

# Hard X-ray Photoelectron Spectroscopy, Chemical Bonding, and First Principle Calculations in Phase Change Memory Materials

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## Abstract

Hard X-ray photoelectron spectroscopy (HXPS) has been performed on phase change memory related alloy systems mainly consisting of IV, V, and VI elements in the periodic table. The electronic structures of this class of materials were revealed to show very similar density of states (DOS) among the materials. That is, DOSs of the materials consist of a topmost p band with ca. 5 eV bandwidth and lone pair s bands well separated from the p band. The results indicate that s-p hybridization is weak, and consequently, tetrahedral bonding is not favorable in these materials. This finding is consistent with a model of the resonance bonding for the crystalline phase, in which the crystal lattices are sustained by half filled p-like bonds. The most important feature in the HXPS results is that remarkable resemblance between crystalline and amorphous phases, showing a strong contrast to tetrahedral bonding material cases such as Si. The HXPS results are discussed basing upon large scale DFT calculations on crystalline and amorphous phases, which apply atomic structural constrictions based upon RMC analysis of XRD result in amorphous phase. Mechanism of the fast and reversible phase change (PC) will be discussed in relation with the specific chemical bonding nature and polymorphism in the average V valence electron materials.

Fast and reversible phase change (PC) in  $(\text{GeTe})_{1-x}(\text{Sb}_2\text{Te}_3)_x$  (GST) pseudo-alloys makes them very ubiquitous in rewritable optical storage devices, such as DVD, Blue-ray discs, and Large scale integrated electronic devices. The mechanism of the NaCl cubic (C) to amorphous (A) phase change has been discussed for a long time. Kim et al. [1] noted that GST is a member of average valence five ( $\langle V \rangle$ ) materials family, thus the PC mechanism is to be closely related to the inherent instability, which manifests in the crystalline polymorphism of this class of materials as shown in Fig. 1. Consensus seems to be established that the resonance bonding specific in the  $\langle V \rangle$  materials [2] is also taking place in the PC materials in cubic phase [3], but the PC mechanism has not yet been fully understood. In order to deepen the understanding, we have performed Hard X-ray photoelectron spectroscopy (HXPS) on phase change memory related alloy systems mainly consisting of IV, V, and VI elements in the periodic table.

GST samples were prepared at Panasonic Corporation, whereas stable GST polycrystalline sample and Bi-Te and Sb-Te polycrystalline samples were prepared at Osaka Prefecture University. HXPS measurements have been performed at BL47XU of SPring-8. High X-ray excitation energies of 6, and 8 keV enable us to have the bulk sensitivity, consequently contributions from surface contaminant are negligible in the observed spectra.

Figure 2 shows comparison of valence band spectra of

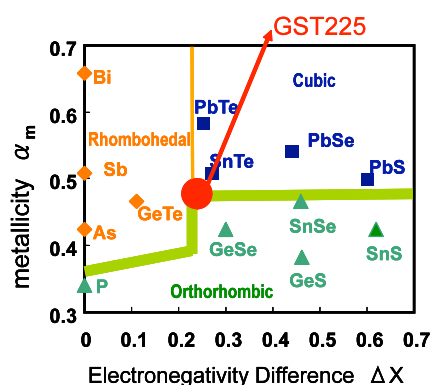


Fig. 1 Polymorphism in  $\langle V \rangle$  family. Note that cubic-rhombohedral and cubic-orthorhombic boundaries are orthogonal each other, suggesting metallicity and electronegativity difference are the independent parameters.

crystalline (a) Sb and  $(\text{GeTe})_{1-x}(\text{Sb}_2\text{Te}_3)_x$  (C phase), (b) stable and meta-stable crystalline GST225, and (c) Bi-Te alloys. Similarity in spectral shapes of these crystalline materials is the most distinguishable, i. e., the valence bands consist of p-bands with ca. 5 eV widths, which are well separated from deep lying lone pair s bands. Sb-Te alloy system also was found to show a very similar valence band spectral shape. These results evidence that s-p hybridization is weak and only the p orbitals sustain the crystalline structures. The meta-stable C phase of GST is considered to be sustained by the resonance bonding of  $p_x$ ,  $p_y$  and  $p_z$  orbitals as in IV-VI compounds. The reported resemblance of valence band spectral shape between A and C phases [1] is well understood chemical bonding in A phase is still sustained by p orbitals, although the resonance bonding is destroyed. We have recently performed large scale DFT-MD calculations constraining to have consistency with the RMC analysis of XRD results [4]. The results are very consistent with the HXPS results.

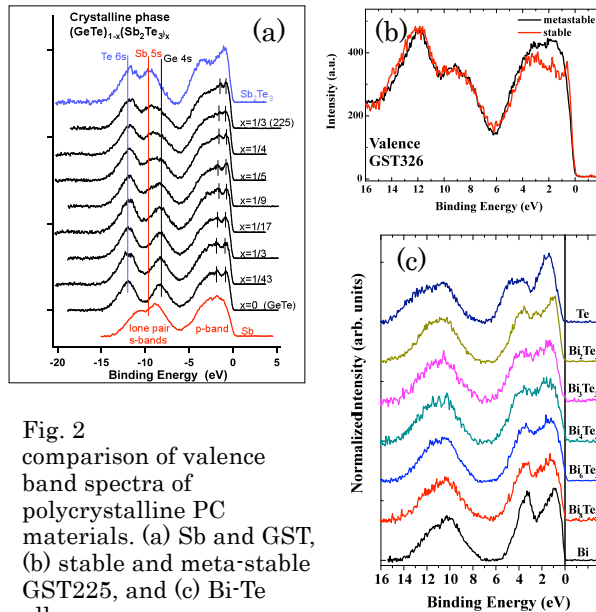


Fig. 2 comparison of valence band spectra of polycrystalline PC materials. (a) Sb and GST, (b) stable and meta-stable GST225, and (c) Bi-Te alloys.

in A phase is still sustained by p orbitals, although the resonance bonding is destroyed. We have recently performed large scale DFT-MD calculations constraining to have consistency with the RMC analysis of XRD results [4]. The results are very consistent with the HXPS results.

Cubic phase in Fig. 1 is essentially metallic with half filled octahedral bonds. This structure is stabilized by the symmetry breaking due to lattice deformation and/or electronegativity difference, introducing a gap around Fermi level. Figure 1 tells that two types of lattice deformation in IV-VI compounds. The difference from the IV-VI compounds is that GST inevitably contains vacancies, which break the translational symmetry. This randomness is considered to play a role in the PC process during quenching from C to A phases and also in the crystallization process. The Bi-Te and Sb-Te alloys do not necessarily involve vacancies. Thus the PC mechanism may different from that in GST.

In conclusion, the crystalline structures in the phase change memory related alloy systems mainly consisting of IV, V, and VI elements in the periodic table are shown to be very similar to those of V elemental and IV-VI compound materials. The high adaptability of p like bonding, which inevitably related with its inherent unstable nature, is considered to be an essential key to the A phase structure and PC mechanism.

## REFERENCES

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## BIBLIOGRAPHIES

Keisuke Kobayashi was born in 1943 in Osaka, Japan. He finished postgraduate course of Osaka University in physics in 1972, and joined Central Research Laboratory of Hitachi Ltd. in the same year. He accepted doctoral degree of science in 1973 from Osaka University. Since the time, he has been engaged in research of semiconductors, including Si, GaAs and other II-V compounds, and IV-VI compounds. From 1978 to 1979, he joined Prof. C. Kunz's group supported by Humboldt Foundation, to start researches of the photoelectron spectroscopy using synchrotron radiation. In 2000, he joined JASRI (Japan Synchrotron Radiation Research Institute) to be in charge of the soft X-ray and infrared beamlines. In 2006, he moved to National Institute for Materials Science as the head of the NIMS contract beamline at SPring-8.