Porous Silica Nanotube Thin Films as Thermally Insulating Barrier Coatings

Derric B. Syme  
*Brigham Young University - Provo*

Jason M. Lund  
*Brigham Young University - Provo*

Brian D. Jensen  
*Brigham Young University - Provo*

Robert C. Davis  
*Brigham Young University - Provo*

Richard R. Vanfleet  
*Brigham Young University - Provo*

*See next page for additional authors*

**Original Publication Citation**


**BYU ScholarsArchive Citation**

https://scholarsarchive.byu.edu/facpub/5086

This Peer-Reviewed Article is brought to you for free and open access by BYU ScholarsArchive. It has been accepted for inclusion in Faculty Publications by an authorized administrator of BYU ScholarsArchive. For more information, please contact ellen_amatangelo@byu.edu.
Porous Silica Nanotube Thin Films as Thermally Insulating Barrier Coatings

Derric B. Syme, Jason M. Lund, Brian D. Jensen, Robert C. Davis, Richard R. Vanfleet, and Brian D. Iverson*

ABSTRACT: The fabrication and examination of a porous silica thin film, potentially for use as an insulating thin film, were investigated. A vertically aligned carbon nanotube (CNT) forest, created by chemical vapor deposition (CVD), was used as scaffolding to construct the porous film. Silicon was deposited on the CNT forest using low-pressure CVD (LPCVD) and then oxidized to remove the CNTs and convert the silicon to silica for electrical or thermal passivation (e.g., thermal barrier). Thermal conductivity was determined using a 1D heat-transfer analysis that equated radiative heat loss in a vacuum with conduction through the substrate and thin film stack. A comparison of the surface temperature differences between a sample film and a reference of comparable thermal resistance enabled determination of the increase in the thermal resistance and of the thermal conductivity of the films. For film thicknesses of approximately 55 μm, the cross-plane thermal conductivity was found to be 0.054−0.071 W m⁻¹ K⁻¹ over 378−422 K. This thermal conductivity value is in the range of other silica aerogels and consistent with the low gravimetric density of 0.15 g cm⁻³ for the samples. The film is also relatively smooth and flat, with an average arithmetic mean roughness of 1.04 μm.

KEYWORDS: silica, carbon nanotube, thin films, insulation, MEMS, thermal barrier, aerogel

Carbone nanotubes (CNTs) can achieve incredible length-to-diameter ratios. With a diameter of just a few nanometers wide, practical length-to-diameter ratios can be greater than 10000:1, providing relatively large surface area with little volume. The thermophysical and geometric properties for CNTs make them attractive for constructing thin-film materials for use in thermal applications. Robust, high-aspect-ratio microstructures, including micoscale films, have been fabricated in a process called CNT-templated microfabrication (CNT-M). In CNT-M, a patterned CNT forest acts as a scaffold, which is infiltrated or coated with additional materials. The conditions and duration of an infiltration procedure can be controlled to result in highly dense or highly porous forest regions. Control of the porosity of the structure and the ability to use insulating materials as scaffolding in a porous thin film makes CNT-M intriguing for use in the creation of a thermally or electrically insulating layer for a microelectromechanical system (MEMS) and other microscale sensors.

Traditional insulating materials in MEMS, such as silicon oxide or silicon nitride, while having a much lower thermal conductivity than silicon, have values larger than that required for many MEMS applications. Further, thermal or electrical cross-talk can affect the sensor sensitivity and accuracy. Attempts to incorporate other insulating materials, such as silica aerogels, into microdevices have failed to preserve the material's low thermal conductivity. Aerogels are lightweight, synthetic materials that can be fabricated from a variety of chemical compounds [including silica (SiO₂)] but they generally lack structural integrity and do not have a clear path for MEMS integration. Recent explorations into using nanostructures to create spectrally selective surfaces for radiative cooling indicate promise in tailoring thermal and structural properties. Silica-based, porous materials constructed from nanoparticles have also appeared in recent literature, demonstrating low thermal conductivities of 0.10−0.16 W m⁻¹ K⁻¹ using sol−gel methods to obtain free-standing silica monoliths.

This work explores the capability of using insulating thin films, constructed using CNT-M, as a thermal barrier in MEMS sensors and similar applications by determining the thermal conductivity of porous silica nanotube thin films. CNT-M affords the method to create insulating thin films that can be integrated into MEMS/nanoelectromechanical system (NEMS) sensor architectures by infiltrating CNT forests with...
low-pressure chemical vapor deposition (LPCVD) of silicon and then oxidizing at high temperatures to simultaneously burn out the carbon and oxidize the silicon. The result is a porous silica structure similar to an aerogel. However, a structure of this kind offers several specific benefits relative to aerogels. First, porous silica films in this work offer the ability to easily and preferentially locate insulating regions on a substrate through lithographic patterning or liftoff of the iron catalyst used for CNT growth. Second, control of the CNT growth height readily offers control of the film thickness (and associated thermal and electrical resistance); the terminal film thickness or CNT growth height is achieved in less than a 1 or 2 min (typically on the order of tens of seconds). Third, our approach offers a rigid, surface-mounted insulating layer. It is this flexibility in patterning and control of the dimensions that make this material particularly attractive, while also providing a low thermal conductivity. It is envisioned that these porous silica thin films may be used to isolate measurements that would otherwise require a suspended MEMS structure, as in the case of a thermal conductivity detector or a microbolometer. Patterned silica structures of this kind have been demonstrated to be effective for use in chromatography. The current work demonstrates that structurally stable, insulating thin films can be created using CNT scaffolds to achieve a porous insulating material and seeks to quantify the cross-plane thermal conductivity.

Porous silica films were produced following the CNT-M procedure shown in Figure 1a–c and procedures similar to those in previous CNT-templated works. Aluminum oxide (50 nm, e-beam evaporation) and iron (4 nm, thermal evaporation) were deposited onto a silicon wafer. CNTs were grown using a chemical vapor deposition (CVD) process of flowing ethylene (C2H4) over an iron catalyst at elevated temperature. In a 2.54-cm-o.d. tube furnace, samples were brought to 750 °C in the presence of flowing hydrogen (H2) at 310 sccm. At temperature and while still flowing H2, 340 sccm of ethylene was introduced for 50 s, growing CNTs of 40–60 μm height (55 μm average). After growth, H2 and ethylene were turned off, and argon was flowed over the samples for 1 min. The furnace heating was then turned off, while argon continued to flow in order to cool the sample. Once grown, CNTs were treated with ozone to improve silicon deposition. Gas-phase ozonation oxidizes the CNTs, which primes and increases the number of nucleation sites on the tubes and facilitates conformal growth of silica along the CNT. To ozone the CNTs, the O3 gaseous reagent is passed over the forest with an Atlas 30 ozone generator (Absolute Ozone, Edmonton, Alberta, Canada) at an O3 flow rate of 6.7 × 10−6 m3 s−1 with the current set at 45%, producing approximately 4.4 g h−1 of ozone. CNT samples were placed in a 2.54-cm-o.d. fused-silica tube, purged for 1 min with oxygen (O2), then exposed to the ozone flow for 45 min, before finally being purged again for 1 min under an O2 flow and then removed. Sample scanning electron microscopy (SEM) images of the CNT template are shown in the Supporting Information.

Figure 1. (a) Vertically aligned CNTs grown using a lithographically patterned catalyst. (b) Uniform silicon infiltration of the CNT forest using LPCVD. (c) Oxidation in an O2-rich furnace, burning away the CNTs and leaving a (d) porous silica structure.
approximately 1–4 cm² area were used for thermal conductivity testing.

The density of the porous silica films was determined by separating the thin film from the substrate with a razor blade and weighing it. The volume of the film was determined from the base area of the growth substrate and measured height of the film. When the mass of the film was divided by its volume, the density of the porous silica film was obtained. Density measurements indicated that the porous silica film is similar to that of an insulating silica aerogel. The volume for a 2 × 2 cm film grown to 15 μm height was 0.006 cm³. A typical sample of this kind weighed 0.9 mg, resulting in a density of 0.15 g cm⁻³. For comparison, the density of silica aerogels can range from 0.001 to 0.7 g cm⁻³. Silicon deposition successfully infiltrated the entire depth of the CNT forest, but deposition was observed to be somewhat thicker at the top of the CNTs than at the base (Figure 1d).

The surface roughness and film height were measured with an optical profilometer (Zeta Instruments 20). Samples were scraped along a segment of the thin film to expose the substrate and measure the height disparity between the substrate and thin film. Sample thicknesses were approximately 55 μm and approximately the same height as the original CNT forest before infiltration and burnout. The surface roughness was determined by interrogating an area of 71 × 95 μm (the largest available aperture area). The average arithmetic mean roughness and root-mean-square roughness of four tested films were 1.04 [standard deviation (SD) = 0.19] and 1.33 μm (SD = 0.28), respectively. The maximum peak height and valley height were 4.93 μm (SD = 0.72) and 5.62 μm (SD = 2.28), respectively. Additional specifics regarding the surface morphology, roughness characteristics, and surface imaging is provided in the Supporting Information.

As a governing parameter in the conduction of thermal energy and to quantify the porous silica’s thermal insulating properties, the thermal conductivity was measured. 1D heat transfer was established, and the thermal resistance across the thin film was determined with the aid of a reference measurement. The layers of material present in the test condition and the associated thermal resistance for each layer are shown in Figure 2 (with the thermal resistance associated with the porous silica film highlighted in blue; Figure 2d).

To heat the silicon substrate to steady state and establish 1D heat transfer, samples were placed on a 5.1 × 2.7 × 1.3 cm copper block to act as a large, isothermal substrate that was heated by an attached thin-film heater. Four T-type thermocouples were placed in the copper block 1.3 cm from each side edge and 0.3 and 0.8 cm from the top surface, embedded half-way into the block to ensure isothermal conditions in the copper. Thermal insulating foam encased the sides and bottom of the copper block and heater to reduce heat loss and further ensure isothermal conditions. Test samples were placed on top of the isothermal copper block and heated via conduction. Accompanying temperature measurements of the copper block at steady state for each test confirmed temperature uniformity, as noted in the Supporting Information.

During testing, a reference sample and one or more test samples were placed on the heated copper substrate. The copper substrate was painted black in regions where the test samples were not located (Figure 2). The black paint (emissivity ε = 0.97; Krylon Ultra Flat Black) enabled use of an IR camera (FLIR SC6103) to measure surface temperature variation of less than 4 μm, heat loss from the sides of the samples was neglected, resulting in 1D conduction heat transfer through the sample thickness and heat loss from the samples radiated to the vacuum chamber walls at ambient temperature. The thermal resistances in the stack are identified by each layer comprising the sample (Figure 2), namely, silicon substrate (Rsi), alumina diffusion barrier (Rdi), iron catalyst (Rcis), porous silica (Rps), and black paint (Rp). The conduction resistance for these

![Figure 2](https://dx.doi.org/10.1021/acsanm.0c00596)
layers can each be calculated using \( R = L / kA \), assuming 1D, steady-state conduction and constant properties (where \( L \) is the thickness, \( k \) is the thermal conductivity, and \( A \) is the area of each layer). An additional contact resistance \( (R_c) \) is present and includes a thin layer of vacuum grease used for good contact between the substrate and sample. The reference test, which excludes the resistance associated with the porous silica material in the test conditions excluding the resistance combined, creating composite resistance associated with all other layers and the film with the porous silica material. This composite resistance can be determined by measuring the temperature difference across the reference sample \( (\Delta T_{\text{ref}}) \) and calculating the radiative heat rate, leaving the surface of the reference sample, as given in eq 2.

\[
q_{\text{comp}} = \frac{\Delta T_{\text{ref}}}{R_{\text{comp}}}
\]

This heat rate \( (q_{\text{comp}}) \) is equivalent to the net radiative heat-transfer rate \( (q_{\text{rad}}) \) shown in eq 3 because the heated surfaces are small relative to the isothermal vacuum chamber.\(^{20}\)

\[
q_{\text{rad}} = \varepsilon \sigma (T_t^4 - T_{\text{surf}}^4)
\]

where \( T_{\text{surf}} = 296.15 \text{ K} \) (as measured by a thermocouple placed on the aluminum chamber wall), \( \varepsilon \) is the emissivity, \( A \) is the surface area, and \( \sigma \) is the Stefan–Boltzmann constant \( (5.67 \times 10^{-8} \text{ W m}^{-2} \text{ K}^{-4}) \). With \( q_{\text{comp}} \) and \( \Delta T_{\text{comp}} \) obtained, the composite resistance is readily calculated and used to determine the resistance to heat transfer across the layers of material in the test conditions excluding the resistance associated with the porous silica film.

A measurement similar to that outlined above for the reference conditions is performed simultaneously for test surfaces that include a porous silica film, introducing an additional layer of resistance. With \( R_{\text{comp}} \) known from measurements associated with the reference conditions, the rate of radiative heat loss (calculated using a new surface temperature \( T_t \) for the test conditions) can be equated to the measured \( \Delta T_{\text{test}} \) divided by the sum of the composite resistance and the resistance associated with the porous silica film, yielding eq 4.

\[
\varepsilon \sigma (T_t^4 - T_{\text{surf}}^4) = \frac{\Delta T_{\text{test}}}{R_{\text{comp}} + R_{ps}} = \frac{\Delta T_{\text{test}}}{\frac{L_{t}}{k_{\text{comp}}} + \frac{L_{ps}}{k_{ps}}}
\]

The only unknown in eq 4 is the cross-plane thermal conductivity of the porous silica film \( (k_{ps}) \), which can now be obtained by inserting the known expression for the thermal conductivity of the composite, yielding eq 5.

\[
T_t \text{ and } T_{\text{comp}} \text{ are the top surface temperatures, read from the thermal camera, of the porous silica and reference composite sample, respectively.}
\]

\[
k_{ps} = \frac{L_{ps}}{\frac{\Delta T_{\text{rad}}}{\varepsilon \sigma (T_t^4 - T_{\text{surf}}^4)} - \frac{\Delta T_{\text{comp}}}{\varepsilon \sigma (T_{\text{comp}}^4 - T_{\text{surf}}^4)}}
\]
Overall thermal conductivity. In air, this occurs in pores of 40 nm diameter and smaller and can reduce the thermal conductivity to less than 0.004 W m⁻¹ K⁻¹. It is possible that changes in the thermal conductivity may also be observed for a ~25% increase in the thermal conductivity when including the influence of the interstitial fluid (air), assuming a ~93% porosity material. However, the Knudsen effect, which occurs when a material’s pore diameter is less than the mean-free path of the gas molecules, may reduce the overall thermal conductivity. In air, this occurs in pores of 40 nm diameter and smaller and can reduce the thermal conductivity to less than 0.004 W m⁻¹ K⁻¹. Additionally, it should be noted that this thermal conductivity measurement method yields an average value over the film thickness at the micron scale for an inhomogeneous material at the nanoscale. It is possible that changes in the thermal conductivity may also be observed for different porous silica thicknesses if the plasma-enhanced CVD coating thickness at the top and bottom of the film is appreciably different or if burnout of the carbon varies for different thicknesses.

This work reports on a fabrication method for porous silica films and determines the thermal conductivity of these films, created using CNTs as a scaffold. The porous silica film may be used in MEMS/NEMS structures because it has excellent thermally insulating properties, with a thermal conductivity of approximately 0.062 W m⁻¹ K⁻¹ in the range of 378–422 K.

This thermal conductivity value is in the range of other silica aerogels and has a very low density of 0.15 g cm⁻³. The film is also relatively smooth and flat, with an average arithmetic mean roughness of 1.04 μm. The porous silica films demonstrate the ability for CNTs to be used as a structural template for the fabrication of micro/nanostructures. Future work includes the use of alternative coating materials besides silicon/silica, opening interesting possibilities in material creation.

**ASSOCIATED CONTENT**

**Supporting Information**
The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acsanm.0c00596.

Images of the CNT template, details on the surface roughness/morphology, results from transmission electron microscopy studies, details of the temperature measurements, and uncertainty analysis (PDF)

**AUTHOR INFORMATION**

**Corresponding Author**
Brian D. Iverson – Brigham Young University, Provo, Utah 84602, United States; orcid.org/0000-0002-4592-3728; Email: bdiverson@byu.edu

**Authors**
Derrick B. Syme – Brigham Young University, Provo, Utah 84602, United States
Jason M. Lund – Brigham Young University, Provo, Utah 84602, United States
Brian D. Jensen – Brigham Young University, Provo, Utah 84602, United States
Robert C. Davis – Brigham Young University, Provo, Utah 84602, United States; orcid.org/0000-0002-6165-4396
Richard R. Vanfleet – Brigham Young University, Provo, Utah 84602, United States; orcid.org/0000-0002-2224-6090

Complete contact information is available at: https://pubs.acs.org/10.1021/acsanm.0c00596

**Notes**
The authors declare no competing financial interest.

**ACKNOWLEDGMENTS**
This material is based on work supported by Brigham Young University.

**REFERENCES**


