Thermal conductivity of bismuth telluride nanowire array-epoxy composite

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The thermal-to-electrical energy conversion efficiency of a thermoelectric material is given by its figure of merit, $ZT = \sigma S^2 T/\kappa$, where $\sigma$ is the electrical conductivity in units of $(\Omega^{-1} \text{m}^{-1})$, $S$ is the Seebeck coefficient in units of $(\text{V/K})$, and $\kappa$ is the thermal conductivity in units of $(\text{W/m K})$. Bulk materials based on Bi$_2$Te$_3$, and its alloys have been known as the best thermoelectric materials for applications near room temperature, delivering $ZT$ values as high as 1. Recently, ball-milled, hot-pressed nanocrystalline bulk (Bi$_2$Sb)$_2$Te$_3$ alloys have shown $ZT$ values of $\sim 1.4$ in the temperature range of 340–370 K.\textsuperscript{1,2} Epitaxial nanostructured thin films have exhibited enhanced $ZT$ values, such as a reported $ZT$ at 300 K of 2.4 for a Bi$_2$Te$_3$/Bi$_2$Te$_3$ superlattice grown by molecular beam epitaxy.\textsuperscript{3} Bi$_2$Te$_3$-based materials, when grown in the form of nanowire arrays, may be expected to deliver even higher $ZT$ values than their bulk and thin film counterparts due to enhanced phonon scattering, elastic relaxation of lattice misfit strain, texture control, and scalability to thicknesses required for thermoelectric applications.

The templated electrodeposition technique\textsuperscript{4–9} employing porous anodic alumina (PAA) templates\textsuperscript{10–14} has been widely used for the fabrication of high density, ordered nanowire arrays for thermoelectric applications. The nanowire/PAA composite provides an opportunity to engineer high density, high aspect ratio, ordered, and texture-controlled nanowire arrays in a PAA matrix, yielding a mechanically robust composite as is necessary to assemble the thermoelectric legs into an array of $p$–$n$ couples. PAA, however, has a reported thermal conductivity of 1.7 W/m K,\textsuperscript{15} which is comparable to that of the Bi$_2$Te$_3$ nanowire array,\textsuperscript{16} thus the PAA matrix will act as a parasitic thermal shunt, reducing the effective $ZT$ of the composite, $ZT_{\text{comp}}$. Based on a simple effective medium model that neglects the effects of solid-solid interfaces that are parallel to the temperature gradient, the $ZT$ of the nanowire/matrix composite is given by $ZT_{\text{comp}} = ZT_{\text{nw}} \left[ \frac{1}{1 + \left( \frac{\kappa_m}{\kappa_{\text{nw}}} \right) \left( \frac{f_{\text{nw}}}{1 - f_{\text{nw}}} \right)} \right]^{-1}$, where $ZT_{\text{nw}}$ is the $ZT$ value of the nanowire, $\kappa_m$ is the thermal conductivity of the matrix, $\kappa_{\text{nw}}$ is thermal conductivity of the nanowire, and $f_{\text{nw}}$ is the volume filling fraction of the nanowires in the composite. To mitigate the detrimental effects of the matrix, the nanowire volume fraction should be maximized and the thermal conductivity of the matrix should be minimized.

If the lattice thermal conductivity of the nanowire can be reduced to values that are close to the theoretical minimum for Bi$_2$Te$_3$, $\sim 0.25$ W/m K,\textsuperscript{5} a matrix with a thermal conductivity below 0.25 W/m K will be required to achieve a composite lattice thermal conductivity below 0.25 W/m K. Parylene-N, a vapor-deposited low thermal conductivity polymer ($\kappa = 0.125$ W/m K) has been previously explored as a supporting matrix for embedded Si nanowire arrays with $f_{\text{nw}} = 0.02\text{.}\textsuperscript{17}$ However, due to the high aspect ratio of the template channels, region between the nanowires (height: diameter $\sim 800:1$), and pore volume fraction ($f_{\text{nw}} \sim 0.7$) in PAA templates, parylene would tend to form a continuous film building up over the nanowire sidewalls and closing the channels.\textsuperscript{18} In this work, we demonstrate a process flow to overcome the challenge of the parasitic thermal shunt in the nanowire array composites by fabricating dense, textured, nanowire arrays in a PAA matrix and then replacing the PAA matrix with epoxy resin.

The criteria for selection of epoxy resin for matrix infiltration included thermal conductivity, viscosity, wetting and adhesion, mechanical stability, shrinkage, and thermal stability. A commercially available epoxy resin, SU-8, which is widely used in the microelectronic industry for high-aspect-ratio and three-dimensional lithographic patterning, was chosen for infiltrating the nanowire array. SU-8 is also used as a permanent and functional material in silicon-on-insulator technologies.\textsuperscript{19,20} The epoxy resin SU-8 has a thermal conductivity $\kappa = 0.2$ W/m K,\textsuperscript{21} which is an order of magnitude lower than that of the PAA matrix. Preliminary results describing the replacement of SU-8 with PAA were reported previously.\textsuperscript{22} In the present work, we describe the fabrication process and demonstrate the efficacy of this approach with measurements of thermal conductivity.

Bi$_2$Te$_3$ nanowires were synthesized by galvanostatic electrodeposition into PAA templates (Anodisc 13, 200 nm diameter, Whatman Inc.). The templates were pore widened.
using a 3 wt % KOH/ethylene glycol solution for achieving 72% ± 2.5% porosity. Platinum was e-beam vaporized on one side of the template to serve as a back electrode for electrodeposition. The electrolyte solution consisted of 0.035M Bi(NO$_3$)$_3$.5 H$_2$O (Alfa Aesar, 99.999%) and 0.05M HTeO$_2$ (Te, Alfa Aesar, 99.999%) in 1M nitric acid, and a pH=1 was maintained throughout the process. The nanowires were electrodeposited for a period of 2–3 h depending on the thickness desired, using 3 s pulses of current density 5 mA/cm$^2$ followed by a standby period of 3 s. Following synthesis, the nanowire arrays were mechanically planarized to overcome any overgrowth or nonuniformity in nanowire lengths.$^{23}$

To fabricate nanowire array/SU-8 composites, the PAA template was entirely removed by etching in a 3 wt % KOH solution for 24 h. To prevent collapse of freestanding Bi$_2$Te$_3$ nanowires as a consequence of capillary forces acting on nanowire sidewalls, the rinsing procedure with de-ionized water (72 mN m$^{-1}$) was followed by a lower surface tension solvent, isopropanol (21.8 mN m$^{-1}$). The isopropanol was allowed to evaporate in the solvent hood. This procedure yielded 40 μm thick freestanding planarized Bi$_2$Te$_3$ nanowire arrays. SU-8 2005 was spin coated on the nanowire array at 2000 rpm for 30 s to obtain a resin matrix thickness of 40 μm. The assembly was then dipped in isopropanol for 1 s to remove excess SU-8 on the top surface. This was followed by a 30 min UV processing in a UV flood curing system (Cure Zone 2, 400 W Hg lamp, intensity 30 mW cm$^{-2}$). SU-8 resin contains acid-labile groups and a photodegradation generator, which on irradiation decompose to generate a low concentration of catalyst acid. Subsequent heating of the polymer activates crosslinking and regenerates the acid catalyst. Solvent removal by soft baking is a crucial step contributing to overall film internal stress during processing through volume shrinkage and mechanical stress accumulation.$^{24}$ Optimizing this step improves the resist-nanowire sidewall adhesion. Irradiation followed by postexposure bake leads to an increased degree of crosslinking and stabilization. Since the purpose of the SU-8 matrix is to provide a permanent structural framework for the thermoelectric element, the composite must be hard baked, typically at 150 ºC. The SU-8 processing steps and baking time are presented in Table I. To accommodate the large SU-8 thickness (40 μm), all baking steps were carried out on a leveled hotplate (by conduction) to avoid dried layer formation on the surface, hindering diffusion of solvent from the interior.

**FIG. 1.** (a) FESEM image showing the pristine fractured cross section of an as-grown Bi$_2$Te$_3$ nanowire array/PAA composite. (b) A magnified view of the composite cross section that shows that the crack through the interface between the PAA and the nanowire rather than through the nanowire, in contrast to the observed behavior of cracks in the nanowire/SU-8 composite [Figs. 2(a) and 2(b)].
0.72 ± 0.025, the effective PAA thermal conductivity is 1.31 ± 0.1 W/m K. This value can be used to estimate the contribution from the Bi$_2$Te$_3$ nanowires in the composite, which is calculated to be 1.44 ± 0.1 W/m K. In the second case, the thermal conductivity of the Bi$_2$Te$_3$ nanowire/ SU-8 composite was measured to be 1.1 ± 0.06 W/m K. Using the volume fraction and thermal conductivity of SU-8 as 0.28 ± 0.025 and 0.2 W/m K, respectively, the effective thermal conductivity of the Bi$_2$Te$_3$ nanowires in the composite is 1.45 ± 0.09 W/m K. The thermal conductivity values obtained for Bi$_2$Te$_3$ nanowires lie within the range of experimental error and in conformation with previously reported data.\(^5\)

In conclusion, we have demonstrated a method for overcoming a significant obstacle to utilizing nanowire arrays as thermoelectric materials. The dense (72% nanowire volume fraction) and mechanically robust nanowire array/SU-8 composites fabricated by replacing the PAA template substantially reduce the matrix thermal shunt. Thermal conductivity measurements by the PA technique reflect a 21% reduction in the composite’s thermal conductivity when the PAA matrix (κ=1.31 W/m K) is replaced with SU-8 epoxy resin (κ=0.2 W/m K). This study with relatively large diameter, nonalloyed Bi$_2$Te$_3$ nanowires represents a baseline for the improvements that might be expected from replacing PAA with SU-8. For example, replacement of PAA with SU-8 in a composite with $f_{nw}=0.7$ and smaller diameter alloyed nanowires with an effective thermal conductivity of 1 W/m K would reduce the composite thermal conductivity from 1.09 to 0.76 W/m K, thereby increasing the ZT of the composite by 44%.

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