SPECIFIC HEAT AND THERMAL CONDUCTIVITY MEASUREMENTS PARALLEL AND PERPENDICULAR TO THE LONG-AXIS OF COBALT NANOWIRES

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Abstract

Rapid progress in the synthesis and processing of materials with structure on nanometer length scales has created a demand for greater scientific understanding of nanoscale thermal transport in individual nanostructures of composite materials. This paper reports the synthesis and sample construction as well as measurements of the specific heat and thermal conductivity of cobalt nanowires (CoNWs). Specific heat ($c_p$) and thermal conductivity ($\kappa$) is measured by an AC calorimetric technique from 300 to 400 K parallel and perpendicular to the CoNW long-axis. The specific heat both parallel ($c_p^\parallel$) and perpendicular ($c_p^\perp$) to the long-axis deviates strongly from the bulk amorphous powder behavior above room temperature. The perpendicular thermal conductivity ($\kappa^\perp$) of CoNWs follows a bulk-like behavior revealing a maximum value near 365 K, indicating the onset of boundary-phonon scattering. The parallel thermal conductivity ($\kappa^\parallel$) increases smoothly with the increase of temperature from 300 to 380 K and appears to be dominated by phonon-phonon scattering.

Introduction

Recent advances in synthesis, processing, and microanalysis are enabling the promising materials with structures that varies on the length scale of several nanometers. Examples such as super-lattices, nanotubes, nanowires, quantum dots, polymer nanocomposites, have advantages in optoelectronics, microelectronics, and micro-mechanical sensors. Many of these nanostructures already have important useful commercial applications. Nanowires are especially attractive for nanoscience studies as well as for nanotechnology applications. Because of their unique density of states, narrow cross-section, and large surface area, nanowires are expected to have significantly different optical, electrical, and thermal properties compared to the bulk. These characteristics may enhanced the exciton binding energy, induce diameter dependent band-gaps, and cause surface scattering of electrons and phonons to dominate the transport properties. In most recent technological applications of nanostructures, thermal management is an important issue in managing undesired heating. Such applications would require highly directional and tunable thermal conductivity and specific heats.

There have been several theoretical studies on the thermal conductivity ($\kappa$) of nanowires [6, 1, 17, 5, 4, 16, 9, 3], which has shed light on the physics of their properties. It was found that nanoscale porosity decreases the permittivity of amorphous dielectrics. But porosity also results in a strongly decreased thermal conductivity [14, 6]. Theory suggests that for nanowires with diameters smaller than the bulk phonon mean-free-path ($\lambda_p^B$) the thermal conductivity
of nanowires will be greatly reduced compared to the bulk \cite{6, 17, 5, 16, 9, 3}. However, there are no predictions regarding the influence of nano-confinement on the behavior of the specific heat ($c_p$). Knowledge of both $c_p$ and $\kappa$ is important in determining the thermal relaxation time of materials. It is notable that there have been comparatively few experimental investigations, especially at room temperature and above. The lack of experimental data is due to the difficulty in preparing nanowire samples with the required specification as well as the challenge of precise measurements on such delicate samples. Another important motivation for gathering detailed experimental data on nanowires is the effect of restricted 1-D dimensionality since it is reasonable to expect some anisotropy of physical parameters parallel and perpendicular to the long-axis of the nanowires.

**Synthesis of Cobalt Nanowires**

CoNWs were synthesized by electrodeposition assisted by a homemade anodic aluminum oxide (AAO) template. The AAO templates were obtained by a well-established two-step anodization process \cite{8, 7}. Briefly, the first anodic oxidation of aluminum (99.999% pure, Electronic Space Products International) was carried out in a 0.3 M oxalic acid solution at an anodizing voltage of 40 V at 10 °C for 16 − 20 hr. The porous alumina layer formed during first anodization process is dissolved by chromic acid at 70 °C. The treated samples are subjected to the second anodization with the same conditions as the first. The thickness of the anodic film was adjusted by appropriately setting the anodization time. The resulting AAO templates were then immersed in a 0.1 M phosphoric acid etching solution at room temperature for 30 min to widen the pores and thin the oxide barrier layer at the pole bottom. Pore diameters were controlled to lie in the range of 80 − 120 nm by varying the anodizing voltage and etching times.

Cobalt nanowires were then electrochemically deposited by AC electrolysis from the bottom of the pores up using 14 V at 100 Hz for 150 mins in an electrolyte solution consisting of 240 g/L of CoSO$_4$+7H$_2$O, 40 g/L of HBO$_3$, and 1 g/L of ascorbic acid \cite{8, 7}.

Structural characterization was performed by means of x-ray diffraction using a Rigaku goniometer with Cu K$\alpha$ radiation ($\lambda = 0.15406$ nm), operated routinely at 37.5 kV and 25 mA with 0.5° divergent and anti-scattering slits coupled with 0.3 mm receiving slits. Diffraction patterns were acquired at 2$\theta$ steps of 0.05° and 5 s/step exposures. The filling of the pores as well as the morphology of the nanowire array before and after removing the alumina template was monitored with a JEOL 982 field-emission scanning electron microscopy (SEM).

For comparison, bulk cobalt was obtained from Aldrich Inc. in a fine powder form (99.9% pure) with particle size in the range of 2 to 10 µm. This bulk powder was used after degassing and drying in vacuum at $\sim$ 100 °C for about 2 hr.

**Sample Configuration**

The CoNW samples were prepared in two different ways for directional measurements of heat flow parallel and perpendicular to the long-axis of the nanowires. The sample+cell configuration for the parallel measurement is shown in Fig. 1-RIGHT BOTTOM. The general sample+cell configuration consists of a sandwich (or stack) arrangement of heater, thin silver sheet (0.1 mm thick and 5 mm square), sample, thin silver sheet, and thermistor, all held together by a thin application of GE varnish.

For the parallel configuration, the CoNWs embedded in an AAO template were first separated from the Al substrate by a 0.1% HgCl$_2$ solution, and the barrier layer was removed.
Figure 1: LEFT: SEM micrographs of (a) Anodic aluminium oxide template with 20 µm long and 80 nm diameter parallel non-interconnected cylindrical cavities, (b) "forest" of CoNWs after acid removal of the AAO membrane, and (c) expanded view of CoNWs having 80 nm diameter and extending through the entire thickness of the AAO membrane. The scale bar is 500 nm (a), 5 µm (b), and 500 nm (c). RIGHT TOP: XRD pattern of CoNWs showing different planes. The peaks with 2θ near 41.685° and 47.57° is assigned to planes of (10\bar{1}0) and (10\bar{1}1) of hcp structure. The peak with 2θ near 51.522° is attributed to (200) of the fcc structure. The remaining peaks indexed as M with 2θ could be a combination of diffraction of planes (0002) and (1120) of hcp structure and peaks near 44° and 75° could be a combination of (111) and (220) of fcc structure. RIGHT BOTTOM: Sample + Cell configuration for thermal study. (a) parallel alignment of CoNWs to heat flow. The CoNWs mat is dispersed and sandwich between two silver sheets. (b) Perpendicular alignment of CoNWs to heat flow. H - heater, θ - thermistor, Ag - silver sheet. CoNW+AAO template is sandwich between the two silver sheet, heater is connected at the bottom of one silver sheet and a microbead thermistor is connected on the top surface of other silver sheet.
by wet etching in 0.5% H$_3$PO$_4$ for 30 mins. To ensure a good thermal contact between the CoNWs and the silver sheets, the AAO template is etched by 0.1 M NaOH solution to expose the tips of the CoNWs from both ends. This 20 µm thick CoNW+AAO sample is then carefully sandwiched between the two silver sheets and secured by a thin layer of GE varnish. A 120 Ω strain-gauge heater is attached on one side of the stack and a 1 MΩ carbon-flake thermistor on the other side by GE varnish. In this arrangement, the applied heat should transfer along the nanowires. A measurement of each element of the sample+cell package was made separately in order to subtract the heat capacity and thermal conductance of the cell and AAO and so, isolate the CoNW contribution.

Measurements with the heat flow perpendicular to the long-axis of the nanowires were conducted in a similar arrangement. The CoNW embedded AAO template was immersed in a 0.1 M NaOH solution to completely dissolve the AAO and release the nanowires. The powder form of CoNWs was then dispersed in a solvent and drop cast onto one of the cell’s silver sheets. This deposition results in a mat-like arrangement of the CoNWs approximately 0.1 mm thick and essentially perpendicular to the stack. The remaining components of the cell are attached again by a thin application of GE varnish. It is important to note that although the geometry has the heat transfer perpendicular to the nanowire long-axis, there are a large number of contacts between the sides of the nanowires in the layer of CoNWs. The bulk powder measurements were done in the same way with a similar film thickness. All sample+cell arrangements had essentially identical areas.

The AC calorimetric technique used to measure heat capacity and thermal conductivity is described elsewhere [12, 11]. Estimation of specific heat and effective thermal conductivity of the bulk cobalt and nanowires is straightforward. Each component of the above described sample+cell arrangement was measured separately to determine the contribution of the thin silver sheets, heater, thermistor, and GE varnish. In addition, an empty AAO template was also measured. The specific heat ($c_p$) is then calculated by subtracting these contributions from the total heat capacity and dividing by the cobalt mass. The thermal conductivity estimation for these macroscopic samples requires the assumption that the entire sample volume of thickness $L$ and area $A$ is filled by the cobalt for the bulk powder and perpendicular configuration samples since the filling fraction is not known. For the parallel configuration, $\kappa_\parallel$ of the nanowires is estimated by assuming that the AAO and CoNWs are in a parallel circuit arrangement. Thus, it is expected that the thermal conductivity measured here is an effective $\kappa$ and would have a higher uncertainty in its absolute value than that for the specific heat.

**Morphology CoNWs**

Figure 1-LEFT shows SEM images of CoNWs embedded in the AAO templates. In Fig. 1-LEFT(a), an oblique view of the sample before etching by NaOH solution showing the highly ordered hexagonal pattern of the AAO pores. The pore diameter and interpore separation are about 80 and 40 nm, respectively. Figure 1-LEFT(b) is an SEM image of the CoNWs with the tips exposed by about 3 µm and Fig. 1-LEFT(c) is a high-magnification image of the cobalt nanowires.

A microstructure study of the resulting CoNWs was performed by x-ray diffraction (XRD) and shown in Fig. 1-RIGHT TOP. From the scattering angle $2\theta$ dependence of the x-ray intensity it is shown that the CoNWs consists of a mixture of fcc and hcp structures. This is consistent with an nuclear magnetic resonance (NMR) study by Strijkers et al. [13] although direct current was applied there to synthesize CoNWs. The XRD peaks at $2\theta$ near 41.685°
Figure 2: LEFT: Specific heat of bulk powder cobalt (triangles) and cobalt nanowires measured perpendicular (solid circles) and parallel (open circles) to the long-axis of the 20 µm long, 80 nm diameter, CoNWs from 300 to 400 K. RIGHT: (a) Effective thermal conductivity of bulk Co as a function of temperature from 300 to 400 K obtained from Aldrich (99.99% pure powder form). (b) Effective thermal conductivity of CoNWs as a function of temperature in long-axis (open circles) and off-axis (dots) from 300 to 400 K. Arrows indicate the temperature where phonon-phonon scattering begins to dominate.

and 47.57° can be assigned to the (10\bar{1}0) and (10\bar{1}1) planes of an hcp structure. The peak at 2θ near 51.522° is attributed to the (200) plane of a fcc structure. The remaining peaks indexed as M in Fig. 1-RIGHT TOP could be a combination of diffraction from the (0002) and (1120) planes of the hcp structure. Alternatively, the peaks near 44° and 75° could be a combination of the (111) and (220) planes of the fcc structure. It is also shown that the fabricated Co nanowires have a preferential orientation (0002). The preferentially oriented growth of the nanowires is attributed to the growth of the nanowires within the pores of the alumina film. No diffraction peaks from cobalt oxide or from the alumina are seen, indicating that cobalt nanowires obtained by AC electro-deposition are of high purity.

Specific Heat of CoNWs

The specific heats of bulk powder cobalt as well as CoNWs in parallel and perpendicular to the long-axis configuration are shown in Figure 2-LEFT. The specific heats of all samples were determined as a function of temperature from 300 to 400 K. The cobalt bulk powder sample yields a $c_p^B = 0.49 \text{ J g}^{-1} \text{ K}^{-1}$ at 300 K and a weak, nearly-linear, temperature
dependence consistent with the literature [10, 2]. The magnitude of the specific heat for the two CoNW samples are $c_p^\parallel = 0.53 \text{ J g}^{-1} \text{ K}^{-1}$ and $c_p^\perp = 0.50 \text{ J g}^{-1} \text{ K}^{-1}$ at 300 K. For the parallel CoNW configuration, $c_p^\parallel$ increases linearly from room temperature to $\sim 320$ K in a bulk-like fashion. Above 320 K, $c_p^\parallel$ increases much more rapidly with temperature than the bulk. In the case of perpendicular measurement, $c_p^\perp$ increases more rapidly than either the parallel or the bulk behavior from 318 to 370 K, above which it begins decreasing.

The differences in $c_p$ observed here are likely due to the composite nature of the sample+cell configuration. The similarity, at least just above room temperature, between $c_p^\parallel$ and $c_B^\parallel$ is understandable as in this heat-flow configuration, the length of the CoNW is comparable to the size of the bulk powder sample. The deviation beginning at $\sim 320$ K may be a consequence of the 1-D nature of the nanowires. As a result, one might expect ”bunching” of the phonons (or phonon-phonon scattering) to dominate at some elevated temperature. For the perpendicular arrangement and although laying flat to the silver sheets, the random deposition of CoNWs within the cell likely results in a very large number of contacts, on the nanometer scale, between individual CoNWs. Thus, the $c_p^\perp$ measured is almost certainly an effective result for the sample+cell composite.

**Thermal Conductivity of CoNWs**

Figure 2-RIGHT(top panel) shows the effective thermal conductivity of bulk powder cobalt at 300 K of $\kappa_B \approx 67 \text{ W m}^{-1} \text{ K}^{-1}$ with a strong temperature dependence reaching a maximum at $\sim 360$ K. The literature value for pure cobalt at 300 K is 90 W m$^{-1}$ K$^{-1}$ and displays a weak temperature dependence [15]. As with $c_p^\perp$, the effective thermal conductivity of bulk powder cobalt measured here is a consequence of the composite nature of micron sized amorphous particles sandwiched in the cell ”stack”. As such, it seems likely that the observed maximum is due to boundary-phonon scattering.

The derived thermal conductivity of the CoNWs for the two heat-flow configurations are shown in Fig. 2-RIGHT(bottom panel). Both $\kappa^\parallel$ and $\kappa^\perp$ have values 83 times less than the bulk at 300 K. However, for increasing temperatures, $\kappa^\parallel(T)$ behaves quite differently from the observed bulk trend, increasing in a smooth manner up to $\sim 380$ K at which a small ”kink” is seen to a nearly constant value of $\kappa^\parallel \approx 4 \text{ W m}^{-1} \text{ K}^{-1}$. Although the uncertainty in absolute values is higher for the measured $\kappa$ compared to $c_p$, the marked reduction of magnitude of $\kappa$ in both configurations with respect to the bulk is consistent with the 1-D nature and boundary scattering. However, for $\kappa^\parallel$, the kink to a constant value at $\sim 380$ K may be an indication of phonon-phonon and defect-phonon scattering. For the perpendicular heat-flow measurement of CoNWs, $\kappa^\perp$ exhibits a similar temperature dependence as the bulk, although of greatly reduced magnitude. As with $\kappa_B$, the observed maximum for $\kappa^\perp$ seen at $\sim 360$ K is again likely due to the composite nature of the sample+cell arrangement. The junctions between the nanowires dominate the heat transfer for $\kappa^\perp$ as the contacts between bulk powder particles were for $\kappa_B$. The difference in temperature for the observed maximum is consistent with the bulk powder particles being of much larger size (microns) compared to the width of the nanowires.

**Conclusions**

This paper reports measurements of the specific heat and effective thermal conductivity of a macroscopic arrangement of cobalt nanowires, CoNWs, with the orientation of the nanowire parallel and perpendicular to direction of the heat-flow and compared with re-
sults for bulk-powder cobalt. The particle nature of the bulk-powder and random deposition of the CoNW(⊥) configuration, lead to strong deviations of both $\kappa$ and $c_p$ from that expected for pure solid cobalt. For these samples, the introduction of peak-like maximums in $\kappa$ and in $c_p$ for the CoNW(⊥), which also has a much stronger temperature dependence, are observed. An analysis suggests that these features are the result of the dominance of phonon-boundary scattering. The more controlled, uniform and oriented, CoNW(∥) sample exhibits smooth temperature dependence of the thermal properties that appears dominated by phonon-phonon or phonon-defect scattering. These results suggest the interesting possibility of engineering both the specific heat and thermal conductivity of composite materials containing nanowires that can be exploited for a wide range of applications.

References


