

Measurement of bulk ESCA and bulk valence band structure in Sb-Te and Ge-Te optical memory alloys

P. Fons, A.V. Kolobov, T. Fukaya, and J. Tominaga

AIST

While phase-change materials are being applied in a variety of memory applications including current (DVD-RAM/RW) and future (SuperRENS) optical storage technologies, there are many fundamental materials aspects that remain to be explored. We have used high-energy x-ray photoelectron spectroscopy (XPS) to investigate the electronic structure of metastable laser-induced amorphous and crystalline phases. The use of a high-energy excitation source (4345 eV) significantly increases the escape depth of photoelectrons changing the measured signal from a surface sensitive probe significantly effected by surface oxides/imperfections to a more "bulk-like" spectroscopy. Based upon the chemical shifts of the constituent elements measured using this technique, we have confirmed that there is no significant charge transfer in both the laser-induced amorphous and crystalline phases of $\text{Ge}_2\text{Sb}_2\text{Te}_5$ and Ag-In-Sb-Te alloys; bonding is essentially covalent. We have also measured bulk-like valence band density of states for both compounds.

Phase-change alloys based upon chalcogenide compounds are now in wide use as re-writable optical media. Two prototypical examples of chalcogenide compounds in wide use include GST and Ag-In-Sb-Te compounds. As optical media have been to date utilized in the far-field limit, the density of information storage has been determined by the diffraction limit given by 2 NA/wavelength , where NA is the numerical aperture of the lens used. While information density can be increase by decreasing the wavelength of the readout laser, the practical limit has already been reach by use of the blue laser in the upcoming BluRay optical disk with a diffraction limit of approximately 240 nm. In the last few years, another alternative has been developed, the so-called Super-RENS optical

disk. By use of thermal lithography in the decomposition of a PtO_x mask layer, recording marks as small as 30 nm can be written. By placing a phase-change alloy underneath this mask layer, it has been shown that such small marks can be read out with excellent signal-noise characteristics by utilizing non-linear properties of these alloys under near-field optical excitation induced by a readout laser via marks recorded in the mask PtO_x layer. While phase-change materials were first suggested for use as memory elements in the late 1960s, their structural and material properties remained largely unknown. Concomitant with the widespread commercial use of phase-change memory in re-writable disks first initiated by Matsushita in the early 1990s, research activity into the properties of such

materials has increased, however much detail still remains to be understood. One common attribute of many phase-change memory alloys is the existence of a metastable structural phase when they are deposited in thin film form. For example, GST is known to form in a trigonal structure with a nine layer stacking sequence, while in contrast, the thin film form has been found to crystallize in a lower density, higher symmetry distorted rocksalt structure. The structure for Sb-Te compounds has also been found to be different in bulk and thin film forms. We have measured both XPS and valence spectra for a variety of Sb-Te optical memory alloys in both the laser-induced amorphous and metastable crystalline states. In all cases, materials were measured in actual devices structures. The sample structures consisted of Al-Cr (100 nm)/ ZnS-SiO₂(30 nm)/ phase-change alloy(20 nm)/ ZnS-SiO₂(130 nm)/ silica substrate (distances are in nm). Samples were grown by RF sputter deposition. Silica substrates were chosen over conventional polycarbonate substrates to increase thermal transfer and avoid heat-induced transformation of the metastable phases during measurement. The as-grown sample were initialized in a customized Pulstec ddu unit due to the lack of the land and groove structure substrate required for conventional laser tracking. Two different annuli of approximately 10 mm width were fabricated laser-amorphized and laser-crystallized, respectively. This assured that the both the amorphized and crystallized samples were of the same composition. The material located above the phase change layers were then removed by a selective etching process leaving the phase-change materials exposed; samples were immediately transferred to a nitrogen ambient for loading into the XPS system at

BL15XU. Fig.1 shows a survey scan taken over a region of approximately 4000 eV. As both Auger and ESCA data are present, the plot indicates both binding (lower) and kinetic (upper) energies. That little surface contamination was minimal compared with the over signal intensity can also be confirmed in Fig.1 in the near background intensity of the omnipresent C 1s photoelectron peak.

The samples were excited just below the Sb L2 edge to avoid peak interference effects using a 4345 eV helically polarized x-ray beam with a resolution in energy of 1:10000. By using this excitation energy, it proved possible to sample a reasonable subspace of ESCA and AES peaks allowing the use of Auger parameter analysis. The x-ray beam spot size was approximately 5 by 10 millimeters on the sample. Figure 1 shows a typical survey spectra observed from a as-loaded Sb-Te alloy sample. No oxygen peak was observed indicating that the decapping procedure was effective. Some slight charging effects were observed for the amorphized samples due to its low conductivity, but these were compensated for using an electron flood gun. Valence-band density of states were also taken. Fig.2 shows two typical spectra for a Ge-Sb-Te and a Sb-Te alloy. As the phase-change materials reported upon in the current experiments are only stable

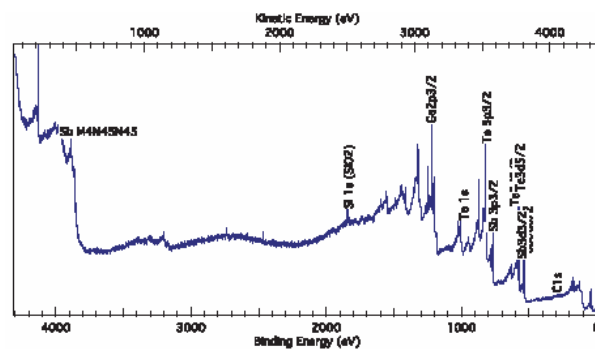


Fig.1 Wide energy scan survey of as-loaded Ge-Sb-Te alloy

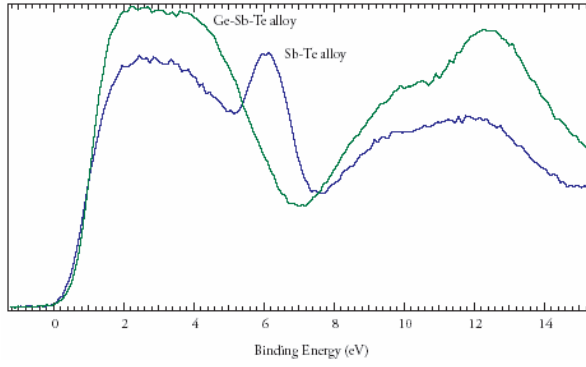


Fig.2 Selected valence band density of states data for a Ge-Sb-Te (top/green) and a Sb-Te (lower/blue) alloy.

in thin film form, the ability to record good quality valence band data, albeit with somewhat reduced resolution, allows the experimental determination of electronic structure is a major achievement. We are now in the process of comparing this experimental data with first-principles electronic structure calculations in an attempt to get further insight into the relationship between structure and electronic properties in phase-change memory alloys. Indeed the comparison of structural observations and first-principles calculations is already showing great promise [1]. Based upon these calculations, a deeper understanding of the mechanisms involved in the super-resolution process will be achieved.

Reference

- [1] W. Welnic, A. Pamungkas, R. Detemple, C. Steimer, S. Blugel, and M. Wuttig. Unravelling the interplay of local structure and physical properties in phase-change materials. *Nature Materials*, **5**(1):56–62, Jan 2006.