

Thermal Conduction in Nanoporous Copper Inverse Opal Films

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ABSTRACT

Copper inverse opal films offer an attractive combination of conduction and convection transport properties that yield a low total thermal resistance for microfluidic heat exchanger applications. In this work, we present an integrated synthesis and characterization strategy to fabricate nanoporous copper inverse opal films and to measure the effective thermal conductivity. We synthesize inverse opal films with sub-micron pore diameters using a sacrificial packed multilayer nanosphere bed to mold the geometry of an electrodeposited copper film. We characterize the effective thermal conductivity using the 3ω method, where the nanoporous copper film is deposited directly above a microfabricated and electrically-passivated 3ω device. The effective thermal conductivity is measured to be as large as $170 \text{ W m}^{-1} \text{ K}^{-1}$. This experimental data is compared to finite element simulations as well as common conduction models for heterogeneous media, including Maxwell's model and differential effective medium theory. This provides insight into the design of nanoengineered surfaces and two-phase vapor-venting microfluidic heat exchangers for ultrahigh heat flux cooling.

KEY WORDS: inverse opal, three omega, electrodeposition, thermal conductivity, Langmuir-Blodgett

NOMENCLATURE

A	deposition area
b	heater half-width
C	volumetric heat capacity
d	diameter
F	Faraday's constant
h	film thickness
I	electrical current
k	thermal conductivity
L	length
M	molar mass
m	mass
P	heater power
Q	electrical charge
R	electrical resistance
T	temperature
t	time
V	voltage
z	charge transferred per ion

Greek symbols

α	thermal diffusivity
ε	volume fraction
η	overpotential
κ	thermal conductivity ratio
Λ	mean free path
ρ	mass density
τ	total deposition time
ω	frequency

Subscripts

$bulk$	bulk property
eff	effective property
f	fluid phase
FS	fused silica
ref	reference electrode
RMS	root-mean-squared
s	solid phase
SS	steady-state

INTRODUCTION

Nanoporous copper (NPC) films with inverse opal geometry are advantageous for high heat flux microfluidic cooling applications due to the combined high thermal conductivity copper scaffold and high density of spherical voids with interconnected fluid-permeable pores. The low thermal resistance allows heat to conduct and spread throughout the NPC film to take advantage of the large surface area available for heat transfer across the solid-liquid interface. Several critical material properties are tunable during the NPC film fabrication to accommodate varying performance requirements, including the base metal composition, film thickness, spherical void diameter, inter-void pore size, and surface chemistry at the solid-liquid interface.

Inverse opal structures have been demonstrated in a variety of applications which leverage the tunable periodicity, diffractive and optical properties, fluid pathways, and high surface area to volume ratio. Photonic crystals with pore sizes comparable to the wavelength of light utilize the high periodicity of inverse opals [1,2]. This nanoscale periodicity also enhances phonon scattering in semiconductor inverse opals, which suppresses the lattice contribution to the thermal conductivity in silicon for thermoelectric applications [3]. Catalytic surfaces comprised of ceria-zirconia inverse opals leverage the low tortuosity but high periodicity structure for chemical oxidation [4]. Multilayered inverse opals have been used in three-dimensional battery architectures to

simultaneously improve both ionic and electronic transport in ultrafast charging and discharging lithium-ion batteries [5]. Biological and chemical sensors can be made from inverse opals, such as functionalized hydrogel inverse opals for use as pH sensors that utilize the relationship between optical properties and geometric structure [6].

Inverse opals have been assembled with different materials, geometries, and surface chemistries either through modification of the initial template (e.g. sphere size, sintering) or through post-fabrication material processing (e.g. interstitial deposition method, surface functionalization). Multilayered sacrificial opal templates have been fabricated from both SiO₂ spheres [7-12] and polymer colloids [1,6,13,14] with diameters ranging from 200 nm [8] to 2.2 μ m [1]. These spheres are self-assembled onto substrates over centimeter-

scale areas using a variety of non-template techniques, including drop casting [15], spin coating [16], convective and vertical deposition [5,11,14], and in flow cells [13]. A more comprehensive review of self-assembly techniques is available in the literature [2, 17]. Different materials have been used to fill the interstitial spaces, including metals [8,13], semiconductors [9,10,12], polymers [6,15], and insulators [14]. Numerous techniques are available to deposit the interstitial material, including electrodeposition [1,13], electroless deposition [8], chemical vapor deposition [9,10,12], and sol-gel processes [6,14]. These inverse opal films have been grown as thick as 100 μ m [13] and over areas as large as a 4-inch silicon wafer [16].

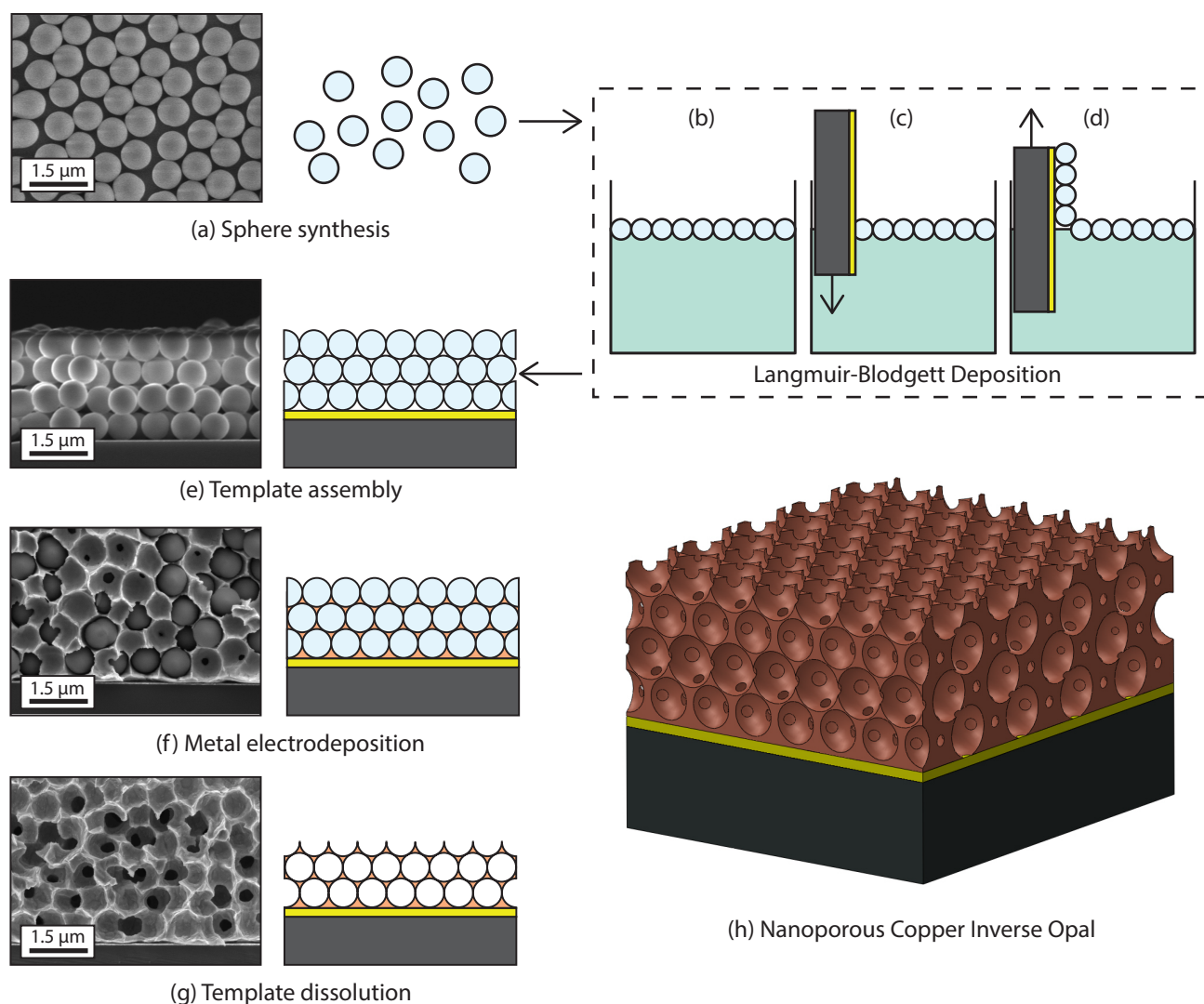


Figure 1: Nanoporous copper fabrication process. (a) Silica nanospheres are first synthesized via the Stöber method and functionalized with an amine terminal group to prevent aggregation. (b) The spheres are dispersed and compressed to be close-packed on a deionized water surface in a Langmuir-Blodgett (LB) trough. (c) A gold-coated substrate is vertically oriented and immersed into the trough. (d) By slowly drawing the substrate up across the water-sphere-air interface, spheres adhere to the substrate surface to form a single monolayer. (e) By repeating steps (c) and (d), the LB method enables precision assembly of multiple monolayers in a three-dimensional close-packed structure. (f) Beginning with the gold surface of the substrate, copper is electrodeposited into the interstitial spaces of the sphere template. (g) The spheres are dissolved using a dilute aqueous HF solution, and (h) this reveals a copper inverse opal film.

There has been relatively little work to characterize relevant thermal transport properties of inverse opals for enhanced microfluidic heat exchangers. In the present work, monodisperse SiO₂ nanospheres are chemically synthesized and self-assembled into a packed bed on a metal-coated substrate using the Langmuir-Blodgett technique. Copper is then electrodeposited into the interstitial spaces, and the spheres are subsequently dissolved. The resulting material consists of a copper inverse opal scaffold containing an interconnected network of spherical voids. The effective thermal conductivity of the resulting material is measured and the results are compared to models for effective conduction in composite media.

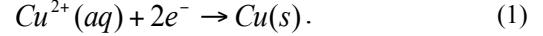
SAMPLE PREPARATION

Template-assisted electrodeposition utilizes the geometry of a sacrificial template to mold the resulting morphology of an electrodeposited interstitial material. In the present work, a packed bed of SiO₂ nanospheres is self-assembled into a close-packed crystal geometry, the inverse of which is referred to as an inverse opal. Silica nanospheres with diameters of 675 nm (Figure 1a) are chemically synthesized (see Appendix) using the Stöber process [18-20], a common technique used to produce highly monodisperse SiO₂ nanospheres with diameters ranging from 50-1000 nm [9,21]. The nanospheres are functionalized with 3-aminopropyl(diethoxy)methylsilane (Sigma-Aldrich) to terminate the silica surface with a positively-charged amine group to prevent sphere aggregation by creating repulsive forces between spheres. The surface of the substrate used to grow the NPC film (both silicon and fused silica are used in the present work) is covered with an adhesion layer (5 nm titanium) and a seed layer (50 nm gold) deposited by electron beam evaporation. The gold-coated substrate is then immersed in a 1M aqueous solution of sodium 3-mercaptopropyl-1-propanesulfonate (MPS) for 30 minutes to form a hydrophilic self-assembled monolayer on the gold surface [1]. The MPS monolayer contains a thiol (HS-) head group that binds to the gold surface and a hydrophilic ionized sodium-terminated sulfite (-SO₃-Na) functional group.

The nanospheres are self-assembled onto the gold-coated substrate using the Langmuir-Blodgett (LB) technique (Figure 1e) [21,22]. In LB deposition, the functionalized nanospheres are dispersed onto the surface of deionized water in a particle-free trough. Compression bars maintain a close-packed monolayer of spheres on the water surface as a substrate is slowly drawn out of the trough, transferring the spheres to the substrate at the fluid interface. Each dip and withdrawal produces a new monolayer of nanospheres on the surface, requiring repeated cycles to build up a multilayered packed bed of spheres. The LB deposition method enables precise control over the number of individual nanosphere monolayers, which nominally form a HCP structure [17,23].

Copper is then deposited into the interstitial spaces of the packed sphere bed (i.e. the “template”) via potentiostatic electrodeposition (Figure 1f), with copper deposition beginning at the gold seed layer on the surface of the substrate and growing up through the spheres. A three-electrode PTFE electrolytic cell (Figure 2a) enables well-controlled

electrodeposition of copper onto the surface of the working electrode from an aqueous acid-salt electrolyte solution (0.6 M CuSO₄ + 30 mM H₂SO₄, pH = 1.74 ± 0.03). The working electrode (cathode) is the surface of the substrate, and Cu²⁺ ions are reduced and deposited as solid copper onto this surface, forming the electrodeposited film. This electrodeposition half-reaction is given by



The counter electrode (anode) supplies current to complete the full reaction and is a solid piece of oxygen-free high-conductivity copper (99.99% pure, Alloy 101, McMaster-Carr) placed in the bulk solution. The Ag/AgCl reference electrode ($V_{\text{ref}} = +207$ mV vs. normal hydrogen electrode, BaSi Inc.) provides a reference voltage for measuring the potential of the working electrode and is nominally non-polarizable. Unless otherwise specified, all electrochemical potentials in this work are reported with respect to the Ag/AgCl reference electrode.

Electrodeposition is performed under potentiostatic conditions, where a constant voltage is fixed at $V_{\text{applied}} = -120$ mV. The standard electrode potential of the redox couple in Equation 1 (for 0.6 M Cu²⁺) is $V_0 = +126$ mV. The corresponding deposition overpotential is then given by $\eta = V_0 - V_{\text{applied}} = 246$ mV. An aperture in the electrochemical cell exposes only a selective region of the substrate (i.e. working electrode) to the electrolyte solution and limits the copper deposition to a desired shape, size, and location. The working electrode on the thermal characterization devices is a circle of diameter $d = 3$ mm with area $A = 7.1$ mm².

The electrical current is proportional to the copper deposition rate, as related by Faraday’s Law of electrolysis:

$$m = \frac{MQ}{Fz} = \frac{M \int_0^{\tau} I(t) dt}{Fz} \quad (2)$$

where m and M are the total mass and molar mass of the deposited species, respectively, Q is the total charge passed during the time interval of length τ , F is Faraday’s constant, z is the magnitude of the charge transferred per ion, and $I(t)$ is the electrical current. Since the aperture maintains a fixed deposition area A , the film height h can be written in terms of the mass and density ρ such that $h = m/(\rho A)$. Once the deposition process reaches steady-state, the current becomes approximately constant, and Equation 2 then linearly relates the film thickness and deposition time:

$$h = \left[\frac{1}{(\rho A)} \frac{MI_{ss}}{Fz} \right] t \quad (3)$$

where I_{ss} is the steady state current. This expression is valid when the deposition time constant is small compared to the total deposition time. This phenomenon was experimentally validated for copper films grown at constant overpotential (Figure 2b), where the height was measured using cross-sectional scanning electron microscopy (SEM). This empirical

deposition rate coefficient enables the growth of films with well-controlled thickness.

The template is removed by dissolving the nanospheres in a 2-5% solution of aqueous hydrofluoric acid using the gold seed layer as an etch stop. This produces a NPC scaffold with the inverse geometry of the original sacrificial template and allows NPC films to be fabricated directly onto substrates and devices (e.g. microfluidic devices, MEMS cantilevers).

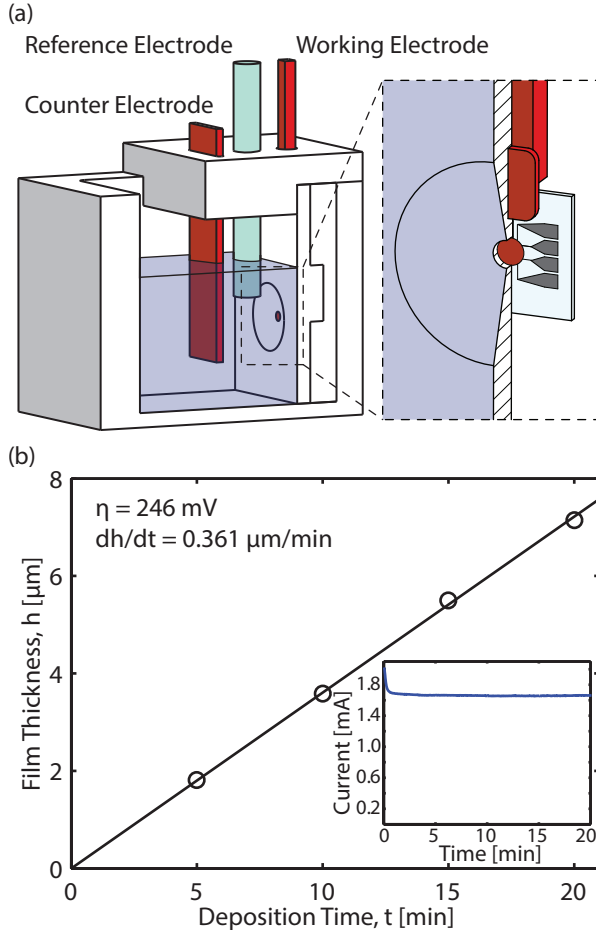


Figure 2: (a) Cutaway view of electrodeposition apparatus. A three-electrode electrochemical cell is used to produce repeatable electrodeposited films over well-defined areas. This setup aligns the film deposition onto the center of the thermal characterization substrates. A machined copper bar is used to contact the working electrode lead on the substrate. (b) Performance characteristics for this electrodeposition setup. The deposited film thickness is a function of both overpotential and deposition time. This growth rate was measured experimentally for a fixed deposition area and overpotential. When the deposition time is much longer than the deposition time constant (see inset), the current reaches a steady state value and the deposition rate follows Equation 3.

THERMAL CHARACTERIZATION

The effective thermal conductivity of NPC films is measured using the 3ω method [24,25]. The 3ω measurement technique utilizes a single patterned metal line by driving an alternating

current (Keithley 6221) through the line at frequency ω , giving rise to Joule heating and corresponding temperature oscillations in the metal line at frequency 2ω . The linear relationship between temperature and resistance in the metal line generates a voltage signal at a frequency 3ω , which is directly measurable using a lock-in amplifier (Stanford Research Systems, SRS830). The spatially-averaged temperature rise in the heater ΔT is then mapped to the measured $V_{3\omega}$ signal [25, 26]:

$$\Delta T = \frac{2V_{3\omega}}{I_{RMS}} \frac{dT}{dR} \quad (4)$$

where dT/dR is the measured linear relationship between temperature and resistance in the metal line (see Appendix) and I_{RMS} is the root-mean-squared current sourced through the metal line. The temperature oscillations at the heater are a function of the thermal properties of the surrounding materials located within the thermal penetration length $L_{thermal} \approx \sqrt{\alpha/\omega}$ of the heater, where α is the thermal diffusivity of the system.

We implement the 3ω method by growing the NPC film directly above an electrically-passivated microfabricated heater structure patterned onto a fused silica substrate. The device design is derived from a structure originally employed by Roy *et al.* for use in high-sensitivity thermal characterization of fluid microdroplets [28]. First, a fused silica wafer is patterned with metal heater lines ($5 \mu\text{m}$ -wide, $1000 \mu\text{m}$ -long) in a four-point probe configuration using photolithography (Figure 3). The metal lines are comprised of a 5 nm titanium adhesion layer followed by a 60 nm platinum layer deposited by electron beam evaporation. Each device contains two decoupled heater configurations arranged symmetrically. A third metal line serving as the working electrode lead connects a contact pad on the substrate perimeter to the center between the two heater lines. The electrode lead line is $500 \mu\text{m}$ -wide and carries current from the electrochemical cell to the working electrode during electrodeposition. Next, a 200 nm-thick SiO_2 passivation layer is deposited onto the surface of the device by plasma-enhanced chemical vapor deposition (PECVD) to electrically isolate the buried metal lines from the conductive samples grown on top of the devices. A high-quality, conformal 20 nm-thick SiO_2 passivation film is deposited via atomic layer deposition above the PECVD film to further ensure complete passivation from the conductive samples. Finally, the electrical contact pads on the perimeter of the device and the tip of the working electrode lead are exposed via wet etching, and the wafer is diced into squares ($9 \text{ mm} \times 9 \text{ mm}$) that each contain a symmetrical pair of heater lines and a single working electrode lead (Figure 3a).

The adhesion layer and seed layer are then deposited directly onto the surface of the device (Figure 3b) using electron beam evaporation through a shadow mask to form a circle above the electrically-isolated heaters and working electrode lead. The nanosphere template and NPC film are assembled and grown directly on top of the gold seed layer on the device by supplying current to the working electrode lead.

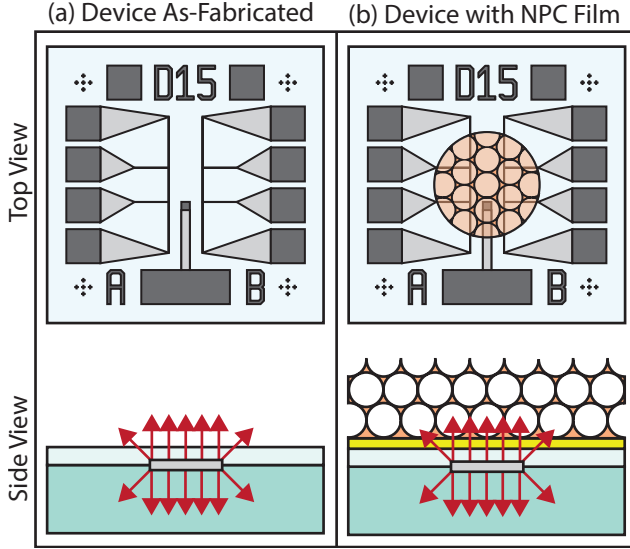


Figure 3: (a) Top and side view of electrically-passivated thermal characterization devices on fused silica immediately following microfabrication. The entire device is covered with ~ 220 nm SiO_2 except for the dark gray regions where metal has been exposed. (b) Top and side view of the same devices after NPC film growth. An aperture isolates the gold seed layer and copper electrodeposition and confines NPC film growth to a circle centered over the electrically-passivated heater lines in the center of the device (spherical voids are not drawn to scale).

The thermal properties of the multilayered stack (Figure 3) can be extracted by comparing the thermal response, $\Delta T(\omega)$, (Figure 4) to the analytical heat diffusion equation [27] using a least-squares fitting algorithm. In this model, the 220 nm-thick SiO_2 passivation layer and the 1 μm -thick NPC film are treated as discrete layers with finite thickness since they are entirely contained within a thermal penetration length of the heater, and the fused silica substrate and air above the film are treated as semi-infinite media. The spatially-averaged temperature rise ΔT at the location of heating for such a defined multilayered system can be derived [27] to be

$$\Delta T = \frac{P}{2\pi L b^2} \int_0^\infty \frac{B^+(m) + B^-(m)}{A^+(m)B^-(m) - A^-(m)B^+(m)} \frac{\sin^2(mb)}{\gamma_j m^2} dm \quad (5a)$$

$$\gamma_j = k_j \sqrt{m^2 - i \frac{\omega}{\alpha_j}} \quad (5b)$$

where P is the heating power, L and b are the length and half-width of the heater, k_j and α_j are the thermal conductivity and diffusivity of the j^{th} layer, and A and B are dimensionless parameters solved using a recursive matrix method.

RESULTS

Each device is calibrated prior to sample deposition using the 3ω method to characterize the heater line half-width b and the heat capacity and thermal conductivity of the fused silica substrate, $C_{\text{v,FS}}$ and k_{FS} respectively (Figure 4). At the driving

frequencies in this work, these devices are thermally insensitive to the passivation film. The sensitivity of the heater is governed by the relationship between temperature and resistance, which for metals is well-approximated as linear near room temperature. This value is determined experimentally for each heater line by differentiating the temperature-dependent resistance, dT/dR , over the temperature range 20-50°C (see Appendix). During the 3ω measurement, a driving current is applied across the heater line over a frequency range of 200-3000 Hz (in intervals of 100 Hz) to obtain a thermal response for each frequency. This method is used to characterize thermal properties of the multilayered stack after the addition of each layer, including the evaporated titanium/gold seed layer (to measure seed layer thickness and composite thermal conductivity) and the NPC film (to measure NPC film thermal conductivity). The driving current is chosen to adjust the temperature rise seen at the heater to ~ 1 -2 K, providing a good signal-to-noise ratio without requiring consideration of any temperature-dependent thermal properties caused by large temperature perturbations.

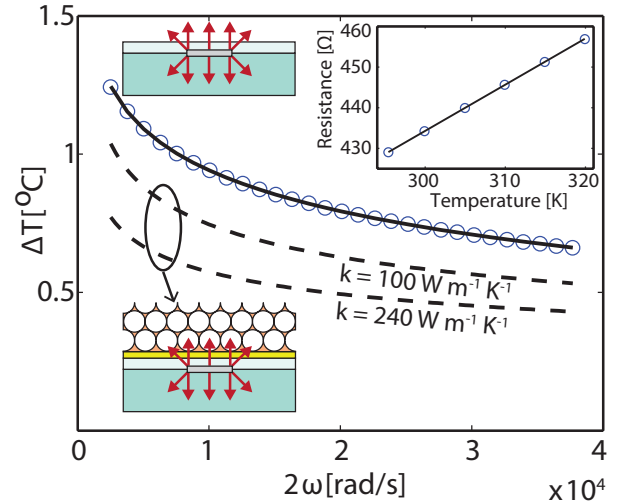


Figure 4: Calibration characteristics for 3ω devices. The calibration data and least-squares fits (circles and solid line, respectively) are shown for a 3ω device without the sample film on top, including the frequency sweep and the heater sensitivity calibration (inset). The dashed lines demonstrate analytical 3ω thermal response curves for a 2 μm -thick NPC film with 60% solid volume fraction for two different possible thermal conductivity values. Since the high-conductivity NPC film dissipates a larger amount of heat compared to air, the signal is improved by increasing the amplitude of the driving current.

In nanostructured materials, as the feature sizes approach the mean free path (MFP) of the thermal energy carriers ($\Lambda_{\text{Cu,electron}} \approx 39$ nm [29,30] at room temperature) the effective thermal conductivity is suppressed with a scaling approximated by Matthiessen's Rule:

$$\Lambda_{\text{eff}} = \left[\frac{1}{\Lambda_{\text{bulk}}} + \frac{1}{L_c} \right]^{-1} \quad (6)$$

where Λ_{eff} is the effective MFP, Λ_{bulk} is the MFP in the constituent bulk material, and L_c is a characteristic length describing the mean proximity of surface scattering sites. In NPC films, there are both regions with bulk-like conduction ($L_c > \Lambda_{bulk}$) and regions of nanoscale constrictions that throttle conduction ($L_c \approx \Lambda_{bulk}$). This becomes increasingly relevant as the feature sizes are reduced. However, for $d = 675$ nm the majority of the inverse opal volume has $L_c > \Lambda_{bulk}$, and the effective thermal conduction through the NPC film is expected to be primarily influenced by diffusive transport.

In the limit of diffusive thermal conduction in a bulk two-component material (where one component has a negligible thermal conductivity compared to the other, e.g. $k_s \gg k_f$ for most solid/fluid heterogeneous media), the upper bound of the effective thermal conductivity, k_{eff} , scales with the solid volume fraction ε :

$$k_{eff} = k_s \varepsilon \quad (7)$$

where $0 \leq \varepsilon \leq 1$ is the volume fraction of the thermally-conductive solid phase. This is equivalent to modeling the two components as parallel resistors.

A simple approximation for the conduction properties of binary composite media is presented by Maxwell [31, 32] for a solid medium with randomly dispersed fluid-saturated spherical voids:

$$k_{eff} = k_s \frac{2\kappa\varepsilon + (3 - 2\varepsilon)}{3\kappa + (1 - \kappa)\varepsilon} \quad (8)$$

where k_f and k_s are the thermal conductivities of the fluid and solid phase, respectively, and κ is the thermal conductivity ratio $\kappa = k_s/k_f \approx 667$ for copper and water. Maxwell's model, while insensitive to microscale geometry, is shown to closely agree with more comprehensive effective medium theory models [33] that account for the specific spherical arrangement. Datta et al. evaluate their model over a range of filling fractions for different cubic systems and demonstrate increasing agreement with Maxwell's model for crystals with increasing close-packed threshold volume fractions [33]. This suggests that Equation 8 accurately models the effective conductivity in highly close-packed structures, such as the face-centered cubic and hexagonal close-packed crystals produced in the present work. Effective medium theory is commonly used to model heterogeneous media under different limiting assumptions and regimes. Garboczi and Berryman [34] apply a form of differential effective medium theory (D-EMT) to a similar system and predict the effective conductivity by solving

$$\left(\frac{k_{eff} - k_f}{k_s - k_f} \right) \left(\frac{k_{eff}}{k_s} \right)^{-1/3} = \varepsilon. \quad (9)$$

For the condition $(k_s, k_{eff}) \gg k_f$, Equation 9 reduces to

$$k_{eff} = k_s \varepsilon^{3/2}. \quad (10)$$

A more comprehensive review of different conduction models for saturated porous media is compiled by Aichlmayr and Kulacki [32].

A finite element analysis is performed on an inverse opal unit cell using the commercial software package FLUENT. The effective thermal conductivity of a single NPC unit cell is computed for a copper solid phase with spherical water inclusions arranged in a face-centered cubic unit cell. The unit cell porosity was tuned by fixing the lattice parameter while varying the spherical liquid diameter. A temperature differential is applied between two opposing faces of the unit cell with adiabatic boundary conditions on the remaining sides. The effective thermal conductivity is then calculated by numerically computing the steady state heat flux for the imposed temperature differential and applying Fourier's law.

The solid volume fraction ε is estimated using two methods. The first method uses image analysis to analyze cross-sectional SEM images (see Figure 1g) to compute the ratio of solid (non-void) area to total cross-sectional area [35]. The second method leverages ε as a fitting parameter in the 3ω analysis, where both the thermal conductivity and heat capacity of the NPC film can be simultaneously fit by assuming that the volumetric heat capacity is proportional to the solid volume fraction. Thermal conductivity data gathered during preliminary experiments suggest that $k_{eff} = (170 \pm 7) \text{ W m}^{-1} \text{ K}^{-1}$ for NPC films grown with a volume fraction of approximately $\varepsilon \approx 0.53 (\pm 0.11)$. Within the uncertainty of ε , this compares favorably to the aforementioned models and simulation results shown in Figure 5.

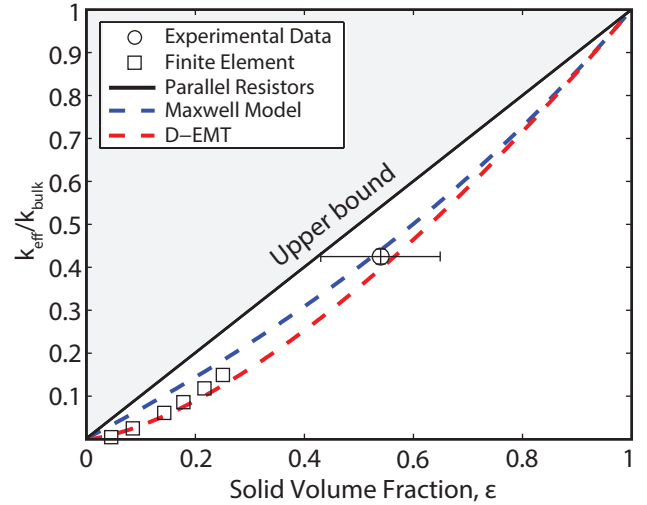


Figure 5: Normalized effective thermal conductivity as a function of copper volume fraction. The volume-fraction scaling of thermal conductivity corresponds to the physical upper bound on diffusive conduction. Maxwell's model and differential effective medium theory (D-EMT) provide more detailed approximations for solid phases containing distributed spherical cavities without considering specific crystallographic arrangement of the voids. A finite element analysis was performed to better capture the geometry. Experimental data obtained using the 3ω method is compared to these models.

CONCLUDING REMARKS

In this work, we demonstrated a fabrication technique, thermal characterization metrology, and measured and modeled the effective thermal conductivity of nanoporous copper. This is the first critical step toward understanding the total heat transfer through this type of structure and provides insight into the design of nanoengineered surfaces and two-phase vapor-venting microfluidic heat exchangers for ultrahigh heat flux cooling. Further experiments are required to generate additional data points across a range of volume fractions and geometric configurations. This requires the ability to tune the internal porosity either by modifying the initial template prior to metal deposition (such as sintering a colloidal crystal to increase neck formation) or by electropolishing the final inverse opal structure to isotropically widen the existing pores. Fluid permeability characterization and measurements of operating convective heat transfer coefficients should then be performed to determine the combined conduction and convection performance and overall heat transfer coefficient of this material for microfluidic heat exchanger applications. This type of material may also benefit heat spreader applications where the porous volume contains a phase change material (such as paraffin wax) to both passively mitigate hot spots and buffer heat flux transients.

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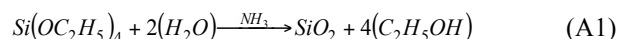
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APPENDIX

Synthesis of 675 nm Silica Nanospheres

The silica nanospheres are created using a modified Stöber synthesis, which utilizes the reaction of tetraethoxysilane (TEOS) with water in the presence of an ammonia catalyst as shown in Equation A1 [19]:



In particular, a 50 mL vial containing a magnetic stir bar is filled with 20 mL of pure ethanol, 7 mL of 30% ammonium hydroxide and 1.3 mL of TEOS. After an hour of mixing at room temperature, 675 nm silica spheres are created and ready for cleaning. The cleaning process consists of 6 centrifuge cycles with solution exchange to replace the initial solution (containing excess reactants and other impurities) with clean ethanol. The spheres are then redispersed in the fresh ethanol via sonication.

Calibration and Uncertainty of 3 ω Heater Line Sensitivity

The metal heater line sensitivity is accurately determined by wirebonding each device to a chip carrier and placing the package in a temperature-controlled vacuum environment (Lakeshore 330). The temperature of the chamber is raised from 295 K to 320 K (stabilized in increments of 5 K), and the resistance is measured by taking an I-V sweep from -100 μA to +100 μA (in increments of 5 μA) at each stabilized temperature point. Low currents are supplied to minimize Joule heating effects. The resistance is equal to the slope of a linear regression applied to the data (Figure 4, inset).

As the temperature of the chamber is incremented, temporary spatial temperature gradients arise within the chamber, leading to a difference in temperature between the internal chamber temperature sensor and the surface of the device (where the metal heater line is located). To reconcile this difference, a continuous direct current of 50 μA is applied across the device to measure the resistance. In this work, the temperature of the device is considered stable once the instantaneous resistance measurement is found to vary by less than $2 \times 10^{-4} \Omega/\text{s}$. For the maximum measured dT/dR value ($\approx 1.20 \text{ K}/\Omega$), this corresponds to a maximum temperature drift of $2.4 \times 10^{-4} \text{ K/s}$. The I-V sweep is performed over 180 seconds, leading to a total temperature uncertainty at each measurement point of $\pm 0.043 \text{ K}$.