Thermal Transport of Tin Dioxide Nanowires

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Abstract. Temperature dependent thermal conductivities of individual Tin Dioxide (SnO$_2$) nanowires have been studied via a suspended microdevice method. Thermal conductivity of SnO$_2$ nanowires is found to be less than 20\% of the bulk value in the whole measurement temperature range and the peak shifts to a higher temperature about 110 K compared with that of its bulk counterpart at around 26 K. This study demonstrated experimental results and analysis of thermal transport property of one-dimensional SnO$_2$ nanostructure.

1. Introduction

Oxide materials has drawn increasing interest and became promising candidates for various novel materials, because they are nontoxic, naturally abundant, stable and durable in air, minimal environment impact and composed of cheap and light elements. Tin dioxide is one of important n-type non-toxic semiconductor with a wide band gap of 3.6 eV at 300K and highly achievable carrier concentration\textsuperscript{1,2}, which is a suitable candidate for a wide range of technological applications in transparent conducting electrodes\textsuperscript{3,4}, gas sensors\textsuperscript{5,6}, varistors\textsuperscript{7}, catalyst supports\textsuperscript{8}, optoelectronic\textsuperscript{9} and thermoelectrics\textsuperscript{10-18}. Its electrical and optical properties with and without doping have been widely studied\textsuperscript{2,20-22}. However, few work\textsuperscript{19} has been done to study the thermal transport property of SnO$_2$, especially for the low dimensional nanostructures, which is unique from the macroscopic properties and independent of its size and geometry. Understanding and managing the thermal transport in nanostructured SnO$_2$ is essential for reliable and efficient operation of related metal oxide applications, such as varistors and thermoelectrics.

In the present work, we fabricated the single crystal SnO$_2$ nanowires using the Au-catalyzed vapor-liquid-solid (VLS) method and subsequently characterized the intrinsic thermal conductivity of SnO$_2$ nanowires by multiple measurement method.
2. Experimental

2.1. Materials Synthesis and Structural Characterization
Single crystalline SnO$_2$ nanowires are synthesized by the Au-catalyzed VLS method. The synthesis of SnO$_2$ nanowires was carried out in a horizontal quartz tube in the three zone furnace. The Sn powder precursor was placed upstream in a quartz boat. The Si substrates with the 10 nm Au particles on it were placed in the same quartz boat downstream of the precursor. The boat was positioned in the center of quartz furnace tube and then heated to 920°C for one hour at a ramping rate of approximately 20 degrees per minute. Argon was used as the carrier gas, and the tube was evacuated and the pressure inside the furnace at around 300 Torr mbar during growing SnO$_2$ nanowires.

The diameter ($D$) of as-synthesized SnO$_2$ nanowires ranges from 70 nm to 150 nm and the length at around tens of microns. The TEM image (Figure 1(a)) and high resolution TEM (HRTEM) image (Figure 1(b)) of a SnO$_2$ nanowires are shown in Figure 1. The corresponding Fourier transform electron diffraction pattern is shown in the inset of Figure 1(b). The Au catalyst nanoparticles are clearly visible on the tips of the nanowires in Figure 1(a), which confirms the VLS growth mode. HRTEM and SAED pattern display that the SnO$_2$ nanowires are single crystals with a tetragonal rutile structure, and the growth direction is [101].

![Figure 1. The scanning transmission electron microscopy (TEM) image (a) and the high resolution transmission electron microscopy (HRTEM) image (b) of a SnO$_2$ nanowire. The inset of (b) gives the SAED pattern. The growth direction of the nanoribbon is [101].](image)

2.2. Thermal Conductivity Characterization
The thermal conductivity of as-synthesized SnO$_2$ nanowires was characterized using suspended microdevices$^{23}$ by the differential method to cancel out the background noises$^{24}$ and the multiple-measurement approach was adopted to estimate the contact thermal resistance and obtain the intrinsic thermal conductivity$^{25}$, which was described in our previous work$^{26}$. Individual SnO$_2$ nanowire was placed like a bridge across the two suspended membranes by a home-made micromanipulator and each SnO$_2$ nanowire was measured four times with different suspended length to determine the contact thermal resistance. In this method, the contact thermal resistances are assumed to be the same among multiple measurements for every sample. After that, two Pt/C contacts formed by electron beam induced deposition (EBID) were deposited on top of platinum electrodes after all the measurements, which has been verified to be an effective way to reduce contact thermal resistance between 1D nanostructures and underneath electrodes$^{26}$. The diameter ($D$) and suspended length ($L_s$) of each measurement was estimated from the SEM images.
3. Results and Discussion
As mentioned above, each SnO$_2$ nanowires were measured four times to estimate the contact thermal resistance ($R_c$). As seen in Figure 2 (a), the total thermal resistance ($R_{tot}$) of Sample 1 (S1: $D = 93$ nm) was measured with suspended length ($L_s$) of 3.3 μm first. Then this sample was transferred and realigned to another device with larger gap. The same measurements were did with 6 μm (Figure 2 (b)), 6.8 μm (Figure 2 (c)) and 8 μm (Figure 2 (d)), respectively.

![Figure 2](image)

**Figure 2** The SEM images of a SnO$_2$ nanowire (S1) with suspended lengths between the two membranes of 3.3 μm (a), 6 μm (b), 8 μm (c), 6.8 μm (d), and 6.8 μm with Pt/C composites on the contacts (d).

As shown in Figure 3 (a), the total thermal resistance per unit length of S1 decrease with increased suspended length due to the reduced ratio of contact thermal resistance to the total thermal resistance, under the precondition of the same contact thermal resistance for all measurements of the same sample. The linear fitting of $R_{tot}$ as a function of $L_s$ at each temperature gives $R_c$ at the y-axis intercept and the inset of Figure 3 (a) plots the case at 300K and gives us $R_c = 8.65 \times 10^6$ K/W. Following the same procedure, we obtained the contact thermal resistance at whole temperature range and the ratio of $R_c$ to $R_{tot}$ with suspended length of 8 μm, shown in Figure 3 (c). The ratio has a maximum value of 20 % at 50 K and then decrease to about 8 % at 400 K. After eliminating the contact thermal resistance, the intrinsic thermal conductivity can be extracted and the values were plotted in the same figure with effective thermal conductivity with four different suspended length. In Figure 3 (b), we can see that the effective thermal conductivity of S1 increases with $L_s$ because of the reduced contribution of $R_c$ to $R_{tot}$. And the calculated intrinsic thermal conductivity is 14.97 W/m-K, which is about 14 % higher than that of effective value (13.14 W/m-K) obtained with $L_s = 8$ μm.
Figure 3 (a) Thermal resistance values per unit length of S1 measured with suspended lengths of 3.3 μm, 6 μm, 6.8 μm, 8 μm, and 6.8 μm with Pt/C composites. The inset shows the measured $R_{\text{tot}}$ as a function of $L_s$ at 300 K. The dash line is the linear fitting of the experimental data and the y-axis intercept gives $R_c = 8.65 \times 10^6$ K/W. (b) Effective and intrinsic thermal conductivities obtained for S1. (c) The ratio of $R_c$ to $R_{\text{tot}}$ measured with $L_s = 6.8$ μm.

After four effective thermal conductivity measurements of S1, a thermal anchor was deposited on the contact area of nanowire and two electrodes with $L_s = 6.8$ m, shown in Figure 2 (e). Pt/C deposition by EBID on top of platinum electrodes has been verified to be an effective way to reduce the contact thermal resistance at the interface between the nanowire and membranes. Thus the thermal resistance of suspended nanowire dominates over that of the contacts and the obtained effective thermal conductivity of the nanowire with Pt/C anchor is very close to the intrinsic value, especially at higher temperature range above 200 K. The value with Pt/C composites in $L_s = 6.8$ m are even larger than effective thermal conductivity with $L_s = 8$ m over the whole temperature range, which is shown in Figure 3 (b). Therefore, the contact thermal contact between the SnO$_2$ nanowires and membranes can be highly enhanced by Pt/C deposition.

Following the same measurements, the effective and intrinsic thermal conductivity of another SnO$_2$ nanowire ($D = 112$ nm) as Sample 2 (S2) was measured. And Sample 3 (S3), a thinner SnO$_2$ nanowire with diameter of 83 nm, was measured just once at one suspended length ($L_s = 9.9$ m) but with Pt/C composites deposited on the contacts. In total, we have measured three SnO$_2$ nanowires and the thermal conductivity of them was displayed in Figure 4. The inset of Figure 4 shows the thermal conductivity comparison of bulk SnO$_2$ and S2 in our measurement. Three features can be seen from the temperature dependence of the thermal conductivity. First, the thermal conductivity of SnO$_2$ nanowires is strongly diameter-dependent, which indicates that enhanced boundary scattering has a strong effect on phonon transport in SnO$_2$ nanowires. Second, the thermal conductivity values were highly suppressed compared to the bulk values. In the temperature range from 20 K to 300 K, the thermal conductivity of our three SnO$_2$ nanowires are in the interval of 2 – 27 W/m-K, which is less than 20% of the bulk value ($k_{\text{bulk}} = 1664$ W/m-K at 27 K and $k_{\text{bulk}} = 84$ W/m-K at 300 K), due to an increased phonon–boundary scattering rate in nanostructured materials. Another striking feature is that the peak of thermal conductivity shifts to around 110 K independent of diameter of nanowires, which is higher than the temperature corresponding to the peak thermal conductivity of the bulk SnO$_2$ single crystal (∼ 26 K). The peak shift suggests that, as the wire diameter is reduced, the phonon mean free path is limited by phonon boundary scattering as opposed to phonon–phonon Umklapp scattering, which decreases the thermal conductivity with an increase in temperature.
Figure 4 The measured thermal conductivities of the three SnO$_2$ nanowires before Ar/O$_2$ plasma treatment. The inset shows the thermal conductivity of bulk SnO$_2$ and S2 in our measurement.

4. Conclusion
In summary, we have measured thermal conductivity of SnO$_2$ nanowires with different diameters. Thermal conductivity is found to be less than 20% of the bulk value in the whole measurement temperature range and the peak shifts to a higher temperature about 110 K compared with that of its bulk counterpart at around 26 K. And thermal conductivity of SnO$_2$ nanowires is temperature and size dependent. With the diameter increasing, the thermal conductivity increases. These results indicate that the phonon boundary scattering dominate in thermal transport of SnO$_2$ nanowires. This work suggests that the compressed thermal conductivity of SnO$_2$ nanowire could benefit the thermoelectric property in thermoelectric application.

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