Electronic Supporting Information

Study on inorganic phase-change resist $Ge_2Sb_{2(1-x)}Bi_{2x}Te_5$ and its mechanism

Jianzheng Li,[a, b, c] Lirong Zheng,[d] Hongzhu Xi, [e] Dingxin Liu, [a] Hongguang Zhang, [f] Ye Tian,[a]

Yong Xie,[a] Xing Zhu,*[a, b] and Qian Liu *[a]

[a] *National Center for Nanoscience and Technology, Beijing 100190, China*

[b] *Academy for Advanced Interdisciplinary Studies and School of Physics, Peking University, Beijing 100871,*

China

[c] *University of Chinese Academy of Sciences, Beijing 100049, China*

[d] *Institute of High Energy Physics Chinese Academy of Sciences, Beijing 100049, China*

[e] *Anhui Huadong Polytechnic Institute, Wuhu 241002, China*

[f] *College of Science, Nanjing University of Posts and Telecommunications, Nanjing 210023, China*

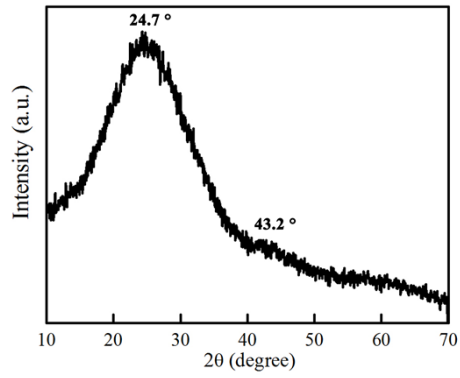*Corresponding authors. E-mails: liuq@nanoctr.cn; zhuxing@pku.edu.cn

Fig. S1 The XRD pattern of the glass substrate.

Table S1. Lattice parameters of c-GST, c-Ge$_2$Sb$_{2(1-x)}$Bi$_{2x}$Te$_5$ (x= 0.1, 0.25, 0.35) and c-GBT

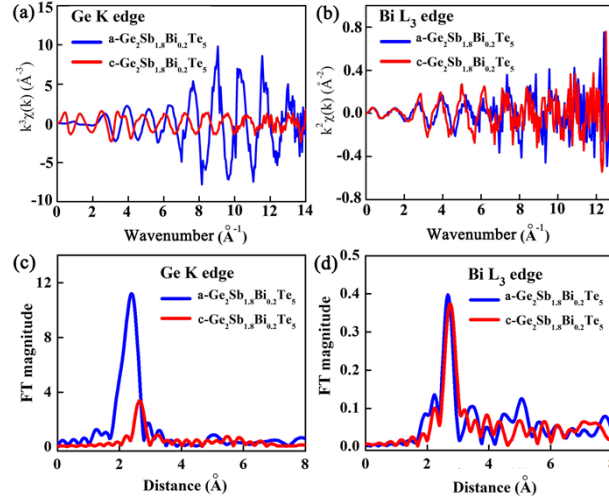|	Lattice parameters (Å)	
	Experimental Value	Value from Vegard's law
c-GST	a= 6.0119 a= 6.0117[1]	——
x=0.1	a= 6.0270	a=6.022
x=0.25	a= 6.0330	a= 6.034
x=0.35	a=6.0480	a=6.046
c-GBT	a=6.1109[2]	——

Fig. S2. (a) Ge K edge k^3-Weighted and (b) Bi L_3 edge k^2-Weighted EXAFS spectra of a-$Ge_2Sb_{1.8}Bi_{0.2}Te_5$ (blue curve) and c-$Ge_2Sb_{1.8}Bi_{0.2}Te_5$ (red curve) in k space. The corresponding Fourier-transforms in r space measured (c) at Ge K edge, (d) at Bi L_3 edge, the peak positions shifted towards lower r for the photoelectron phase shift of the EXAFS oscillations.
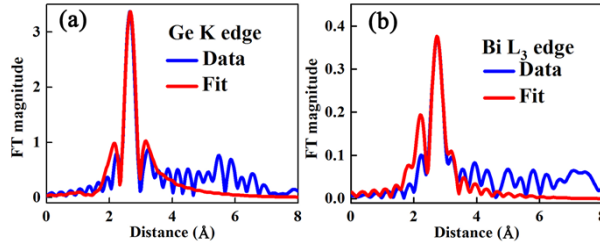

Fig. S3 The corresponding Fourier transforms (blue curves) and the fitting results (red curves) of the EXAFS spectra of c-$Ge_2Sb_{1.8}Bi_{0.2}Te_5$ at (a) Ge K edge and (b) Bi L_3 edge in r space.
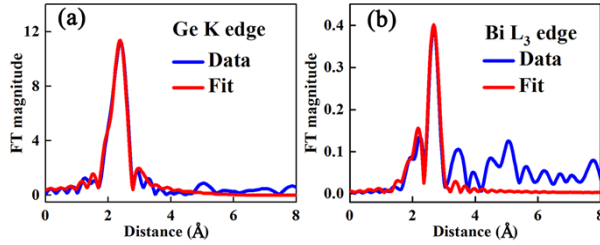

Fig. S4 The corresponding Fourier-transforms (blue curves) and the fitting results (red curves) of the EXAFS spectra of a-$Ge_2Sb_{1.8}Bi_{0.2}Te_5$ at (a) Ge K edge and (b) Bi L_3 edge in r space.

The XAFS energies at Ge K edge and Bi L_3 edge, which are 11103 eV and 13419 eV respectively, are located in the signal-best range of the X-ray energy (4~25 KeV) of Beamline 1w1b at Beijing Synchrotron Radiation Facility (BSRF), so we measured the XAFS spectra of $Ge_2Sb_{1.8}Bi_{0.2}Te_5$ at Ge K edge and Bi L_3 edge. Fig. S2 shows the EXAFS spectra of Ge and Bi in k space and the corresponding Fourier-transforms in r space. The fits of these experimental spectra were performed by using the EXAFS equation which is expressed as follows,

$$\chi(k) = \sum_i \frac{N_i S_0^2(k) F_i(k)}{k R_i^2} \exp[-2k^2\sigma_i^2] e^{-2R_i/\lambda_i(k)} \sin\left(2kR_i + \phi_i(k) - \frac{4}{3}C_{3i}k^3\right).$$

Here, i stands for the scatting path with degeneracy of N_i, and R_i represents the half-path distance. $F_i(k)$ is the

scatting amplitude and S_0^2 is the amplitude reduction factor. σ_i^2 is the squared Debye-Waller factor, which is temperature-dependent and also has effects owing to structural disorder. $\lambda_i(k)$ is the energy-dependent mean free path of XAFS, and ϕ_i and C_{3i} in the term of $\sin(2kR_i + \phi_i(k) - \frac{4}{3}C_3 k^3)$ are the phase shift of the final state and the third-order accumulation, respectively. The Fourier transforms and the fitting curves of the EXAFS spectra of c-$Ge_2Sb_{1.8}Bi_{0.2}Te_5$ and a-$Ge_2Sb_{1.8}Bi_{0.2}Te_5$ in r space are shown in Fig.S3 and Fig.S4, respectively. The fitting results are shown in Table S2 below.

Table S2 Fitting results of Ge K edge and Bi L_3 edge EXAFS in c-$Ge_2Sb_{1.8}Bi_{0.2}Te_5$ and a-$Ge_2Sb_{1.8}Bi_{0.2}Te_5$

Sample	Central atom	Chemical Bond	CN^a	Bond length (Å)	σ^2 (Å^2)	R-factor
Crystalline	Ge	Ge-Te	6.1 ± 0.3	$^S 2.86 \pm 0.03$	0.0145	0.0053
				$^L 3.16 \pm 0.03$	0.0135	
	Bi	Bi-Te	5.7 ± 0.3	$^S 2.99 \pm 0.01$	0.0072	0.0039
				$^L 3.13 \pm 0.04$	0.0115	
Amorphous	Ge	50% Ge-Te	4.1 ± 0.3	2.61 ± 0.01	0.0032	0.0079
		50% Ge-Te	3.0 ± 0.3	3.01 ± 0.05	0.0090	
	Bi	Bi-Te	2.7 ± 0.1	2.93 ± 0.01	0.0075	0.0028

[a] CN, coordination number.

^{S} and ^{L} stand for short bonds and long bonds in c-$Ge_2Sb_{1.8}Bi_{0.2}Te_5$, respectively.

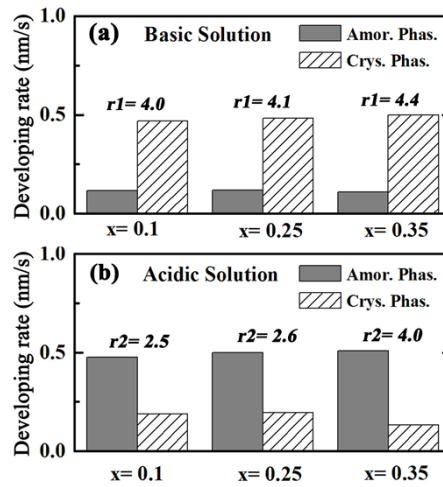Fig. S5 (a) The ratio of developing rate ($r1 = v_c/v_a$) between c-GSBT (x= 0.1, 0.25, 0.35) and corresponding a-GSBT (x= 0.1, 0.25, 0.35) in the basic solution (KOH(1%):H_2O_2(30%)= 20:1) at 22 °C. (b) The ratio of developing rate ($r2= v_a/v_c$) between a-GSBT (x= 0.1, 0.25, 0.35) and corresponding c-GSBT (x= 0.1, 0.25, 0.35) in the acidic solution (HNO$_3$(65%):H_2O:H_2O_2(30%)= 1:6:1) at 22 °C. v_c and v_a stand for the developing rate of c-GSBT and a-GSBT respectively.
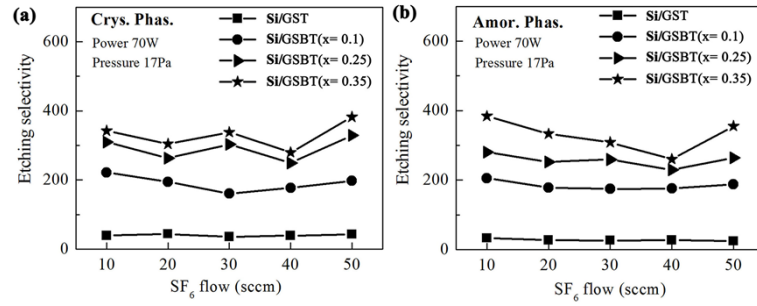
Fig. S6 (a) The etching selectivity between Si and c-GST or c-GSBT(x= 0.1, 0.25, 0.35), and (b) the etching selectivity between Si and a-GST or a-GSBT (x= 0.1, 0.25, 0.35) with the etching power of 70 W, the etching pressure of 17 Pa and different flows of SF_6.

References：

1.   T. Nonaka, G. Ohbayashi, Y. Toriumi, Y. Mori and H. Hashimoto, *Thin Solid Films*, 2000, **370**, 258.

2.   T. Matsunaga, R. Kojima, N. Yamada, K. Kifune, Y. Kubota and M. Takata, *Acta Crystallogr., Sect. B: Struct. Sci.*, 2007, **63**, 346.