

# High density p-type $\text{Bi}_{0.5}\text{Sb}_{1.5}\text{Te}_3$ nanowires by electrochemical templating through ion-track lithography

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High density p-type  $\text{Bi}_{0.5}\text{Sb}_{1.5}\text{Te}_3$  nanowire arrays are produced by a combination of electrodeposition and ion-track lithography technology. Initially, the electrodeposition of p-type  $\text{Bi}_{0.5}\text{Sb}_{1.5}\text{Te}_3$  films is investigated to find out the optimal conditions for the deposition of nanowires. Polyimide-based Kapton foils are chosen as a polymer for ion track irradiation and nanotemplating  $\text{Bi}_{0.5}\text{Sb}_{1.5}\text{Te}_3$  nanowires. The obtained nanowires have average diameters of 80 nm and lengths of 20  $\mu\text{m}$ , which are equivalent to the pore size and thickness of Kapton foils. The nanowires exhibit a preferential orientation along the {110} plane with a composition of 11.26 at.% Bi, 26.23 at.% Sb, and 62.51 at.% Te. Temperature dependence studies of the electrical resistance shows the semiconducting nature of the nanowires with a negative temperature coefficient of resistance and band gap energy of  $0.089 \pm 0.006$  eV.

## 1. Introduction

Thermoelectric devices which convert heat into electricity and *vice versa* utilize the Seebeck effect for power generation and the Peltier effect for cooling. The ideal thermoelectric device contains over hundreds of n-p semiconductor couples connected electrically in series and thermally in parallel. Such devices present many advantages, including solid-state operation with no moving parts, long operating lifetime, zero emission, maintenance free and high reliability.<sup>1</sup> Nonetheless, their use has been limited to a rather specific range of applications because of the relatively low energy-conversion efficiency. The efficiency of thermoelectric materials is evaluated in terms of a dimensionless figure of merit ZT, given by  $ZT = S^2\sigma T/\kappa$  where  $S$ ,  $\sigma$ ,  $T$  and  $\kappa$  are the Seebeck coefficient, electrical conductivity, absolute temperature and thermal conductivity, respectively.<sup>2</sup> In order to enhance the efficiency of thermoelectric energy conversion, a high Seebeck coefficient, an increased electrical conductivity, and a decreased thermal conductivity are required for thermoelectric materials, but these physical properties are often inter-related for bulk systems, making it very difficult to control these variables independently.

Nanostructuring thermoelectric material has recently emerged as a successful strategy to achieve enhancement in ZT due to quantum confinement effects in nanoscale system which offers opportunities to vary  $S$ ,  $\sigma$ , and  $\kappa$  independently.<sup>3–5</sup> Theoretical analysis indicates that the enhancement of ZT in nanostructured system is mainly due to the increased density of states, but an additional factor is the reduced lattice thermal conductivity resulting from the increased phonon

surface scattering in nanostructured system.<sup>6,7</sup> These theoretical predictions have been verified in two-dimensional (2D)  $\text{PbTe}/\text{Pb}_{1-x}\text{Eu}_x\text{Te}$  quantum-well structures<sup>8</sup> and  $\text{Bi}_2\text{Te}_3/\text{Sb}_2\text{Te}_3$  thin film superlattices.<sup>3</sup> Even more exciting are the theoretical predictions for one-dimensional (1D) nanostructured thermoelectric materials,<sup>9,10</sup> which are thought to have remarkable enhancements in ZT compared to 2D systems. These predictions have stimulated research interest in the preparation of 1D nanostructured thermoelectric materials.

Heavily doped  $\text{Bi}_2\text{Te}_3$  based semiconductors (*e.g.* n-type  $\text{Bi}_2\text{Te}_{2.7}\text{Se}_{0.3}$  and p-type  $\text{Bi}_{0.5}\text{Sb}_{1.5}\text{Te}_3$ ) are considered to be the most efficient materials for thermoelectric device application because of their superior ZT near room temperature.<sup>1,11</sup> These materials are therefore one of the best targets for the preparation of 1D nanostructures. A variety of approaches have been reported to prepare n-type  $\text{Bi}_2\text{Te}_3$  1D nanostructures, including templated electrodeposition using anodic alumina,<sup>12–16</sup> surfactant-mediated solvothermal techniques,<sup>17,18</sup> step edge selective electrodeposition,<sup>19</sup> high-temperature organic solution synthesis,<sup>20</sup> low-temperature and template-free synthesis<sup>21</sup> and most recently the galvanic displacement reaction.<sup>22</sup> However, there are only very few reports on the preparation of p-type  $\text{Bi}_{0.5}\text{Sb}_{1.5}\text{Te}_3$  1D nanostructures. Stacy's group made an effort to produce  $\text{Bi}_{0.5}\text{Sb}_{1.5}\text{Te}_3$  nanowire arrays by electrodeposition using anodic alumina templates.<sup>23</sup> Due to the insufficiency of the amount of Sb in the electrolyte solution, they applied a negative deposition potential in order to obtain the correct composition of  $\text{Bi}_{0.5}\text{Sb}_{1.5}\text{Te}_3$ , resulting in rough and dendritic growth and poor wetting of nanowires inside the pores. More recently, Myung's group modified the deposition conditions and obtained  $\text{Bi}_{0.5}\text{Sb}_{1.5}\text{Te}_3$  nanowires using commercial polycarbonate membranes as templates.<sup>24,25</sup>

In this paper, we report the preparation of p-type  $\text{Bi}_{0.5}\text{Sb}_{1.5}\text{Te}_3$  nanowire arrays by combining electrodeposition with ion-track lithography technology. Ion-track lithography

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1 technology is well known as a low-cost process to form deep  
vertical and high aspect ratio channels for nanowire growth.<sup>26</sup>  
In considering nanowire growth in templates for thermoelec-  
tric applications, the contribution of the host materials must  
5 be considered. Here we choose polyimide-based Kapton as a  
template for electroplating  $\text{Bi}_{0.5}\text{Sb}_{1.5}\text{Te}_3$  nanowires. Com-  
pared to the anodic alumina templates, Kapton templates  
have several beneficial properties, *e.g.* high heat resistance,  
flexural capability, chemical resistance and low dielectric con-  
stant.<sup>27</sup> In particular Kapton has a thermal conductivity of  
10  $0.14 \text{ W m}^{-1} \text{ K}^{-1}$  which is low enough to be especially inter-  
esting for thermoelectric applications.<sup>28</sup> Furthermore, since  
both electrodeposition and ion-track lithography are compa-  
15 sible with silicon integrated circuit processing, our approach is  
promising for building MEMS (microelectromechanical sys-  
tem) thermoelectric nanodevices.

## 2. Experimental

### 20 Materials

Bi powder (Alfa Aesar 99.999%), Te powder (Alfa Aesar  
99.999%),  $\text{SbCl}_3$  (Sigma-Aldrich 99+%),  $\text{C}_6\text{H}_8\text{O}_7 \cdot \text{H}_2\text{O}$   
( $\text{H}_3\text{Cit}$ , Aldrich 99.5%),  $\text{Na}_3\text{C}_6\text{H}_5\text{O}_7 \cdot 2\text{H}_2\text{O}$  ( $\text{Na}_3\text{Cit}$ , Sigma-  
25 Aldrich 99%), and  $\text{HNO}_3$  (Fisher 70%) were all used as  
received. All aqueous solutions were freshly prepared using  
reagent grade water ( $15 \text{ M}\Omega \text{ cm}^{-1}$  resistances) from an ELGA  
water purification system. Polyimide Kapton foils ( $20 \mu\text{m}$   
thick from Dupont) were irradiated at GSI (Darmstadt,  
30 Germany) with  $\text{Pb}^+$  ions (kinetic energy  $4 \text{ MeV u}^{-1}$ , fluence  
 $5 \times 10^9 \text{ ions cm}^{-2}$ ). The ion-tracked Kapton foils were pre-  
etched in  $\text{H}_2\text{O}_2$  (Fisher 30%) solution at  $60 \text{ }^\circ\text{C}$  for 100 min  
followed by etching in  $\text{NaClO}$  (Arcros Organics, 13% active  
chlorine, pH  $\sim 12.5$ ) solution at  $60 \text{ }^\circ\text{C}$  for 2.5 min. Prior to use  
35 as a template for nanowire deposition, one side of the ion-  
track-etched Kapton foils was coated with a thin layer of  
evaporated gold and then mounted onto a glass slide substrate  
using double-sided adhesive copper tape (Agar). The com-  
pleted substrate was then masked using insulating tape to  
40 leave only the unmetallized side of the foil exposed to the  
electrolyte solution. This was served as a working electrode for  
nanowire deposition.

### Electrodeposition

45 Electrochemical experiments were carried out in a three-  
electrode cell using an Autolab potentiostat/galvanostat. A  
large area platinum gauze and saturated calomel electrode  
(SCE) were served as counter and reference electrodes, respec-  
tively. The working electrodes for film deposition were made  
50 by evaporating 15 nm chromium onto glass slides followed by  
200 nm thick layer of gold. Both films and nanowires were  
deposited under potentiostatic control at room temperature in  
unstirred electrolyte solutions containing of  $0.001 \text{ M Bi}^{3+}$ ,  
 $0.01 \text{ M HTeO}_2^+$ ,  $1 \text{ M HNO}_3$ ,  $0.02 \text{ M Sb}^{3+}$ ,  $0.1 \text{ M H}_3\text{Cit}$  and  
55  $0.05 \text{ M Na}_3\text{Cit}$ . After deposition the Kapton templates were  
removed either by dissolving them in organic solvent mixtures  
of *N*-methyl-2-pyrrolidone (NMP, 30 wt%) and monoethano-  
lamine (MEA, 70 wt%) at  $100 \text{ }^\circ\text{C}$  for 1–5 min or by oxygen  
plasma etching in an Oxford Plasma Technology RIE80plus

Etcher at an oxygen pressure of 0.08 T and 300 W at room  
temperature for 40 min.

### Characterization

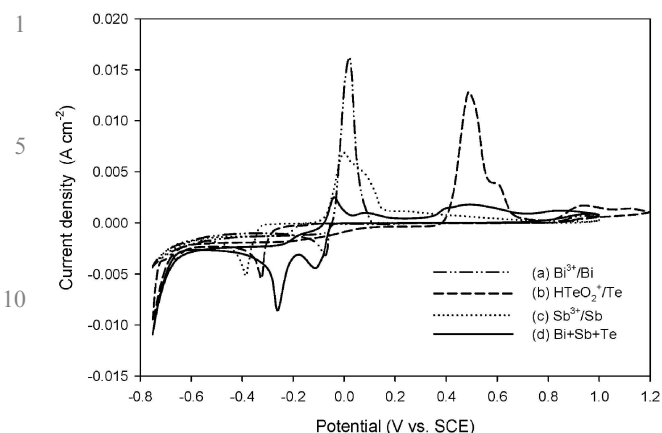
The surface morphology and compositions of the deposited  
5 films and nanowires were characterized using a LEO 1455VP  
scanning electron microscope (SEM) or JSM-6500F SEM  
equipped with energy dispersive X-ray (EDX) microanalysis  
(Oxford Inca 300) and operated at 20 kV. X-Ray diffraction  
10 (XRD) data were collected using a Siemens D5000 X-ray  
diffractometer with  $\text{Cu K}\alpha$  radiation ( $\lambda = 1.5406 \text{ \AA}$ ). The  
transport properties of the deposited films were measured  
using the standard van der Pauw technique with a dc current  
of 19 mA and a permanent magnetic field of 0.55 T at room  
15 temperature on a commercial Hall effect measurement system  
(HMS 300 from Ecopia). In order to eliminate the influence of  
the underlying gold substrates on the electrical conductivity  
measurements, the films were peeled off from the substrates  
using epoxy resin.<sup>29</sup> The peeled film has an area of  $1 \times 1 \text{ cm}$ .  
Ohmic contact was made by soldering copper wires with In–Sn  
20 solder onto the four corners of the film. An average of  $\sim 10$   
measurements was performed to ensure the reproducibility of  
the data. The Seebeck coefficient of the film was determined  
using a custom made Seebeck measurement unit.

The temperature dependence of the electrical resistance of  
25  $\text{Bi}_{0.5}\text{Sb}_{1.5}\text{Te}_3$  nanowires was measured using two-point contact  
technique. Before each measurement, a thin layer of gold spot  
was evaporated on the top of the nanowire array to serve as a  
top contact and a gold seed layer as a bottom contact. Contact  
to the sample was made using silver paint with gold wires. The  
sample was mounted in a cryogenic chamber at temperature  
30 ranging from 1.5 to 295 K.  $I$ – $V$  curves of the nanowires were  
recorded by a source-meter (Keithley 199) and the resistance  $R$   
was extracted by using  $R = dV/dI$ .

## 3. Results and discussion

### 3.1 Electrodeposition of p-type $\text{Bi}_{0.5}\text{Sb}_{1.5}\text{Te}_3$ films

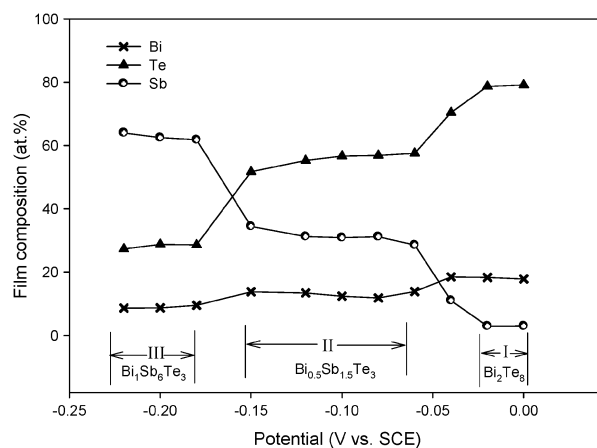
In order to ascertain the appropriate deposition conditions for  
40  $\text{Bi}_{0.5}\text{Sb}_{1.5}\text{Te}_3$  nanowires, a series of experiments was carried  
out to examine the effect of deposition conditions on composi-  
tion, homogeneity, crystallinity and transport properties of the  
deposited films. The optimal conditions for film deposition are  
then used as a starting point for the deposition of  $\text{Bi}_{0.5}\text{Sb}_{1.5}\text{Te}_3$   
45 nanowires in Kapton templates. Previous studies have shown  
that electrodeposition of  $\text{Bi}_{0.5}\text{Sb}_{1.5}\text{Te}_3$  films is quite challen-  
ging due to the fact that it is difficult to achieve sufficient  
amounts of Sb in the aqueous solution.<sup>23–25,30</sup> In this study,  
citric acid was chosen as a complexing agent to increase the  
50 solubility of Sb in the electrolyte solution because citric acid  
was found to readily form complexes with  $\text{Sb}^{3+}$  and has been  
used as an efficient agent for extraction of Sb in environmental  
sample analysis.<sup>32</sup> Fig. 1(a–c) shows the cyclic voltammograms  
(CV) recorded in various electrolyte solutions containing the  
55 individual elements. The deposition of Bi, Te and Sb are  
occurred at  $-0.08 \text{ V}$ ,  $-0.3 \text{ V}$  and  $-0.4 \text{ V vs. SCE}$ , respectively.  
In the CV recorded in the electrolyte solution containing all  
three elements (Fig. 1d) there are only two obvious cathodic



**Fig. 1** Cyclic voltammograms of gold working electrodes in various electrolyte solutions containing: (a) 0.001 M  $\text{Bi}^{3+}$  + 1 M  $\text{HNO}_3$ ; (b) 0.01 M  $\text{HTeO}_2^+$  + 1 M  $\text{HNO}_3$ ; (c) 0.02 M  $\text{Sb}^{3+}$  + 0.1 M  $\text{H}_3\text{Cit}$  + 0.05 M  $\text{Na}_3\text{Cit}$ ; and (d) 0.001 M  $\text{Bi}^{3+}$  + 0.01 M  $\text{HTeO}_2^+$  + 0.02 M  $\text{Sb}^{3+}$  + 0.1 M  $\text{H}_3\text{Cit}$  + 0.05 M  $\text{Na}_3\text{Cit}$ . All voltammograms were recorded at 20 °C at a scan rate of 10  $\text{mV s}^{-1}$ .

peaks observed around  $-0.09$  V and  $-0.26$  V vs. SCE, respectively. The first peaks can be attributed to the deposition of Bi and the second one accounts for the co-deposition of Te and Sb, which is shifted towards positive potentials in comparison to those for individual Te and Sb depositions. The behaviour is consistent with previous reports on the deposition of  $\text{Bi}_2\text{Te}_3$  binary<sup>33</sup> and  $\text{Bi}_2\text{Te}_{3-x}\text{Se}_x$  ternary compounds<sup>34</sup> and can be explained by an induced co-deposition mechanism or underpotential deposition mechanism as proposed by Kröger.<sup>35</sup> According to Kröger's analysis, when the two reversible (Nernst) potentials for the two separate elements are closer than  $\sim 0.25$  V the deposition of both elements can take place at more positive potentials than those of where either element deposits individually. This process is driven by the free energy associated with the formation of compounds from the elements, in this case, *i.e.*  $\text{BiSbTe}$  ternary compounds. Based on the CV studies, the potentials for deposition of  $\text{BiSbTe}$  can be set above the deposition potential of Sb *i.e.*  $-0.4$  V vs. SCE, and below the potential where Bi reduction begins, *i.e.*, 0 V vs. SCE.

To produce stoichiometric films of  $\text{Bi}_{0.5}\text{Sb}_{1.5}\text{Te}_3$  the composition of the deposited films was monitored as a function of the applied deposition potential and determined by EDX. As shown in Fig. 2 for a range of applied potentials, from 0 V to  $-0.3$  V vs. SCE there are three distinct regions in which the composition of the films is almost constant whatever the deposition potential is. In the first region of potentials between 0 V and  $-0.02$  V vs. SCE the films are composed of almost pure  $\text{Bi}_2\text{Te}_8$  with only  $\sim 3$  at.% Sb, indicating that Sb cannot be easily reduced within this positive potential range. For the second region of potentials between  $-0.06$  V and  $-0.15$  V vs. SCE the film composition is approximately  $\sim 10$  at.% Bi,  $\sim 30$  at.% Sb, and  $\sim 60$  at.% Te, close to stoichiometric  $\text{Bi}_{0.5}\text{Sb}_{1.5}\text{Te}_3$ . As potentials are shifted towards the third region, *i.e.* more negative than  $-0.18$  V vs. SCE the film composition changes to  $\text{Bi}_1\text{Sb}_6\text{Te}_3$  with a large excess of Sb.



**Fig. 2** Film compositions as a function of the applied deposition potentials.

It was found that the deposition potentials also had a significant effect on the surface morphology and crystal structure of the films. Fig. 3 show representative SEM images (a–c) and the corresponding XRD patterns (d–f) for typical films deposited within the different potential regions. The films deposited at  $-0.02$  V (region I) show a granular structure with excellent adhesion on substrates and a prominent  $\{015\}$  crystalline orientation. All of the films with close to stoichiometric composition of  $\text{Bi}_{0.5}\text{Sb}_{1.5}\text{Te}_3$  deposited in region II (between  $-0.06$  V and  $-0.15$  V vs. SCE) exhibit a cauliflower-like morphology (as typically shown in Fig. 3b) and good adhesion to the substrates and are grey in color. Fig. 3e shows the XRD pattern collected from a particular film which was deposited at  $-0.08$  V vs. SCE. According to the standard ICDD PDF card (49–1713), all the detected diffraction peaks can be indexed as those from the rhombohedral  $\text{Bi}_{0.5}\text{Te}_{1.5}\text{Se}_3$  ternary crystal [space group (R3m)(166)] except for the gold substrate peaks. This film has a preferential orientation along  $\{110\}$  and  $\{015\}$  planes and the  $\{110\}$  plane is considered to be the optimal crystal orientation for achieving the best thermoelectric performance.<sup>1,23,25</sup> Interpreting the width of the diffraction peaks using the Debye–Sherrer formula gives a grain size of 14 nm. For the films deposited in region III the surface of the films became much rougher and show dendritic growth with poor adhesion to the substrates. The films are black in appearance. The complicated XRD pattern indicates that the resulting film could be a mixture rather than a single phase compound. Taken together, the EDX, SEM and XRD results indicate that the appropriate potential for producing  $\text{Bi}_{0.5}\text{Sb}_{1.5}\text{Te}_3$  films should be around  $-0.08$  V vs. SCE at which the deposited films have closest stoichiometric composition and the ideal crystalline orientation for thermoelectric performance.

The transport properties (*i.e.* electrical resistivity, carrier concentration, and Hall mobility) of the  $\text{Bi}_{0.5}\text{Sb}_{1.5}\text{Te}_3$  film deposited at  $-0.08$  V vs. SCE were measured at room temperature using a Hall measurement system. The thickness of the film was 10  $\mu\text{m}$  as observed using SEM. Hall measurement showed that the film was a p-type semiconductor, which was evident by the positive sign of the Hall voltage. The electrical resistivity of the film was about 0.13  $\Omega\text{ cm}$  as determined using

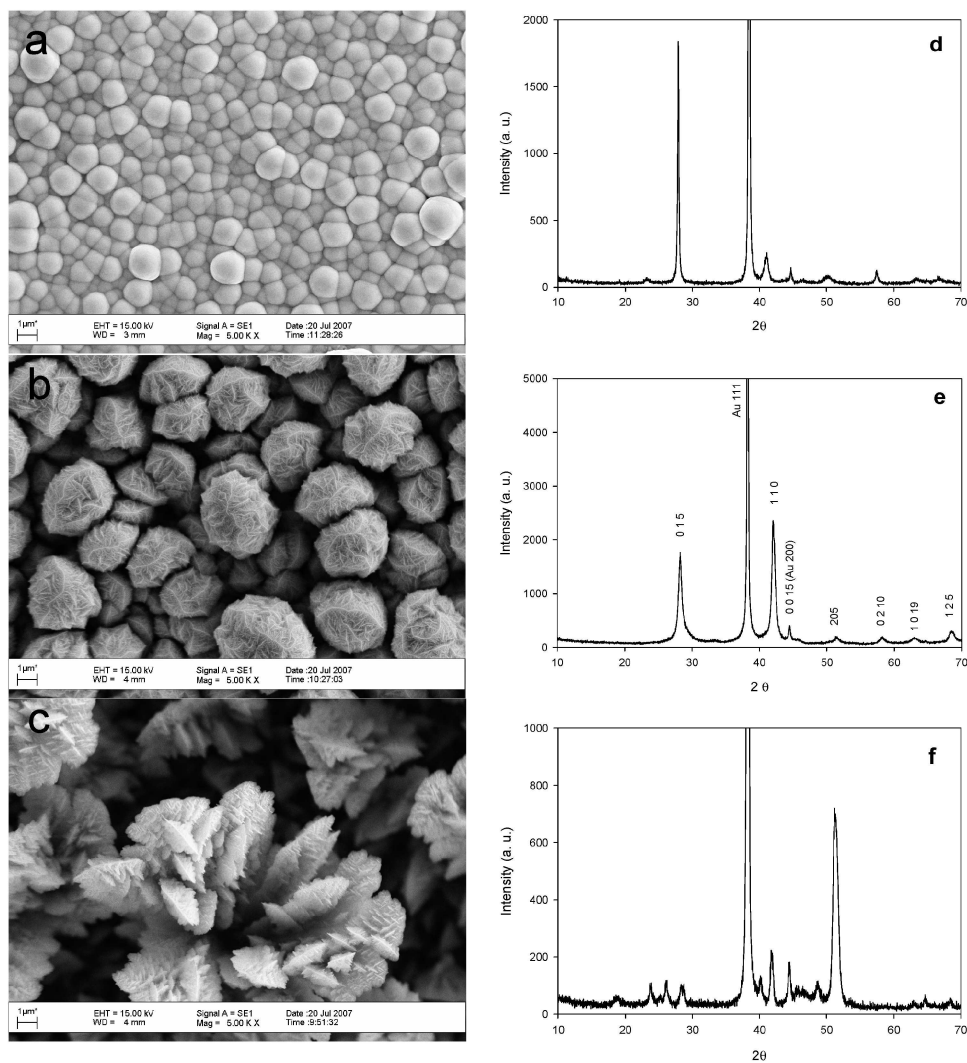


Fig. 3 Representative SEM images (a–c) and corresponding XRD patterns (d–f) for typical films deposited at different potential regions.

the van der Pauw technique. The carrier concentration, Hall mobility and Hall coefficient of the film was found to be  $4.7 \times 10^{18} \text{ cm}^{-3}$ ,  $10.8 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ , and  $1.5 \text{ cm}^3 \text{ C}^{-1}$ , respectively. The measured Seebeck coefficient of the film was  $122 \mu\text{V K}^{-1}$  at room temperature. The positive value confirmed that the film is p-type, which is in good agreement with the Hall measurement.

### 3.2 Electrodeposition of p-type $\text{Bi}_{0.5}\text{Sb}_{1.5}\text{Te}_3$ nanowires

Based on the above studies for film deposition, stoichiometric p-type  $\text{Bi}_{0.5}\text{Sb}_{1.5}\text{Te}_3$  nanowires can be deposited at a potential of  $-0.08 \text{ V vs. SCE}$  using ion-track etched Kapton foils. Fig. 4 shows the SEM image of the etched Kapton foil. The pores are round in shape with an average pore diameter of  $\sim 80 \text{ nm}$ . The pore diameter is monitored by etching conditions such as etching time, temperature and pH of etching solution.<sup>36</sup> By carefully controlling these conditions, polyimide-based templates with pore diameters below  $20 \text{ nm}$  have been achieved.<sup>37</sup> This demonstrates the possibility of further reducing the nanowire diameter and achieving a high aspect ratio to enhance the thermoelectric properties. The Kapton foil be-

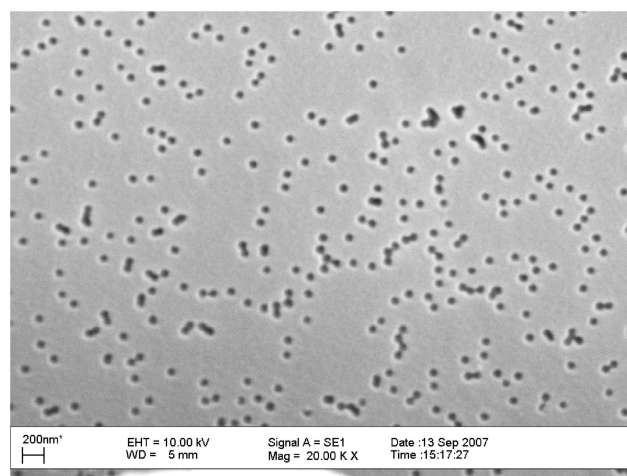
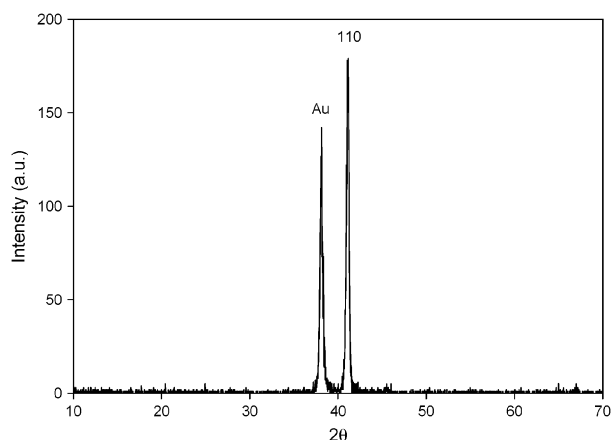


Fig. 4 SEM image of ion-track etched Kapton foils.

came uniformly dark-grey in color during deposition, indicating that the pores were etched through the whole foil and resulted in the smooth deposition of nanowires inside the

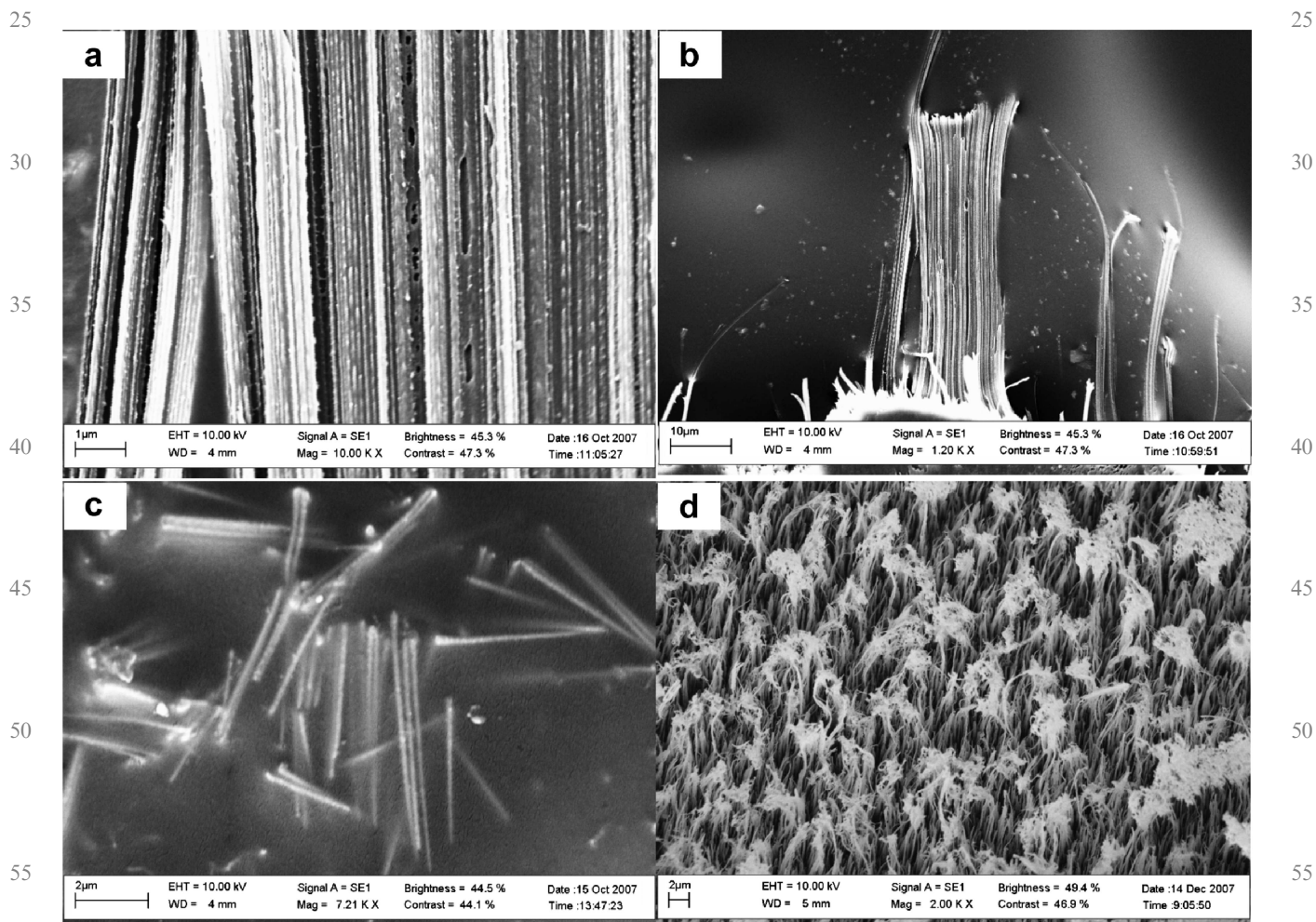
1 pores. Nanowire growth was monitored by a current–time  
transient curve and stopped when a rapid increase in current  
was observed, which indicated that some of the pores were  
filled and the overgrowth of the nanowires occurred across the  
top surface. Cross sectional SEM image (Fig. 5a) show that  
the wires were continuous and dense with  $\sim 80$  nm in diameter  
and  $\sim 20 \mu\text{m}$  in length, which were the same as the pore size  
and thickness of the Kapton foil used. EDX analysis revealed  
the composition of the nanowires to be 11.26 at.% Bi, 26.23  
10 at.% Sb, and 62.51 at.% Te.

After electrodeposition, the Kapton foils can be removed  
either by dissolution in organic solvent mixtures of NMP/  
MEA or by oxygen plasma etching. When dissolved in organic  
solvent mixtures at  $100^\circ\text{C}$  for 1 min, as shown in Fig. 5b the  
15 foil was partially removed and the nanowires retained within  
the foil as bundles. After dissolving for 5 min the nanowires  
were thoroughly liberated from the foils (Fig. 5c). The ob-  
tained wires have an average diameter of 80 nm which is  
equivalent to the pore size of the Kapton foils. In the case  
20 using oxygen plasma for etching, it can be seen from Fig. 5d  
that freestanding nanowires in the form of highly-ordered  
arrays can be obtained. An XRD pattern of the nanowires  
embedded in Kapton foils is shown in Fig. 6. Except for the



**Fig. 6** XRD pattern for  $\text{Bi}_{0.5}\text{Sb}_{1.5}\text{Te}_3$  nanowires embedded in Kapton foil. The peak around  $38^\circ$  can be attributed to gold that was used as a seed layer for electrodeposition.

gold peak that originates from the evaporated seed layer only  
the  $\{110\}$  peak of the  $\text{Bi}_{0.5}\text{Sb}_{1.5}\text{Te}_3$  can be seen clearly. It  
indicates that the preferred growth direction for the nanowires  
is along the  $\{110\}$  plane.



**Fig. 5** SEM images of  $\text{Bi}_{0.5}\text{Sb}_{1.5}\text{Te}_3$  nanowires embedded in Kapton foil (a), and liberated from Kapton foil by dissolving in organic solvent of NMP/MEA at  $100^\circ\text{C}$  for 1 min (b), and 5 min (c), or by oxygen plasma etching at 0.08 T and 300 W for 40 min (d).

### 3.3 Electrical transport properties of p-type $\text{Bi}_{0.5}\text{Sb}_{1.5}\text{Te}_3$ nanowires

From 1.5–295 K all the  $I$ - $V$  curves obtained from the  $\text{Bi}_{0.5}\text{Sb}_{1.5}\text{Te}_3$  nanowires show linear behavior, confirming good Ohmic contact to the nanowires. Fig. 7(a) shows the temperature dependence of the resistance of the nanowire array (solid line),  $R(T)$ , normalized to the resistance at 295 K,  $R_0$ . It can be observed that the resistance of the nanowires decreases with increasing temperature, which indicates the semiconducting nature of the nanowires. The measured resistance as a function of temperature changes from a linear-like temperature dependence ( $T > 50$  K) to an exponential-like dependence ( $T < 50$  K) as the temperature decreases. This feature is quite different from that observed on the  $\text{Bi}_{0.5}\text{Sb}_{1.5}\text{Te}_3$  film in which the resistance decreases with increasing temperature at all temperature range from 1.5–295 K (dash line) and can be explained in terms of the relative importance of carrier-phonon scattering and carrier-boundary scattering.<sup>38</sup> At high temperature ( $T > 50$  K), the phonon scattering dominates and the resistance rises with decreasing temperature. As the temperature decreases below 50 K, the boundary scattering becomes more and more important and dominates the scattering mechanism. Since the nanowires studied in the present work are polycrystalline with potentially

many grain boundaries, the contribution of scattering from wire walls together with the grain boundaries may give rise to a more temperature dependent resistance. Therefore, the resistance at low temperature exhibits more temperature variation than that at high temperature. Further analysis shows that the nanowires have a negative temperature coefficient of resistance, which decreased to  $-0.09 \text{ K}^{-1}$  with decreasing temperature from 295 to 1.5 K.

By applying an equation that reflects the temperature dependence of the intrinsic carrier density in a semiconductor:  $R(T) = R_0 \exp(E_g/2k_B T)$ ,<sup>39,40</sup> the energy band gap  $E_g$  (or thermal activation energy  $E_a$ <sup>25</sup>), can be determined. The fit of the high temperature data for the nanowire array and film can be calculated from Fig. 7(b) according to the equation. The value of  $E_g$  ( $E_a$ ) for the nanowires was found to be  $0.089 \pm 0.006$  eV, which is higher than that of the film,  $0.045 \pm 0.011$  eV. This increased band gap may be due to size effects or carrier localization.<sup>25</sup> Currently, further investigations are being undertaken to prepare p-type  $\text{Bi}_{0.5}\text{Sb}_{1.5}\text{Te}_3$  nanowires with various diameters down to 20 nm to confirm the above experimental result and to observe some quantum confinement effects.

## 4. Conclusions

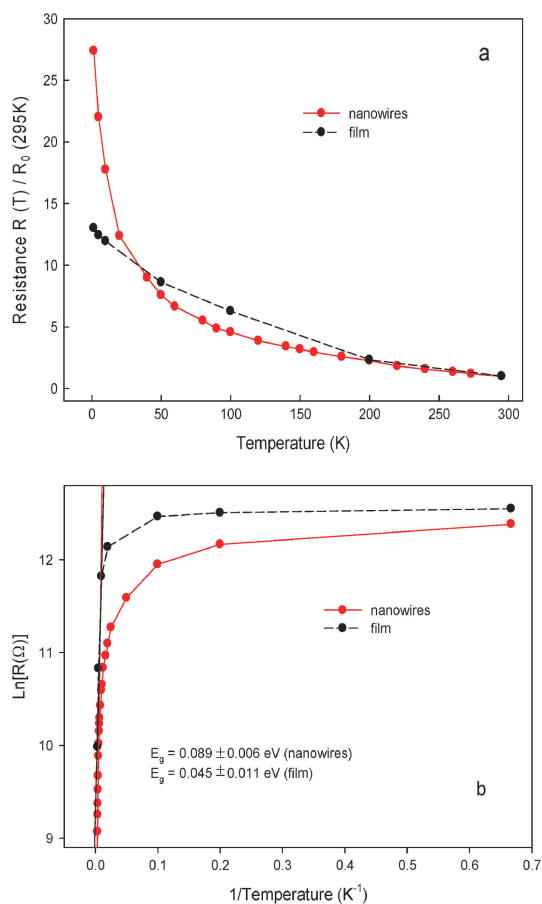
High density p-type  $\text{Bi}_{0.5}\text{Sb}_{1.5}\text{Te}_3$  nanowire arrays have been produced by combining electrodeposition with ion-track lithography technology. The electrodeposition conditions have significant effects on composition, homogeneity, crystallinity and transport properties of the deposited materials. It is found that the stoichiometric  $\text{Bi}_{0.5}\text{Sb}_{1.5}\text{Te}_3$  nanowires can be obtained at deposition potential of  $-0.08$  V vs. SCE. Polyimide-based Kapton foils are good candidate for ion track irradiation and nanotemplating the  $\text{Bi}_{0.5}\text{Sb}_{1.5}\text{Te}_3$  nanowires. The obtained nanowires have average diameters of 80 nm and lengths of 20  $\mu\text{m}$  which are equivalent to the pore size and thickness of the Kapton foils. The nanowires exhibit a preferential orientation along the  $\{110\}$  plane and a stoichiometric composition of 11.26 at.% Bi, 26.23 at.% Sb, and 62.51 at.% Te. The study of the temperature dependence of the electrical resistance indicates that the nanowires are semiconducting with a band gap energy of  $0.089 \pm 0.006$  eV, which is higher than that of the film,  $0.045 \pm 0.011$  eV.

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**Fig. 7** Temperature dependence of the electrical resistance (a) and the determination of energy band gap (b) of  $\text{Bi}_{0.5}\text{Sb}_{1.5}\text{Te}_3$  nanowire array (solid line) and film (dash line).

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