Supporting Information for

Electron beam lithography of GeTe through polymorphic phase transformation

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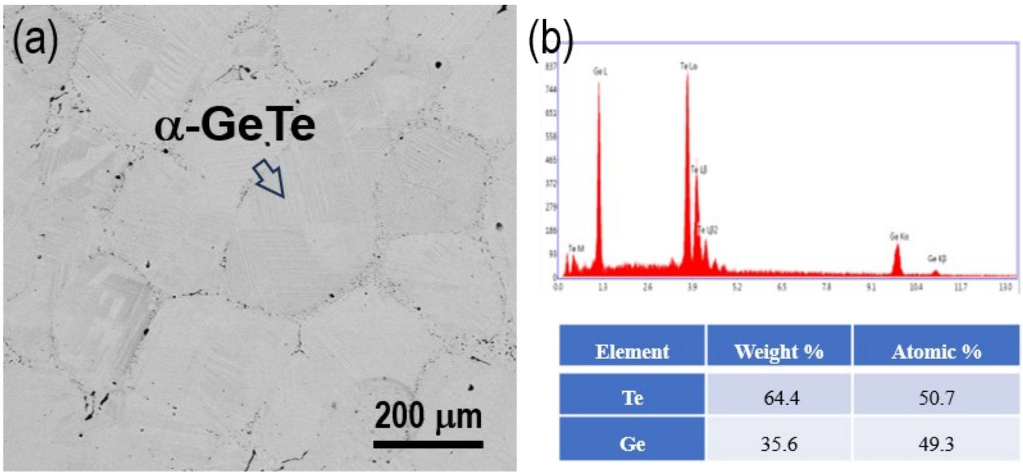

Element	Weight %	Atomic %
Te	64.4	50.7
Ge	35.6	49.3

Fig. S1 The microstructure and stoichiometry of the α-GeTe phase in the as-prepared sample. (a) Back-scattered scanning electron microscopy (SEM) image of the polished GeTe sample. The α-GeTe phase is indicated by an oblique arrow. (b) The chemical composition of the α-GeTe phase measured by energy-dispersive X-ray spectroscopy (EDS) in SEM.

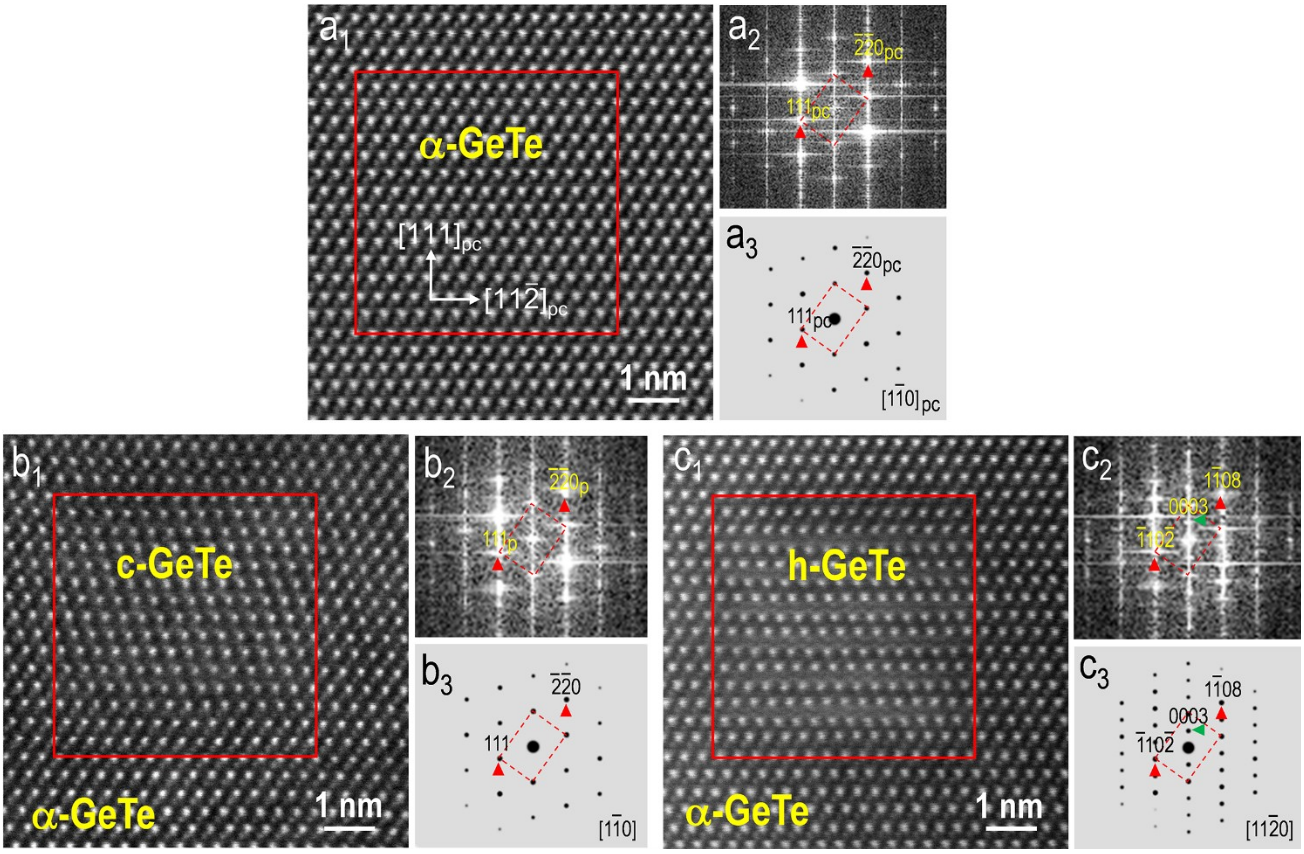

Fig. S2 Atomic-scale HAADF-STEM images, fast Fourier transform (FFT) patterns of the region of interest (ROI), and calculated electron diffraction patterns of α-GeTe, c-GeTe, and h-GeTe. The viewing direction of the HAADF-STEM image is $[1\bar{1}0]_{pc}$ in (a_1), $[1\bar{1}0]$ in (b_1), and $[11\bar{2}0]$ in (c_1), respectively. The ROI is marked by a red solid-line square frame in the HAADF-STEM image. The FFT pattern of the ROI in (a_1), (b_1), and (c_1) is displayed in (a_2), (b_2), and (c_2,), respectively. The calculated electron diffraction pattern in (a_3), (b_3), and (c_3) is the $[1\bar{1}0]_{pc}$ zone axis of α-GeTe, the $[1\bar{1}0]$ zone axis of c-GeTe, and the $[11\bar{2}0]$ zone axis of h-GeTe, respectively.

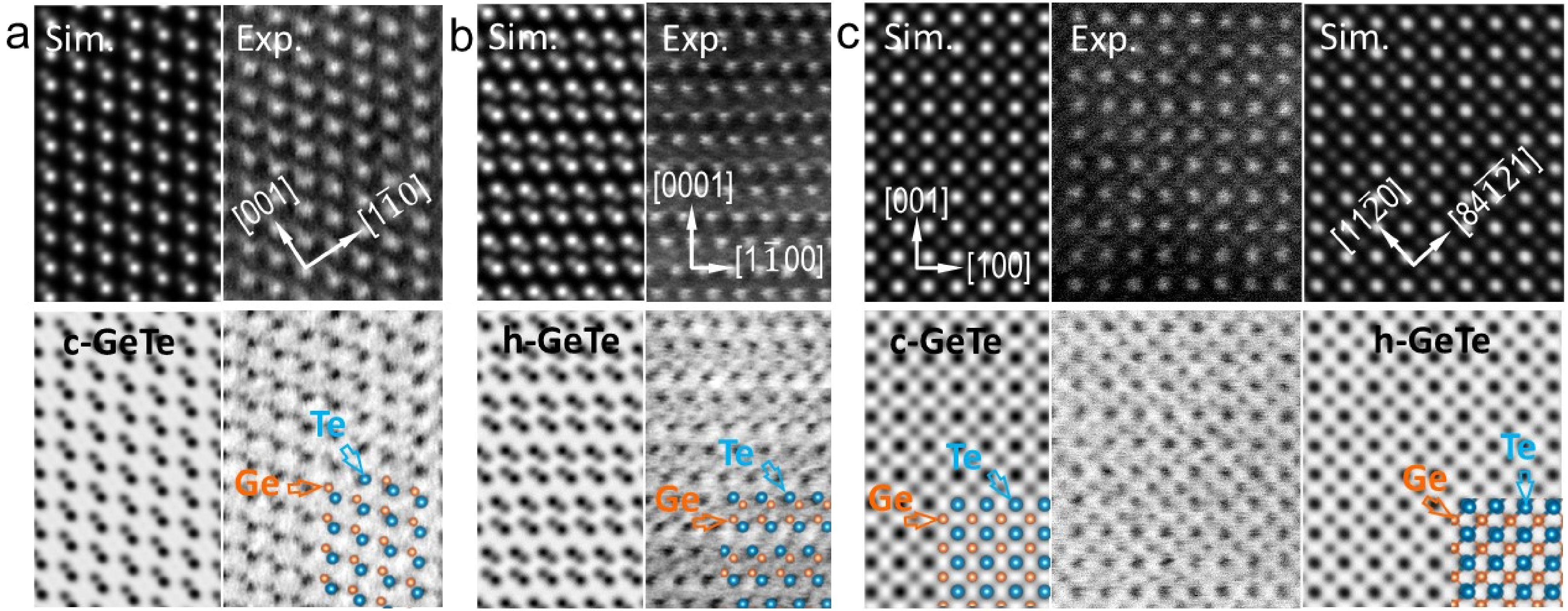

FIG. S3 Experimental and simulated HAADF- (upper) and ABF-STEM (bottom) images of c-GeTe (F$\bar{4}$3m) and h-GeTe (R$\bar{3}$m). (a) Experimental and simulated images of c-GeTe in the [110] zone axis. (b) Experimental and simulated images of h-GeTe in the [11$\bar{2}$0] zone axis. (c) Comparison of simulated images of c-GeTe in the [010] zone axis and h-GeTe in the [$\bar{4}$401] zone axis with respect to experimental images. Atomic structure models of c-GeTe and h-GeTe are superposed in (a-c) for visualization. The lattice parameters used for simulations are a=0.5900 nm and α=β=γ=90° for c-GeTe, and a=b=0.4172 nm, c=2.0438 nm, α=β=90°, and γ=120° for h-GeTe.

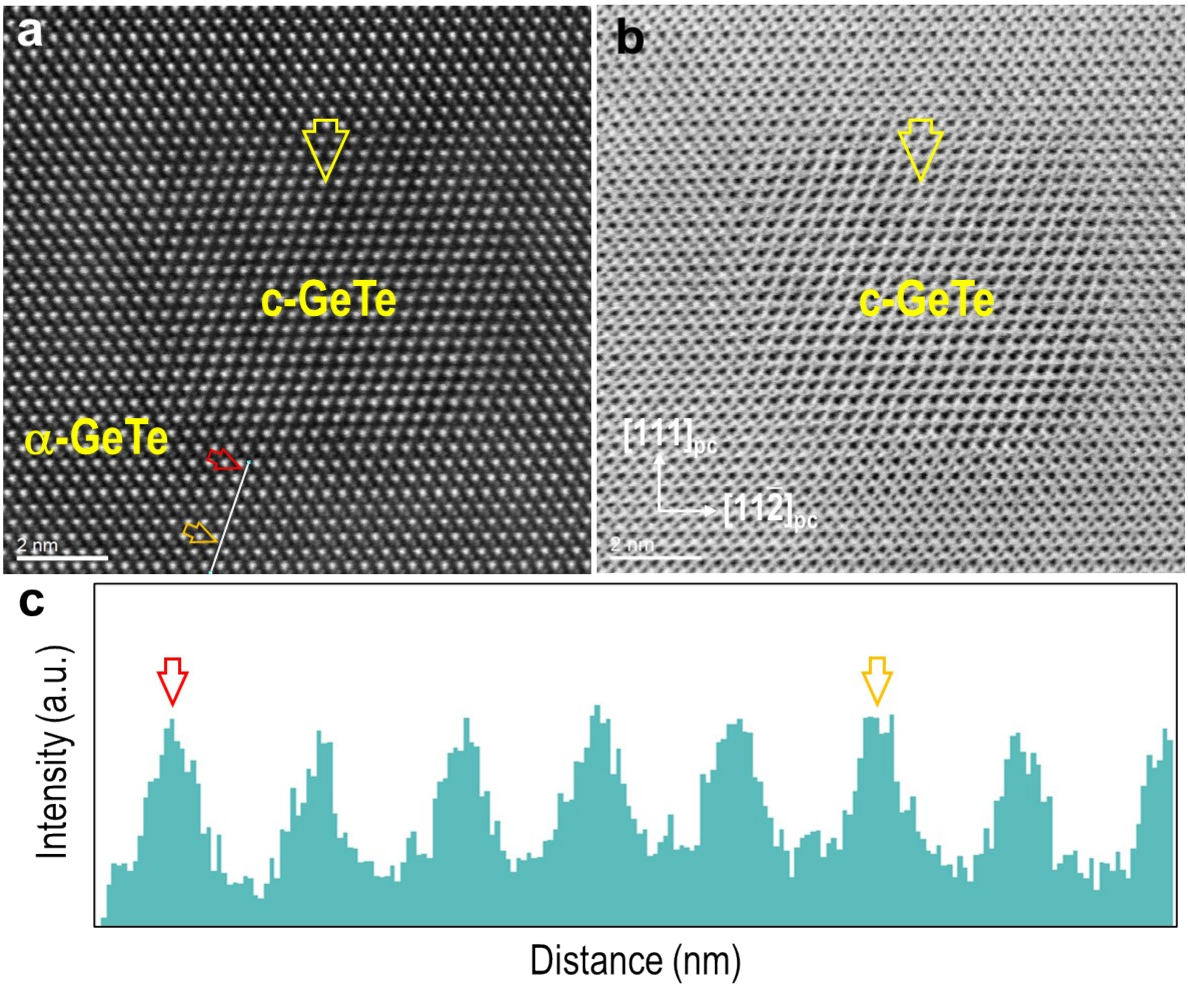

Fig. S4 Evaluation of concentration gradient of Ge atoms around ROI in the α-GeTe matrix. (a, b) Atomic-scale HAADF- and simultaneously recorded ABF-STEM images showing the phase transformation from α-GeTe to c-GeTe driven by electron beam irradiation. The ROI of c-GeTe is indicated by a vertical yellow arrow. The viewing direction is the $[1\bar{1}0]_{pc}$ zone axis of α-GeTe. (c) The intensity profiles of the line marked in (a). Note that the Ge atomic columns have almost identical intensity around the ROI, as illustrated by the red arrow and the orange arrows in (a) and (c), indicating no apparent Ge diffusion between the ROI and the surrounding matrix.

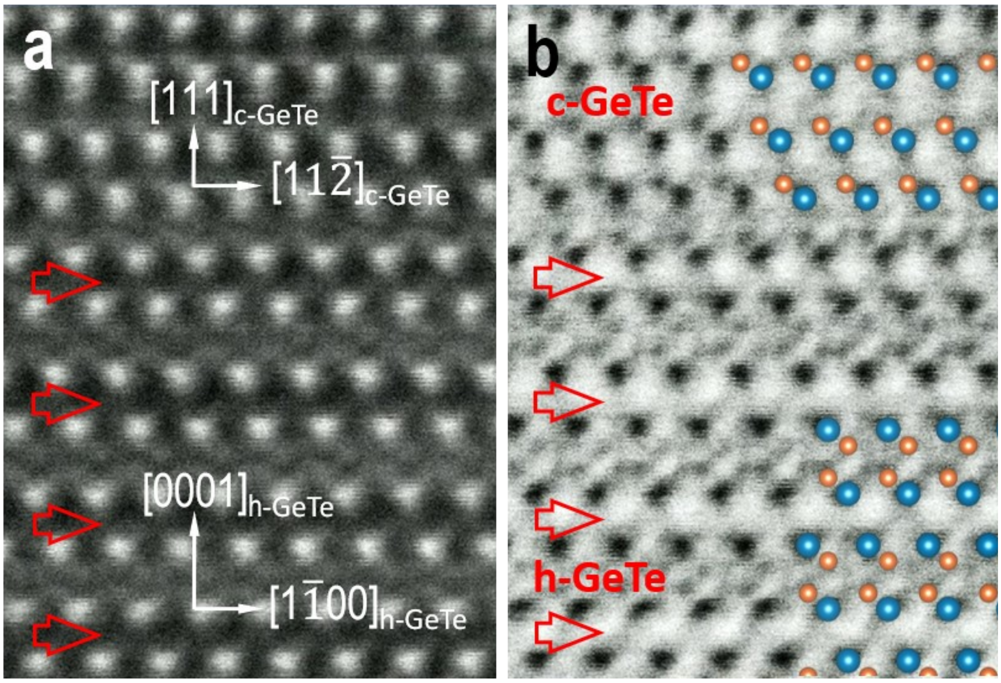

FIG. S5 Illustration of the coexistence of c-GeTe and h-GeTe phases in the ROI under electron beam irradiation. (a, b) HAADF- and ABF-STEM images containing both c-GeTe and h-GeTe phases in the ROI. The horizontal red arrows mark the vdW gap in h-GeTe. The structure models of c-GeTe and h-GeTe are superimposed in (b).

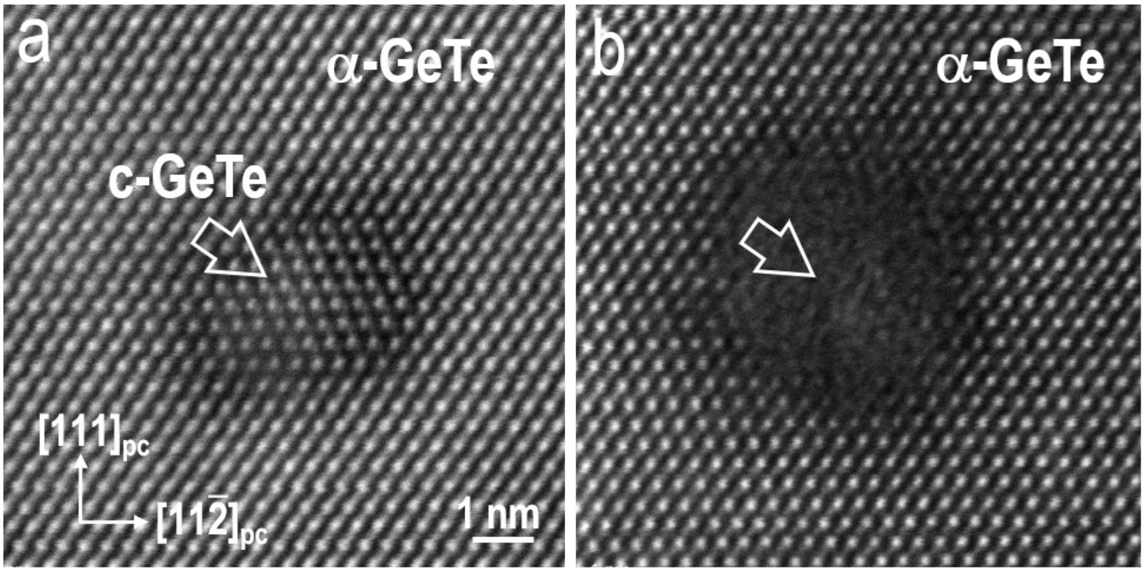

FIG. S6 The chemical composition of GeTe phases measured by EDS in STEM mode. (a, b) High-resolution HAADF-STEM images show the formation of the c-GeTe phase and the amorphization of GeTe during the chemical composition measurement by EDS. The EDS analysis region is indicated by a white arrow. A probe current of approximately 23 pA (acquisition time: 150 seconds).

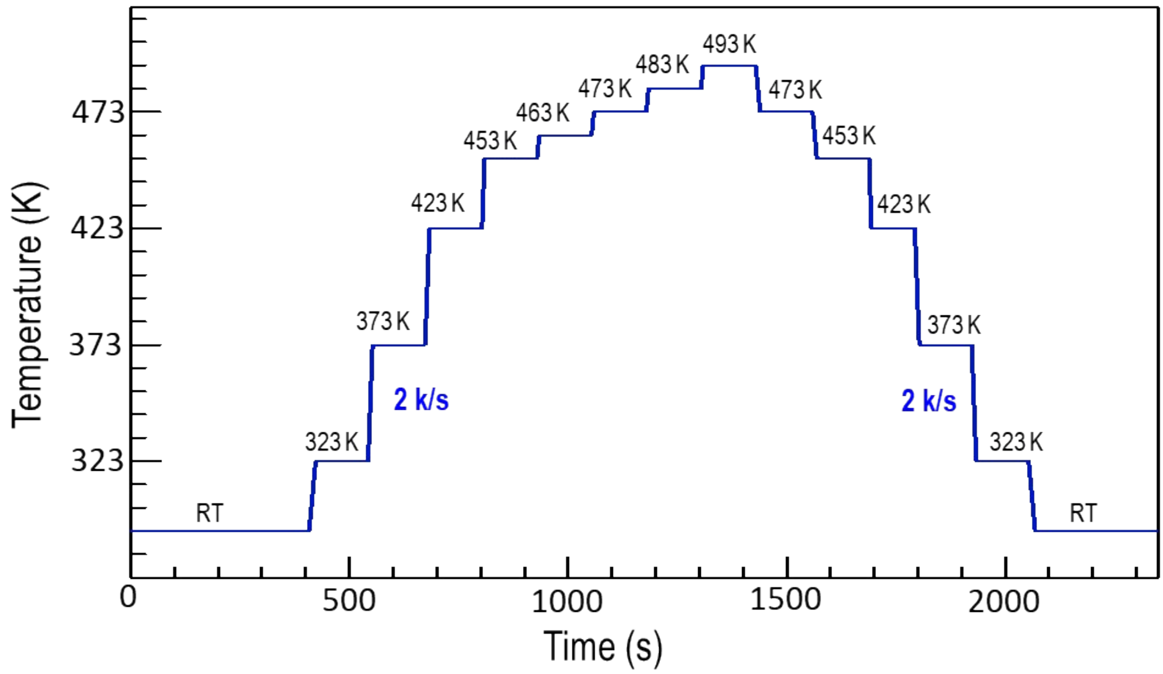

FIG. S7 Temperature profile for *in-situ* thermal cycling experiments.

Movie S1 *In-situ* structure evolution of GeTe under electron beam irradiation. The electron beam irradiation was realized in a JEOL ARM200F scanning transmission electron microscope (STEM) operated at 200 keV, equipped with a probe aberration corrector. The video was recorded in HAADF-STEM mode. The ROI was irradiated at the probe current density of 1.6×10^{26} $e\cdot m^{-2}\cdot s^{-1}$.