Nanostructured Surface Phonon Polariton Systems for Mid-Infrared Nanophotonics

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In this article, novel, phonon-based silicon carbide nanopillar antenna arrays are described. Using fabricated SiC structures, sub-diffractional, localized resonances are observed with exceptionally high quality factors (40-305) and corresponding high modal confinements in the mid-infrared (IR) spectral region. These results exceed the theoretical limit of plasmonic systems and establish a basis for nanophotonics in the mid-IR and beyond, opening the door to a wide range of applications in sensing, lithography, optical circuitry and more.

Introduction

The manipulation of light at sub-wavelength dimensions has become a compelling field of research, as the limits imposed by classical diffraction can now be largely surpassed.[1] Initially observed on metal films,[2] surface plasmon polaritons (SPPs) are electromagnetic excitations that exhibit sub-diffractional confinement of optical fields. The discovery of these SPPs led, in part, to the field of plasmonics, nanophotonics[3] and metamaterials,[4] which in turn have led to advancements in optics and electronics.[5, 6] However, much of the promise of these SPPs has not been realized due to the high optical losses in these metals at optical frequencies.[7-9] Further, such materials have very large, negative permittivities at longer wavelengths, limiting their efficacy for nanophotonics beyond the near-infrared (IR) regime. These issues have motivated a search for alternative materials and strategies that can provide low optical losses, while also extending the operational polaritonic bands into the IR and terahertz (THz) regimes.

Polar dielectrics such as SiC afford an opportunity to achieve sub-wavelength confinement with low optical losses and operation in the mid-IR through surface *phonon* polaritons (SPhPs). This spectral region offers a tremendous variety of applications, including an atmospheric window for free-space communications between 8-12 μm, near-room temperature black-body emission peaks (~10 μm), and a variety of IR-active molecular vibrational resonances, useful for the identification of chemical species. SPhPs are a consequence of a coupling between incident electromagnetic fields (light) and the polar optic phonons present in polar dielectric materials. This results in a coherent oscillation of these charged ionic species enabling the formation of these SPhPs and the ability to confine light at these frequencies to sub-diffractional dimensions. The corresponding operating frequency bands exist between the transverse optic (TO) and longitudinal optic (LO) phonon modes, a region known as the Reststrahlen band,[10, 11] within which extremely high reflectivity occurs (Figure 1). As these SPhP

are phonon-based, their loss is derived from the scattering lifetimes of optic phonons, which are on the order of picoseconds.[11, 12] This provides

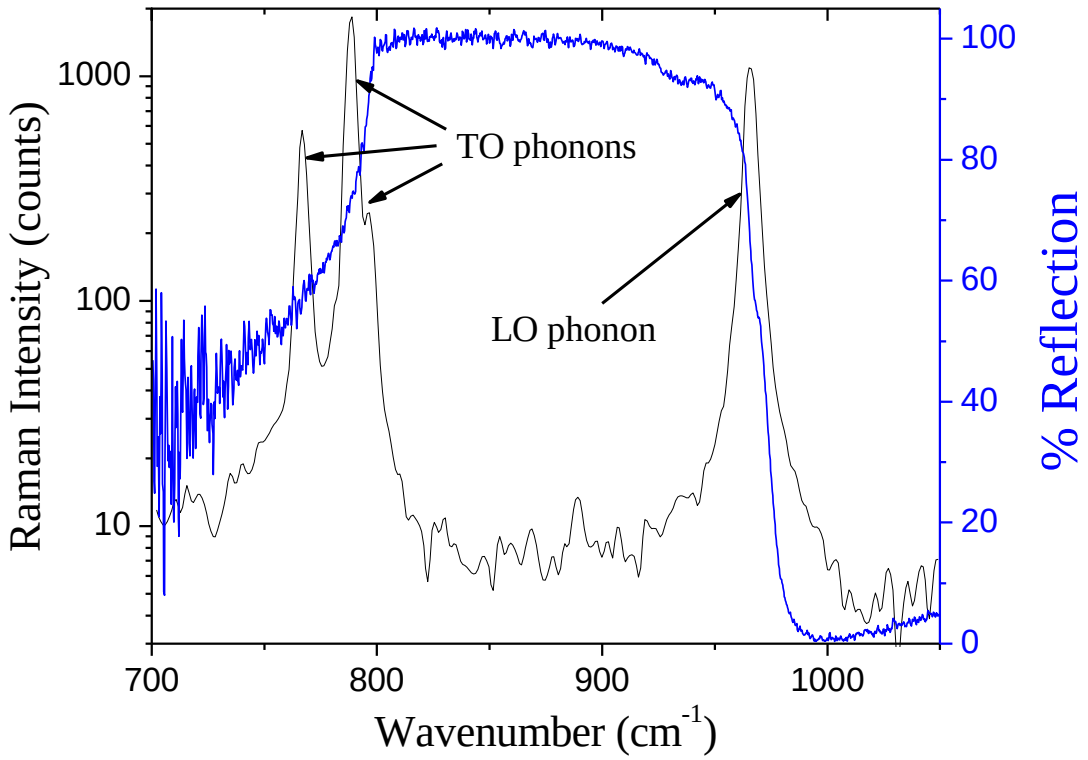

Figure 1: Raman spectra (black line) and reflection spectra (blue line) of un-patterned 6H-SiC. The phonon resonances are seen in the labeled Raman peaks which bound the highly reflective Reststrahlen band.

a dramatic improvement over their SPP-based analogues, whose electron scattering lifetimes are orders of magnitude shorter.[13, 14]

Nanostructured surface phonon polariton systems

Within the highly reflective Reststrahlen band, the reflection of incident light approaches 100% (Figure 1).[10] This is due to the coherent oscillations of bound charges on the atomic lattice, which screen out the incident electromagnetic fields and are manifested in a negative real part of the dielectric function.[15] This situation is analogous to the highly reflective behavior of metals at frequencies below the plasma frequency of that material, in which case coherent free electron oscillations.[12] In either case, the dispersion relation can be approximated as a Lorentz oscillator, however, for the case of SPhPs, the ability to stimulate and support polaritonic modes only exists within this Reststrahlen band. The local electromagnetic fields resulting from the SPhP decays evanescently as one moves away from the polar dielectric surface into a dielectric medium with positive permittivity (air, for example).

Similar to SPPs, the momentum mismatch between the incident light and the SPhP modes, requires a means to reduce the momentum of light such that an overlap between the light line, $k = \omega/c$ and the SPhP dispersion curve can be established. This mismatch can be overcome with a high index prism,[16, 17] diffraction gratings, a scanning near field microscopy (SNOM) tip,

[18, 19] or via nanostructuring the material into sub-wavelength elements.[15, 18]

In order to probe the fundamental SPhP excitations within these polar media, we fabricated a variety of nanostructured arrays (Figure 2) in high quality, ~350 μm thick semi-insulating 4H- and 6H-SiC samples using a JEOL JBX 6300-FS direct-write electron beam lithography (EBL) system. The wide-bandgap and low-background doping of the semi-insulating SiC results in poor electron transport through the substrate, severely limiting the resolution of traditional EBL techniques due to charging and back scattering.[20] We attempted several methods to mitigate these effects and found that a commercially available charge dissipation solutions (eSpacer, Showa Denko) provided the best results via spinning a thin coating on top of the resist stack. We used a bilayer PMMA resist consisting of a 120 nm bottom layer (molar mass = 495k Da) and a 50 nm top layer (molar mass = 950k Da), which greatly improved liftoff success rates. Further, by employing proximity correction techniques and writing at a 100 kV beam energy, we were able to resolve structures with lateral dimensions as small as 50 nm and gaps as small as 25 nm over large area arrays (>300 um). After ebeam writing and development, a 30 nm Al/Cr hard mask was deposited via electron beam evaporation and then lifted off in a 60° C n-methyl-2-pyrrolidone solution.

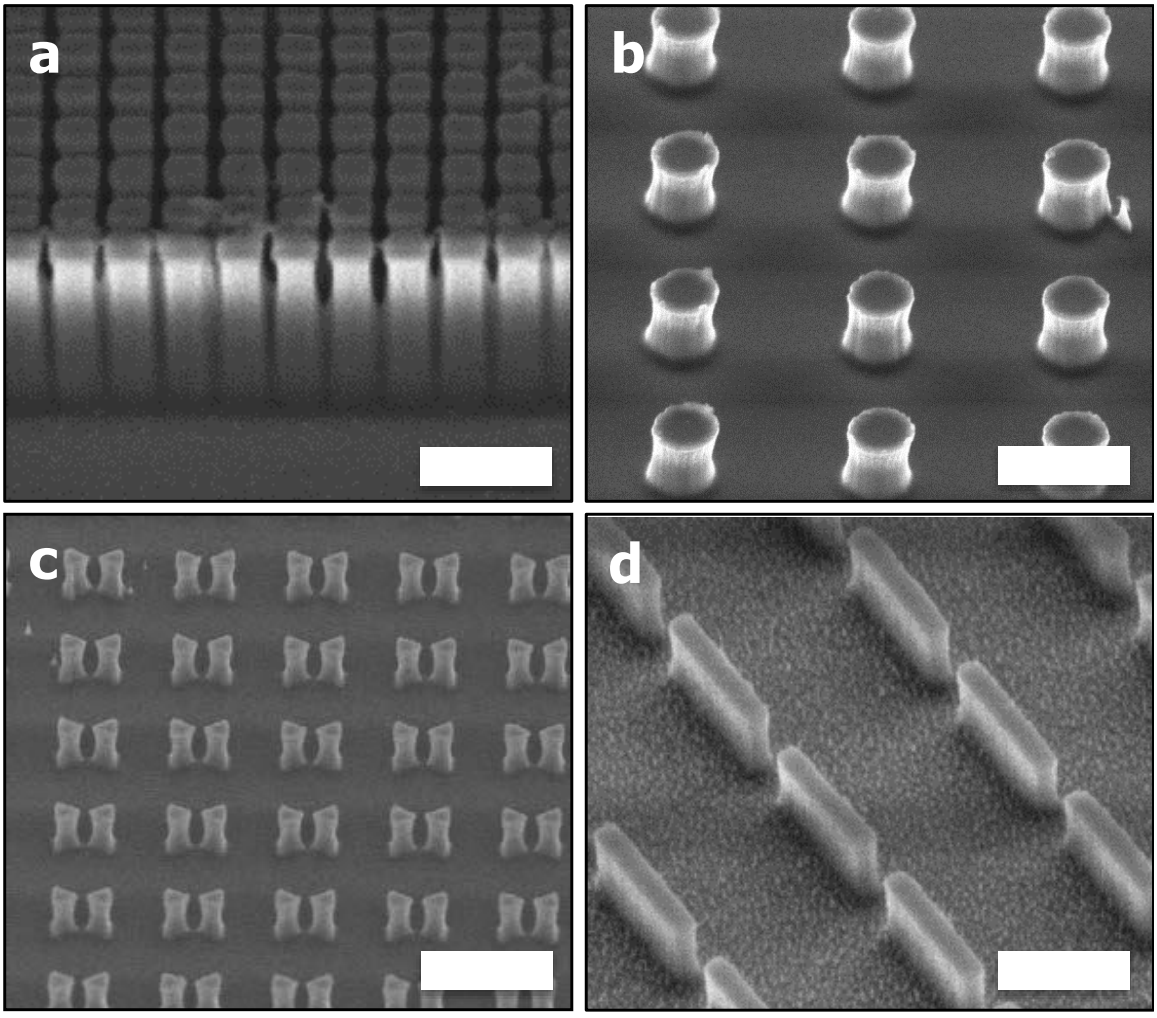

Figure 2: Different designs of phonon polariton nanoantennas fabricated in SiC. All scale bars are 1000 nm. **a** Closely spaced nanopillar array. **b** Widely spaced nanopillar array. **c** Coupled bowties. **d** High aspect ratio cuboids.

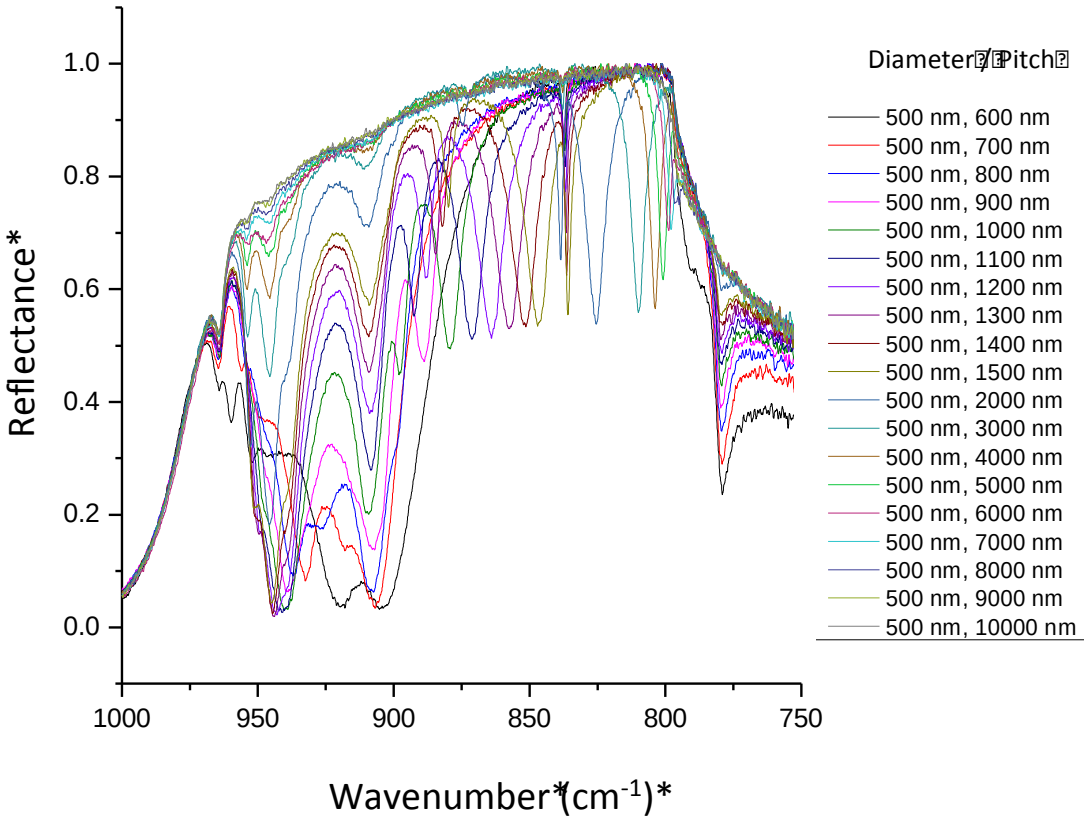

Figure 3: SPhP resonances in nanopillar arrays of 500 nm diameter SiC pillars. By varying the center to center distance (pitch) of the pillars in these arrays, one can precisely tune the spectral positions of these absorptive resonances.

The sample was then characterized optically before reactive ion etching (RIE) was carried out. Equal partial pressures of SF_6 and Ar were used at 150 W RF power at 25° C for 38 minutes, resulting in an etch depth of approximately 800 nm. After the RIE process, the metal caps were removed in consecutive baths of 50° C 16:1:1:2 HNO_3:H_3PO_4: CH_3COOH:H_2O and 25° C 2:3:28 $HClO_4$:$Ce(NH_4)_2(NO_3)_6$:H_2O to remove the Al and Cr, respectively. Several methods were investigated to repair residual surface damage associated with fluorine and other etch gas contaminants during the RIE process. The surface condition of these resonators is especially important as the SPhP modes are confined to the surface, and therefore are extremely sensitive to any morphological or chemical defects. We obtained the highest quality factors via a post-process treatment of the structures in a 70° C mixture of 2-(2-aminoethoxy) ethanol, hydroxylamine and 1,2-dihydroxybenzene (commercially sold as DuPont™ PlasmaSolv® EKC-265™) for 60 minutes. This process removes most chemical surface contaminants, while leaving the morphology of the SiC features relatively unharmed. FTIR spectroscopy was used to characterize the mid-IR reflectance properties of these nanopillar arrays. A 15x, 0.58 NA objective was used to illuminate the sample with a SiC glow bar at incident angles between 10-35° off normal, with a weighted average angle of 25°. This experimental setup provided polarization vector components both in

plane and out of plane (with respect to the substrate surface), exciting modes in both the transverse and longitudinal directions. The spectra were collected at a 0.5 cm^{-1} resolution with 128 scans averaged. The aperture was set to a 50 x 50 μm square, in order to coincide with the dimensions of the each array. Freshly deposited, optically thick Au films were used to collect background spectra at the same spectral resolution.

Tunable, high quality, sub-diffractional SiC nanoresonators

Figure 3 illustrates the tremendous tunability of the resonant properties of the SPhP modes within these SiC nanopillar arrays, providing high quality factor, highly absorptive resonances at almost any spectral position within the Reststrahlen band. For any damped oscillator, the ratio of the resonance linewidth (FWHM) to resonance frequency, is defined as the quality factor *Q*, and represents the rate of energy loss compared to the stored energy within the resonator. For the 100-500 nm diameter nanopillars we measured quality factors ranging from 40-305.[19, 21] This is in excess of any reported values for single particle plasmonic resonator, with silver having a theoretical limit for a spherical particle of about 40.[9] Further, it is important to realize the scale of confinement within these structures. Incident free-space photon wavelengths are on the order of 10-12.5 μm, while nanopillar dimensions are on the order of 100 nm, providing exceptionally sub-wavelength field confinements and dramatic electric field enhancements. Simulations suggest electric field enhancements of 5000x,[22] while enhancements as high as 27,700 were calculated for a single mode. Electromagnetic simulations of such nanopillars further suggested two fundamental types of modes: A transverse dipole that oscillates in-plane and a longitudinally oscillating 'monopole' mode that is supported by the SiC substrate. The latter is not seen in isolated plasmonic structures as they do not possess a polaritonic substrate (ground plane) to support the opposite charge. We have found that we can preferentially excite each of these types of modes by changing the polarization angle of the incident field: The stronger a vertical component of polarization is, the stronger the monopole resonance is; the stronger the in plane component of polarization is, the stronger the transverse dipole resonances are. We discuss this is more detail in a recent article.[22]

Beyond cylindrical nanopillars, we have recently explored the effect of nanopillar shape, observing that specific geometries can allow for the excitation of over a dozen distinct modes that cannot be excited in structures with higher degrees of symmetry (i.e. spheres or cylinders). Further, these resonances can be tuned spectrally without affecting the near-field profile of the mode.These SPhP modes can be highly complex three dimensional field geometries that are able to concentrate charge and electromagnetic fields to exceptionally small areas of the pillar, providing an avenue towards nanoscale control of electromagnetic field patterns for tailored, narrow band thermal emitters[23, 24] that can provide 'LED'-like performance in the mid- to far-IR with a simple, low-cost, solid-state device consisting of the nanostructured material and an integrated heater. .[25]

Summary

In summary, we have demonstrated fabrication of high quality SiC nanostructure arrays in a variety of shapes, sizes and spacings. These nanostructures exhibit strong localized surface phonon polariton (SPhP) resonances, which are highly tunable both spectrally and geometrically with respect their near field profiles. These modes are derived from optic phonons and thus have long modal lifetimes and exceptionally narrow linewidths, corresponding to quality factors as well in excess of any previously reported polaritonic material systems. The phonon

polariton materials described in this article open up new opportunities not accessible to plasmonic materials, such as reciprocal hyperbolicity,[18, 26] tuning via modulation of the carrier concentration,[27] broadband operation via multi layered materials,[28] and more. It is our hope that this approach will stimulate further research and new advances in mid-infrared nanophotonics and beyond.

Acknowledgements

The author acknowledges support from the National Research Council (NRC) NRL Postdoctoral Fellowship Program. Funding was provided via the Office of Naval Research and distributed by the Nanoscience Institute at the Naval Research Laboratory.

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