

Study of GeCu_2Te_3 by Hard X-ray Photoelectron Spectroscopy

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Abstract

The most interesting point in the novel phase change material $\text{Ge}_1\text{Cu}_2\text{Te}_3$, recently reported by Sutou et al. is that this material has 4 sp valence electrons per atom. The material takes a sp^3 bonded crystalline structure, thus very different from standard PC materials such as $\text{GeTe-Sb}_2\text{Te}_3$ pseudo-binary alloy system conventional PC materials. In order to clarify the PC mechanism in this material, hard X-ray photoelectron spectroscopy studies on GCT films with Ge-rich, stoichiometric, and Cu-rich films have been performed using a monochromatic Cr $K\alpha$ X-ray photoelectron spectrometer. The results indicate coexistences of different charge states in Ge, Cu and Te both in amorphous and crystalline phases. The behaviors of these different components upon annealing depend on deviation from stoichiometry, suggesting controllability of the PC in this material. A PC mechanism is proposed basing upon the present experimental results.

Introduction

Recently, Sutou et al. has discovered that GeCu_2Te_3 (GCT) exhibits reversible phase change (PC) phenomena [1,2]. The most interesting point in this new class of PC materials is that it has 24 sp valence electrons per molecule (4 sp electrons/atom) thus takes a tetrahedral bonded chalcopylite related structure in the crystal phase as shown in Fig. 1. In the standard PC materials of GST and related compounds, average valence

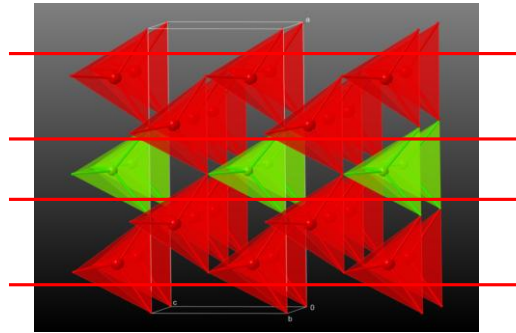


Fig. 1 Crystal structure of GeCu_2Te_3

electron number is approximately 5/atom, corresponding to s^2p^3 valence electron configuration. The s^2 electrons form lone pair band, and p^3 electrons mainly sustain crystal bonding, resulting in the inherent instability in NaCl type cubic crystal lattice. Mechanism of reversible PC phenomena in these

average 5 valence electron family have been discussed in relation with this characteristic valence electron configuration.

In case of GCT, however, tetrahedral s-p hybridized bonds are too rigid, consequently not favorable for the PC. This implies that the PC in this material requires another freedom in the crystal bonding which brings flexibility in the bond configurations.

In order to investigate the problem, we have performed hard x-ray photoelectron spectroscopy (HAXPES/HXPES) to observe variations in valence band and core levels of GCT samples with various compositions (deviations from stoichiometry) and annealing temperatures. Among those spectra, core level spectra of Ge show distinctive changes due to deviations from stoichiometry and annealing, suggesting that Ge atoms play a key role in the PC mechanism in GCT.

Experimental

Stoichiometric, Ge-rich, and Cu-rich films were deposited at Tohoku University by co-sputtering with GeTe, and CuTe targets onto Si substrates covered with 20 nm of SiO_2 , and then C capping layers of few nm were deposited soon after the sputtering. The

compositions of the films were controlled by microwave power ratio for the two targets. The compositions were determined by ICP-MS in several samples as shown in Table I. The XRD measurements indicate that all the films are in single phase, in spite of considerably large deviation from stoichiometry in Ge-rich and Cu-rich films. Samples

Table I

作製条件	Composition (at.%)			備考
	Cu	Ge	Te	
Single phase film by co-sputtering	33.6	17.4	49.0	ICP-MS
Ge-rich film by co-sputtering	31.7	19.1	49.2	ICP-MS
Cu-rich film by co-sputtering	37.9	13.1	49.0	ICP-MS

were then annealed at various temperatures. Electric resistances of these films were found to show typical phase change behaviors as shown in Fig. 2. That is, the resistance steeply decreases at a temperature range between 200-250 C due to amorphous to crystalline phase change. Further increase of annealing temperature results in slight decrease of resistance. The crystalline phase samples then show metallic behavior with positive temperature coefficients of the resistances.

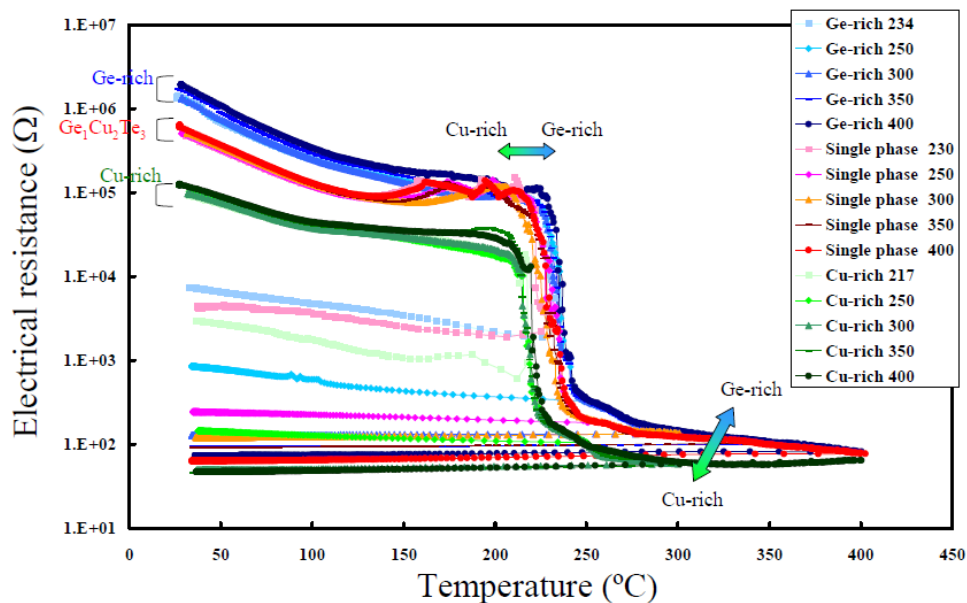


Fig. 2 Temperature dependence of Electric resistance

The hard X-ray photoelectron spectra of the samples were measured by **HEARP Lab** (**H**igh **E**nergy **A**ngle **R**esolved **P**hotoelectron Spectrometer for **L**aboratory **U**se) system, which consists of a monochromatic Cr K α (5.4 keV) source, a wide acceptance objective lens, and a VG Scienta high energy analyzer. [3,4]. Total energy resolution is 0.55eV. The information depths of the measurements are estimated ca. 10 nm, due to the high kinetic energy of photoelectrons. The C capping layers give no detectable traces in the valence band and core levels spectra because of the smaller photoionization cross sections comparing to those of Ge, Cu and Te.

Results

Figure 3(a) shows annealing temperature dependence of valence band spectra for stoichiometric films. A remarkable change is recognized at the topmost band, which spans from Fermi level (E_f) to about 6 eV below E_f . Dominant contribution to this band

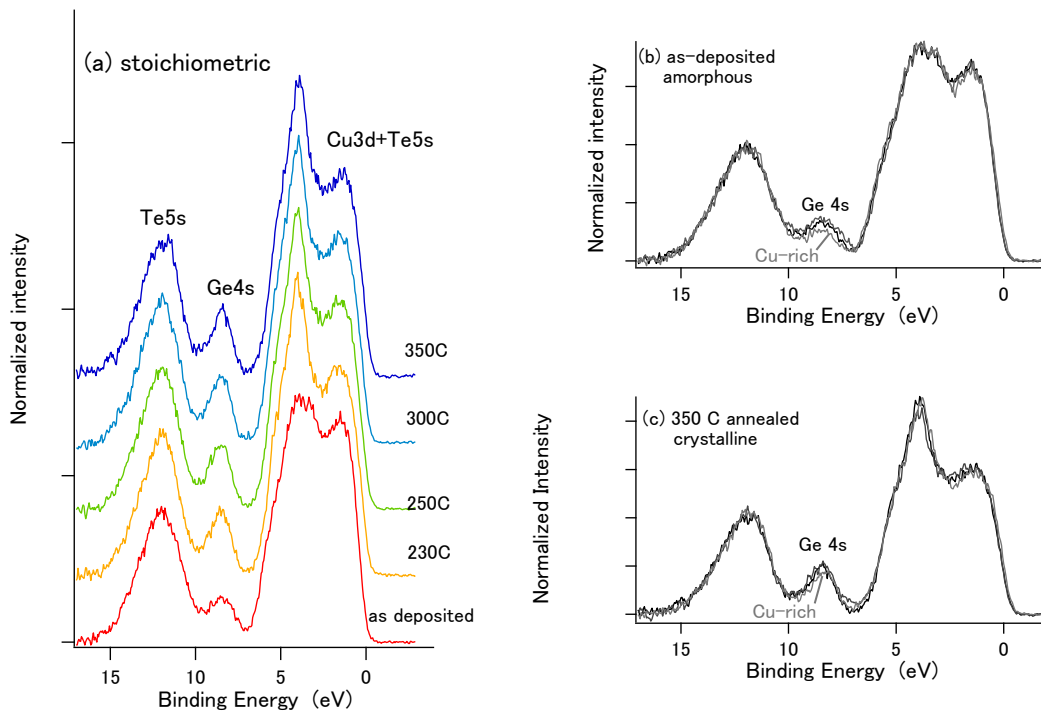


Fig. 3 Valence band spectral of GCT.

(a) Annealing temperature dependence for stoichiometric film. (b) and (c) dependence on deviation from stoichiometry.

comes from Cu 3d, and somewhat smaller contribution comes from Te 5d. The Ge 4p participation is negligible. Two broad peaks are seen at 1.4 eV and 3.7 eV binding energies (E_b) in the as-deposited amorphous film. Upon annealing at 230 K, the high E_b peak becomes sharp and its intensity increases. The Ge 4s band which peaks at around

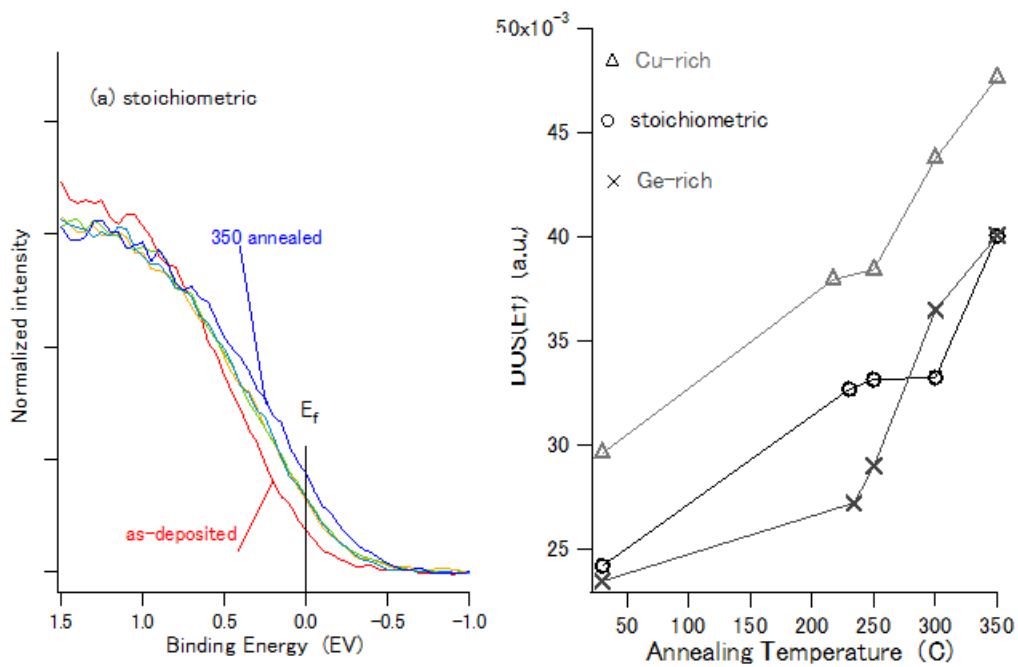


Fig. 4 (a) Valence band spectra near Fermi level. (b) annealing temperature dependence of $DOS(E_f)$.

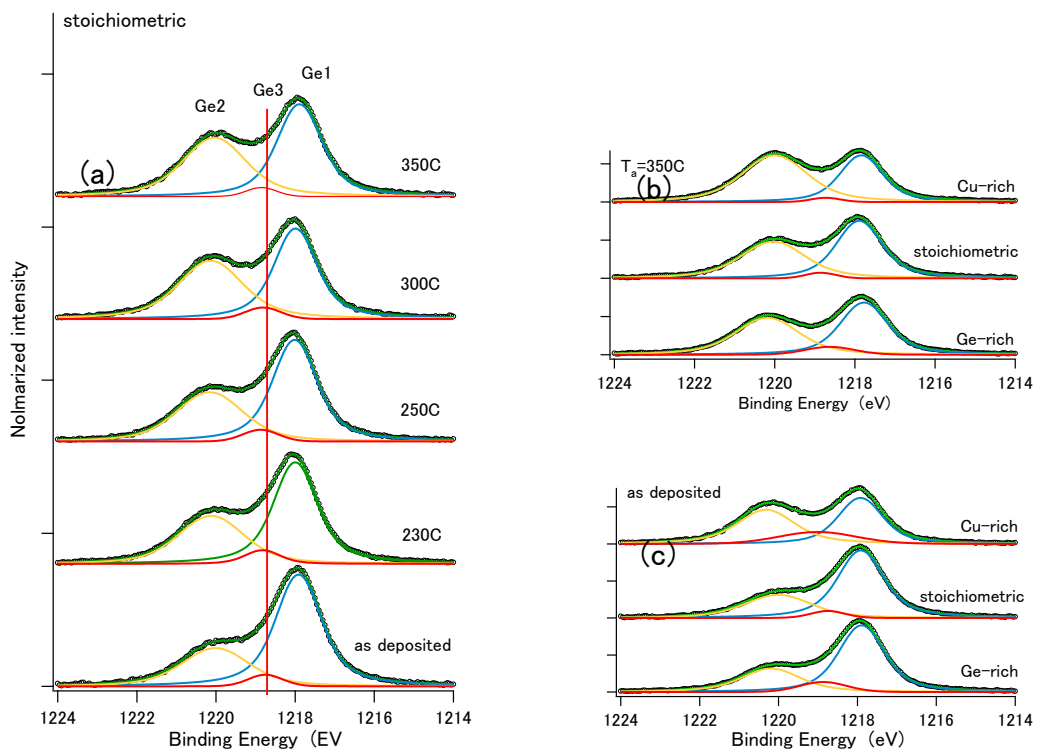


Fig. 5 (a) annealing temperature dependence of $Ge2p_{3/2}$ spectra for stoichiometric film. Dependence on deviation from stoichiometry for (b) 350 C annealed and (c) as deposited films.

7.5 eV becomes narrower and peak height increases. The further increase of annealing

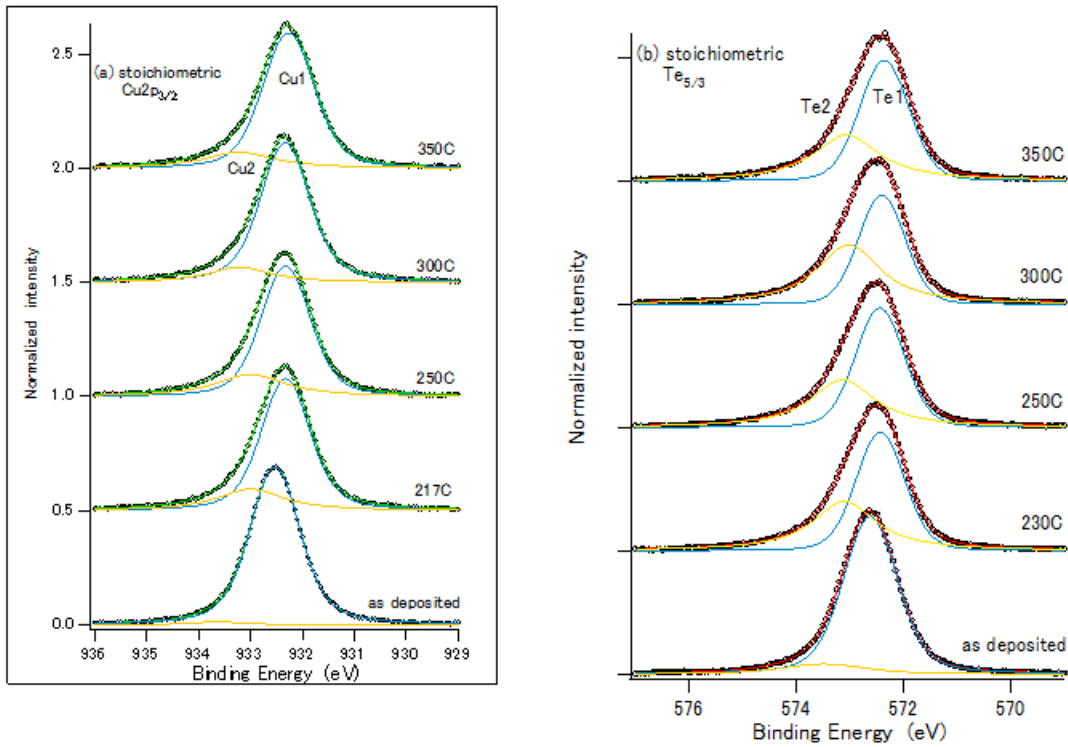


Fig. 6 (a) annealing temperature dependence of Cu 2p_{3/2} and (b)Te_{5/3} spectra.

temperature does not change the spectral shape distinctively. The valence band spectra of as-deposited and 350 C annealed samples of stoichiometric, Ge-rich and Cu-rich films are compared in Fig. 3(b) and 3(c), respectively. The Ge 4s band shows a difference due to differences in Ge composition. However, the rest of spectral shape shows no other distinctive difference. The recognizable spectral shape variation seems to complete already at lowest annealing temperature of from 217 C (for Cu-rich sample) to 234 C (for Ge-rich sample); however, to see more closely, we find the state density at around E_f clearly increases by annealing in Fig. 4(a). Figure 4(b) shows annealing temperature dependences of integrated density of states $DOS(E_f)$ in the binding energy range of -0.5 eV–0.5 eV at around E_f for stoichiometric, Ge-rich and Cu-rich films. The increasing behavior of $DOS(E_f)$ are consistent with electric resistance decreases in Fig. 2.

Annealing temperature dependence of Ge 2p_{3/2} spectrum in stoichiometric film is shown in Fig. 5. The Ge 2p spectrum consists of 3 components denoted as Ge1, Ge2, and Ge3 in this figure. Ge1 appears at 1217.9 eV, which correspond to Ge 2p_{3/2} binding energy of covalent Ge (1218.0 eV in GeTe). Ge2 shift about 2.2 eV toward higher binding energy, thus considered to come from Ge atoms in ionic bonding states. Weaker Ge3 is in between. Upon annealing, Ge1 apparently decreases whereas Ge2 increases.

Figure 5(b) and 5(c) show comparisons of Ge2p_{3/2}spectra for Ge-rich, stoichiometric, and Cu-rich samples of as deposited and 350 C annealed films. The Ge2/Ge1 ratio increase

as Cu/Ge composition ratio increases. Annealing also causes increase in Ge2/Ge1 ratio. Evolutions of Cu $2p_{3/2}$ and Te $3d_{5/2}$ with annealing for stoichiometric samples are shown in Fig. 6(a) and (b), respectively. Both the Cu and Te spectra consist of two components, as denoted Cu1 and Cu2, and Te1 and Te2 in this figure. Cu2 component is very weak in as deposited film, whereas Te2 is somewhat stronger. Annealing causes distinctive enhancement of Te2 component. The variations of these components are summarized in Fig. 7, showing the relative intensities of each component by bars.

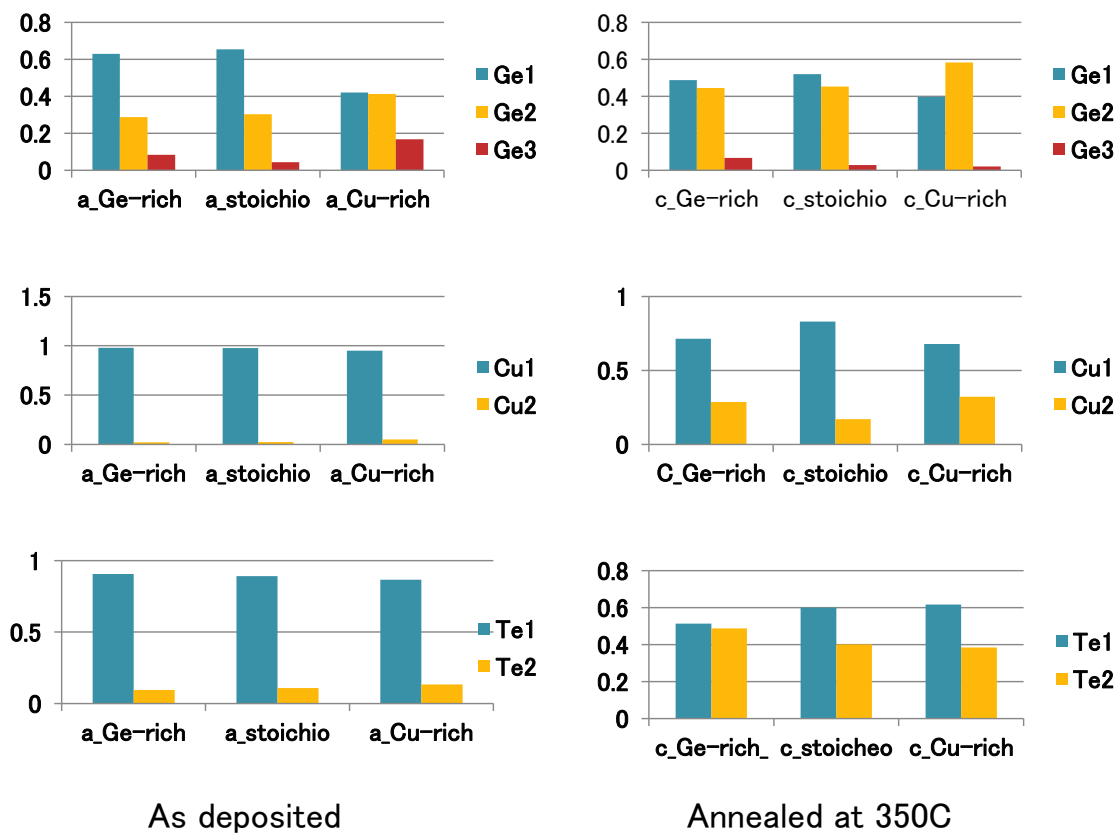


Fig. 7 Relative intensity variations due to annealing.

Discussion

The present results clarify followings

- 1) Variation of valence band spectral shape is already completes at 217–230 C, where the electric resistances are on the half way of steep decreases. As valence band DOSs are considered to be determined dominantly by local bonding characteristics, the present results suggest annealing at rather low temperature already results in bond reconstructions, which is connected to PC.

- 2) The DOS(E_f) changes due to annealing are consistent with the resistance changes, however, amount of DOS(E_f) increase is apparently not enough large to explain the resistance drops. Thus main cause of the high resistance in amorphous phase is considered to be due to randomness of atomic arrangements.
- 3) Ge 2p spectra evidence three kinds of Ge atoms. In amorphous (as deposited) film, Ge2 concentration is less in stoichiometric films, whereas it is almost equal to Ge1 in Cu-rich film. In the crystalline film annealed at 350 C, Ge1 and Ge2 concentration becomes almost equal, and Te2 increases up to about 40% in stoichiometric film.
- 4) The relative compositions and their variations with annealing depends on deviations from stoichiometry. This implies that PC behaviors in GCT can be controlled by compositions of films.
- 5) As shown in Fig. 1, GCT crystalline structure consists of tacking of CuTe-GeTe-CuTe

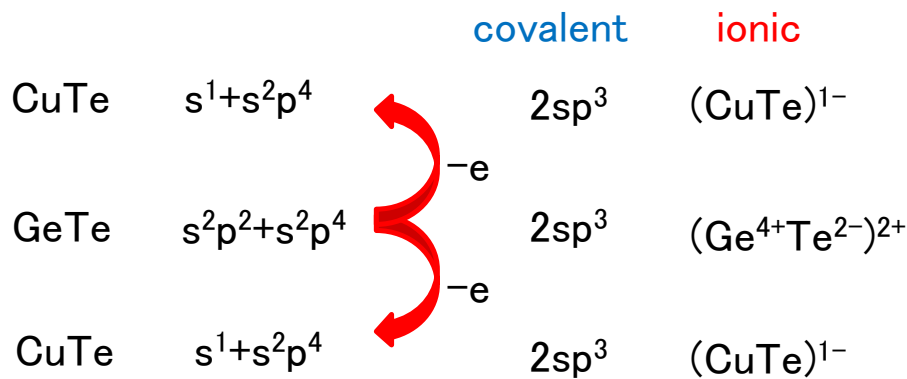


Fig. 8 Schematic explanation of coexistence of two charge state in Ge..

layered unit. In the formal charge framework, we can consider coexistence of two different charge states for Ge atoms as schematically shown in Fig. 8. That is, sp^3 like covalent bonding state and $(Ge^{4+}Te^{2-})^{2+}$ states. The 2+ charges are compensated by 1+ charge in two CuTe layers. If we assume these + charges are delocalized in CuTe layers, we have Ge^{4+} and Te^{2-} of the same concentrations in ionic states. This is consistent with the present results. The Te2 appears a little higher binding energy than Te1, although the binding energy difference is relatively small. Te1 is considered to come from covalent whereas Te2 come from ionic Te (negatively charged). This discrepancy may be due to difference in relaxation energies.

- 6) Existing XRD measurements [5] seem not to support coexistence of the two different

Ge charge states in crystalline GCT. This may be explained by assuming random distribution of the two charge states or dynamical alteration between the two charge states.

- 7) The coexistence of the two charge state in Ge could offer a kind of freedom in the rearrangements of atoms without introducing broken sp^3 bonds, thus enables reversible PC in this material.

Summary

We have investigated novel PC materials GCT by bulk sensitive hard X-ray photoelectron spectroscopy using laboratory HXPES system at 5.4 keV excitation energy with 0.55 eV resolutions. Present results indicate that valence band change takes place by annealing at low temperatures of 217–234 C. The behaviors of valence band and core level spectra were found to depend on deviations from stoichiometry. Density of states at Fermi level increases upon annealing indicating increases in metallic nature due to crystallization, however, amount of DOS increase alone does not explain the drop of electric resistances due to annealing. Ge 2p spectra indicate coexistence of neutral and ionic Ge both in amorphous and crystalline phases. Te and Cu spectra also exhibit coexistence of two different states in both Te and Cu. These coexistences of different charge states may introduce a kind of freedom in atomic arrangements in GCT, which enables fast reversible phase change.

References

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