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

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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.

These predictions have stimulated research interest in the preparation of 1D nanostructured thermoelectric materials. These predictions have been verified in two-dimensional (2D) PbTe/Pb$_{1-x}$Eu$_x$Te quantum-well structures and Bi$_2$Te$_3$/Sb$_2$Te$_3$ thin film superlattices. Even more exciting are the theoretical predictions for one-dimensional (1D) nanostructured thermoelectric materials, which are thought to have remarkable enhancements in ZT compared to 2D systems. 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 Bi$_2$Te$_3$ 1D nanostructures, including templated electrodeposition using anodic alumina, surfactant-mediated solvothermal techniques, step edge selective electrodeposition, high-temperature organic solution synthesis, low-temperature and template-free synthesis and most recently the galvanic displacement reaction. However, there are only very few reports on the preparation of p-type Bi$_{0.5}$Sb$_{1.5}$Te$_3$ 1D nanostructures. Stacy’s group made an effort to produce Bi$_{0.5}$Sb$_{1.5}$Te$_3$ nanowires by electrodeposition using anodic alumina templates. 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 Bi$_{0.5}$Sb$_{1.5}$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 Bi$_{0.5}$Sb$_{1.5}$Te$_3$ nanowires using commercial polycarbonate membranes as templates.

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

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technology is well known as a low-cost process to form deep vertical and high aspect ratio channels for nanowire growth.\textsuperscript{26} In considering nanowire growth in templates for thermoelectric applications, the contribution of the host materials must be considered. Here we choose polyimide-based Kapton as a template for electropolating Bi\textsubscript{0.5}Sb\textsubscript{1.5}Te\textsubscript{3} nanowires. Compared to the anodic alumina templates, Kapton templates have several beneficial properties, e.g. high heat resistance, flexural capability, chemical resistance and low dielectric constant.\textsuperscript{27} In particular Kapton has a thermal conductivity of 0.14 W m\textsuperscript{-1} K\textsuperscript{-1} which is low enough to be especially interesting for thermoelectric applications.\textsuperscript{28} Furthermore, since both electrodeposition and ion-track lithography are compatible with silicon integrated circuit processing, our approach is promising for building MEMS (microelectromechanical system) thermoelectric nanodevices.

2. Experimental

Materials

Bi powder (Alfa Aesar 99.999%), Te powder (Alfa Aesar 99.999%), \textit{SbCl}_3 (Sigma-Aldrich 99\%\), \textit{C}_6\textit{H}_5\textit{O}_7\cdot\textit{H}_2\textit{O} (H\textit{Cit}, Aldrich 99.5\%), \textit{Na}_3\textit{C}_6\textit{H}_5\textit{O}_7\cdot2\textit{H}_2\textit{O} (Na\textit{Cit}, Sigma-Aldrich 99\%), and \textit{HNO}_3 (Fisher 70\%) were all used as received. All aqueous solutions were freshly prepared using reagent grade water (15 MΩ cm\textsuperscript{-1} resistances) from an ELGA water purification system. Polyimide Kapton foils (20 μm thick from Dupont) were irradiated at GSI (Darmstadt, Germany) with Pb\textsuperscript{2+} ions (kinetic energy 4 MeV u\textsuperscript{-1}, fluence 5 × 10\textsuperscript{8} ions cm\textsuperscript{-2}). The ion-etched Kapton foils were pre-etched in \textit{H}_2\textit{O}_2 (Fisher 30\%) solution at 60 °C for 100 min followed by etching in Na\textit{ClO} (Arcros Organics, 13% active chlorine, pH \textasciitilde 12.5) solution at 60 °C for 2.5 min. Prior to use 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 completed substrate was then masked using insulating tape to leave only the unmetallized side of the foil exposed to the electrolyte solution. This was served as a working electrode for nanowire deposition.

Electrodeposition

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, respectively. The working electrodes for film deposition were made 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 M Bi\textsuperscript{3+}, 0.01 M HTeO\textsubscript{3}\textsuperscript{+}, 1 M HNO\textsubscript{3}, 0.02M Sb\textsuperscript{3+}, 0.1 M H\textsubscript{2}Cit and 0.05 M Na\textsubscript{Cit}. After deposition the Kapton templates were removed either by dissolving them in organic solvent mixtures of \textit{N}-methyl-2-pyrrolidone (NMP, 30 wt\%) and monoethanolamine (MEA, 70 wt\%) at 100 °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 films and nanowires were characterized using a LEO 1455VP scanning electron microscope (SEM) or JSM-6500F SEM equipped with energy dispersive X-ray (EDX) microanalyzer (Oxford Inca 300) and operated at 20 kV. X-Ray diffraction (XRD) data were collected using a Siemens D5000 X-ray diffractometer with Cu Kα radiation (λ = 1.5406 Å). 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 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.\textsuperscript{29} The peeled film has an area of 1 × 1 cm. Ohmic contact was made by soldering copper wires with In-Sn solder onto the four corners of the film. An average of ~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 Bi\textsubscript{0.5}Sb\textsubscript{1.5}Te\textsubscript{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 ranging from 1.5 to 295 K. \textit{I}–\textit{V} curves of the nanowires were recorded by a source-meter (Keithley 199) and the resistance \textit{R} was extracted by using \textit{R} = d\textit{V}/d\textit{I}.

3. Results and discussion

3.1 Electrodeposition of p-type Bi\textsubscript{0.5}Sb\textsubscript{1.5}Te\textsubscript{3} films

In order to ascertain the appropriate deposition conditions for Bi\textsubscript{0.5}Sb\textsubscript{1.5}Te\textsubscript{3} nanowires, a series of experiments was carried out to examine the effect of deposition conditions on composition, 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 Bi\textsubscript{0.5}Sb\textsubscript{1.5}Te\textsubscript{3} nanowires in Kapton templates. Previous studies have shown that electrodeposition of Bi\textsubscript{0.5}Sb\textsubscript{1.5}Te\textsubscript{3} films is quite challenging due to the fact that it is difficult to achieve sufficient amounts of Sb in the aqueous solution.\textsuperscript{28,31} In this study, citric acid was chosen as a complexing agent to increase the solubility of Sb in the electrolyte solution because citric acid was found to readily form complexes with Sb and has been used as an efficient agent for extraction of Sb in environmental sample analysis.\textsuperscript{32} Fig. 1(a–c) shows the cyclic voltammograms (CV) recorded in various electrolyte solutions containing the individual elements. The deposition of Bi, Te and Sb are occurred at −0.08 V, −0.3 V and −0.4 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 Bi$^{3+}$ + 1 M HNO$_3$; (b) 0.01 M HTeO$_2$$^+$ + 1 M HNO$_3$; (c) 0.02 M Sb$^{3+}$ + 0.1 M H$_3$Cit + 0.05 M Na$_2$Cit; and (d) 0.001 M Bi$^{3+}$ + 0.01 M HTeO$_2$$^+$ + 0.02 M Sb$^{3+}$ + 0.1 M H$_3$Cit + 0.05 M Na$_2$Cit. All voltammograms were recorded at 20°C at a scan rate of 10 mV s$^{-1}$.

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 Bi$_{0.5}$Sb$_{1.5}$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 Bi$_{0.5}$Te$_{1.5}$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.1,23,25 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 Bi$_{0.5}$Sb$_{1.5}$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 Bi$_{0.5}$Sb$_{1.5}$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 µm 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 Ω cm as determined using
the van der Pauw technique. The carrier concentration, Hall mobility and Hall coefficient of the film was found to be $4.7 \times 10^{18}$ cm$^{-3}$, 10.8 cm$^2$ V$^{-1}$ s$^{-1}$, and 1.5 cm$^3$ C$^{-1}$, respectively. The measured Seebeck coefficient of the film was 122 $\mu$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 Bi$_{0.5}$Sb$_{1.5}$Te$_3$ nanowires

Based on the above studies for film deposition, stoichiometric p-type Bi$_{0.5}$Sb$_{1.5}$Te$_3$ nanowires can be deposited at a potential of $-0.08$ 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 $\sim 80$ nm. The pore diameter is monitored by etching conditions such as etching time, temperature and pH of etching solution. By carefully controlling these conditions, polyimide-based templates with pore diameters below 20 nm have been achieved. This demonstrates the possibility of further reducing the nanowire diameter and achieving a high aspect ratio to enhance the thermoelectric properties. The Kapton foil became 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
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 \( \sim 20 \) \( \mu \)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 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 °C for 1 min, as shown in Fig. 5b the 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 obtained wires have an average diameter of 80 nm which is equivalent to the pore size of the Kapton foils. In the case 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 gold peak that originates from the evaporated seed layer only the \{110\} peak of the Bi\(_{0.5}\)Sb\(_{1.5}\)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 Bi\(_{0.5}\)Sb\(_{1.5}\)Te\(_3\) nanowires embedded in Kapton foil (a), and liberated from Kapton foil by dissolving in organic solvent of NMP/MEA at 100 °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).

**Fig. 6** XRD pattern for Bi\(_{0.5}\)Sb\(_{1.5}\)Te\(_3\) nanowires embedded in Kapton foil. The peak around 38° can be attributed to gold that was used as a seed layer for electrodeposition.
3.3 Electrical transport properties of p-type Bi$_{0.5}$Sb$_{1.5}$Te$_3$ nanowires

From 1.5–295 K all the $I$–$V$ curves obtained from the Bi$_{0.5}$Sb$_{1.5}$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 Bi$_{0.5}$Sb$_{1.5}$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. 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 $-0.09$ 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: $R(T) = R_0 \exp(E_g/2k_B T)$, the energy band gap $E_g$ (or thermal activation energy $E_a$), 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 $E_a$ ($E_g$) for the nanowires was found to be 0.089 ± 0.006 eV, which is higher than that of the film, 0.045 ± 0.011 eV. This increased band gap may be due to size effects or carrier localization. Currently, further investigations are being undertaken to prepare p-type Bi$_{0.5}$Sb$_{1.5}$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 Bi$_{0.5}$Sb$_{1.5}$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 Bi$_{0.5}$Sb$_{1.5}$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 Bi$_{0.5}$Sb$_{1.5}$Te$_3$ nanowires. The obtained nanowires have average diameters of 80 nm and lengths of 20 µm 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 ± 0.006 eV, which is higher than that of the film, 0.045 ± 0.011 eV.

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