

# Hard X-ray Photoelectron Spectroscopy of Crystalline and Amorphous $\text{Ge}_1\text{Cu}_2\text{Te}_3$

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## Abstract

Valence band structures and chemical bonding states of amorphous (A) and crystalline (C) phases of an average- four- valence- electrons- material  $\text{Ge}_1\text{Cu}_2\text{Te}_3$  were investigated by hard X-ray photoelectron spectroscopy. Prominent spectral shape differences between the two phases which correspond to the electric resistivity difference between A- and C-phases were observed. The results strongly suggest that  $\text{Ge}_1\text{Cu}_2\text{Te}_3$  is expected to be a new class of phase change memory materials, in which the change in bonding coordination of Ge may play an essential role in the phase change mechanism.

## Introduction

Crystalline (C)  $\text{Ge}_1\text{Cu}_2\text{Te}_3$  (GCT) has 24 s-p electrons per molecule, i. e., 4 electrons per atom. It takes chalcopyrite related structure with 4 fold coordinated bonds. Amorphous (A) phase of this compound is possible to be obtained by quenching. Recently, Sutou et al. reported that the electrical resistivity of the A-phase is 2-3 orders of magnitude larger than that of C-phase [1]. Being interested in the A-C phase change of this material, we have conducted hard X-ray photoelectron spectroscopy (HXPS) observation[2].

## Experimental

Samples were prepared by sputtering of a Ge-Cu-Te alloy target on  $\text{SiO}_2$  (20 nm)/Si substrates at Tohoku University. In order to avoid oxidation of the sample surfaces, carbon layers of few nm in thickness were deposited immediately after the deposition. As-deposited GCT films were verified to be amorphous by the X-ray diffraction pattern. The crystalline samples were prepared by annealing the as-deposited amorphous films at 250 °C. The electrical resistance drastically decreases by this annealing procedure, indicating crystallization of the films. HXPS measurements were done at BL15XU of

SPring-8, NIMS contract beamline, using horizontally polarized undulator X-ray photons of 6 keV with band width of ca. 55 meV. The total energy resolution of the HXPS measurements was set to 230 meV. Due to the large information depth of HXPS in this photon energy region, electronic as well as chemical states of the samples were observable down to as deep as ca. 20 nm from the sample surface. Both the valence band and core level spectra were measured in C- and A-phases of the thin film samples. The carbon capping layers did not manifest in the observed spectra due to its smaller photoionization cross sections comparing to those of Ge, Cu and Te.

### Results and Discussions

Figure 1 shows whole valence band spectra (a) and near Fermi edge spectra (b) of A- and C-phase films. The whole valence band spectra exhibit similar shapes each other, with Te 5s, Ge 4s, and mixed bands among Te 5p, Ge 4p, and Cu 3d, in the binding energy regions of 15-10, 10-7.5, and 7.5-0 eV, respectively. However, several apparent differences are recognized as mentioned below. The Ge 4s band becomes more distinguishable in C-phase than in A-phase. The topmost band (7.5-0 eV) shape is different between A- and C-phases. The width is broader in A-phase than that in C-phase. Intensity distribution of three peaks and a shoulder is also different. Figure 1 (b) verifies that C-phase samples show finite density of states at the Fermi level, whereas the Fermi level locates just above the onset of the valence band in A-phase samples. This coincides with the resistivity behavior mentioned above.

A distinguishable difference was found in the Ge 2p spectra. In C-phase, the Ge 2p spectrum showed a double-peak structure with almost the same intensities, while the higher binding energy component became stronger than the lower binding energy one in A-phase. On the other hand, the Cu and Te core spectra did not show significant changes (not shown in the figure).

The differences between A- and C-phases observed in the present experiments are apparently dissimilar from that in Si, which is a typical tetrahedral bonding material. It is strongly suggested that the change in s-p hybridization of the Ge-Te bonds is to play a key role in the A-C phase change in  $\text{Ge}_1\text{Cu}_2\text{Te}_3$ .

We are going to verify the reversible phase change in this material, expecting that possibility as a new candidate of materials for the phase change memory devices.

### Conclusion

The present HXPS results on the  $\text{Ge}_1\text{Cu}_2\text{Te}_3$  sputtered films revealed that a sudden electrical resistivity decrease due to annealing of as-deposited films at 250 C is caused

by the valence band structure change. The change also accompanied by change in Ge chemical bonding states, which suggests a kind of Ge bonding coordination transition takes place at the amorphous to crystalline phase change in this material.

### Acknowledgements

The authors are grateful to HiSOR, Hiroshima Univ. and JAEA/SPring-8 for the development of HX-PES at BL15XU of SPring-8.

### References

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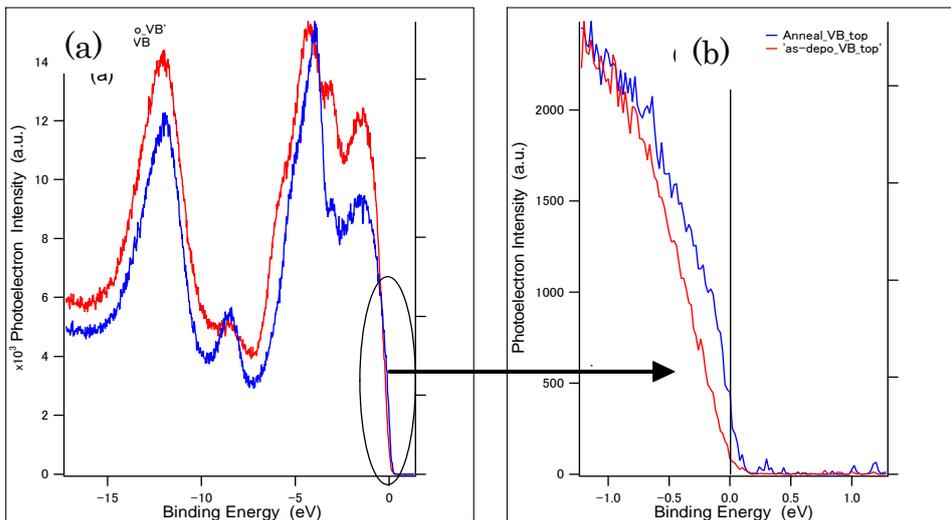


Fig. 1 (a) Whole valence band spectra of as-deposited (red) and annealed (blue)  $\text{GeCu}_2\text{Te}_3$ . (b) Spectra near the Fermi level. X-ray energy: 5.95 keV.

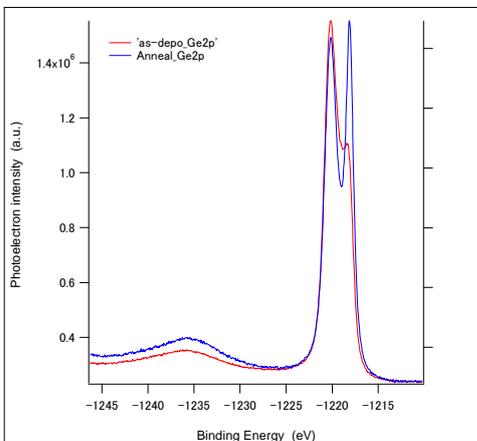


Fig. 2  
Ge 2p<sub>3/2</sub> spectra of as-deposited (red) and annealed (blue) samples.  
X-ray energy: 5.95 keV.