Hard X-ray Photoelectron Spectroscopy of Crystalline and Amorphous $Ge_1Cu_2Te_3$

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ABSTRACT

Valence band structures and chemical bonding states of amorphous and crystalline phases of an average-four-valence-electrons-material $Cu_2Ge_1Te_3$ were investigated by hard X-ray photoelectron spectroscopy. Valence band spectrum in crystalline phase does not resemble easer those of typical tetrahedral semiconductors such as Si, Ge and GaAs, or average-five-valence-electron-materials such as GST. Weak Ge 4s band intensity suggests that Ge 4s electrons transfer to Te empty states. Small metallic state is recognized at Fermi level in crystalline phase, whereas it diminishes in amorphous phase, consistently with large resistivity increase observed at the crystalline to amorphous phase change. Ge and Te core spectra indicate coexistence of neutral and ionic Ge-Te bonds, which is consistent with the weak Ge 4s contribution to valence band spectrum. Significant spectral-shape-differences between the two phases were observed both in valence band and core level spectra. The results strongly suggest that $Cu_2Ge_1Te_3$ is expected be a new class of phase change memory materials, in which coexistence of neutral and ionic Ge-Te bonds may play an essential role in the phase change mechanism.

Key words: $Cu_2Ge_1Te_3$, HXPS, tetrahedral sp^3 bonding, ionic bonding

1. INTRODUCTION

Phase change (PC) materials, which show fast reversible change between crystalline and amorphous phases, have widely been investigated for the developments of rewritable memory devices. DVD and Blu ray discs are the one of the most successful applications. Recently many efforts have been made to realize large scale integrated electronic rewritable memory devices. Pseudo-binary alloy system $(GeTe)_{1-x}$-$(Sb_2Te_3)_x$ (GST) has been investigated as a typical materials for theses PC memory devices. Materials quests have been conducted, for instance by replacing Sb by Bi and introducing I and III elements such as Ag and In, in various research groups. All these materials belong to the family of approximately three p electrons per atoms in average. The phase change mechanism in this class of materials has been discussed in relation to this specific valence electron configuration. The two s electrons form lone pair bands and three p electrons sustain the 6 fold NaCl cubic structure by resonance bonding as in the case of average-five-valence-electron materials such as V elemental and IV-VI compounds. [1-8] This results in the formation of an unstable half-filled metallic band of p character. Displacive transitions from 6-fold to the two types of 3-fold phases (rhombohedral A7 and orthorhombic B16 phases) take place by introducing a gap around the Fermi level. The phase change in GST is understood essentially as electronic transition from 6-fold NaCl structure to random distribution of 3-fold bonding structure.[7,8] Recently $Ag_{3.5}In_{3.8}Sb_{75.0}Te_{17.7}$ (AIST) is clarified as another class of average three p electrons material. The crystalline AIST takes A7 structure with periodically alternating three long and three short bonds aligned in order. In the amorphous phase, directions of resultant vector of short bonds distribute randomly. Upon the re-

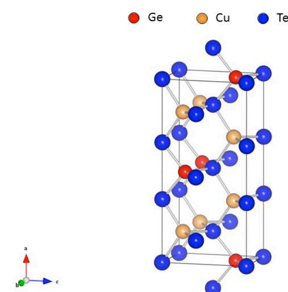

Fig. 1 Crystal structure of Cu2GeTe3

crystallization, the randomly distributed resultant vectors become realigned to have the crystalline order through bond exchange mechanism.[9] Recently, Sutou et al. reported that the electrical resistivity of $Ge_1Cu_2Te_3$ (GCT) in the A-phase is 2-3 orders of magnitude larger than that in C-phase.[10] They also found that this resistivity change is reversible, suggesting CGT has a potential as a new PC material. The most interesting point in these new findings is that CGT does not belong to the average-five-valence-electron family. Crystalline (C) has 24 s-p electrons per molecule, i. e., 4 electrons per atom in average. It takes chalcopyrite related structure with 4 fold coordinated bonds as shown in Fig. 1. This indicate that CGT is a completely new PC material with very different PC mechanism from those in average three p electron materials such as GST and AIST. Being interested in the A-C phase change of this material, we have conducted bulk sensitive hard X-ray photoelectron spectroscopy (HXPS, HXPES, or HAXPES) [11,12] observation to investigate PC mechanism from electronic structures and chemical bonding states viewpoints.

2. EXPERIMENTS

Samples were prepared by sputtering of Ge-Cu-Te alloy target on SiO_2 (20 nm)/Si substrates at Tohoku University. In order to avoid oxidation of the sample surfaces, carbon layers of few nm thicknesses were deposited immediately after the deposition. As-deposited GCT films were verified to be amorphous by the XRD 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 230 meV. Due to 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, thus the resultant spectra are assured not to be affected by surface conditions. [10, 11] Both the valence band and core level spectra were measured in C- and A-phases of thin film samples. The carbon capping layers of few nm thicknesses did not manifest in the observed spectra due to the large attenuation length of the photoelectrons, and also smaller photoionization cross sections of C valence electrons comparing to those of Ge, Cu and Te.

3. RESULTS & DISCUSSION

Figure 2 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 as a whole, with Te 5s, Ge 4s and Te 5p-Ge 4p-Cu 3d mixed bands, in the binding energy regions of 15-10, 10-7.5, and 7.5-0 eV, respectively. No significant difference is seen in Te 5s band. The Ge 4s band is apparently weaker than Te 5s band expected from experimental results in GST.[8] It becomes even weaker in A-phase. The topmost band (7.5-0 eV) shape is several different features between A- and C-phases. Three peaks are recognized at 1.4 eV, 3.2 eV, and 3.9 eV in C-phase topmost band. In the A-phase, the three peaks appear at the same positions; however, intensity distribution among them is changed. In addition, a shoulder appears at around 6.2 eV. The photoionization cross section of Cu 3d is the strongest, and those of Te 5s, Te 5p, and Ge 4s are smaller than that of Cu 3d at the photon energy of 6 keV. The photoionization cross sections of Cu 4s and Ge 4p are more than one order of magnitude weaker than that of Cu 3d. Thus the topmost valence band consists mainly of Cu 3d, and Te 5p mixed states. Figure 2 (b) evidences that C-phase samples show finite density of states at Fermi level, whereas Fermi level locates just above the onset of the valence band in A-phase

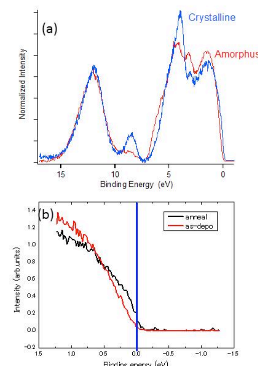

Fig. 2 (a) Valence band spectra. (b) Valence band spectra near the Felmi level.

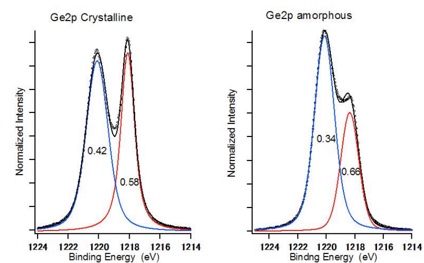

Fig. 3 Ge 2p3/2 spectra

samples. This coincides with the large resistivity change upon the PC mentioned above.

Ge $2p_{3/2}$, Te 4d and Cu $2p_{3/2}$ spectra are shown in Fig. 3, Fig.4, and Fig.5, respectively. A significant difference is apparent in Ge $2p_{3/2}$ spectra. In C-phase, Ge $2p_{3/2}$ spectrum exhibits double peaks at 1218.1 eV and 1220.1 eV with almost the same intensities as shown in Fig. 3. The intensity ratio for the low to the high binding energy components was estimated at 0.58/ 0.42. The position of the low binding energy component coincides with that of Ge $2p_{3/2}$ in GeTe. Thus we assign this component is originated from neutral Ge. The energy difference between the two components is 2.0 eV, which is comparable to the Ge $3d_{5/2}$ binding energy difference of 2.9 eV between GeTe and GeO_2, strongly suggesting that it comes from Ge positively charged up to nearly 4+. The lower binding energy component is stronger than the higher binding energy one in A-phase. The intensity ration is 0.34/0.66. Te 4d core spectra also show distinguishable two spin-orbit doublet pairs at (40.04 eV-40.28 eV, and 40.49 eV-40.38 eV) with almost the equal intensities in C-phase. The high binding energy component in this case appears at the same binding energy position of Te 4d in GeTe, indicating that it is attributed to neutral Te. Consequently, the lower binding energy component is identified as negatively charged Te. The intensity ratio of the low binding energy to the high binding energy components is at 0.49/0.51. In A-phase, the ratio is 0.35/0.65. The low binding energy pair shifts to higher binding energy side by amount of 0.25 eV, whereas, the high binding energy pair stays at the same position that of in C-phase. Cu 2p core spectra in C-phase exhibit a weak component in 0.35 eV higher binding energy side of the main component at 932.74 eV. This component intensity becomes even weaker in A-phase.

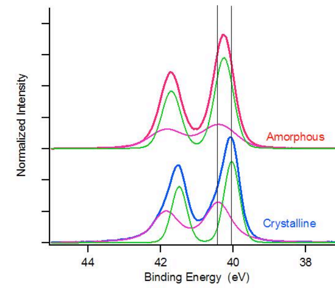

Fig.4 Te4d spectra of crystalline and amorphous CGT.

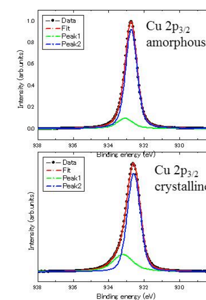

Fig 5 Cu2p3/2 spectra

Basing upon the experimental results on CGT, here we propose a model for the electronic structure and chemical bonding states of C-phase CGT, and a possible explanation of PC in this new class of materials. Viewing from <010> and <001> direction, CGT crystal consists of stacks of (CuTe)-(GeTe)-(CuTe). In order to form tetrahedral sp^3 bonding, the (GeTe) layer donates two electrons per molecule to the sandwiching two (CuTe) layers. There are two possible valence electron configurations to realize this. One is to form the sp^3 bonding between Ge and Te by donating excess electrons to the (CuTe) layers. Another possible configuration is that Ge and Te take Ge^{4+} and Te^{2-} charged states, respectively. Excess two electrons again donate the (CuTe) layers. Since XRD experiments has shown no evidence of super lattice formation in CGT[13], Ge^0 and Ge^{4+} are considered to be randomly distributed in the (GeTe) plane in C-pahse. The weakness of Ge 4s band in the C-phase valence band spectrum also supports existence of Ge^{4+} state. Cu atoms may be also affected by the difference in Ge charge states, however, the effect is considered to be weaker, because they are affected through Te atoms. In A-phase, both Ge and Te spectra show that decreases in neutral components and increases in ionized components. Almost complete disappearance of Ge 4s band in the valence band spectrum is also consistent with the change in core spectra mention above. Increase in the Ge-Te ionic bonding, which is expected to be less un-isotropic than neutral sp^3 bonding, may play a role in the PC mechanism in the material.

4. CONCLUSION

The present HXPS results on $Ge_1Cu_2Te_3$ sputtered films revealed that a sudden electrical resistivity decrease due to annealing of as-deposited films at 250 C is caused the valence band structure change, which gives rise to a small metallic edge at the Fermi level. The valence band and core level spectra indicate coexistence of neutral and ionized Ge and Te. In A-phase, concentrations of ionized Ge and Te contributions increase. This may play an essential role in

this new type of PC-mechanism. It is strongly suggested that degree of freedom due to coexistence of the ionic and neutral bonding states in the Ge-Te bonds plays a key role in the A-C phase change in $Ge_1Cu_2Te_3$. The electronic structure and chemical bonding states in CGT are very different from GST and related materials as discussed above. Thus we may expect fruitful results in the quest of possible candidates for advanced PC devices in this class of materials. Further investigations on the reversible phase change in this material are needed to prove the PC mechanism and to verify the possibility as a new candidate of materials for the phase change memory devices.

5.Ackonowledgements

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Biographies

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 doctral 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 Japan Synchrotron Radiation Research Institute (JASRI) to be in charge of the soft X-ray and infrared beamlines. In 2006, He moved to National Institute for Materials Science (NIMS). He was the group leader of the NIMS contract beamline at Spring-8 until March 2011. Now he is a research advisor of NIMS beamline group and a guest professor of Hiroshima Synchrotron Radiation Center, Hiroshima University.