

## EXAFS study of Sb-Te alloy films

Katsuhiko Tani,<sup>a\*</sup> Noriyuki Yiwata,<sup>a</sup> Makoto Harigaya,<sup>a</sup> Shuichi Emura,<sup>b</sup> Yoshiyuki Nakata<sup>c</sup>

<sup>a</sup>R&D Center, Ricoh co.Ltd., Yokohama 224-0035, JAPAN.

<sup>b</sup>ISIR, Osaka University, Osaka 567-0047, JAPAN.

<sup>c</sup>Iwaki Meisei University, Iwaki 970-8551, JAPAN.

Email:tani@rdc.ricoh.co.jp

The local structures of three phases; stable compound  $\text{Sb}_2\text{Te}_3$ , metastable crystalline c-SbTe and amorphous a-SbTe films having the atomic ratio  $\text{Sb}/\text{Te}=3$ ; in Sb-Te system have been studied by EXAFS. The c-SbTe has a partly similar local structure to crystalline  $\text{Sb}_2\text{Te}_3$ . The a-SbTe film has a local structure of NaCl-type, which is topologically analogous to the crystalline form. The amorphous phase has shorter bond distances 2.86Å (around Sb-site) and 2.83Å (around Te-site) than the corresponding distances 2.89Å and 2.87Å in the crystalline phase. This unbalanced bond distances between the Sb-site and Te-site implies that site-disordering occurs. Shortening of bond distances in the amorphous phase is due to the relaxation of locally distorted crystalline structure.

**Keywords:** EXAFS, Sb, Te, binary alloy, phase-change

## 1. Introduction

The binary alloy system Sb-Te is a fundamental and key material to reversible phase-change optical recording. Nevertheless, crystal structures of the binary system are little known yet. Only accepted crystalline structure is the stoichiometric stable compound  $\text{Sb}_2\text{Te}_3$ :  $R\bar{3}m$ ;  $a_0=4.25$ ,  $c_0=30.4$  with hexagonal 3-point-cell. The structure of this compound is regarded as a layered structure along the  $c_0$  axis, in the succession of a cubic close-packing; -Sb-Sb-Te-Te-Te-Sb-Sb-Te-Te-Te...; the interatomic distances in the structure are  $\text{Te-Te}=3.65$ ,  $4.25\text{\AA}$  and  $\text{Sb-Te}=2.98$ ,  $3.18\text{\AA}$  [Anderson and Krause, 1974; Wyckoff, 1980]. Ternary compounds such as  $\text{AgSbTe}_2$  and  $\text{Ge}_2\text{Sb}_2\text{Te}_5$  were also reported to have crystalline forms. The high temperature form of  $\text{AgSbTe}_2$  has a face-centered cubic statistically NaCl-type structure  $Fm\bar{3}m$ , whereas the low temperature form a rhombohedral structure  $R\bar{3}m$  [Geller and Wernick, 1959];  $\text{AgSbTe}_2$  film was reported to have a NaCl lattice-type by use of electron diffraction [Lakshminarayana, 1990]. The structure of  $\text{Ge}_2\text{Sb}_2\text{Te}_5$  was also found NaCl-type  $Fm\bar{3}m$ , where Ge, Sb and 20% vacancy populate the (4a)-site and Te the (4b)-site, by use of Reitveld calculation [Nonaka et al., 1999]. In order to investigate structures of the binary alloy SbTe, EXAFS measurements have been made at the Sb and Te K-edges.

## 2. Experimental

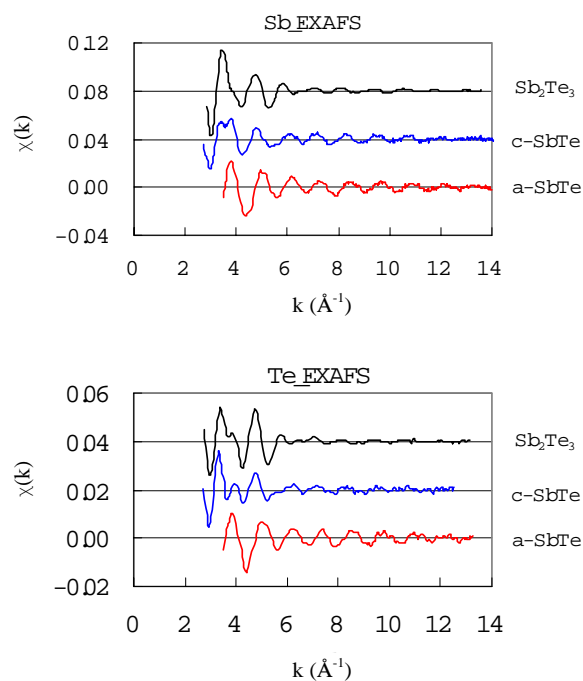
Films with 200nm thick of binary alloy SbTe, in which the atomic ratio  $\text{Sb}/\text{Te}=3$ , were deposited by sputtering on polycarbonate substrates with 0.6mm thick. The film was sandwiched with  $\text{SiO}_2/\text{ZnS}$  55nm dielectric layers. Films as deposited are amorphous phase (a-SbTe) and films scanned with laser beam are transformed into crystalline phase (c-SbTe). Each the sample film was diced into 4mmx12mm chips. EXAFS

spectra were recorded in transmission mode with a pile of these chips; a pile of 200 sheets for Te-edge and 100 sheets for Sb-edge measurements. The accumulated binary alloy film thickness is 40µm including polycarbonate moiety 120mm for a pile of 200 sheets. The EXAFS spectra of stable crystalline compound  $\text{Sb}_2\text{Te}_3$  were recorded on the powder sample in transmission mode.

Absorption spectra were measured with Si (311) double-crystal monochromator at BL01B1 in Spring-8; higher harmonics was rejected by mirror with an inclination angle of 1.3 mrad. All spectra were measured at room temperature. The incident and transmitted X-ray intensities monitored with ionization chambers with Ar+15%Kr and Kr gases respectively.

Figure 1

Raw EXAFS for  $\text{Sb}_2\text{Te}_3$  crystalline powder, c-SbTe and a-SbTe films.



## 3. Results and discussion

Figure 1 shows K-edge EXAFS spectra of Sb and Te measured on the three samples: crystalline powder of  $\text{Sb}_2\text{Te}_3$ , c-SbTe and a-SbTe films. The Te-edge EXAFS for c-SbTe is featured by somewhat resembling to crystalline  $\text{Sb}_2\text{Te}_3$ .

### 3.1. $\text{Sb}_2\text{Te}_3$

Spectra of the stable crystalline compound  $\text{Sb}_2\text{Te}_3$  was measured in order to estimate unknown parameters such as Debye-Waller factors  $\sigma^2$ . Crystal structure of  $\text{Sb}_2\text{Te}_3$  belongs to  $R\bar{3}m$ ; one Te in the (3a)-site; the other two Te and two Sb in the (6c)-site. Thus, the site-symmetry of averaged Te atom is reduced due to the superposition of different two types of site-symmetry at the Te1 (3a) and Te2 (6c), whereas the site-symmetry of Sb atom consists of single type. Scattering paths are calculated based on the structural model by use of FEFF6.01 code [Zabinsky et al., 1995] and the averaged coordination number and averaged

EXAFS for Te atom are estimated from the values at the two Te-sites (Te1 and Te2) with their multiplicity. Fourier transforms of  $k^3$ -weighted [Fig. 2] and  $r$ -range fit was down by use of WINXAS1.2 code [ Ressler, 1997].  $R$ -range fit was down with four shells for Sb-site and three shells for Te-site. Structural parameters obtained for Sb-site and Te-site are listed in Table 1. Debye-Waller factors  $\sigma^2$  are estimated  $0.011\text{\AA}^2$ (Sb-Te),  $0.020\text{\AA}^2$  (Sb-Sb),  $0.013\text{\AA}^2$  (Te-Sb) and  $0.019\text{\AA}^2$  (Te-Te). The rapid damping of Te EXAFS is considered due to the mutual cancellation of the two different Te sites. Thus, Debye-Waller factor for Te is estimated to be such large value.

Figure 2

Fourier Transforms of  $k^3$ -weighted for  $\text{Sb}_2\text{Te}_3$ .

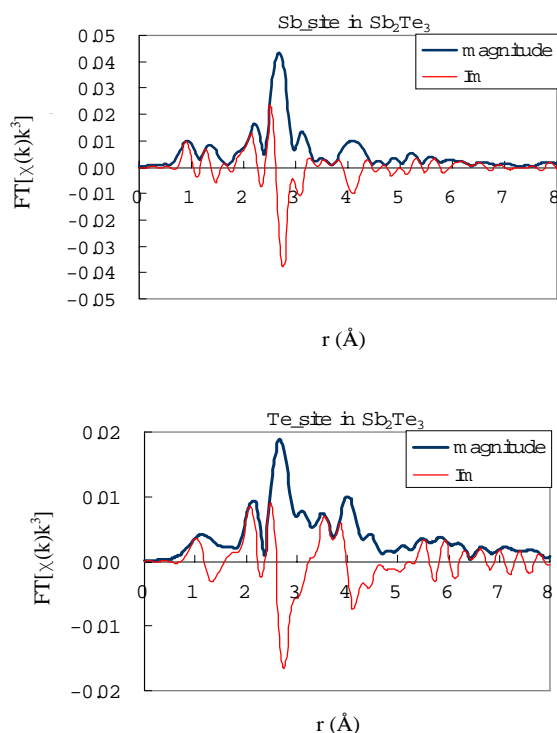
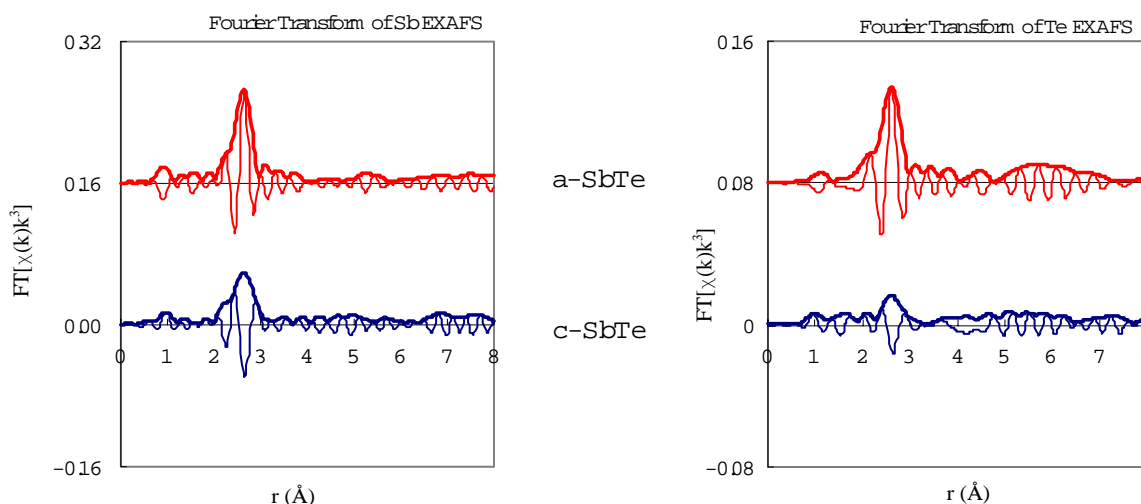


Figure 3 (a, b)

Fourier Transforms of  $k^3 \cdot \chi(k)$  for SbTe films.



### 3.2. a-SbTe and c-SbTe

Raw Sb-edge and Te-edge EXAFS signals for the SbTe films are shown in Fig. 1. Fourier transforms of  $k^3$ -weighted EXAFS for a-SbTe and c-SbTe are shown in Figs. 3a (at the Sb-site) and 3b (at the Te-site).  $R$ -range fit was done in the  $r$ -region of 1.8-3.2Å. Fitting structural parameters with single-shell on the assumption of NaCl structure show unbalanced bond distances: 2.89Å at the Sb-site and 2.87Å at the Te-site in the crystalline; 2.86Å at the Sb-site and 2.83Å at the Te-site in the amorphous. Such the unbalanced bond distances are unacceptable as long as the SbTe has ordered NaCl structure. Then, it is concluded that the SbTe structure is inevitably involving randomization of Sb-site and Te-site. Two-shell fit was also applied to the Fourier transforms for c-SbTe, since their imaginary parts indicate two shells. Fitting results are shown in Table 2.

This conclusion is consistent with our powder X-ray diffraction results. The X-ray diffraction pattern on the c-SbTe film shows the extinction rule of NaCl-lattice type: the lattice constant  $a_0=6.01\text{\AA}$ . The intensity of (111)-reflection is reduced almost to negligible, and this means that the Na-site and Cl-site are filled with atoms of equal electron densities. Since the adjacent atoms Sb and Te possess almost equal number of electrons, such the amount of vacancy as reported in  $\text{Ge}_2\text{Sb}_2\text{Te}_5$ , is unacceptable in the case of c-SbTe structure. Non (or little) site-vacancy model is also supported by the SbTe film density  $\rho=6.9$  obtained from our X-ray reflection data.

The bond distance averaged around Sb-site is little longer than Sb-Te bond owing to involve Sb-Sb bonds; the bond distance averaged around Te-site is little shorter than the Sb-Te bond owing to involve Te-Te bonds. Thus, the unbalanced bond distances obtained from SbTe films is explained by mixing of the Sb and Te atom-sites. This mixing involves local distortion in the crystalline phase.

### 4. Conclusions

It is concluded that the structure of c-SbTe is globally statistical NaCl-type and distorted locally. Shortening of bond distances in a-SbTe occurs due to the relaxation of distorted crystalline structure. EXAFS analysis provides an evidence of disordering between Sb-site and Te-site and the local distortion in c-SbTe.

Table 1: Fitting structural parameters for the Sb<sub>2</sub>Te<sub>3</sub> compound.

Sb-site	Coord. No.	Distance[Å]	$\sigma^2$ [Å <sup>2</sup> ]	Residual[%]
Sb-Te	3.8(4)	2.95(1)	0.011(1)	6.2
Sb-Te	1.9(2)	3.14(1)	0.011	
Sb-Sb	7.3(9)	4.24(1)	0.020(1)	
Sb-Sb	2.2(4)	4.55(3)	0.020	

Te-site	Coord. No.	Distance [Å]	$\sigma^2$ [Å <sup>2</sup> ]	Residual[%]
Te-Sb	1.9(3)	3.14(1)	0.013(1)	2.7
Te-Sb	2.5(4)	2.95(1)	0.013	
Te-Te	2.5(4)	3.69(1)	0.020(1)	

Table 2: Fitting structural parameters for a- and c-SbTe films.

		Coord. No.	Distance [Å]	$\sigma^2$ [Å <sup>2</sup> ]	Residual [%]
Sb-site	a-SbTe	2.8(5)	2.86(2)	0.011	5.6
	c-SbTe	2.7(6)	2.89	0.007	18.8
	two-shell fit	2.2 ; 4.7	2.81 ; 3.09	0.011	6.5
Te-site	a-SbTe	2.0(5)	2.83(1)	0.013	5.8
	c-SbTe	1.1(5)	2.87	0.006	11.5
	two-shell fit	1.2 ; 2.2	3.1 ; 2.9	0.013	12.3

The authors thank Dr. Tomoya Uruga, the SPring-8, for his valuable advice on instrumentation. This work was performed under the approval 1999A0304-NX-np and 1999B0332-NX-np of the SPring-8.

## References

- Anderson, T. L. & Krause, H. B. (1974). *Acta Cryst.*, 30B, 1307-1310.  
 Geller, S. & Wernick, J. H. (1959). *Acta Cryst.*, 12, 46-53.  
 Lakshminarayana, D. (1991). *Thin solid films*, 201, 91-96.  
 Nonaka, T., Amioka, T., Ohbayashi, G., Hashimoto, H. & Nagai, N. (1999). *Proc. of PCOS*, 70-73.  
 Ressler, T. (1997). *J. Physique*, IV 7, C2-269.  
 Wyckoff, R. W. G. (1966). *Crystal Structures*, Wiley, 30.  
 Zabinsky, S. I., Rehr, J. J., Ankudinov, A., Albers, R. C. & Eller, M. J. (1995). *Phys. Rev. B*, 52, 2995.