well-controlled GeTe/Sb₂Te₃ super-lattices [8]. Therefore, this observation is not the result of a sample preparation artefact (namely: the thinning procedure for TEM analyses) but intrinsic to this system. The structural details of these systems in a variety of growth conditions and composition variations will be also shown in detail giving important clues in order to unveil the origin of the switching mechanism in such IPCM.

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Biographies

F. d’Acapito graduated in physics in 1992 at the Rome university ‘La Sapienza’ and obtained his PhD in physics in 1997 at the Grenoble university ‘Joseph Fourier’. Since 1993 he works at the European Synchrotron Radiation Facility (ESRF) and he is responsible of the Italian CRG beamline LISA. He is author of about 230 papers and thematic book chapters. He is an expert on X-ray Absorption Spectroscopy (XAS) both from the point of view of development of experimental instrumentation (grazing incidence XAS, XEOL, beamline design, pump-and-probe experiments) and from the point of view of advanced data analysis (analysis of Refl-EXAFS data, ab-initio simulation of XAS spectra). His interests are focused on materials science, in particular on the relationship between local atomic environment and macroscopic properties of the systems. He has conducted studies on dopants in glasses and semiconductors in the fields of waveguides, optic fibers, high- κ dielectrics, low-dimension systems (Quantum Dots, 2Dim materials, ..), magnetic semiconductors, Phase Change Materials, luminescent materials. He has exploited his expertise also in the field of cultural heritage for the analysis of pigment degradation and characterization of ancient ceramics and glasses.