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Ryan A. Duncan, Giuseppe Romano, Marianna Sledzinska, Alexei A. Maznev, Jean-Philippe M. Péraud, Olle Hellman, Clivia M. Sotomayor Torres, and Keith A. Nelson
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Ryan A. Duncan,1,a) Giuseppe Romano,2 Marianna Sledzinska,3 Alexei A. Maznev,1 Jean-Philippe M. Péraud,4 Olle Hellman,5 Clivia M. Sotomayor Torres,3,6 and Keith A. Nelson1

AFFILIATIONS
1 Department of Chemistry, Massachusetts Institute of Technology, 77 Massachusetts Ave., Cambridge, Massachusetts 02139, USA
2 Department of Mechanical Engineering, Massachusetts Institute of Technology, 77 Massachusetts Ave., Cambridge, Massachusetts 02139, USA
3 Catalan Institute of Nanoscience and Nanotechnology (ICN2), CSIC and BIST, Campus UAB, Bellaterra, 08193 Barcelona, Spain
4 Computational Research Division, Lawrence Berkeley National Laboratory, 1 Cyclotron Road, Berkeley, California 94720, USA
5 Department of Applied Physics and Materials Science, California Institute of Technology, Pasadena, California 91125, USA
6 ICREA, Pg. Lluís Companys 23, 08010 Barcelona, Spain

a)Author to whom correspondence should be addressed: raduncan@mit.edu

ABSTRACT

In this study, we use transient thermal gratings—a non-contact, laser-based thermal metrology technique with intrinsically high accuracy—to investigate room-temperature phonon-mediated thermal transport in two nanoporous holey silicon membranes with limiting dimensions of 120 nm and 250 nm, respectively. We compare the experimental results with 

I. INTRODUCTION

Nanoscale thermal transport has become a topic of much recent interest due to the novel transport phenomena that emerge at the micro- and nanoscale1,2 and their relevance to technological fields such as microelectronics and thermoelectrics.3,4 In semiconductor systems with feature sizes comparable to the phonon mean free path (MFP), size effects can lead to strong reductions in thermal conductivity—making thermal management in microelectronic devices a significant engineering challenge.5 In the field of thermoelectrics, nanostructuring has emerged as a key strategy for enhancing the thermoelectric figure of merit ZT by reducing the thermal conductivity without significantly affecting the electronic properties of the material.6,8 Traditionally overlooked for thermoelectric applications, silicon has generated recent interest as a material for thermoelectric devices due to the strongly reduced thermal conductivity achievable through nanostructuring.7 Experimental results on silicon nanowires have shown thermal conductivity values two orders of magnitude lower than the bulk value and ZT values approaching unity.8–10 Two-dimensional “holey silicon” nanostructures—suspended silicon membranes with a periodic array of nanopores—have exhibited thermal conductivity reductions comparable to nanowires11–15 while retaining superior relative mechanical strength. Such nanostructures hold great promise for thermoelectric applications due to the wide variety of well-established and scalable fabrication and manufacturing techniques available for silicon.

Thermal transport at the nanoscale differs significantly from macroscopic, diffusive thermal transport. In structures with feature
sizes comparable to the MFP of heat-carrying phonons, thermal transport no longer obeys the heat diffusion equation. One of the earliest attempts to account for non-Fourier phonon-mediated thermal transport in nanostructures was by Casimir, whose model featured particle-like phonon transport with diffuse scattering at boundaries. Although Casimir’s original model was concerned with thermal transport in rods, the broader formalism of semiclassical particle-like phonon transport with diffuse boundary scattering is expected to be valid for any nanostructure for which \( \lambda_{th} \ll \ell \) and \( \lambda_{th}/2\pi \ll R \), where \( R \) is the surface roughness, \( \lambda_{th} \) is the representative wavelength of heat-carrying phonons, and \( \ell \) is the limiting dimension of the nanostructure. Heat-carrying phonons at room temperature in silicon have single-digit nanometer wavelengths, which is of the order of lithographically realistic surface roughnesses. Thus, silicon nanostructures with feature sizes \( \ell > 10 \text{ nm} \) should be well described by the Casimir formulation of thermal transport—that is, particle-like phonon transport according to the phonon Boltzmann transport equation (BTE) with diffuse scattering from surfaces. Studies comparing experimental results with \textit{ab initio} theory based on the BTE have shown that the Casimir formulation is indeed valid for nanoscale silicon membranes and silicon nanobeams. However, there have been highly conflicting reports regarding the validity of the Casimir formulation for thermal transport in nanoporous holey silicon membranes. Several studies have reported room-temperature effective thermal conductivities reduced by up to an order of magnitude relative to the Casimir formulation predictions for such structures, while others have found good agreement between the Casimir formulation and experiment. In some cases, measurements showing deviations from the Casimir formulation predictions for holey silicon nanostructures have been invoked as evidence of “coherent” thermal transport effects at room temperature. This notion, however, has been challenged by recent experimental and theoretical works, in which no effect of nanopore lattice disorder on the room-temperature thermal transport was found. It should be noted that reports of “below Casimir” thermal conductivity rely on the measurements of the absolute values of thermal conductivity, which are challenging even for bulk samples. If far-reaching conclusions are to be drawn from the absolute value of thermal conductivity, then a technique with high absolute accuracy is desirable.

Transient thermal gratings (TTGs) is a non-contact optical technique that measures the time evolution of an impulsively generated sinusoidal temperature profile. The experimental observable is the amplitude of this sinusoidal temperature profile, which decays as heat spreads from the peaks to the nulls of the grating. For a one-dimensional TTG, the amplitude of the thermal profile and, therefore, the intensity of the heterodyned TTG signal is given by

\[
I(t) \propto e^{-t/\tau},
\]

where \( \tau = 1/\alpha q^2 \), \( \alpha \) is the thermal diffusivity, \( q = 2\pi/L \) is the transient grating wavevector, and \( L \) is the transient grating period. The only parameter other than \( \alpha \) that affects the decay rate is \( L \), which can be measured with high accuracy. Thus, the thermal diffusivity can be determined to high accuracy from the decay rate of the TTG signal. Furthermore, TTG’s non-contact nature reduces additional sources of error due to the absence of any interfaces with metrological structures.

In this paper, two 250 nm-thick holey silicon membrane nanostructures are investigated with the TTG technique. The experimental results from TTG measurements are compared to the results of two \textit{ab initio} numerical Boltzmann transport techniques: the OpenBTE computational framework developed by Romano and Grossman and the energy-based devotional Monte Carlo BTE simulation technique developed by Péraud and Hadjiconstantinou. Quantitative agreement between numerical calculations and experiment is found for both the unpatterned silicon membrane and holey silicon structures, confirming the validity of the Casimir formulation for room temperature heat transport in silicon nanostructures with feature sizes on the order of 100 nm.

II. EXPERIMENTAL

A. Sample fabrication

The holey silicon structures were fabricated using electron beam lithography (EBL) and reactive ion etching (RIE) of a 250 nm-thick freestanding silicon membrane \( 3 \times 3 \mu m \text{ window area} \), obtained from Norcada Inc. Each of the two structures was a 100 \( \mu \text{m} \)-diameter region of the freestanding membrane patterned with a square lattice of nanopores. SEM micrographs of the regions are shown in Fig. 1. “Region A” had a pitch size (nanopore periodicity) of 400 nm and a nanopore diameter of 280 nm, and “region B” had a pitch size of 500 nm and a nanopore diameter of 250 nm.

B. Transient thermal grating (TTG) measurements

As shown in Fig. 2(a), two “pump” laser pulses are crossed at the sample, where optical interference and subsequent absorption lead to the establishment of a transient sinusoidal temperature profile with spatial period \( L = \lambda_2/2 \sin(\theta/2) \), where \( \lambda_2 \) is the pump wavelength and \( \theta \) is the crossing angle for the two pump beams. Through the temperature dependence of the material’s complex index of refraction \( n = n + ik \)—where \( n \) is the real index of refraction and \( k \) is the absorption coefficient—this sinusoidal temperature profile is accompanied by a spatially sinusoidal modulation in

![FIG. 1. Scanning electron micrographs of the patterned holey silicon regions—(a) region A (400 nm pitch, 280 nm nanopore diameter) and (b) region B (500 nm pitch, 250 nm nanopore diameter).](image)
A quasi-continuous "probe" beam then impinges on the sample, diffracting from this transient optical grating. As the amplitude of the temperature grating diminishes due to heat transport from the peaks to the troughs, the amplitude of the diffracted signal—diminishes accordingly. In this way, the time dependence of the diffracted signal can be directly related to the thermal diffusivity according to Eq. (1).

TTG measures the thermal transport dynamics over a length scale set by the period of the transient grating, which can be tuned by changing the crossing angle of the pump beams. Further details regarding this technique can be found in Ref. 34.

The pump beams were derived from a 515 nm source with a 60 ps pulse duration and 1 kHz repetition rate, and the probe beam was derived from a continuous-wave 532 nm source. A "reference" beam was derived from the same source as the probe beam, and the relative phase between the two was controlled by tilting a highly parallel optical flat through which the probe beam passes to achieve heterodyne detection. At the sample, the probe beam diffracts from the transient grating and becomes superposed with the transmitted reference beam, and the combined heterodyned signal is collected by a fast photodiode detector and recorded on an oscilloscope. The \( 1/e^2 \)-intensity radius of the pump and probe beams were 100 μm and 40 μm, respectively. While the pump spot size is commensurate with the patterned regions, the probe spot size is much smaller. Thus, although our pump may be exciting a grating pattern that extends somewhat outside of the patterned region, our experiment is only sensitive to the transport dynamics within the region bounded by the much smaller probe spot. The pump pulse energies ranged from 170 to 340 nJ, and the instantaneous power of the probe beam at the sample ranged from 0.8 to 1.6 mW. The probe beam was shuttered by an electro-optic modulator with a duty cycle of 5% to prevent steady-state heating of the sample.

The thickness of the membrane was smaller than the optical penetration depth of silicon for the wavelengths involved in the measurements, which permitted measurements in the transmission geometry as shown in Fig. 2(a). The raw TTG data obtained from the two holey regions and the unpatterned silicon membrane at a grating period of 4.25 μm are shown in Fig. 2(b). Measurements were performed under medium vacuum at a pressure of 1 mbar. The maximum amplitude of the temperature grating was determined to have an upper bound of 35 K. Upper bounds on the average heating of the sample due to the pump and probe beams were determined to be 20 K each.

The TTG signal for a one-dimensional thermal grating exhibiting diffusive thermal transport is given by Eq. (1). The low-dimensionality of the dynamical parameter space and the fact that neither precise knowledge of the magnitude of the temperature variation nor of the magnitude of the heat flux is required in the analysis of the data allow for the determination of the thermal diffusivity with high absolute accuracy. Further discussion regarding the accuracy of transmission-geometry TTG experiments on nanomembranes can be found in Ref. 34. The traces were truncated such that fitting began 5 ns after pump incidence to ensure that the fitted region corresponds only to thermal transport signal without any potential contribution from the fast electronic response shown in the inset of Fig. 2(b). The acquired fits are plotted alongside the data as well. A quasi-continuous "probe" beam then impinges on the sample, diffracting from this transient optical grating. As the amplitude of the temperature grating diminishes due to heat transport from the peaks to the troughs, the amplitude of the grating in \( \bar{n} \)—

\[ \tau = \alpha \]
raw TTG data in Fig. 2(b). Figure 2(c) shows the measured thermal diffusivity values obtained according to Eq. (1) as a function of TTG period for each of the three regions measured. Each raw TTG trace consisted of 50,000 individual measurements. The statistical error of the measurement was determined by partitioning the data into subsets of 10,000 measurements, fitting each subset to Eq. (1) and taking the standard error of the mean of the resulting distribution of \( \tau \) values. In addition to the statistical error of the measurement, the systematic error due to laser heating effects was also considered. The effects of laser heating were determined by performing each measurement three times—once at a baseline set of pump and probe powers, and two additional times at which the pump and probe powers, respectively, were doubled. Linearly extrapolating the measured values of \( \tau \) to zero pump and probe laser power allows us to determine the systematic error due to laser heating, which was then added to the appropriate side of the error-bars for each point to account for this systematic heating effect. We note that the upper bounds on laser heating reported above are non-negligible relative to room temperature. However, since the effect of laser heating is experimentally quantified in our error analysis, we can still compare our experimental results with calculations that use room-temperature material properties. Despite the somewhat high upper bounds on laser heating, we nevertheless note that the effect of laser heating on the experimentally determined values of \( \alpha \) was generally found to be less than 10%.

For grating periods from 4.25 to 7.5 \( \mu \)m, we find that the experimental values of thermal diffusivity are independent of \( L \) for both the unpatterned membrane and the holey membranes, consistent with preliminary TTG results on holey silicon structures. The exponential form of the TTG data and the invariance of thermal diffusivity as a function of grating period indicates that the transport kinetics are “effectively diffusive” over the TTG experimental length scales, albeit with “effective” thermal diffusivity values \( \alpha_{\text{eff}} \) reduced relative to the bulk because of the non-Fourier size effect due to nanostructuring.

It should be noted that occasionally an additional transient with a characteristic timescale much longer than the acquisition timescale (i.e., approximately a constant offset from the pre-pump baseline) was observed in some of the obtained TTG traces. However, we determined that the presence of this contribution to the signal (which is roughly on the timescale that would correspond to thermal diffusion out of the pump spot) was not associated with any change in the \( \alpha_{\text{eff}} \) value that was calculated from the time constant of the exponentially decaying contribution to the signal observed on the 10s–100s of ns timescale (which we took to be the true TTG signal) that remained after subtracting out this approximately constant offset. This issue is more thoroughly addressed in the supplementary material.

Experimental values of the effective thermal conductivity \( \kappa_{\text{eff}} \) were calculated from the data in Fig. 2(c) according to

\[
\kappa_{\text{eff}} = (1 - \phi)c_0\alpha_{\text{eff}},
\]

where \( \phi \) is the void fraction of the holey silicon membrane and \( c_0 \) is the bulk volumetric specific heat of silicon. The resulting experimental values of \( \kappa_{\text{eff}} \) are shown in Fig. 3, where the effective thermal conductivity values are plotted against the neck width \( \ell_n \) (i.e., the difference between the pitch size and the nanopore diameter).

### III. COMPARISON TO FIRST-PRINCIPLES NUMERICAL CALCULATIONS

Numerical calculations of the thermal transport through the membranes were performed according to the linearized isotropic phonon Boltzmann transport equation (BTE) under the single-mode relaxation time approximation (RTA), which is given by

\[
\frac{\partial f_{kp}}{\partial t} + \mathbf{v}_{kp} \cdot \nabla f_{kp} = \frac{f_0 - f_{kp}}{\tau_{kp}},
\]

where \( f_{kp}(r, t) \) is the occupation function for a mode traveling with wavevector \( k \) and polarization \( p \). \( \tau_{kp} \) is the (isotropic) group velocity, \( f_0(\hbar\omega, T_L(r, t)) \) is the Bose–Einstein distribution, \( T_L(r, t) \) is the local temperature field defined such that energy is locally conserved, \( \hbar \omega \) is the phonon energy, and \( \tau_{kp} \) is the (isotropic) single-mode relaxation time (where \( k = |k| \)).

The simulation domain is one pore-centered unit cell of the nanopore lattice with the cylindrical axis of the pore chosen to be oriented along \( \hat{z} \). Periodic boundary conditions are applied along both the \( x \) - and \( y \) -axes. The phonon group velocities and relaxation times were determined, respectively, from the harmonic and anharmonic force constants, which were obtained from density functional theory (DFT) calculations using the temperature dependent effective potential (TDEP) method. Naturally occurring isotope disorder was taken into account. Details on the DFT calculations can be found in the supplementary material.
The OpenBTE computational technique of Romano and Grossman and the energy-based deviational Monte Carlo BTE (MC-BTE) technique of Péraud and Hadjiconstantinou were both used for ab initio calculations of $\kappa_{\text{eff}}$ for both the holey and unpatterned membranes.

For the OpenBTE case, Eq. (3) is transformed into the following form:

$$\delta(\hat{\Omega}) \cdot \mathbf{V}(\hat{\Omega}, \hat{r}, \hat{\Lambda}) + \hat{T}(\hat{r}, \hat{\Omega}, \hat{\Lambda}) = T_{\text{L}}(\hat{r}),$$

$$T_{\text{L}} = \left( \int_{0}^{\infty} \frac{K(\Lambda)}{\Lambda^2} d\Lambda \right)^{-1} \int_{0}^{\infty} \frac{K(\Lambda')}{\Lambda'^2} \langle \hat{T}(\hat{r}, \hat{\Omega}, \hat{\Lambda}') \rangle d\Lambda',$$

where $\hat{\Omega}$ is the unit vector for the propagation direction $\Omega$, $\hat{T}(\hat{r}, \hat{\Omega}, \hat{\Lambda})$ is the “effective temperature” of phonons with MFP $\Lambda$ traveling in direction $\Omega$ (i.e., the sum of their energy densities divided by $c_0$), $K(\Lambda)$ is the bulk MFP distribution (i.e., the derivative of the thermal conductivity accumulation function with respect to $\Lambda$), and $\langle \hat{T}(\hat{r}, \hat{\Omega}, \hat{\Lambda}) \rangle$ is the angular average over all propagation directions. Equation (4) is derived by imposing steady-state conditions on Eq. (3), as well as assuming that $\delta(\hat{\Omega}) = (1/4\pi) \int_{0}^{\infty} \hat{x} \delta(\Omega) d\Omega$ is the angular average over all propagation directions. To overcome numerical instability due to small-MFP phonons, OpenBTE switches to a modified Fourier law to compute the diffusive component to heat transport for region A and a near order of magnitude reduction in $\kappa_{\text{eff}}$ is observed due to the nanopore superlattice patterning, resulting in a reduction of $\kappa_{\text{eff}}$ by a factor of 3 relative to the bulk value. Two computational techniques in excellent agreement with each other), which indicates that the Casimir formulation is valid for nanostructures of this kind.

IV. CONCLUSIONS

We have used the non-contact optical TTG method to investigate thermal transport in holey regions and an unpatterned region of the same silicon membrane. We observe effective diffusive transport at grating periods larger than 4$\mu$m and a reduction in effective thermal conductivity by nearly an order of magnitude relative to the bulk value. Two ab initio numerical techniques simulating transport according to the semiclassical phonon Boltzmann transport equation yielded excellent agreement with the measurements. Our results indicate that the Casimir framework of semiclassical particle-like phonon-mediated thermal transport with diffuse boundary scattering is adequate for describing thermal transport in holey silicon structures with limiting dimensions of $\sim$100 nm.
SUPPLEMENTARY MATERIAL

See the supplementary material for discussion regarding the long-time contribution to the obtained TTG signals that appears in some of the measurements, details regarding the density functional theory calculations, and discussion of computational uncertainties.

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DATA AVAILABILITY

The data that support the findings of this study are available from the corresponding author upon reasonable request.

REFERENCES

43. Thus, \( \kappa_{eff} \) is defined as the thermal conductivity of a solid membrane that would have the same conductance per unit area as the nanoporous membrane. This definition is consistent with Eq. (2) used to obtain the experimental value of \( \kappa_{eff} \) from the measured thermal diffusivity.