



# Single-crystalline $\text{Ag}_2\text{Te}$ nanorods prepared by room temperature sputtering of GeTe

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## Abstract

We report a facile, single-crystalline  $\text{Ag}_2\text{Te}$  nanorod formation based on electrochemical diffusion of Ag. The nanorods were grown non-epitaxially by sputtering deposition of GeTe on  $\text{Ag}_2\text{Te}$  nanoparticles at room temperature. For the nanorod growth, the source of the Ag supply is not deposition but the diffusion of Ag from the nanoparticles. The growth of the single-crystalline  $\text{Ag}_2\text{Te}$  nanorods required GeTe deposition onto  $\text{Ag}_2\text{Te}$  nanoparticles, in contrast to the growth of amorphous  $\text{Ag}_2\text{Te}$  nanorods caused by Te deposition onto Ag nanoparticles and the growth of other nanostructures caused by GeTe deposition on Ag nanoparticles. The GeTe deposition onto the  $\text{Ag}_2\text{Te}$  nanoparticles of an amount equivalent to a 100-nm-thick film produced nanorods of a length ranging from 3 to 5  $\mu\text{m}$  and a diameter ranging from 100 to 400 nm. We propose a model for the nanorod growth based on solid-state electrochemical reaction between GeTe and movable Ag ions, inducing nanoscale phase separation and precipitation of amorphous Ge. We suggest that the nanorod structure with a crystalline  $\text{Ag}_2\text{Te}$  core and an amorphous Ge shell is useful for thermoelectric applications.

**Keywords** GeTe ·  $\text{Ag}_2\text{Te}$  · Nanorod · Nanowire · Nanoparticle · Electrochemical reaction · RF magnetron sputtering

## 1 Introduction

The electrochemical reaction of Ag in amorphous chalcogenides of solid electrolytes has been investigated intensively because of the fundamental interests in anomalous diffusion [1], modified phase change characteristics [2, 3], and optical properties [4–6] and also because of the potential device applications [7] such as RAM memories, sensors, and batteries. For example, the operation of conductive bridge RAM (CBRAM) devices [8, 9] is based on the formation of conductive filaments via the electrochemical reaction of Ag ions. We have directly observed the formation of conductive filaments in GeTe [10], which is a typical phase change material used in phase change RAM [11, 12], radio frequency switches [13, 14], CBRAM [15, 16], and thermoelectric devices [17–19].

Such an electrochemical reaction has also been used for crystal growth in silver chalcogenides [20, 21]. Bulk

single crystals of  $\text{Ag}_2\text{S}$  and  $\text{Ag}_2\text{Se}$  were grown based on the electrochemical diffusion of Ag that determined the growth rate [22, 23]. Amorphous [24] or polycrystalline [25]  $\text{Ag}_2\text{Te}$  films were obtained by electrochemical interdiffusion between deposited Te and an Ag film at room temperature. Not only bulk crystals, but also nanostructures can be produced by the electrochemical reaction [26–28].  $\text{Ag}_2\text{S}$  whiskers or nanowires were grown electrochemically from an Ag plate, placed in a sulfur vapor environment, and kept at a fixed temperature for more than an hour. In this paper, we report on the electrochemical formation of single-crystalline  $\text{Ag}_2\text{Te}$  nanorods by magnetron sputtering at room temperature with a normal deposition rate of  $\sim 1$  A/s. Formation of a single-crystalline  $\text{Ag}_2\text{Te}$  nanorod requires deposition of “GeTe” onto “ $\text{Ag}_2\text{Te}$ ” nanoparticles. This contrasts with the formation of amorphous  $\text{Ag}_2\text{Te}$  nanorods that requires deposition of “Te” onto “Ag” nanoparticles [29]. Electrochemical phase separation of Ge as

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well as the  $\text{Ag}_2\text{Te}$  seeds is essential for the crystallization. To the best of our knowledge, this is the first report on electrochemical formation of the single-crystalline one-dimensional structures produced by dry or vacuum-deposition processes such as evaporation, sputtering, and chemical vapor deposition, which are compatible with semiconductor technology.

$\text{Ag}_2\text{Te}$  is a narrow gap semiconductor [30, 31] that has various attractive properties, including near-infrared light emission [32, 33], large magnetoresistance [34, 35], structural phase transition [36], topological insulating behaviors [37, 38], and a high thermoelectric figure of merit ZT [39–41]. One-dimensional structures including nanofibers, nanorods, or nanowire can modify the properties. An enhancement of the ZT in one-dimensional  $\text{Ag}_2\text{Te}$  has been reported [42, 43] and was attributed to modified phonon scattering [44, 45] and electronic contribution [46]. Such one-dimensional structures of  $\text{Ag}_2\text{Te}$  have also been applied to flexible thermoelectric [47, 48] and electronic [49] devices. The flexible devices require lower temperatures for growth or processing than the decomposition temperatures of the flexible substrates, which are typically between 100 and 300 °C [50].

The one-dimensional  $\text{Ag}_2\text{Te}$  nanostructures have been fabricated mostly via chemical solution synthetic routes [42–51] such as electrochemical transformation in an electrochemical solution from Ag nanofibers to  $\text{Ag}_2\text{Te}$  nanotubes [52], possibly because chemical solution synthetic routes were potentially mass-producible and low cost. On the other hand, dry or vacuum-deposition processes such as evaporation, sputtering, and chemical vapor deposition have been little used despite their advantages for avoiding contamination and their high purity. Reported single-crystalline  $\text{Ag}_2\text{Te}$  nanowires grown by a dry or vacuum process without the help of an electrochemical reaction have generally required high growth temperatures around 1000 °C [53, 54] and a relatively long reaction time of more than several tens of minutes in a furnace. No facile deposition methods around room temperature have yet been presented.

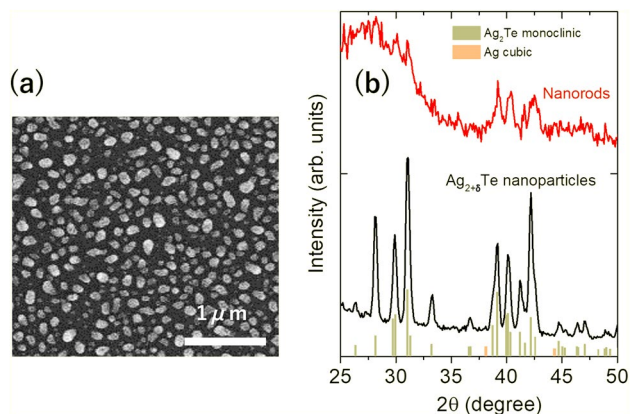
## 2 Materials and methods

The  $\text{Ag}_2\text{Te}$  nanoparticles used as the seeds for the nanorod growth were prepared by thermal annealing of an Ag film in Te vapor. A 10-nm-thick Ag film was formed by RF magnetron sputtering with an Ag target (99.99% purity) on a 300-nm-thick  $\text{SiO}_2$  layer thermally oxidized on a (100) Si substrate. The Ag film was annealed at 500 °C for three hours in Te vapor that was evaporated from Te powder placed upstream to the Ag film and was carried by Ar gas at a flow rate of 10 sccm. The fabricated seed nanoparticles

had an average diameter of about 100 nm and a density of about  $5 \times 10^9/\text{cm}^2$  (Fig. 1a). The structure was identified as monoclinic  $\text{Ag}_2\text{Te}$  crystal slightly including cubic Ag on the basis of the X-ray diffraction (XRD) pattern (Fig. 1b). The XRD measurement was performed in an asymmetric,  $2\theta$  scan mode with a small incident angle fixed at  $0.5^\circ$ , using a Rigaku Smart Lab diffractometer with a Cu source at an acceleration voltage of 45 kV and a current of 200 mA.

Nanorods were spontaneously grown by depositing GeTe on the slightly Ag-rich  $\text{Ag}_{2+\delta}\text{Te}$  nanoparticles by RF magnetron sputtering without intentional heating. A temperature increase of less than 50 °C during the deposition was confirmed by a label-type temperature indicator. The GeTe was deposited at a rate of 1.2 Å/s using a GeTe target (99.99% purity), with a plasma discharge power of 50 W, under an argon flow of 30 sccm, and at a pressure of 0.7 kPa. We emphasize here that the nanorods were grown without an Ag supply from the deposition. The only possible source of Ag was the diffusion from the nanoparticles of  $\text{Ag}_{2+\delta}\text{Te}$ . Because GeTe deposition lowers the concentration of Ag near the surface, the Ag ions are continuously driven by the concentration gradient from the nanoparticles toward the surfaces. The diffusion constant of monoclinic  $\text{Ag}_2\text{Te}$  was reported to be around  $10^{-4} \text{ cm}^2 \text{ s}^{-1}$  at 110 °C [55]. The diffusion constant was three orders of magnitude lower than that of the high-temperature cubic phase, which is a well-known super ionic semiconductor [56, 57], but the diffusion was still significant in micro-scale. Extrapolation assuming the Arrhenius law suggests  $\sim 10 \mu\text{m}^2 \text{ s}^{-1}$  at RT. Thus, the ion diffusion rate was faster than the deposition rate of 1.2 Å/s.

The structure and the composition of a nanorod were identified by transmission electron microscopy (TEM), electron diffraction measurement, and energy-dispersive



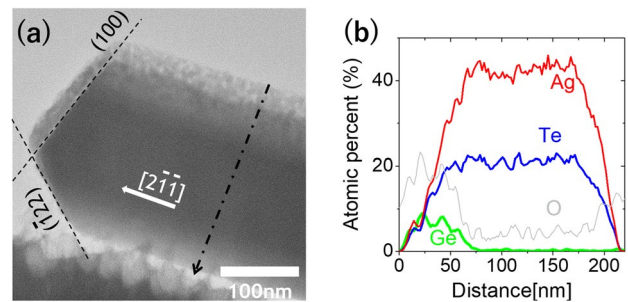
**Fig. 1** **a** SEM image of the  $\text{Ag}_{2+\delta}\text{Te}$  nanoparticles. **b** XRD patterns of the nanoparticles and those after GeTe deposition producing nanorods. Standard crystalline patterns of monoclinic  $\text{Ag}_2\text{Te}$  (# 00-034-0142) and cubic Ag (# 01-071-4613) are also shown

X-ray (EDX) spectroscopy using a JEOL JEM-ARM200F with an accelerating voltage of 200 kV.

### 3 Results and discussion

The GeTe deposition onto the  $\text{Ag}_{2+\delta}\text{Te}$  nanoparticles of an amount equivalent to a 100-nm-thick film spontaneously produced nanorods of a length ranging from 3 to 5  $\mu\text{m}$  and a diameter ranging from 100 to 400 nm (Fig. 2a). The nanorods grew at a density of about  $8 \times 10^7/\text{cm}^2$  with no preferred growth orientation. A typical cross-sectional TEM image of a nanorod is shown in Fig. 2b. Electron diffraction patterns were measured at the core (A–D) and the cover layer (E) of the nanorod (Fig. 2c). All the diffraction patterns measured along the nanorod core (A–D) were successfully indexed as monoclinic  $\text{Ag}_2\text{Te}$  (JCPDS No. 00-034-0142) and were the same in geometric arrangements and the orientation: Some difference in spot contrast was attributed to an extrinsic bending caused during the specimen fabrication for the TEM measurement. This demonstrates that the nanorod core consists of a single-crystalline  $\text{Ag}_2\text{Te}$ . The growth of crystalline  $\text{Ag}_2\text{Te}$  was also confirmed by the XRD measurement on the nanorod sample (Fig. 1b). Sharp peaks of monoclinic  $\text{Ag}_2\text{Te}$  were superimposed on a broad spectrum of Ag-diffused amorphous GeTe arising from the other regions than the nanorods. The different relative intensity of the  $\text{Ag}_2\text{Te}$  peaks between the nanorod sample and the seed sample suggests the nanorod growth having a different orientation tendency with the seed nanoparticles.

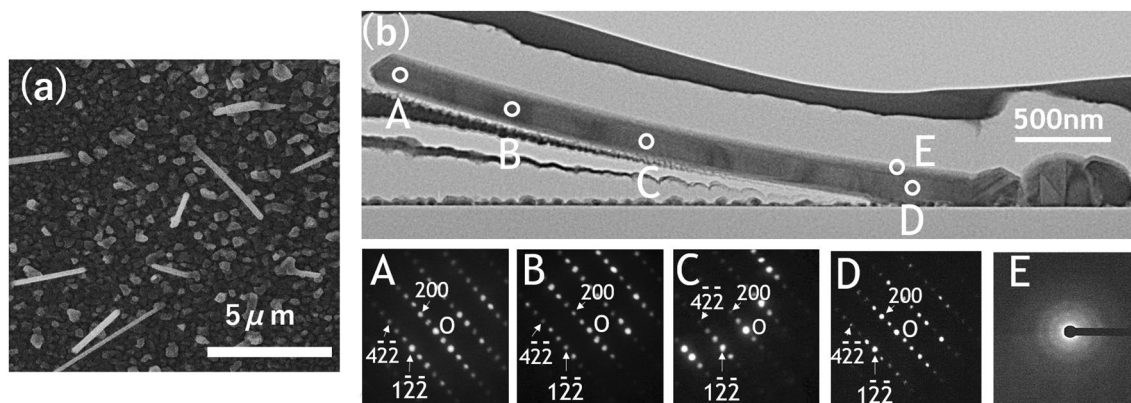
The position of the diffraction spot of (4–2–2) shows that the nanorod grew along [4–2–2] or [2–1–1], and the positions of the spots of (200) and (1–2–2) represent that two facet planes on the top are (100) and (–122), respectively. As shown in Fig. 3a, the facet of (100) was capped



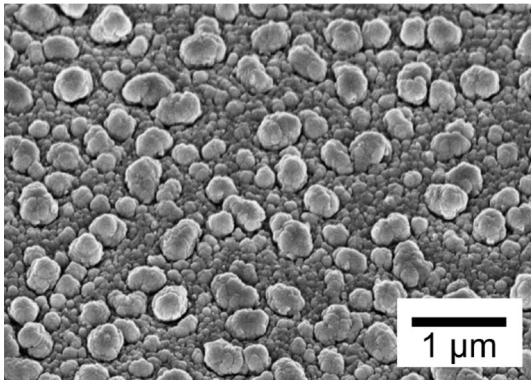
**Fig. 3** **a** TEM image enlarged near the tip of the nanorod of Fig. 2b. **b** Line profiles of EDX spectrometry along the line indicated by a dashed-and-dotted arrow in (a)

with a cover layer about 10 nm thick, while that of the (–122) plane was not capped. EDX mapping in a radial direction shows that the cover layer consists of  $\text{Ge}_x\text{O}_{1-x}$  (Fig. 3b). The electron diffraction of the cover layer (E) showed a halo pattern, characteristic of an amorphous structure in contrast to the diffraction of the core (A–D) that showed the spot patterns from the  $\text{Ag}_2\text{Te}$  crystal. The  $\text{Ge}_x\text{O}_{1-x}$  most likely resulted from extrinsic oxidation of Ge after exposure to the ambient air because the base vacuum for the deposition was less than  $5.0 \times 10^{-5}$  Pa. In other words, the cover layer intrinsically consisted of amorphous Ge. The EDX mapping also shows twice as much Ag as Te in the nanorod core, which confirms that the core consisted of  $\text{Ag}_2\text{Te}$  (Fig. 3b).

GeTe was deposited mainly as free atoms. The free Te atoms deposited onto an Ag-rich part of the  $\text{Ag}_{2+\delta}\text{Te}$  nanoparticles react with Ag to form  $\text{Ag}_2\text{Te}$ . However, direct Te deposition at similar deposition conditions onto  $\text{Ag}_{2+\delta}\text{Te}$  nanoparticles did not produce nanorods (Fig. 4). Because the free energy of formation of Ag–Te is much lower than that of Ge–Te, Ge is phase-separated and is precipitated. The cover layer formation of amorphous Ge in our  $\text{Ag}_2\text{Te}$



**Fig. 2** **a** SEM image of nanorods. **b** TEM image of a nanorod and electron diffraction patterns taken with an incident electron beam along [0–11], measured at the points A–D indicated by white circles. The diffraction patterns at A–D are indexed as monoclinic  $\text{Ag}_2\text{Te}$



**Fig. 4** SEM image of  $\text{Ag}_{2+\delta}\text{Te}$  nanoparticles after Te deposition onto them. Te deposition at  $1.2 \text{ \AA/s}$  of an amount equivalent to a 100-nm-thick film produced no nanorods

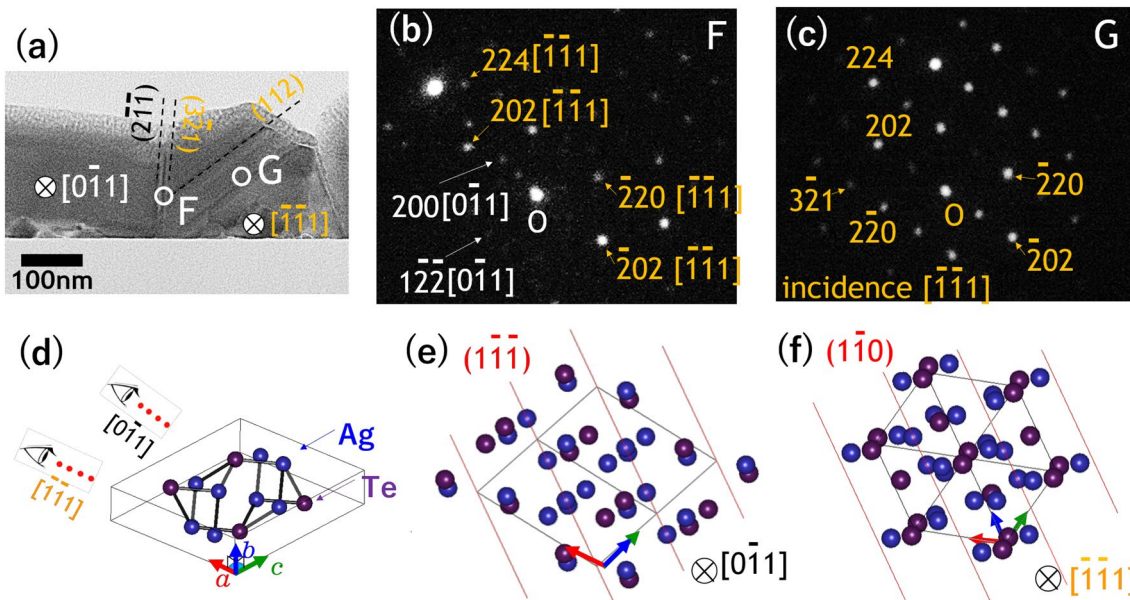
nanorods is attributed to the amorphous Ge precipitation that occurs as a result of the nanoscale phase separation to form  $\text{Ag}_2\text{Te}$ . The nanoscale phase separation resulting in precipitated amorphous Ge regions was also observed in the case of the GeTe deposition onto Ag nanoparticles [58]. We suggest that the supply of Ge that leads to the precipitation is required to grow the reacted  $\text{Ag}_2\text{Te}$  into the 3–5- $\mu\text{m}$ -long single-crystalline  $\text{Ag}_2\text{Te}$  nanorods. The importance of the Ge precipitation for the  $\text{Ag}_2\text{Te}$  crystalline nanorod formation is supported by the observations that Te deposition onto Ag nanoparticles at the deposition condition produced *amorphous*  $\text{Ag}_2\text{Te}$  nanorods [29]. Thus, forming single-crystalline nanorods requires a supply of Ag via diffusion, a supply of Ge, and the  $\text{Ag}_{2+\delta}\text{Te}$  nanoparticles as the seed.

The nanorod grew along  $[2-1-1]$  and had two facets of (100) and  $(-122)$  on the top. The facet of (100) was capped with an about 10-nm-thick amorphous Ge layer, while that of the  $(-122)$  plane was not capped. The nanorod growth along  $[2-1-1]$  is attributed to the characteristic of monoclinic Ag chalcogenides that forms dendritic whiskers for the restricted supply of silver ions via diffusion and the competitive growth along  $[100]$  and  $[1, 2]$ . The direction  $[100]$  is one of the favorable growth directions in the Ag–Te topotactic reaction when depositing Te onto Ag film [59]. Kasugabe demonstrated that monoclinic  $\text{Ag}_2\text{S}$  whisker grew along several peculiar branching directions such as  $[310]$  and  $[410]$  after the saturation of the growth along the principal growth direction of  $[100]$  due to the restricted supply [26]. In the case of our  $\text{Ag}_2\text{Te}$  nanorod growth, we suggest that the growth along  $[100]$  was slowed down due to the formation of the amorphous Ge regions. The growth along  $[100]$  was not stopped because the amorphous Ge region still allows for the diffusion to supply Ag. Assuming three times faster growth along  $[100]$  than  $[1, 2]$

results in the growth along  $[2-1-1]$ . The Ge layer formed on the (100) growth plane can decrease the growth rate along  $[100]$ . We suggest that the slowed growth along  $[100]$  induced additional growth along  $[1, 2]$ . The growth along  $[1, 2]$  did not suffer from Ge precipitation because the  $(1-2-2)$  plane was face-down and was shadowed from the GeTe deposition.

The interface between the bottom of the nanorod and the nanoparticle was studied by TEM and electron diffraction measurements (Fig. 5a–c). At point F, which is a point on the interface, the diffraction patterns were observed in two series. One was the same as the patterns of the nanorod core found at points A–D in Fig. 3b, and the other was the same as that of the nanoparticle found at point G. The two patterns were of the monoclinic  $\text{Ag}_2\text{Te}$  in different orientations. The electron beam incident direction corresponded to the  $[0-11]$  direction for the nanorod and the  $[-1-11]$  direction for the nanoparticle. The interface consisted of the  $(2-1-1)$  plane of the nanorod and the  $(3-21)$  plane of the nanoparticle. The different atomic arrangements of the two planes indicated that the nanorod growth was not epitaxial. One key feature of the nanorod–nanoparticle orientation was that the  $(1-1-1)$  plane of the nanorod, which consisted of only Ag atoms, is in parallel to the  $(1-10)$  plane of the nanoparticle, which also consisted of only Ag atoms (Fig. 5c, d). We suggest that the parallel Ag-only plane pair with movable Ag atoms forms a locally Ag-rich region that facilitates Ag diffusion and eases the non-epitaxial growth to form  $\text{Ag}_2\text{Te}$  nuclei. The important role of the parallel Ag-only planes on the nanorod growth explains the low nanorod yield of about 2%. In other words, the low yield can be improved if the orientation of the seed nanoparticles is controlled.

In light of all these considerations, we propose a model for nanorod growth: (1) A solid-state interdiffusion reaction occurs between GeTe and Ag when GeTe is deposited on an  $\text{Ag}_{2+\delta}\text{Te}$  seed nanoparticle with locally Ag-rich regions, such as Ag-only layers. (2) The reaction induces a nanoscale phase separation of Ge to form  $\text{Ag}_2\text{Te}$  and to precipitate Ge. (3) Further deposition of GeTe and subsequent interdiffusion partly reduces the Ag concentration in the formed  $\text{Ag}_2\text{Te}$  region, which serves to retain the Ag diffusion from the seed nanoparticle toward the top, and repeats the solid-state reaction between GeTe and Ag to form  $\text{Ag}_2\text{Te}$ . (4) When the size of the  $\text{Ag}_2\text{Te}$  region becomes greater than the critical nucleus size, the embryo starts to grow, and mobility of Ag atoms on Ag-only planes of monoclinic  $\text{Ag}_2\text{Te}$  eases the formation of the nucleus and the non-epitaxial growth. The indirect supply of Ag allows for an appropriate rate of one-dimensional crystal growth.



**Fig. 5** **a** Cross-sectional TEM image enlarged near the bottom of the nanorod. **b** Electron diffraction pattern, measured at point F, and **c** at point G, whose positions are indicated by the circles in **(a)**. Both diffraction patterns at F and G are indexed as monoclinic  $\text{Ag}_2\text{Te}$ . **d** Atomic arrangement in a unit cell of the monoclinic  $\text{Ag}_2\text{Te}$

displayed in a bird's eye view. **e** Cross-sectional atomic arrangement, perpendicular to the electron beam direction, around a unit cell of the nanorod and **f** that of the nanoparticle, oriented like those shown in the TEM image **(a)**. The atomic arrangements were obtained using the ReciPro software package [60]

## 4 Conclusions

We have demonstrated a facile, room temperature, dry-deposition-based growth of single-crystalline monoclinic  $\text{Ag}_2\text{Te}$  nanorods with a thin amorphous cover layer of Ge. The single-crystalline  $\text{Ag}_2\text{Te}$  nanorods were grown by GeTe deposition onto  $\text{Ag}_{2+\delta}\text{Te}$  nanoparticles, in contrast to the amorphous  $\text{Ag}_2\text{Te}$  nanorods grown by Te deposition onto Ag nanoparticles and the broccoli-like nanostructures formed by GeTe deposition onto Ag nanoparticles. We propose a model for non-epitaxial single-crystalline nanorod growth on the basis of the electrochemical diffusion of Ag and reaction with GeTe, involving nanoscale phase separation.

The nanorod structure with a crystalline  $\text{Ag}_2\text{Te}$  core and an amorphous Ge shell has two advantages for thermoelectric applications. One arises from the crystalline core/amorphous shell structure. The crystalline core/amorphous shell structure modifies the vibrational modes to decrease the thermal conductivity [61, 62]. The other arises from the combination of the materials of  $\text{Ag}_2\text{Te}$  and Ge. The bandgap of  $\text{Ag}_2\text{Te}$  [63] is lower than that of Ge and thus confines electronic carriers in the core, while the thermal conductivity of  $\text{Ag}_2\text{Te}$  [40] is comparable to or smaller than Ge [64] and thus induces phonon transport in the shell, resulting in decoupled electronic and phononic transport [65].

**Acknowledgements** This work was supported in part by MEXT KAKENHI Grant Numbers 18H01480 and by specially promoted academic research from Sophia University.

## Compliance with ethical standards

**Conflict of interest** The authors declare that they have no conflict of interest.

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