Supporting information

Disproportination of Thermoelectric Bismuth Telluride Nanowires as a Result of an Annealing Process

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1. The investigation of overgrown Bi-Te film after annealing

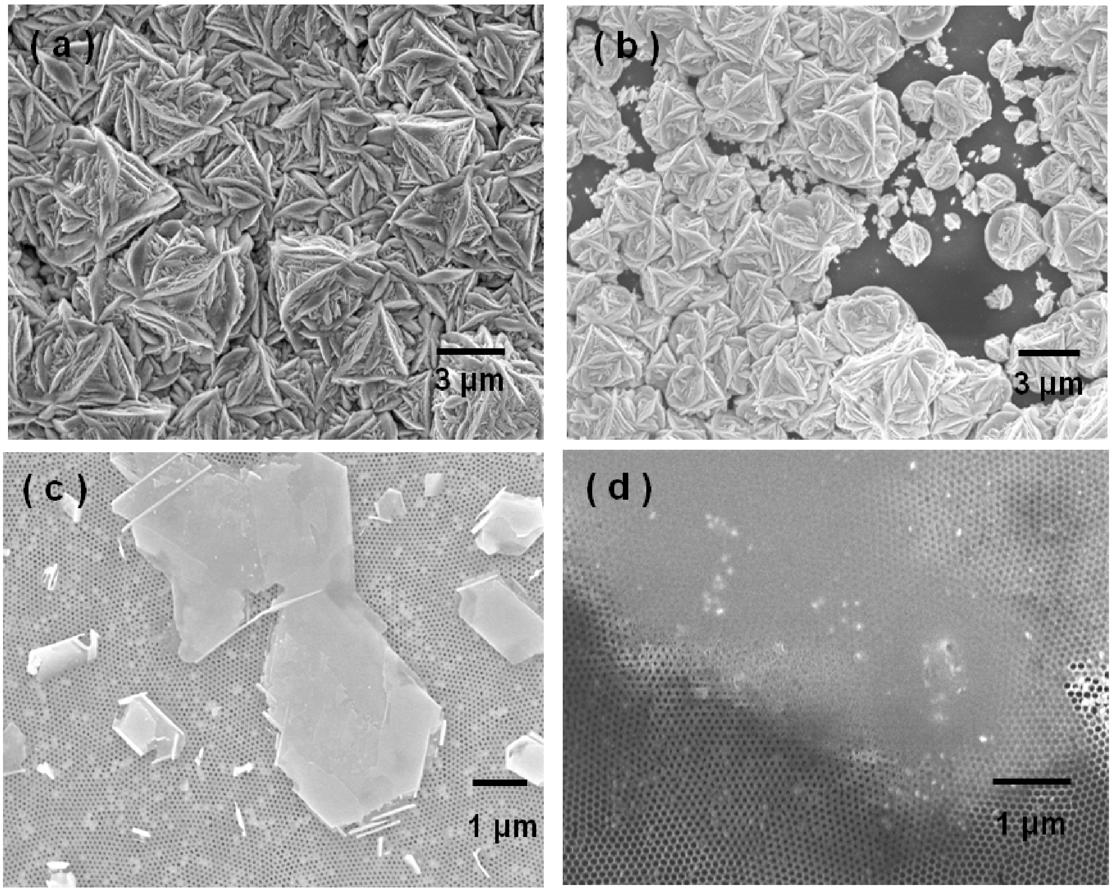

Figure 1. Morphology change of the overgrown Bi-Te film on the AAO membrane with an increase of the annealing temperature. (a) as-prepared, (b) annealed at 423 K, (c) 523 K and (d) 673 K.

Table 1. Compositional variations of overgrown Bi-Te film as a the function of the annealing temperature

Annealing temperature	as-prepared	423K	523K	673K
Bi (at %)	41.28	39.44	44.51	50.11
Te (at %)	58.72	60.56	55.49	49.89
Atomic ratio (Te / Bi)	1.422	1.535	1.246	0.995

Figure 1 shows the morphology change of an overgrown Bi-Te film on an AAO membrane as a function of the annealing temperature. The surface morphology depicted in figure 1 (a) is a typical Bi_2Te_3 feature. With an increase in the annealing temperatures, the overgrown Bi_2Te_3 film vaporized and almost peeled off at 673 K (figure 1 (d)). The composition of the film was investigated by EDX attached to an SEM. As summarized in Table 1, the Te compound had a tendency to incongruently sublimate above the annealing temperature of 423 K, leading to a Bi-rich Bi-Te compound. Furthermore, the composition of the individual nanowires was investigated by EDX attached to a TEM performing a line scan across the nanowire.

2. XRD patterns of annealed Bi-Te nanowires

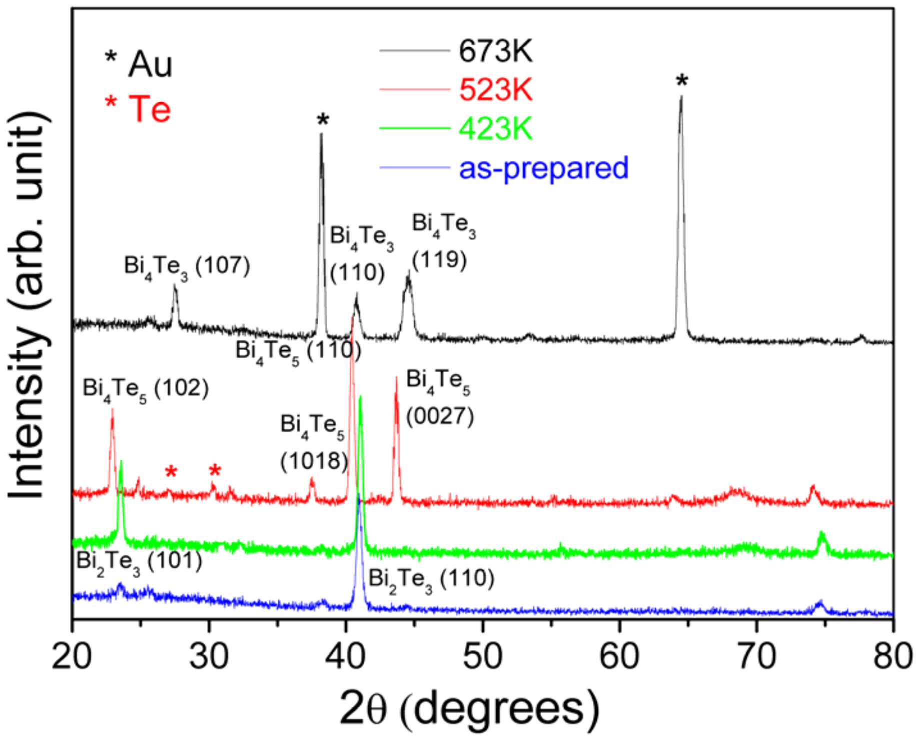

Figure 2. XRD patterns of as-prepared nanowires and nanowires annealed at different temperatures, respectively. Notice that Au peaks came from not complete removal of Au electrode where was placed in the bottom of AAO for the growth of Bi-Te nanostructures.

Figure 2 shows XRD patterns of Bi-Te nanowires annealed at the set temperatures (423 K, 523 K, and 673 K). As-prepared nanowires and the nanowires annealed at 423 K showed a similar crystalline structure (rhombohedral ($R\bar{3}m$) space group, *a* = 4.385 Å and *c* = 30.48 Å, ref. JCPDS No.150863) with a Bi_2Te_3 phase. The highly preferred oriented direction [110] was observed with different intensities and the intensity of the oriented direction [101] was slightly lower for the nanowires annealed at 423 K. However, as the annealing temperature increased (523 K and 673 K), in the spectra peaks of new bismuth telluride phases (Bi_4Te_5 and Bi_4Te_3) appeared due to the loss of tellurium (Te) and the subsequent recrystallization, remaining in the same crystalline structure (rhombohedral ($P\bar{3}m1$) and ($R\bar{3}m$) space group (*a* = 4.41 Å, *c* = 54.33 Å and *a* = 4.451 Å, *c* = 41.88 Å, ref. JCPDS No.220115 and 330216), respectively). In particular, Bi_4Te_5 and Te peaks were observed in the XRD pattern for the nanowires annealed at 523 K due to the coexistence of the observed black spots (Te) and the Bi_4Te_5 phase in the nanowires, which is consistent with the previous EDX results. For the nanowires annealed at 673 K, Te peaks were not observed anymore and Bi_4Te_3 phase peaks were found in the XRD pattern. This indicates that the Te crystallites had been sublimated and recrystallized with the Bi-Te alloy nanowires. Together with the consisting loss of Te, this lead to a transformation to a Bi_4Te_3 phase. Furthermore, the Bi_4Te_3 and Bi_4Te_5 [110] peaks shifted slightly into the negative direction compared with the Bi_2Te_3 [110] peak, in agreement with reference JCPDS No. 220115 and 330216.