

# Bismuth Telluride (Bi<sub>2</sub>Te<sub>3</sub>) Nanowires Synthesized by Cyclic Electrodeposition/Stripping Coupled with Step Edge Decoration

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## ABSTRACT

Polycrystalline bismuth telluride (Bi<sub>2</sub>Te<sub>3</sub>) nanowires have been prepared by the step edge selective electrodeposition of Bi<sub>2</sub>Te<sub>3</sub> on highly oriented pyrolytic graphite (HOPG) surfaces. Bi<sub>2</sub>Te<sub>3</sub> nanowires were obtained from an aqueous plating solution containing Bi<sup>3+</sup> and HTeO<sub>2</sub><sup>+</sup> using a three-step procedure: (1) potentiostatic oxidation of the graphite surface at +0.8 V (vs saturated calomel electrode, SCE), (2) potentiostatic nucleation of Bi<sub>2</sub>Te<sub>3</sub> at -0.6 V for 5 ms, (3) growth of Bi<sub>2</sub>Te<sub>3</sub> from these nuclei by cyclic electrodeposition (of both Bi<sub>2</sub>Te<sub>3</sub> and bismuth) and stripping (of bismuth only) between +0.30 V and -0.05 V at 20 mV s<sup>-1</sup>. Control of the number of electrodeposition/stripping scans allowed the diameter of Bi<sub>2</sub>Te<sub>3</sub> nanowires to be specified in the range from 100 to 300 nm. Bi<sub>2</sub>Te<sub>3</sub> nanowires were narrowly dispersed in diameter (RSD<sub>dia</sub> = 10–20%), were up to 1.0 mm in length, and were organized into parallel arrays containing hundreds of wires.

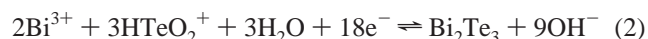
Thermoelectric (TE) generators produce electrical power from a temperature gradient. The efficiency of a particular thermoelectric material for power generation can be expressed in terms of the dimensionless quantity  $ZT$ <sup>1</sup>:

$$ZT = \frac{S^2 \sigma T}{\kappa} \quad (1)$$

where  $Z$  is the thermoelectric figure of merit,  $T$  is the mean temperature of the material,  $S$  is the thermoelectric power or Seebeck coefficient,  $\sigma$  is the electrical conductivity, and  $\kappa$  is the thermal conductivity. The best thermoelectric materials at room temperature are members of the Bi<sub>2(1-x)</sub>Sb<sub>2x</sub>Te<sub>3(1-y)</sub>Se<sub>3y</sub> family and possess a  $ZT \approx 1$  near room temperature (300–450 K).<sup>1</sup> Theoretical investigations have suggested that low-dimensional materials may exhibit  $ZT$  values considerably larger than 1.0 as a consequence of enhanced  $S$  and  $\sigma$ ,<sup>2–6</sup> and/or depressed  $\kappa$ <sup>7–12</sup> relative to the corresponding properties of bulk material.

These predictions have stimulated interest in the synthesis of Bi<sub>2</sub>Te<sub>3</sub> nanowires. Until now template synthesis<sup>13–15</sup> has been exclusively used to obtain Bi<sub>2</sub>Te<sub>3</sub> nanowires by both Martin<sup>16</sup> and Stacy<sup>17–19</sup> who electrodeposited Bi<sub>2</sub>Te<sub>3</sub> into the pores of a porous alumina membrane. Both research groups

employed an electrodeposition recipe similar to that originally described by Magri et al.:<sup>20</sup>



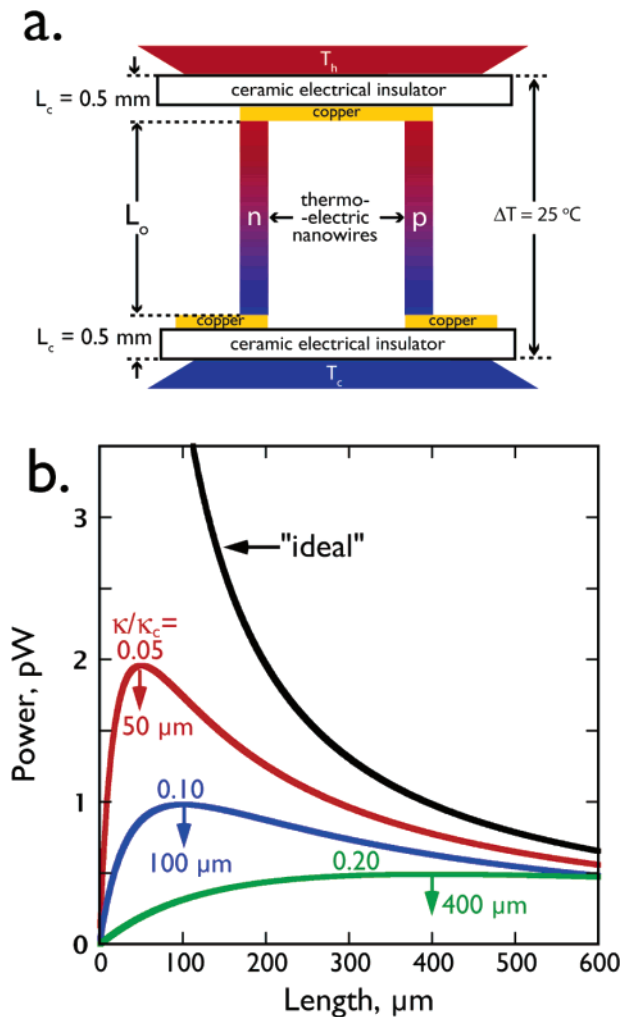
Nanowires with minimum diameters of 280 and 40 nm, respectively, were obtained by these two research groups, whereas the lengths of the nanowires prepared by template synthesis range from 10 to 50  $\mu\text{m}$ .

Efficient thermoelectric devices are likely to require nanowires that are not only extremely narrow but also extremely long – in excess of 50  $\mu\text{m}$ . Min and Rowe<sup>1,21–23</sup> have derived equations that allow performance metrics (power, efficiency, etc.) to be calculated for two-element Peltier devices, like that shown in Figure 1a. These equations include a consideration of the properties of the electrical and thermal contacts. One important metric is the electrical power generated by such a device:<sup>1</sup>

$$P = \frac{\pi r^2 (S \Delta T)^2}{\rho L_o (1 + (2\rho_j / \rho L_o)) (1 + (2\kappa L_c / \kappa_c L_o))^2} \quad (3)$$

where  $\Delta T$  is the temperature difference measured at the external surfaces of the ceramic layers,  $r$  is the radii of the two cylindrical thermoelements,  $\rho$  is the electrical resistivity

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**Figure 1.** (a) Schematic diagram of a two-element thermoelectric device showing parameters contained in eq 3. (b) Plot of total power generated,  $P$ , from the device shown in (a) as a function of the nanowire length,  $L_o$ . Shown are plots for three values of the ratio  $\kappa/\kappa_c$  as indicated. Arrows mark the optimum nanowire length for each value of  $\kappa/\kappa_c$ . The values of the other parameters indicated in eq 2 are as follows:  $r = 10 \times 10^{-6}$  mm,  $S = 2.00 \times 10^{-4}$   $\mu\text{V}/\text{K}$ ,  $\Delta T = 25$  K,  $\rho_c = 7$  k $\Omega$ ,  $\rho = 0.01$   $\Omega$ , and  $L_c = 0.5$  mm (taken from ref 1). The power generated by a device with ideal contacts, indicated by the black trace, is:  $P_{\text{ideal}} = (\pi r^2 (S \Delta T)^2 / 2 \rho L_o)$ .

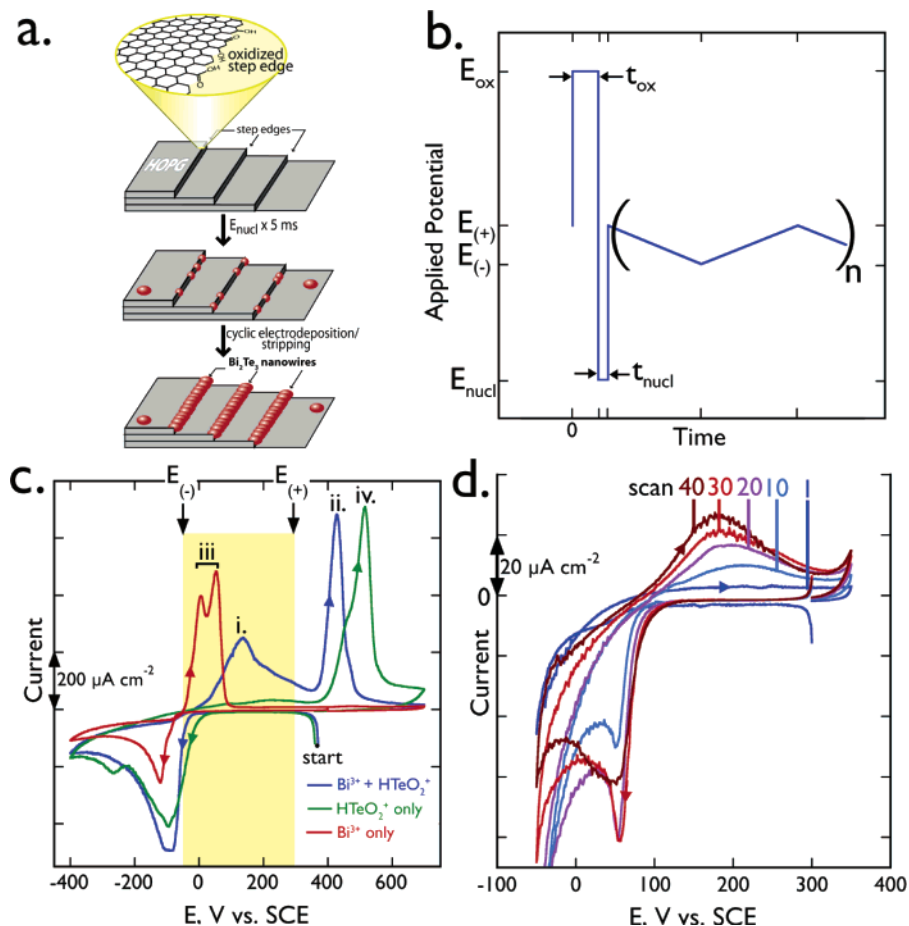
of the nanowires with length  $L_o$  and thermal conductivity  $\kappa$ , and  $\rho_c$  is the electrical resistance of the contacts of total thickness (insulator + conductor)  $L_c$ , having a net thermal conductivity  $\kappa_c$ . When realistic values<sup>24</sup> are substituted for these parameters, the effect of nanowire length can be assessed. For example, the dependence of  $L_o$  on  $P$  is plotted in Figure 1b for three different values of the ratio  $\kappa/\kappa_c$  (0.05, 0.1, and 0.2). Figure 1b shows that  $P$  is maximized for nanowires that are 50  $\mu\text{m}$  in length (for  $\kappa/\kappa_c = 0.05$ ) or longer ( $\kappa/\kappa_c > 0.05$ ) and that  $P$  falls rapidly with decreasing nanowire length below these optimum values. The plots of Figure 1b were calculated for nanowires with a diameter of 10 nm, but the optimum nanowire lengths, indicated by the arrows, are identical across the diameter range from 1 to 100 nm. Since a value of  $\kappa/\kappa_c = 0.10$  is typical for state-

of-the-art devices,<sup>23</sup> we conclude that nanowires longer than any synthesized to date may be required for device applications.

In this letter we describe a method for preparing arrays of hundreds of  $\text{Bi}_2\text{Te}_3$  nanowires that are 100–300 nm in diameter and up to 1 mm in length. This method, a variant of the electrochemical step edge decoration (ESED) method developed in our lab,<sup>25–31</sup> involves the electrodeposition of  $\text{Bi}_2\text{Te}_3$  selectively at the step edges present on a graphite surface, as shown schematically in Figure 2a. The potential program for our method is shown in Figure 2b and consists of three steps: (1) mild oxidation of the basal plane step edges on a piece of highly oriented pyrolytic graphite (HOPG) at +0.80 V for 5 s; (2) nucleation of nanoscopic  $\text{Bi}_2\text{Te}_3$  particles along the oxidized step edges at –0.60 V for 5 ms; (3) co-deposition of  $\text{Bi}_2\text{Te}_3$  and excess bismuth during a negative-going potential scan from +0.3 to –0.05 V and subsequent anodic stripping of excess bismuth, producing a stoichiometric  $\text{Bi}_2\text{Te}_3$  deposit, during a positive-going potential scan from –0.05 V to 0.30 V. Step 3 is then repeated a number of times (“ $n$ ” in Figure 2b) until the  $\text{Bi}_2\text{Te}_3$  particles grow large enough to coalesce, forming continuous  $\text{Bi}_2\text{Te}_3$  nanowires. This cyclic electrodeposition/stripping strategy is identical in concept to the method described by Sailor<sup>32</sup> for the electrodeposition of stoichiometric thin films of CdSe.

The electrochemical deposition of  $\text{Bi}_2\text{Te}_3$  was carried out in a 50 mL, one-compartment, glass and Teflon three-electrode cell. The plating solution consisted of 1.5 mM bismuth(III) nitrate pentahydrate (Aldrich, 99.999%) and 1 mM tellurium oxide (Aldrich, 99.999%) in 1 M nitric acid prepared according to the published procedure.<sup>20</sup> This plating solution was prepared using Nanopure water ( $\rho > 17.6$  M $\Omega$ ) and was purged with  $\text{N}_2$  prior to each experiment. A saturated calomel reference electrode (SCE) and a 2 cm<sup>2</sup> Pt foil counter electrode were also employed. The working electrode for these electrodeposition experiments was the basal plane surface of ZYA or ZYB grade HOPG crystals from GE Advanced Ceramics Inc. (Cleveland, OH). The basal plane surface was cleaved with adhesive tape prior to use, and a circular area of 0.2 cm<sup>2</sup> of was exposed, using an O-ring, to this plating solution. After deposition, the HOPG working electrode was removed from solution, rinsed with Nanopure water, and air-dried prior to characterization. Scanning electron microscopy (SEM) images and energy-dispersive X-ray fluorescence (EDX) analyses were acquired on a Philips Model XL-30FEG operating at 20 kV. Samples were mounted on aluminum SEM stubs using adhesive carbon dots from Ted Pella. Powder X-ray diffraction (XRD) spectra were acquired on a Siemens D5000 diffractometer operating at 40 keV and 30 mA. Transmission electron microscopy (TEM) and selected area electron diffraction (SAED) data were acquired on a Philips model CM20 operating at 200 kV.

Cyclic voltammograms (CVs) for a  $\text{Bi}_2\text{Te}_3$  plating solution (Figure 2c) show a cathodic deposition peak at approximately

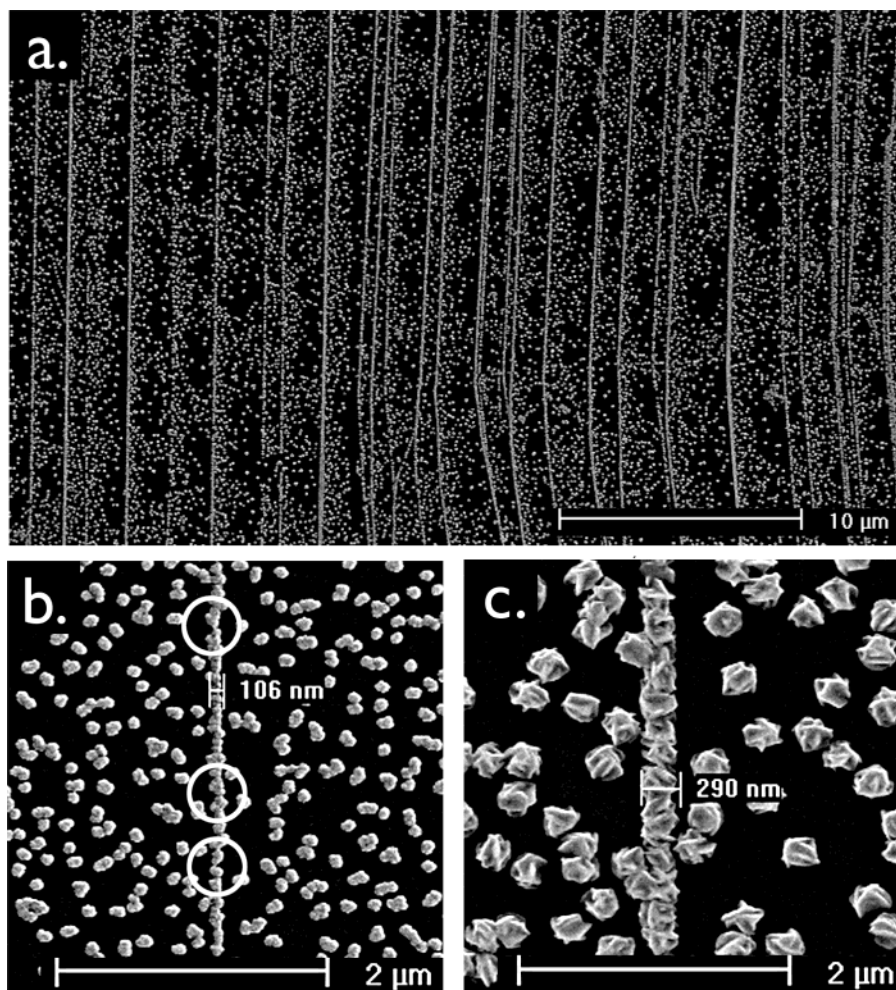


**Figure 2.** (a) Schematic diagram of the three-step method employed here for synthesizing  $\text{Bi}_2\text{Te}_3$  nanowires by cyclic electrodeposition/stripping coupled with ESED. (b) Potential program, plotted as potential versus time, used for the synthesis by cyclic electrodeposition/stripping of  $\text{Bi}_2\text{Te}_3$  nanowires. The electrodeposition of  $\text{Bi}_2\text{Te}_3$  consisted of three steps: (1) potentiostatic oxidation of step edges on the HOPG surface at  $E_{\text{ox}} = 0.80$  V vs SCE for a time  $t_{\text{ox}} = 5$  s; (2) potentiostatic nucleation of  $\text{Bi}_2\text{Te}_3$  at  $E_{\text{nucl}} = -0.6$  V for  $t_{\text{nucl}} = 5$  ms; and, (3) cyclic electrodeposition of stoichiometric  $\text{Bi}_2\text{Te}_3$  involving  $n$  potential cycles at  $20$  mV  $\text{s}^{-1}$  between a positive limit of  $E_{(+)}$  ( $+0.30$  V) and a negative limit of  $E_{(-)}$  ( $-0.05$  V). (c) Cyclic voltammograms, CVs, for the HOPG basal plane in contact with the plating solution employed for  $\text{Bi}_2\text{Te}_3$  nanowire growth (blue line). This solution contained:  $1.5$  mM  $\text{Bi}(\text{NO}_3)_3$  and  $1.0$  mM  $\text{TeO}$ , in  $1$  M  $\text{HNO}_3$ . Also shown are CVs acquired in plating solutions containing just  $\text{Bi}^{3+}$  (red line) and just  $\text{TeO}_2^+$  (green line). (d) CVs acquired during the growth of  $\text{Bi}_2\text{Te}_3$  nanowires using cyclic electrodeposition/stripping. The scan number,  $n$ , is indicated at top.

$-0.1$  V, as well as two anodic peaks at  $+0.175$  V (peak i) and  $+0.425$  V vs SCE (peak ii). CVs of  $1.5$  mM  $\text{Bi}^{3+}$  in  $1$  M  $\text{HNO}_3$  and  $1$  mM  $\text{HTeO}_2^+$  in  $1$  M  $\text{HNO}_3$  (Figure 2c) suggest that the broad anodic peak at  $+0.175$  V can be assigned to the stripping of excess bismuth from a bismuth-rich  $\text{Bi}_2\text{Te}_3$  deposit. These CVs also suggest that the anodic peak at  $+0.425$  V is the stripping of  $\text{Bi}_2\text{Te}_3$ , not Te stripping, as this occurs at a potential (peak iv) more than  $100$  mV positive of this. These assignments, which are identical to those of Stacey et al.,<sup>17</sup> are also supported by EDX elemental analysis of the electrodeposits formed in each solution. One departure from the observations of Stacey et al.<sup>17</sup> concerns the potential at which the deposition of  $\text{Bi}_2\text{Te}_3$  commences. In our case, this onset is at  $-50$  mV and is well negative of the onset for tellurium deposition at  $0.00$  V; exactly the opposite was reported by Stacy et al.<sup>17</sup> for experiments conducted at platinum electrodes. The explanation, we believe, is the presence at the HOPG electrode of large nucleation overpotentials that are absent, or insignificant, at

polycrystalline platinum electrodes. The existence of this nucleation overpotential for  $\text{Bi}_2\text{Te}_3$  is exposed by the CVs recorded during  $\text{Bi}_2\text{Te}_3$  deposition (Figure 2d) which show a prompt  $+80$ – $100$  mV shift in the  $\text{Bi}_2\text{Te}_3$  deposition onset, accompanied by a dramatic sharpening of the cathodic wave at  $+60$  mV, after just one deposition scan. The deposition CVs of Figure 2d show a second cathodic process occurring in the potential range from  $+0.02$  V to  $-0.05$  V, and this is assigned, based on EDX analysis, to the electrodeposition of pure bismuth, which is subsequently stripped (peak i) on the anodic return scan. We demonstrate below that the cyclic electrodeposition of  $\text{Bi}_2\text{Te}_3$  provides a robust method for the production of near-stoichiometric  $\text{Bi}_2\text{Te}_3$  wires.

Low magnification SEM images (Figure 3a) confirm that  $\text{Bi}_2\text{Te}_3$  nanowires, and nanoparticles, are formed by the cyclic electrodeposition/stripping procedure detailed above. The nanowires are formed at step edges present on the HOPG surface, and both the step edges and the  $\text{Bi}_2\text{Te}_3$  nanowires



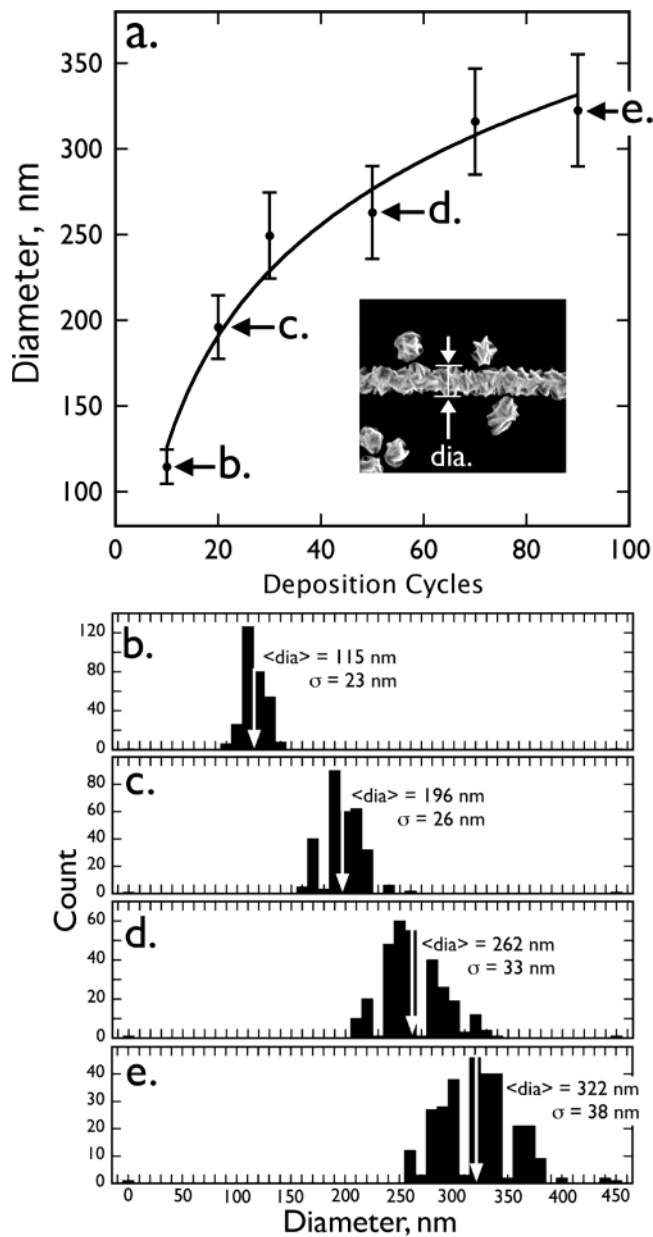
**Figure 3.** (a) Low magnification scanning electron microscope (SEM) image of  $\text{Bi}_2\text{Te}_3$  nanowires prepared by cyclic electrodeposition/stripping.  $\text{Bi}_2\text{Te}_3$  nanowires that nucleate and grow on step edges are arranged in parallel arrays. These nanowires are up to 1 mm in length. (b) High magnification SEM image of  $\text{Bi}_2\text{Te}_3$  nanowires prepared using 10 electrodeposition/stripping cycles. The mean, outermost diameter of these nanowires is 115 nm; however, such wires are characterized by periodic constrictions, indicated by circles, that are 20 nm in diameter or smaller. (c) SEM image of  $\text{Bi}_2\text{Te}_3$  nanowires prepared using 90 electrodeposition/stripping cycles.

formed on them can be a millimeter in length (i.e., the diameter of a columnar grain in the HOPG crystal). However, long nanowires are obtained only after the coalescence of  $\text{Bi}_2\text{Te}_3$  nuclei has proceeded to completion along each step edge. Our data show that the smallest  $\text{Bi}_2\text{Te}_3$  nanowires that are continuous over distances of more than 100  $\mu\text{m}$  are 60–80 nm in diameter. The individual  $\text{Bi}_2\text{Te}_3$  crystallites comprising each nanowire can be observed in higher magnification SEM images, like those shown in Figure 3b and c.

Once nanowires are formed by the coalescence of these crystallites, the deposition of additional  $\text{Bi}_2\text{Te}_3$  serves to increase the diameter of the nanowires. The diameter of the  $\text{Bi}_2\text{Te}_3$  nanowires that are produced is a function of the number of growth cycles,  $n$ , as shown in Figure 4a. The populations of nanowires produced in a particular synthesis experiment are narrowly distributed in diameter, with a relative standard deviation of the diameter ( $\text{RSD}_{\text{dia}}$ ) that ranged from 10 to 20%, as shown in the histograms plotted in Figure 4b–e. The granular morphology of these  $\text{Bi}_2\text{Te}_3$

nanowires leads, frequently, to the presence of constrictions (circled regions in Figure 4b) of 20 nm or less at interparticle boundaries. This morphology contrasts with the smooth, cylindrical  $\text{Bi}_2\text{Te}_3$  wires that are usually obtained in a template synthesis experiment.<sup>16,18,19,33–35</sup>

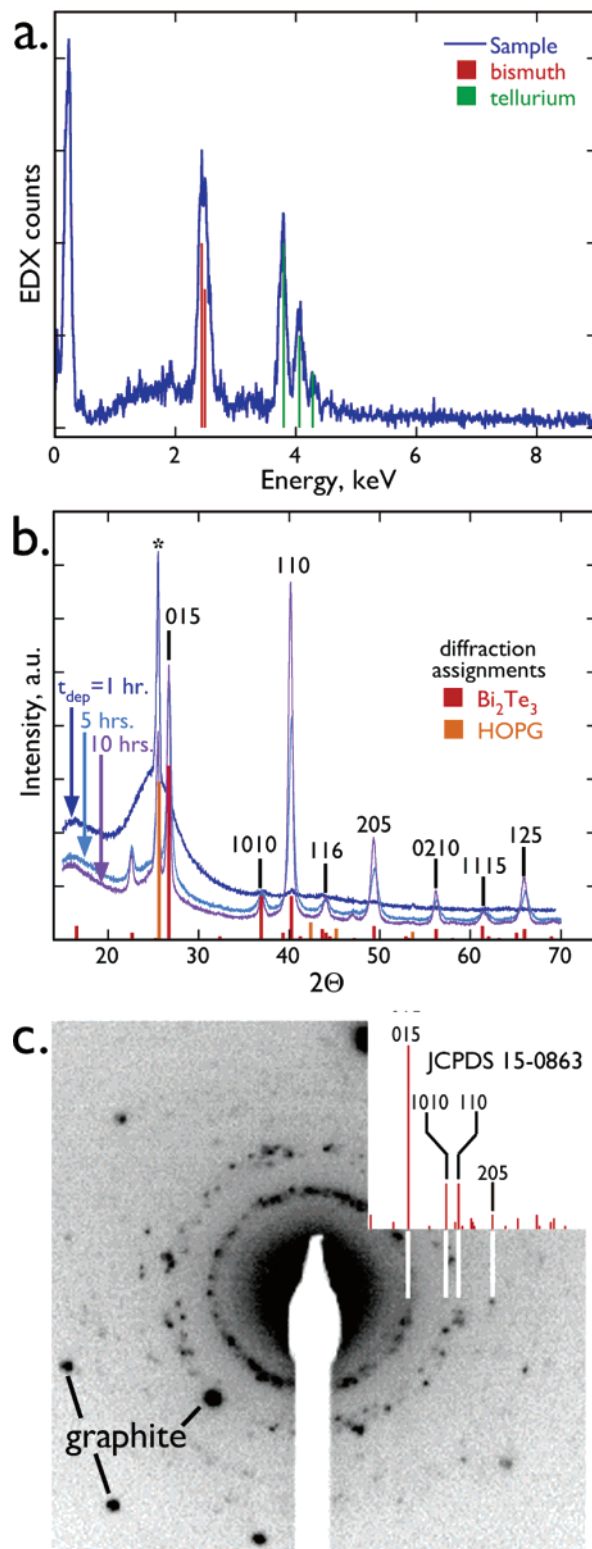
An attribute of the cyclic electrodeposition/stripping method is its propensity to produce material that is close to stoichiometric. EDX elemental analysis of  $\text{Bi}_2\text{Te}_3$  nanowires (Figure 5a) shows them to be slightly tellurium rich with a Bi/Te ratio of 2:3.4, in agreement with the composition predicted from the Bi–Te phase diagram.<sup>36</sup> XRD analysis (Figure 5b) further confirms that the deposited material is the hexagonal phase of  $\text{Bi}_2\text{Te}_3$ . However, diffractions corresponding to out-of-plane periodicities, including 110, 205, 116, and 125, are more intense than expected for isotropically distributed crystallites relative to 015, and in-plane periodicities 1010 and 1115 are weaker than expected. As XRD is most sensitive to the out-of-plane periodicities, this skewing means that a crystallographically preferred growth direction exists along 110. This conclusion is supported by selected



**Figure 4.** (a) Plot of the diameter of  $\text{Bi}_2\text{Te}_3$  nanowires as a function of the number of electrodeposition/stripping cycles,  $n$ . The diameter plotted here is the outermost diameter of these nanowires, measured as indicated in the SEM image (inset). The diameter error bars shown in this plot represent  $+1\sigma$  for the diameter measured from  $\approx 300$  nanowires. (b,c,d,e) Histograms of the outermost diameter for nanowires prepared using 10, 20, 50, and 90 electrodeposition/stripping cycles,  $n$ , respectively.

area electron diffraction (SAED) which, in contrast to XRD, is most sensitive to in-plane periodicities. In the SAED pattern of Figure 5c the 205 reflection is absent (the diffraction spot shown there derives from graphite), but 015 is observed and consistent with hexagonal  $\text{Bi}_2\text{Te}_3$ .

We have demonstrated that cyclic electrodeposition/stripping can be coupled with step edge decoration to produce  $\text{Bi}_2\text{Te}_3$  nanowires size-selectively. Uniquely, this method is capable of producing  $\text{Bi}_2\text{Te}_3$  nanowires that are up to 1 mm in length and organized into parallel arrays of hundreds of wires. In future investigations, we are interested in under-



**Figure 5.** (a) Energy-dispersive X-ray fluorescence (EDX) for  $\text{Bi}_2\text{Te}_3$  nanowires prepared by cyclic electrodeposition/stripping. The Bi/Te ratio calculated from this spectrum is 2:3.4 corresponding to 63 atomic percent tellurium, within the expected range based on the Bi–Te phase diagram.<sup>36</sup> (b) Powder X-ray diffraction for three  $\text{Bi}_2\text{Te}_3$  samples prepared by cyclic electrodeposition/stripping for 1 h, 5 h, and 10 h. The 5 and 10 h samples were continuous films of  $\text{Bi}_2\text{Te}_3$ , whereas the 1 h sample consisted of wires with a mean diameter of approximately 500 nm. (c) Selected area electron diffraction pattern for a  $\text{Bi}_2\text{Te}_3$  nanowire synthesized using cyclic electrodeposition/stripping.

standing whether the crystallographic disorder present in these nanowires, coupled with the presence of narrow interparticle constrictions, enhances  $S^2\sigma/\kappa$  and increases  $ZT$ .

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