Bulk ESCA and Valence Band measurements of Ge-Sb-Te based Optical Memory Alloys

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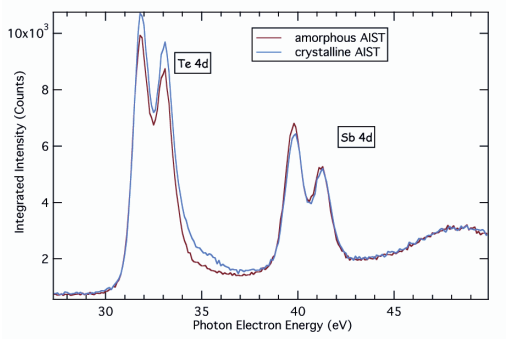
Phase-change alloys based upon chalcogenide compounds are now in wide use as re-writable optical media. Ge-Sb-Te compounds, specifically those lying along the GeTe - Sb_2Te_3 pseudo-binary tie-line are known to exhibit nanosecond scale transitions between the crystalline and amorphous phases and are now in widespread commercial use. Despite their wide use and over thirty-five year history, the properties of the utilized phase transition are only now becoming understood. We recently proposed a structural model (Nature Materials 3(10), 703 (2005)) that describes the local ordering changes occurring in the amorphous-crystalline phase transition based upon our measurements at SPring-8 on the Ge-Sb-Te alloy $Ge_2Sb_2Te_5$. We believe our model is general and with minor modifications can also describe the local structural changes occurring in other Ge-Sb- Te alloys.

As a first step, it is important to investigate the electronic structure of $Ge_2Sb_2Te_5$ in particular and optical memory alloys in general. Using the structures recently determined by our group, we intend to use *ab initio* calculations to determine the corresponding electronic structure of these materials. The ability to predict structural aspects and response functions on the basis of theoretical models is of great importance to understand many of the fundamental properties of chalcogenide alloys. In particular, the application of phase-change alloys to new technology such as Super-RENS readout which utilizes local thermal heating to generate readout properties beyond the conventional diffraction limit. While the technological aspects of these super-resolution readout mechanisms are already being applied, a grasp of the fundamental material properties that lead to localized enhanced of the readout signal are not understood. In addition, as the characteristic length scales of Super-RENS lie below 100 nm and characteristic time scales are on the order of 100 ns, the difficulty of carrying out comprehensive experimental studies cannot be over-emphasized. The value of carrying out such *ab initio* calculations is thus two fold. They allow investigation of material properties as a function of readout conditions which are difficult to measure via experiment and they also allow the preliminary investigation of differing allow composition and/or doping effects to allow the time-consuming experimental verification to focus on worth candidate materials. To this end, it is essential to

verify the accuracy of the electronic structure predicted from *ab initio* calculations which use as input a structural model derived such as ours. It is also of prime importance to look at actual device structures in thin film form. The use of the unique facilities at SPring-8 BL15XU in which a high intensity, high-energy resolution x-ray beam is used to excite photoelectrons. The use of a high-energy x-ray beam as an excitation source results in the generation of high-energy photoelectrons which can except from depths on the order of 100 nm into the bulk and in so doing transform what is normally a surface sensitive technique to practical device structures which may have thin (several nanometer) oxide layers present due to the nature of the disk fabrication process. We have measured both XPS and valence spectra for various $Ge_2Sb_2Te_5$optical memory alloys in both the laser-induced amorphous and metastable crystalline states. The sample structure consisted of Al-Cr (100)/ ZnS-SiO2(30)/ AgInSbTe(20)/ ZnS SiO2(130)/ quartz substrate (distances are in nm). Samples were grown by RF sputter deposition. The as-grown sample was then mounted in a Pulstec ddu unit. Two different annuli of approximately 10 mm width were then laser-amorphized and laser-crystallized, respectively. This assured that the both the amorphized and crystallized samples were of the same composition. Immediately before measurement, the samples were chemically etched to remove the metallic and dielectric layers; the samples were transported to the vacuum chamber in a nitrogen ambient. 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 the 4d spin doublets for Te and Sb in an laser-crystallized and laser-amorphized AgInSbTe alloy. While in all likelyhood, the 4dorbitals are localized, there is some broadening of the 4d doublets in the amorphous state. Although no large shift in position was detected for the 4d peaks of Sb and Te, there was a significant difference observed in the valence band structure implying that significant structural rearrangement had occurred as might be expected from the large change in reflectivity seen between the amorphous and crystalline phases of AgInSbTe optical memory alloys. This also serves to confirm that the structural changes are minor between the two phases and that local order is likely preserved.



4d doublets for laser-crystallized (blue) and laser-amorphized (red) AgInSbTe