

Semiconductor Thermal and Electrical Properties Decoupled by Localized Phonon Resonances

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Thermoelectric materials convert heat into electricity through thermally driven charge transport in solids or vice versa for cooling. To compete with conventional energy-conversion technologies, a thermoelectric material must possess the properties of both an electrical conductor and a thermal insulator. However, these properties are normally mutually exclusive because of the interconnection between scattering mechanisms for charge carriers and phonons. Recent theoretical investigations on sub-device scales have revealed that nanopillars attached to a membrane exhibit a multitude of local phonon resonances, spanning the full spectrum, that couple with the heatcarrying phonons in the membrane and cause a reduction in the in-plane thermal conductivity, with no expected change in the electrical properties because the nanopillars are outside the pathway of voltage generation and charge transport. Here this effect is demonstrated experimentally for the first time by investigating device-scale suspended silicon membranes with GaN nanopillars grown on the surface. The nanopillars cause up to 21% reduction in the thermal conductivity while the power factor remains unaffected, thus demonstrating an unprecedented decoupling in the semiconductor's thermoelectric properties. The measured thermal conductivity behavior for coalesced nanopillars and corresponding lattice-dynamics calculations provide evidence that the reductions are mechanistically tied to the phonon resonances. This finding paves the way for high-efficiency solid-state energy recovery and cooling.

1. Introduction

Thermoelectric (TE) materials enable electrical power generation, refrigeration, and heating, all in the solid state. Since no moving mechanical components, fluid systems, or chemical reactions are involved, TE devices provide good reliability, stability, and overall practicality.^[1] On the other hand, their low efficiency, around 3-6% in commercial devices, is a significant obstacle that impedes competitive wide-scale use as a replacement to traditional electrical power generation and fluid-based refrigeration/heat pump technologies.^[2] The performance of a TE material under a temperature gradient is based on a well-defined figure of merit, $ZT = [(S)^2 \sigma/k]T$, where S is the Seebeck coefficient, σ is the electrical conductivity, k is the thermal conductivity, and T is the average temperature between the hot and cold sides of the material. The main challenge facing TE material performance is the tight coupling between these properties among nearly all classes of inorganic and organic materials; in particular, there

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Figure 1. Prime mechanisms of thermal conductivity reduction in a semiconductor for TE conversion. a) Bulk and reduced-dimension configurations where the key factors for *k* reduction are phonon–phonon scattering (top), and phonon confinement and scattering off rough surfaces (bottom), respectively; b) corresponding configurations where optimized internal scattering obstacles such as holes, inclusions, and interfaces dominate the scattering (contemporary approach); c) NPM configuration in the form of a nanopillared membrane where the prime mechanism of *k* reduction is resonance hybridization and the resulting phonon group velocity reductions and mode localizations (current approach).

is an inherent trade-off between exhibiting a low *k* while simultaneously possessing a high σ and a high *S*—a combination of attributes needed for a significant increase in *ZT*. This trade-off has stood as a key limitation to TE technological development and proliferation since the early days of discovery of the Seebeck^[3] and Peltier^[4] effects close to two hundred years ago.^[5]

An increase of ZT by thermal conductivity reduction is a widely pursued strategy. Central to this path are phonon confinement^[6] and the key scattering mechanisms available for impeding phonon transport; these include phonon-phonon scattering (which increases with temperature),^[7] boundary scattering (such as rough boundaries),^[8-10] and scattering by impurities and internal barriers^[11] (Figure 1a,b). With the advent of nanotechnology, nanostructuring has enabled precise access and control of the internal microstructure of existing materials, especially semiconductors. A prevailing approach is the introduction of obstacles, such as holes, inclusions, and interfaces, within the interior of the TE medium to enhance phonon scattering and reduce $k^{[12,13]}$ However, in addition to scattering the phonons, the motion of charge carriers is likely to be impeded by the same obstacles. While it is possible to tune the separation distances between scattering centers to selectively scatter

phonons with longer mean free paths (MFPs) and minimize electron/hole scattering at shorter MFPs, the problem remains constrained because the allowable range of selective scattering is limited by the inherent overlap in the intrinsic phonon and charge carrier MFP distributions of the material.^[14,15] This in turn negates the possibility of a true decoupling of the phononic and electronic properties and subsequent realization of a substantial increase in *ZT*.

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2. Results and Discussion

Departing from this constraining trade-off strategy, here we demonstrate decoupling of the thermal conductivity reduction from the remaining TE properties by mechanistic means. This is done by forming a thin, suspended membrane of Si with a random arrangement of closely-packed GaN nanopillars standing on its top surface, that is, exterior to the membrane nominal cross-section. The membrane thickness and nanopillar spacing are selected to fall within the range of the phonon MFP distribution for Si, which is estimated to average at around 200-300 nm at room temperature.^[16,17] Similarly, the nanopillar feature sizes, that is, the height and width, are selected to fall within the MFP distribution of GaN; ab initio calculations predict that most of the thermal conductivity of GaN arises from phonons with MFPs greater than 200 nm.^[18] The dominant portion of the heat transported in this nanostructured material is carried by traveling phonons because generally, the electronic contribution to the thermal conductivity in silicon is negligible, even with heavy doping.^[19,20] The atoms making up the nanopillars, on the other hand, generate vibrons, or wavenumber-independent phonon resonances. These two types of waves, the traveling and the standing, couple (Figure 1c) and cause a substantial portion of the energy of the heat-carrying phonons to modally localize in the nanopillars. In addition, the coupling causes the base-membrane phonon group velocities to drop significantly. These two effects lead to a reduction in the lattice thermal conductivity along the membrane portion and form the basis of the notion of a nanophononic metamaterial (NPM).^[21-27] This mechanism of phonon hybridizations and resonance localizations-which, in principle, takes place across the full phonon spectrum—is independent of the mechanisms of voltage generation and electrical charge transport and is therefore not expected to affect the Seebeck coefficient or the electrical conductivity. This aspect breaks a longstanding tradeoff between competing properties in thermoelectricity.

Previous theoretical investigations using molecular dynamics (MD) simulations have shown the presence of phonon-vibron couplings^[23] and predicted up to two orders of magnitude reduction in thermal conductivity.^[25] However, these studies were done on model sizes on the order of 10–20 nm for the base membrane thickness due to computational limitations. Small nanostructures are more amenable to coherent wave effects; the key challenge is sustaining these effects at larger scales closer to the average MFP.^[27–29] Here, we demonstrate the first experimental evidence for both the thermal conductivity reduction by nanoresonators (designated as the *NPM effect*^[21]) and the decoupling with the electrical properties, *S* and σ . Importantly, this demonstration is accomplished with device-scale structures,





Figure 2. Nanofabricated samples of GaN-on-Si NPMs and corresponding lattice dynamics properties. a) Schematic of the NPM unit cell, b) SEM image of GaN nanopillars on a Si membrane. c) Optical microscope image of a suspended membrane, which appears lighter due to its partial transparency in the visible spectrum. The nanopillars produced a textured appearance and d) schematic of the Raman thermometry measurement geometry. e) Conventional unit cell of Si; primitive unit cell of GaN; f) atomic displacements for a bare membrane mode indicating intense motion (left) and for a corresponding NPM mode indicating localized motion in the nanopillars and minimal motion in the base membrane (right). g) Phonon band structure, and h) group velocity (left) and mode participation (right) distributions of Si membrane with (red) or without (blue) GaN nanopillars standing on the surface. The resonance hybridization (phonon-vibron) coupling phenomenon is illustrated in the circular inset in (g).

with the smallest dimension being the membrane thickness of 200 nm. The thermal conductivity along the base membranes decreases as the nanopillars increase in height, consistent with NPM theory.^[25] Electrical conductivity and Seebeck coefficient measurements on the same structures show that the nanopillars do not degrade the electrical properties. We also show that the behavior of the thermal conductivity for coalesced nanopillars provides evidence that the reductions are due primarily to phonon resonances and not boundary scattering.

The thermal conductivity test structures are illustrated in **Figure 2**. The GaN nanopillars were grown on silicon-on-insulator

(SOI) substrates via plasma-assisted molecular-beam epitaxy (MBE), see Figure 2b. The GaN nanopillars formed spontaneously at high growth temperatures and a high N:Ga flux ratio.^[30] Specimen sets with varying nanopillar heights were grown with the expectation that taller, more massive nanopillars would produce more vibrons and therefore a greater reduction in the thermal conductivity.^[25] The samples are of two types, Set A in which GaN nanopillar growth was initiated directly on the Si after a brief nitridation step and Set B in which an 8-nm AlN buffer was grown prior to nanopillar growth. As described in more detail in the Supplemental Information, the sets differ

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in their electrical conductivity variation with nanopillar height because of different degrees of diffusion of Ga and Al into the membrane during high-temperature nanopillar growth. Set A displays an increase in electrical conductivity as a function of nanopillar height, while Set B displays approximately constant electrical conductivity. Suspended membranes were formed by etching from the backside of the substrate to the buried oxide layer, then removing the oxide layer. The as-purchased SOI device layer thickness of 200 nm thus becomes the final membrane thickness. We note that SOI substrates with such thin device layers are only available with very light p-type doping, and therefore the electrical conductivity of these structures is not optimal for high ZT. This limitation is not fundamental and does not interfere with the novelty of the mechanism for thermal conductivity reduction. The membranes were heated with a strongly absorbed UV laser beam incident from the unpatterned lower side, and the specimen temperature was measured at the center of the hot spot using a green laser beam incident from the top side (Figure 2d). The temperature was determined by the shift in frequency of the Si Raman peak appearing near 520 cm⁻¹ at room temperature. Raman thermometry is a non-contact technique that has been widely used to measure the thermal conductivity of a variety of thin membranes.^[10,31-34]

Following the development given in ref. [31] for bare (unpillared) membranes, the lateral thermal transport is governed by a radial heat equation with a source heating term. We find $\Delta T(r) = T(r) - T_{amb} = P_{abs} \ln(r/R) \beta(r) / (2\pi d_i k_i)$, where P_{abs} is the absorbed power from the heating laser with beam radius r_0 , r is the radial distance from the center of the laser spot, $T_{\rm amb}$ is the ambient temperature, R is the radius of the membrane (to the boundary where it attaches to the silicon wafer), and d_i and k_i are the effective conductive thickness and thermal conductivity, respectively, where *i* represents either a bare membrane "Mem" or a nanopillared-covered membrane "NPM." As described in the Supporting Information, the radial temperature variation is small within the probe beam diameter, and thus the measured temperature difference relative to T_{amb} can be equated to $\Delta T(0)$, for which $\ln (r/R)\beta(r)$ becomes $\ln (R/r_0) + \gamma/2$, where γ is the Euler constant = 0.57721 to five significant digits. In this study, we are primarily interested in the effects of the added nanopillars on the surface of the Si membranes. In order to single out the nanopillar effects on the thermal conductivity, we differentiate the previous equation with respect to the absorbed laser power and take the ratio of this differential expression for the specimens with nanopillars and the specimens with bare membranes, that is,

$$\frac{\partial \Delta T_{\text{Mem}} / \partial P_{\text{abs}}}{\partial \Delta T_{\text{NPM}} / \partial P_{\text{abs}}} = \frac{k_{\text{NPM}} d_{\text{NPM}}}{k_{\text{Mem}} d_{\text{Mem}}}$$
(1)

In our measurements, the power of the 325 nm beam was varied and the slope of the temperature versus absorbed power was used to derive the relative ratio of the thermal conductivities. We convert the relative changes in k to estimates of absolute thermal conductivity by multiplying a typical thermal conductivity of 200-nm thick Si membranes, 60 W m⁻¹ K^{-1,[34,35]} by the ratio of the inverse slope of each sample to the average value of the inverse slope for membranes without nanopillars, 0.0251 mW K⁻¹. Although d_{NPM} is greater on average than

 $d_{\rm Mem}$ because of the presence of the nanopillars, we make the assumption that these two thicknesses are equal and cancel in Equation (1). This assumption tends to underestimate the thermal conductivity reduction by the NPM effect. In the Supporting Information, we discuss how surface roughness variation and heat loss to the environment are not consequential in our experiments.

As can be seen in Figure 3a, the thermal conductivity for the specimens displays a significant reduction as the height of the nanopillars increases, with a maximum reduction of $21\% \pm 0.4\%$ (1 std. dev.). The source of this reduction is explained by examining the phonon band structure of the NPM unit cell. For our models, we consider a representative unit cell with a Si base width of 85 nm and thickness of 200 nm, supporting a GaN nanopillar with a square cross-section, a width of 55 nm, and a height targeted to vary from 0.5 to 4 µm. A corresponding atomic model was created with all dimensions ≈15 times smaller for feasible computation (see Figures 2e,f and Experimental and Modeling Section). As shown in Figure 2g, the nanopillars fundamentally transform the membrane band structure by adding a population of localized modes that appear as horizontal lines spanning the Brillouin zone; these represent the resonance/vibron modes that couple with the underlying membrane phonon dispersion modes throughout the spectrum (the NPM effect). The localizations manifest physically as illustrated in the atomic motion close-up inserts in Figure 2f. The outcome is strong reductions in the phonon group velocities v_{g} and their mode participation ratios p_{r} which quantify the extent of mode localization in the NPM unit cell; see definitions in Experimental and Modeling Section. These two factors directly contribute to reducing the in-plane thermal conductivity.^[25] Equilibrium MD simulations were also conducted on the same atomic-scale NPM model, followed by the application of the Green-Kubo method, producing a trend similar to the experimental trend of a reduction in k with nanopillar height (see the green curve in Figure 3a and Experimental and Modeling Section). The MD results indicate a reduction of nearly 92%, which is higher than the experimental reduction because of the smaller feature sizes compared to the phonon MFP distributions of Si and GaN. This similarity in trends shows that the NPM effect describes the data we observe experimentally.

Unlike strategies of introducing defects that also slow electronic carrier transport, we see no negative impact on the electrical conductivity of the specimens (Figure 3b), while both sets display similar reductions in k. As Figure 3b,c shows, the σ and S values for Set B are unaffected by the presence of increasingly taller nanopillars, while k is reduced for all but the severely coalesced specimen. The low value of σ , around 200 Sm⁻¹, is due to the low doping in the samples (see Experimental and Modeling Section and Supporting Information). This data rules out the possibility of scattering-induced reductions in carrier mobility or density from the presence of the nanopillar forest. As explained previously, Set A shows an increase in electrical conductivity that we attribute to coincidental Ga diffusion and not to improvement in mobility. The Seebeck coefficients for Set A show the typical decrease as carrier concentrations increase.^[19,36,37] Thus, we have clearly shown that the thermal properties and electrical properties of the nanopillared membranes have been decoupled.







Figure 3. Measurements of TE properties of GaN-on-Si NPMs with varying nanopillar height. a) Thermal conductivity, b) electrical conductivity, c) Seebeck coefficient, and d) ZT^* figure of merit normalized with respect to bare membrane value. In (a), thermal conductivity predictions by MD simulations for smaller (by a factor of \approx 15) but proportionally-sized models are shown in green; arrows point to relevant axes. The AIN buffer layer (Set B) minimized diffusion of GaN into the Si membrane that dominated electrical properties in Set A. Data points circled in blue represent samples with coalesced nanopillars and were excluded from the curve fittings. Solid (dashed) curves represent phenomena influenced (uninfluenced) by the nanopillar vibrons. Uncertainty values are for one standard deviation.

Under ideal circumstances, theory predicts that having larger nanopillars attached to the Si membranes should reduce the thermal conductivity by increasing the number of vibrons available for coupling with the base-membrane phonons.^[25,26] As can be seen in Figure 3a, the initial decreases in k with increasing nanopillar height reverse themselves for Set B, with the NPM effect extinguished at a nanopillar height of 5.7 µm. This reversal is explained by an unavoidable coalescence of neighboring nanopillars as the nanopillar height increases. We observe that the coalescence occurs predominantly near the tips rather than at the roots. A comparison of two extreme cases is given in Figure 4a-d. We quantify the coalescence by calculating an average tip area using standard image analysis techniques; the complete image set is available in the Supporting Information. The tip areas plotted in Figure 4e show that most of the specimens in this study display some degree of coalescence, and the effect is significantly ($\approx 3 \times$) stronger for the tallest nanopillars in Set B. The nullification of the observed NPM thermal conductivity reduction by coalescence is also seen in quasiharmonic lattice dynamics calculations, as shown in Figure 4f-i. The phonon band structure shows that vibron states (horizontal black lines) move to higher frequencies when the nanopillars touch at the tips and thus reduce the NPM effect at the lower frequency regime which is dominant in the thermal transport.^[21] Furthermore, an increase in the

average group velocities across the spectrum is observed due to having less isolated nanoresonators. These changes cause an increase in k relative to nanopillars with unconnected tips, which provides further proof that the thermal conductivity reduction is due primarily to the NPM effect and not the scattering of phonons from the nanopillar roots. More broadly, the results offer an experimental demonstration of the role of wave effects in thermal transport in nanostructures with feature sizes on the order of a few hundred nanometers, at room temperature. This finding establishes a unique analogy with acoustics, given that the introduction of substructures to induce intrinsic local resonances has been widely utilized in the form of acoustic metamaterials;^[38] here the concept is experimentally realized—for the first time—at the nanoscale for influencing the thermal conductivity.

3. Conclusions

The ultimate target of decoupling TE properties is to enable a route for increasing *ZT*. In Figure 3d, we see that the NPM effect has increased the relative *ZT* by a factor of 2.7, raising the absolute value from 0.42×10^{-3} for the bare membrane to 1.12×10^{-3} . The theory predicts that significantly larger enhancements are possible in more ideal specimens with a larger ratio





Figure 4. Nanopillar coalescence: Evidence of NPM effect. SEM images of the specimen with a) least coalescence and b) greatest coalescence, both in tilt view 45°. Top views of (a) and (b) are shown in (c) and (d), respectively. e) Plot of average tip area versus nanopillar height showing that coalescence increased with nanopillar height. Atomic model of the unit cell f) without coalescence and g) with coalescence (base membrane brown, nanopillar purple), and corresponding h) phonon band structure and group-velocity distribution. The average group velocity for NPM normalized with respect to the corresponding bare membrane is shown to increase by 53% with coalescence.

of nanopillar-to-membrane volume.^[25,26] Our results demonstrate that these gains are obtained by the NPM effect without degradation in the electrical properties of membranes. By increasing doping in the base membrane, the numerator in the ZT expression will also increase to provide significant additional gains in the ZT absolute value. Furthermore, these results have been demonstrated in base membranes with robust dimensions and in a material that is technologically advanced and inexpensive. The enhancement through nanostructure-induced resonances would apply to other semiconductors as well, including common TE materials,^[40] provided the phonon MFP distribution has significant overlap with the nanostructure features. Together, these results point to a longsought solution to the problem of maximizing TE material performance by breaking the coupling between the thermal and electrical properties.

4. Experimental and Modeling Section

Nanopillar Synthesis: MBE Growth: GaN nanopillars were grown by catalyst-free MBE with a plasma-assisted nitrogen source onto the Si(100) device layer prior to membrane etching and release. The SOI substrates (SEH America^[39]) had device, buried oxide, and carrier layer thicknesses of 200 nm, 380 nm, and 675 μ m, respectively. The device layer was lightly boron doped with a resistivity of 28 Ω cm; as noted above, these thin device layers were not available in any other doping types or concentrations. The nanopillars initially covered the entire surface of the substrate but were selectively removed with photolithography for the electrical test structures.^[41] Nanopillar height was varied by adjusting the nanopillar growth period, with the longest growth period being 12 h. The ratio of the *N* equivalent growth rate to the Ga equivalent growth rate during nanopillar growth was 6:1 for Set A and 3:1 for Set B. The nanopillars were grown at approximately 810 °C. More details are provided in the Supporting Information.

Sample Fabrication: After nanopillar growth, each 2 cm \times 2 cm chip was fabricated into a testing platform to measure its thermoelectric properties. Each completed chip yielded two four-point electrical resistivity devices, two Seebeck coefficient devices, and 92 thermal conductivity test membranes ranging in nominal size from 400 μ m \times 400 μ m to 700 μ m \times 700 μ m. Ohmic contact pads were formed using 20 nm Ti/200 nm Al metal stacks annealed in argon at 500 °C for 1 min.

Raman Thermometry: A 325 nm He–Cd laser was used as a heating source that was propagating anti-parallel to a low intensity 532-nm laser used as a Raman probe. The nanopillared Si membranes were positioned such that the side with nanopillars was exposed to the low intensity 532-nm Raman probe, while the 325-nm beam was absorbed on the unpatterned side of the membrane. This optical alignment allowed for a more accurate estimation of absorbed laser power due to the ~60-nm

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The average group velocity ratio G_r is a quantity that characterizes the reduction in the group velocities across the entire phonon spectrum.^[25] It is defined as $G_r = G_{\text{NPM}} / G_{\text{Mem}}$, where G_i is the average group velocity of either an NPM or a membrane calculated by $G_i = (1/n_{\kappa}n_m) \sum_{\kappa}^{n_m} r_g(\kappa,m)$. Here, κ is the wave number (a scalar component of the wave vector κ

along the $\Gamma - X$ direction), *m* is the branch number, n_{κ} is the number of wave-number points considered, and $n_m = 3N$ is the total number of phonon branches. The group velocity $v_g(\kappa, m)$ is defined as the slope of the phonon frequency with respect to the wave number κ for branch *m*.

For the characterization of nanopillar resonant mode localization, we examined the mode shape corresponding to each point in the phonon band structure. We then computed the mode participation ratio p_r , which is defined for a mode at wave vector κ and branch number *m* by refs. [22,25]

$$p_{r}(\kappa,m) = \frac{1}{N \sum_{i=1}^{N} [\sum_{j=1}^{3} \phi_{ij}^{*}(\kappa,m) \phi_{ij}(\kappa,m)]^{2}}$$
(2)

where $\phi_{ij}(\kappa,m)$ is the displacement component corresponding to atom *i* and direction *j* of the normalized mode shape. The formula comprises two summations. The first is over the total number of atoms *N* in a unit cell, that is, $N = N_{\text{base}} + N_{\text{pillar}}$ for an NPM, where N_{base} is the number of atoms in the base membrane and N_{pillar} is the number of atoms in the nanopillar. The second summation is over the three directions of motion per atom. The inverse of this quantity p_r indicated the degree of modal localization over the entire unit cell considered without being specific to a particular region, for example, the nanopillar or base membrane portion of an NPM unit cell. This calculation was performed for both an NPM and a bare membrane. In an NPM, a large number of the modes exhibited high concentrations of vibrations in the nanopillar portion, yielding a low value of p_r .

Molecular Dynamics Simulations: Equilibrium molecular dynamics (EMD) simulations were executed to predict the in-plane lattice thermal conductivity of the GaN-on-Si NPMs sized at nearly 1/15 of the nominal experimental unit cell, with the height of the nanopillar being varied (see atomic model dimensions in Figure 2). A single unit cell was used as the simulation cell with periodic boundary conditions applied along the x- and y-directions and free boundary conditions applied in z-direction and around the nanopillar. The empirical interatomic potentials were identical to those used in the LD calculations. The time integration step was set as $\Delta t = 0.5$ fs. First, a canonical ensemble MD with a Langevin heat reservoir was allowed to run for 0.3 ns to enable the whole system to reach equilibrium at 300 K. Then, a microcanonical ensemble (NVE) was run for 3 ns; meanwhile, the heat current was recorded at each time step. At the end of the simulations, the thermal conductivity was calculated by the Green–Kubo formula,^[48] $k = 1/(2Vk_BT^2) \int_0^{\infty} \langle J(\tau) \cdot J(\tau) \rangle d\tau$ where $k_{\rm B}$ is the Boltzmann constant, V is the system material volume, and J is the heat flux along the direction of transport. Finally, the thermal conductivity was averaged over the two in-plane directions over six simulations with different initial velocities (i.e., a total of 12 cases), and the statistical errors were obtained according to the method described in ref. [48]. All EMD simulations were performed in LAMMPS.^[49]

Supporting Information

Supporting Information is available from the Wiley Online Library or from the author.

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absorption depth at the 325-nm wavelength, precluding transmission to the nanopillars on the opposite side of the membrane. The beam diameters at the $1/e^2$ points were 25 and 0.8 μ m for the 325 and 532 nm lasers, respectively. The nanopillars were transparent to the green probe beam though some scattering occurred as the beam passed through them. The reflectance R of the bottom side of the membranes was measured to be 0.57 for the UV beam, and the absorbed beam power was calculated as the incident beam power multiplied by (1 - R). The beam power was measured with an optical power meter close to where it impinged on the specimen and then corrected for transmission of the intervening optics. The temperature dependence of the Si Raman peak was calibrated by heating a Si chip with a strip heater and measuring its temperature with a thermocouple while acquiring Raman data. The resulting data was fit with the quadratic equation T (°C) = 23.2 – 50.4(Δv – 1.1(Δv)²) where Δv is the temperature-induced shift in the Raman peak position in wavenumbers (cm⁻¹). The linear term of this equation agreed well with previous evaluations that report $\Delta T/\Delta v = -46$ K/cm⁻¹, initially by the work of Mendez and Cardona and verified by others including Reparaz et al.^[42,43]

Seebeck Coefficient: The Seebeck coefficient measurement was performed via a steady-state method with the geometry shown in Figure S4, Supporting Information. Two meandering Ti/Al wires were lithographically defined 10 µm from the Si device layer to serve as thermometers with a \approx 100 Ω resistance. Prior to measurement, both resistors R_1 and R_2 were calibrated to within 0.1 K. An additional pair of Ti/Al wires was patterned in direct contact with either end of the Si device layer to measure the Seebeck voltage. Two 1-k Ω chip resistors, serving as heaters, were glued to one end of the chip and used to provide a thermal gradient along the length of the Si device layer. The heaters provided up to 25 mW of power yielding a maximum ΔT of 3.5 K. The heater current, thermopower voltage V_{th} , temperatures at R_1 and R_2 , and temperature gradient across the Si device layer ΔT were recorded as a function of time with an initial sample temperature at 277 K. All calibrations and measurements were performed in ice water to maintain a constant bath temperature.

Electrical Resistivity: The electrical resistivity was measured using a standard four-point probe test structure shown in Figure S4, Supporting Information. The quantity ΔV across the two inner contacts was measured as a function of current across the two outer contacts over the range of 0–100 nA. All tested devices showed a linear, ohmic response, allowing for resistivity ρ to be calculated from the membrane width w, thickness t, length L, and measured resistance R as $\rho = Rwt/L$.

Atomic Models: The theoretical investigations were based on atomic models comprising a Si membrane with GaN nanopillars standing on the surface. Both material portions were modeled as single crystals under room-temperature equilibrium conditions. The Tersoff potential was used for the interatomic interactions. The parameters of the Si-Si and Ga-N interactions were taken from refs. [44, 45], respectively. For the Si-Ga and Si-N interactions, the potential parameters were mixed following the Tersoff multicomponent combination rules.^[46] Two sizes of NPMs were investigated: one that is nearly 15 times smaller than a nominal experimental unit cell (shown in Figure 2f, right), and a smaller version for the coalescence investigation (shown in Figure 4g). In the model of the coalesced NPM, the top of the nanopillar was laterally extended to partially connect with adjacent nanopillars. This was done by adding three primitive-cell layers of GaN around the tip of the nanopillar forming a cross-like cross section when viewed from the top (cut view A-A in Figure 4g).

Lattice Dynamics Calculations: The phonon band structures for the examined GaN-on-Si NPM unit cells were obtained by solving the quasiharmonic lattice dynamics eigenvalue problem using the GULP software.^[47] Bloch periodic boundary conditions were applied along in-plane directions and free boundary conditions were applied in the *z*-direction and around the nanopillar. The phonon frequencies were computed at a set of allowed wave vectors ranging from Γ to X in the Brillouin zone with a resolution of 128 points. There are 3N phonon branches in the band structure, where N is the total number of atoms in the unit cell.



Conflict of Interest

The authors declare no conflict of interest.

Data Availability Statement

The data that support the findings of this study are available in the supplementary material of this article.

Keywords

gallium nitride, nanophononic metamaterials, nanopillars, thermal transport, thermoelectrics

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