

DEVICE FOR CONFINING SURFACE PHONON-POLARITONS AND METHOD FOR FORMING THE SAME

Cross-Reference To Related Application

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[0001] This application claims the benefit of priority of Singapore patent application No. 10202003847T, filed 27 April 2020, the content of it being hereby incorporated by reference in its entirety for all purposes.

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Technical Field

[0002] Various embodiments relate to a device for confining surface phonon-polaritons and a method for forming a device for confining surface phonon-polaritons.

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Background

[0003] Phonon-polaritons (PhPs) are quasiparticles in a form of photons coupled with electric dipole oscillations of deformable ions in the crystal lattice. They exist in polar crystals at infrared frequencies, hold great promise for low-loss chip-scale nanophotonics and are considered as an alternative to plasmonics. Being observed in various material systems, phonon-polaritons can form electromagnetic waves bound to the bulk, surface and edges of the crystal, and can be efficiently controlled by dielectric permittivity and architecture of the device. Moreover, PhPs may carry remarkably large wave vectors compared to the momentum of light travelling in free space. This unique property, also typical of other polaritonic waves, has been attracting tremendous attention in the past decade as it enables new platforms for high-density optical integration and strong light-matter interactions at the nanoscale. This opens new opportunities in a number of practical applications, including sub-diffraction elements (resonators, waveguides, metamaterials, photonic crystals) and sensing.

[0004] Highly-confined (i.e., large-momentum) PhPs have been extensively studied in natural layered anisotropic two-dimension materials, BN (boron nitride) and α -MoO₃ (α -molybdenum trioxide), where they form intrinsic modes with hyperbolic dispersion. However, the growth of

large-scale high-quality uniform films, capable of supporting intrinsic hyperbolic modes, is a significant challenge, which limits phononic applications of the two-dimension materials to exfoliated-flake-based microscale devices. More recently, another approach employing nearly isotropic polar crystals with ultra-thin dielectric or semiconductor coating layers revealed even larger-momentum phonon-polaritons at the crystal surface. Such surface PhPs (SPhPs) are practically important as they can exist in numerous combinations of technology-ready polar substrates and coatings, that broadens the scope of their applications. The substrate here serves as the source of SPhPs, while their confinement is achieved by reducing the thickness of the coating layer to extremely sub-diffraction nanometric scale (typically 2 - 4 orders of magnitude smaller than the wavelength in free space). The remarkable sensitivity of the ultra-confined SPhPs to the thickness and the index of coating layers opens new avenue for ultra-compact tunable devices and infrared applications at the nanoscale. The cutting-edge performance in practical platform implementations remains a challenge, as reported approaches are limited either by the coating layer quality or the absence of technology to fabricate the high-quality layer at reasonably large scale.

Summary

[0005] The invention is defined in the independent claims. Further embodiments of the invention are defined in the dependent claims.

[0006] According to an embodiment, a device for confining surface phonon-polaritons is provided. The device may include a polar crystal substrate configured to support the surface phonon-polaritons in the device, and a layer having elemental germanium, the layer being arranged on the polar crystal substrate to confine the surface phonon-polaritons, wherein the layer has a thickness of about 50 nm or less.

[0007] According to an embodiment, a method for forming a device for confining surface phonon-polaritons is provided. The method may include forming a layer having elemental germanium on a polar crystal substrate, the polar crystal substrate being configured to support the surface phonon-polaritons in the device, and the layer being configured to confine the surface phonon-polaritons, wherein the layer has a thickness of about 50 nm or less.

Brief Description of the Drawings

[0008] In the drawings, like reference characters generally refer to like parts throughout the different views. The drawings are not necessarily to scale, emphasis instead generally being placed upon illustrating the principles of the invention. In the following description, various

embodiments of the invention are described with reference to the following drawings, in which:

[0009] FIG. 1A shows a schematic perspective view of a device for confining surface phonon-polaritons, according to various embodiments.

[0010] FIG. 1B shows a schematic perspective view of a device for confining surface phonon-polaritons, according to various embodiments.

[0011] FIG. 1C shows a method for forming a device for confining surface phonon-polaritons, according to various embodiments.

[0012] FIGS. 2A to 2D show experimental and theoretical analysis of surface phonon-polariton wavelength (λ_p) scaling.

[0013] FIGS. 3A and 3B show the topography of a 1000×500 nm germanium resonator on silicon carbide.

[0014] FIGS. 4A and 4B show results for analysis of germanium film oxidation.

[0015] FIGS. 5A to 5G show results for highly-confined surface polariton modes on 7-nm thick germanium nanoresonators. All scale bars represent 300 nm.

[0016] FIGS. 6A to 6I show results for tuning germanium resonator modes by sub-nm oxidation. All scale bars represent 300 nm.

[0017] FIGS. 7A to 7D show results for tuning near-field patterns on germanium resonators by changing the excitation frequency. All scale bars represent 300 nm.

[0018] FIG. 8 shows surface phonon-polariton (SPhP) wavelength scaling calculated for $\omega = 930 \text{ cm}^{-1}$.

[0019] FIGS. 9A to 9D show results of numerical simulations supporting corresponding data in Table 1.

Detailed Description

[0020] The following detailed description refers to the accompanying drawings that show, by way of illustration, specific details and embodiments in which the invention may be practiced.

5 These embodiments are described in sufficient detail to enable those skilled in the art to practice the invention. Other embodiments may be utilized and structural, logical, and electrical changes may be made without departing from the scope of the invention. The various embodiments are not necessarily mutually exclusive, as some embodiments can be combined with one or more other embodiments to form new embodiments.

10 [0021] Embodiments described in the context of one of the methods or devices are analogously valid for the other methods or devices. Similarly, embodiments described in the context of a method are analogously valid for a device, and vice versa.

[0022] Features that are described in the context of an embodiment may correspondingly be applicable to the same or similar features in the other embodiments. Features that are described
15 in the context of an embodiment may correspondingly be applicable to the other embodiments, even if not explicitly described in these other embodiments. Furthermore, additions and/or combinations and/or alternatives as described for a feature in the context of an embodiment may correspondingly be applicable to the same or similar feature in the other embodiments.

[0023] In the context of various embodiments, the articles “a”, “an” and “the” as used with
20 regard to a feature or element include a reference to one or more of the features or elements.

[0024] In the context of various embodiments, the term “about” as applied to a numeric value encompasses the exact value and a reasonable variance.

[0025] As used herein, the term “and/or” includes any and all combinations of one or more of the associated listed items.

25 [0026] As used herein, the phrase of the form of “at least one of A or B” may include A or B or both A and B. Correspondingly, the phrase of the form of “at least one of A or B or C”, or including further listed items, may include any and all combinations of one or more of the associated listed items.

[0027] Plasmonics on metal-dielectric interfaces was widely seen as the main route for
30 miniaturization of components and interconnect of photonic circuits. However recently, ultra-confined surface phonon-polaritons in high-index chalcogenide films of nanometric thickness

have emerged as an alternative to plasmonics. In the techniques disclosed herein, using mid-IR near-field imaging, tunable surface phonon-polaritons in CMOS-compatible interfaces of few-nm thick germanium (Ge) on silicon carbide (SiC) is demonstrated. The resonators disclosed herein may include a germanium-based structure (or patch) and a SiC substrate, where the physical size of the Ge-based structure or patch defines the size of such Ge-SiC resonator on the SiC substrate. As will be described herein, Ge-SiC resonators with nanoscale footprint can support sheet and edge surface modes excited at the free space wavelength hundred times larger than their physical dimensions. Owing to the surface nature of the modes, the sensitivity of real-space polaritonic patterns may provide pathway for local detection of the interface composition change at sub-nanometer level. Such deeply subwavelength resonators may be of interest for high-density optoelectronic applications, filters, dispersion control and optical delay devices.

[0028] Various embodiments may provide phonon polariton devices (e.g., mid-infrared (mid-IR) phonon polariton devices) on CMOS (complementary metal-oxide-semiconductor) compatible platform. Due to CMOS compatibility, the devices may be fabricated at wafer scale.

[0029] Various embodiments may provide resonant nanostructures for highly-confined and ultra-sensitive surface phonon-polaritons. The devices of various embodiments may enable the phonon-polaritons to be highly confined and, thus, can be applied for nanophotonics applications. Confinement may be defined as the ratio between the free-space wavelength of the excitation light and the SPhP wavelength. Being "highly confined" may be associated with a confinement ratio that may be significantly larger than 1 (i.e., confinement ratio $\gg 1$), e.g., a few times larger, or tens, and even hundreds of times larger.

[0030] In the techniques disclosed herein, deeply subwavelength planar resonators supporting extremely confined and tunable SPhPs on group IV semiconductor platform, having a silicon carbide (SiC) substrate coated with a nanometric germanium (Ge) film of deeply subwavelength thickness, are described. While this system enables ultracompact low-loss on-chip phononic devices with optical features more than two orders smaller than free-space wavelength (λ_0), it also bears potential in wafer-scale fabrication compatible with CMOS technology. In various embodiments, the few-nm or tens of nm thick Ge film may be fabricated with high quality and uniformity (down to atomic scale). Being of "high quality and uniformity" may mean that the roughness of the topography of the film may be close to the atomic scale (i.e., about few Angstroms, which is a typical distance between atoms - the bottom

limit of the roughness). This may be seen, for example, from FIG. 3A to be described further below, where there are a few places with sporadic ‘dots’ that should be excluded as they are related to the quality of the lithographic patterning process used and not the film roughness itself.

5 **[0031]** The resonators of various embodiments are made of few-nm or tens of nm thick Ge patches or layers or slabs of sub-micron/nanoscale sizes on top of a SiC substrate. As a non-limiting example, a general function of the resonator is to interact with an incident light and to concentrate it on deeply subwavelength scale. The optical response of the resonators is usually characterised either in real-space measurements (e.g., using s-SNOM (scattering-type scanning
10 near-field optical microscopy)), or using far-field techniques (e.g., FTIR (Fourier-transform infrared spectroscopy)) detecting its spectral response (for the latter approach, an array of resonators in the form of metamaterial may be fabricated to make spectroscopic measurements possible as will be described further below in relation to Table 1 and FIGS. 9A to 9D). The output information of the real-space near-field imaging is the direct field distribution on the
15 resonator, typically showing a number of optical modes. The output of the far-field spectroscopic characterization is the position of the resonance peak in the reflection spectrum. By monitoring changes in either of these two outputs, various contaminants or chemicals present in the environment to which the resonator is exposed to may be potentially detected, and/or how stable various materials (used as top layers) are may be checked against different
20 environments down to atomic-scale material change (in vertical direction). The approach based on real-space nanoimaging using highly-confined SPhPs provides an advantage of performing such detection locally, at sub- μm scale (in the plane of the substrate). Accordingly, the devices disclosed herein may be employed in sensing applications.

[0032] For other potential applications, such as filters and dispersion control elements as non-limiting examples, a metamaterial array of resonators (rather than working with a single
25 resonator) may be constructed. As a non-limiting example, 10 metamaterial arrays (made of multiple patches of Ge on SiC) with different functionalities may be fabricated on one large SiC wafer; optionally the wafer may be diced in, e.g., 10 smaller pieces to separate each of the device or use the whole wafer (it would depend on convenience or industrial needs). The term
30 ‘metamaterial’ may mean (or equal to) an array of Ge-SiC resonators of sufficiently subwavelength sizes (this condition is applicable to all the resonators described; typically such

definition is used when the size of the resonator is about twice (or any larger value) smaller than the wavelength of light). Physically, such an array may perform (as a whole) as a man-made artificial ‘material’ in aspects of how it interacts with light, which yield to its name (i.e., ‘metamaterial’). It should be appreciated that the number of metamaterial arrays is not so limited. The number of metamaterial arrays may depend on the size of each metamaterial (which would depend on application needs) and the size of the wafer (which would depend on the application and industrial requirements). For example, if as compact metamaterial array as possible is to be fabricated (e.g., performing like a single ‘pixel’ with designed optical properties), the number of such arrays on a wafer may be few orders of magnitude more than 10 (e.g., a million, as non-limiting example); in some other applications (such as building optical filters), a large-scale uniform metamaterial array across the whole wafer or across typical sizes of commercial optical elements may be needed (one inch, as non-limiting example). By tuning parameters of the metamaterials (including but not limited to at least one of size of the resonator, spacing between resonators, or Ge (or alternative top layer material) thickness), the intensity and/or the spectrum of the incident light reflection from such arrays may be tuned on-demand. Exploiting highly-confined SPhPs (which allow deeply subwavelength resonators) may enable dramatically shrinking footprints of such metamaterial arrays and making devices two - three orders of magnitude smaller in area compared to metamaterials based on conventional plasmonic compounds (which are not based on highly-confined SPhPs).

[0033] FIG. 1A shows a schematic perspective view of a device 100 for confining surface phonon-polaritons, according to various embodiments. The device 100 includes a polar crystal substrate 102 configured to support the surface phonon-polaritons in the device 100, and a layer 104 having elemental germanium 106, the layer 104 being arranged on the polar crystal substrate 102 to confine the surface phonon-polaritons, wherein the layer 104 has a thickness of about 50 nm or less.

[0034] In other words, a device 100 capable of confining surface phonon-polaritons (SPhPs) may be provided. The device 100 includes a polar crystal substrate (or a substrate including a polar crystal) 102 capable of supporting the surface phonon-polaritons in the device 100. The polar crystal substrate 102 has a negative real part of dielectric permittivity in the operation frequency range of the device (e.g., in the IR or mid-IR range). Polar crystal substrates or polar crystals are built from polarizable molecules, which enable excitation of dipole moments in the

material yielding to SPhPs existence at relevant frequencies. The polar crystal substrate 102 may be capable of supporting propagation of the surface phonon-polaritons in the device 100. Nevertheless, in embodiments of extremely tiny devices, the surface phonon-polaritons may be localized/confined on the device 100 than propagate.

5 **[0035]** The device 100 may further include a layer (or slab) 104 supported on the polar crystal substrate 102 to confine the (propagating) SPhPs. The layer 104 may include elemental germanium (Ge) 106 (i.e., germanium in the element form). The layer 104 may have a thickness, t , of about 50 nm or less (i.e., ≤ 50 nm), for example, ≤ 40 nm, ≤ 30 nm, ≤ 20 nm, ≤ 10 nm, or ≤ 7 nm. The layer 104 may confine SPhP modes. The layer 104 may act or function
10 as part of a resonator, and may physically define the size or dimension of the resonator. The wavelength of the SPhPs may be dependent, at least in part, on the material composition of the layer 104.

[0036] In the context of various embodiments, the device 100 is capable of supporting sheet and/or edge surface modes of the SPhPs.

15 **[0037]** In the context of various embodiments, the layer 104 may have a thickness, t , of about 7 nm or less (i.e., ≤ 7 nm), for example, ≤ 5 nm, or ≤ 3 nm.

[0038] The layer 104 may further include germanium oxide (GeO_x, e.g., GeO₂). The elemental Ge material 106 may be present in the core or the inner part or within the layer 104 and the germanium oxide may surround the elemental Ge 106. The germanium oxide may be in the
20 form of a layer or film on at least one surface of the elemental Ge 106. The germanium oxide may be present as a surface film as part of the layer 104. In other words, the layer 104 may include the germanium oxide on at least one surface of the layer 104. In various embodiments, part of the elemental Ge 106 may become oxidised to form the germanium oxide, where the part of the layer 104 containing the germanium oxide may make up part of the overall thickness
25 of the layer 104. As a non-limiting example, the layer 104 having the elemental Ge 106 may be formed on the polar crystal substrate 102. With exposure to air or ambient environment, the elemental Ge 106 may become oxidised to form the germanium oxide.

[0039] In various embodiments, the layer 104 may include a (surface) film having the germanium oxide, wherein a thickness of the film is between about 2.5 nm and about 4 nm,
30 e.g., between about 2.5 nm and about 3.7 nm, between about 2.5 nm and about 3.5 nm, between about 2.5 nm and about 3 nm, between about 2.7 nm and about 4 nm, between about 2.7 nm

and about 3.5 nm, or between about 3.2 nm and about 3.7 nm, e.g., about 2.7 nm, about 3 nm, about 3.2 nm, about 3.5 nm, or about 3.7 nm. The part of the layer 104 having the elemental Ge 106 make up the remaining thickness, e.g., having a thickness of between about 3 nm and about 4.5 nm in the presence of the germanium oxide. The part containing the elemental Ge and the part containing the germanium oxide may together result in a thickness of about 7 nm.

[0040] In various embodiments, the polar crystal substrate 102 may include silicon carbide (SiC). It should be appreciated that other suitable polar crystal substrates may be used.

[0041] The device 100 may further include an optical antenna configured to generate a near-field light for excitation of the surface phonon-polaritons (propagating) in the device 100. The optical antenna may receive a far-field light (e.g., infrared, e.g., mid-infrared (mid-IR)) and convert the far-field light into the near-field light. The far-field light may be incident or illuminated on the optical antenna. The far-field light may be provided by a laser source, e.g., an IR laser. It should be appreciated that any deeply subwavelength objects or features (e.g., geometrical features) may be employed as the optical antenna.

[0042] In various embodiments, the optical antenna may include a (sharp) metal tip (or metallised tip). The apex of the metal tip may have deeply subwavelength size. As a non-limiting example, the metal tip may include or may be an atomic force microscopy (AFM) tip.

[0043] In various embodiments, the layer 104 may be patterned to define the optical antenna. This means that the layer 104 may include a patterned feature that defines the optical antenna.

For example, the layer 104 may include a surface pattern. The patterned feature may include but not limited to at least one of a grating, a ridge, a groove, or any suitable subwavelength feature(s).

[0044] In various embodiments, the layer 104 may include a (optical) grating (as the patterned feature in or on the layer 104) to define the optical antenna. FIG. 1B shows a schematic perspective view of a device 100b having a grating 108. Similar to the device 100 of FIG. 1A, the device 100b includes a polar crystal substrate 102, and a layer 104 having elemental germanium 106 of a thickness of about 50 nm or less. The grating 108 may be defined in the layer 104. The layer 104 may be partially or fully perforated (down to the surface of the substrate 102) to define the grating 108. The period and gap values for the grating 108 may be suitably varied. FIG. 1B illustrates a non-limiting example of a patterned grating 108, and it should be appreciated that more complex geometry gratings are also possible to implement.

[0045] In various embodiments, the layer 104 may have or may be of a shape of a rectangle, a square or a rod. Nevertheless, it should be appreciated that other suitable shapes may be possible.

[0046] The device 100 may be compatible with CMOS technology.

5 [0047] FIG. 1C shows a method 120 for forming a device for confining surface phonon-polaritons, according to various embodiments. The method 120 includes forming a layer having elemental germanium (Ge) on a polar crystal substrate, the polar crystal substrate being configured to support the surface phonon-polaritons in the device, and the layer being configured to confine the surface phonon-polaritons, wherein the layer has a thickness of about
10 50 nm or less (i.e., ≤ 50 nm).

[0048] In various embodiments of the method, the layer may have a thickness of about 7 nm or less (i.e., ≤ 7 nm).

[0049] In various embodiments of the method, the layer may further include germanium oxide. The layer may include a film having the germanium oxide, wherein a thickness of the film may
15 be between about 2.5 nm and about 4 nm.

[0050] The polar crystal substrate may include silicon carbide (SiC).

[0051] The method may further include forming an optical antenna configured to generate a near-field light for excitation of the surface phonon-polaritons (propagating) in the device. This may include patterning the layer to define the optical antenna. Patterning the layer may include
20 forming a grating in the layer to define the optical antenna.

[0052] In various embodiments, the layer may have or may be of a shape of a rectangle, a square or a rod. Nevertheless, it should be appreciated that other suitable shapes may be possible.

[0053] It should be appreciated that description in the context of the device 100 may
25 correspondingly be applicable in relation to the method 120.

[0054] Various embodiments or techniques will now be further described in detail.

[0055] Various embodiments may provide few-nm Ge-SiC interfaces for highly-confined SPhPs. Using scattering-type scanning near-field optical microscopy (s-SNOM), infrared SPhP modes in ultra-thin (thickness $\sim \lambda_0/1500$) germanium slabs and nanoresonators on silicon
30 carbide may be investigated. As a “gold standard” high-index material for the fabrication of ultra-smooth, wafer-scale and low-loss nanometric coatings, Ge provides excellent conditions

for support of high-quality mid-IR SPhP modes. At the same time, it also allows the formation of surface oxidized layer (i.e., Ge oxide), which may provide the opportunity to trace polaritons dynamics under chemical interactions with the environment. s-SNOM technique may provide direct information on changes in the SPhP wavelength (λ_p) and mode field distribution, which
5 may be modelled with the evolution of the device material composition.

[0056] FIGS. 2A to 2D show experimental and theoretical analysis of surface phonon-polariton wavelength (λ_p) scaling, e.g., in the case of high confinement. FIG. 2A shows a perspective schematic of an s-SNOM imaging or experiment using the device 200 of various embodiments. The device 200 includes a silicon carbide (SiC) substrate 202, and a germanium (Ge) or
10 germanium-based structure 204 on the SiC substrate 202. The germanium-based structure 204 and the SiC substrate 202 may together define a resonator. The structure 204 may include a layer 206 of elemental Ge material (e.g., as an inner material or core) and a film 208 of oxide (i.e., Ge oxide) on one or more surfaces of the Ge material 206. The Ge oxide layer 208 may be
15 on the top surface and/or side surface(s) of the Ge material 206 or the Ge structure (or layer) 204. The inset in FIG. 2A shows a schematic of the device or sample cross-section, which includes a four-layer system having a bulk SiC substrate 202, nanometric elemental germanium 206 and oxide 208 layers, and air 280. White dashed lines are provided in the four-layer system in the inset to trace the boundaries or interfaces between adjacent layers.

[0057] Depending on the applications, an oxide layer (e.g., Ge oxide 208) may or may not be
20 desirable. The device 200 can suitably work without the Ge oxide 208. The oxide layer (e.g., Ge oxide 208), in general, reduces the quality factor of the device 200. However, as long as a reasonable amount of elemental Ge is left non-oxidized (e.g., in the form of Ge material 206), the device 200 may be suitably employed in various applications. Using sensing as a non-limiting example, the device 200 may be suitably used even in the presence of the Ge
25 oxide 208, in addition to reasonable amount of elemental Ge material 206, as it may be natural or expected for resonant sensors to have reduced quality factors in the process of sensing since additional materials/contaminants may be absorbed by the device 200.

[0058] The SiC substrate 202 serves as the source of SPhPs. The SiC substrate 202 has a negative real part of the permittivity, which is the physical reason that it supports SPhPs at the
30 interfaces with positive-permittivity materials (e.g., air, Ge). The Ge structure 204 itself may not support SPhPs; however, working co-operatively with the SiC substrate 202, the Ge

structure 204 dramatically reduces the wavelength of SPhPs existing in the resulting SiC-Ge-air system. Adding few-nm or tens of nm Ge layer results in appearance of the highly-confined mode.

[0059] Laser radiation (represented by the inward directional arrow 272), of a wavelength in the mid-IR range, within the reststrahlen band of SiC may be provided. The incident laser radiation 272 may excite SPhPs by means of sub-diffraction optical antenna (e.g., in the form of a metallized tip 270, e.g., a standard atomic force microscopy (AFM) metal-coated silicon (Si) tip) for simultaneous launching and detection of polaritonic waves. These waves undergo reflections from the edges of the Ge structure (or the walls of resonators) 204, forming interference patterns which may be mapped together with the topography upon scanning the sample 200. In FIG. 2A, the outward directional arrow 274 represents back-scattered light by the device 200. While not shown, the setup may use the same objective for illumination of the sample or device 200 with the incident light 272, and for collection of the scattered light 274, which the sample 200 scatters.

[0060] The sharp metallic tip 270 works here as a deeply subwavelength antenna for simultaneous launching and detection of SPhP electric field (e.g., a converter of the far-field illumination to the near-field waves in the form of SPhPs). Upon sample or device 200 illumination, the tip-launched SPhP wave travels to an edge of the resonator (in the form of the germanium-based structure 204), reflects back and forms a standing SPhP pattern, which is further mapped by the tip 270 during scanning of the device 200. The SiC/Ge resonator 200 works as a medium which supports highly-confined SPhPs and may allow their propagation. Bare SiC (outside of the Ge resonator 204) does not support highly-confined SPhPs, so that adding the Ge structure 204 is required for generating such highly-confined SPhPs and making the device 200 work. Referring to the four-layer system shown in the inset in FIG. 2A, the introduced or generated highly-confined SPhP is, intrinsically, a wave which simultaneously exists and which may propagate along all the layers or portion thereof (i.e., SiC 202, Ge 206, oxide 208 and air 280) at the same time. The highly-confined SPhP may also propagate along the respective interfaces of two adjacent layers of the four-layer system. The apex of the tip 270 has deeply subwavelength size (around 50 nm), which helps to overcome momentum mismatch between far-field illumination (holding small wave vector) and the SPhPs (holding few tens

larger wavevector). Without the tip 270, the efficiency of highly-confined SPhPs excitation may be much lower. Therefore, it should be appreciated that the tip 270 may be optional.

[0061] It should be appreciated that any deeply subwavelength objects may be used as (optical) antennas. However, the excitation efficiency may be very different depending on the geometry and/or materials. For example, the edges of the resonator, e.g., the edges of the germanium-based structure 204, can also help to launch the SPhPs, so that the resonators can be excited in known spectroscopic regime (without the tip 270 or additional/external optical antennas) as shown in simulation as will be described further below in relation to Table 1 and FIGS. 9A to 9D. In general, the surface phonon-polaritons (SPhPs) have smaller wavelength (and larger wavevector, called momentum, correspondingly) compared to free-space radiation, which may forbid their excitation by direct illumination due to momentum mismatch. Optical antennas may be employed to help convert the low-momentum far-field radiation to the higher-momentum near-field waves. This may be naturally achieved by using an antenna with geometrical features (such as tip apex size) at the subwavelength scale, or deeply subwavelength scale when described in the context of the current platform described herein based on highly-confined SPhPs. Further, it should be appreciated that, as non-limiting examples, in patterned devices (e.g., which may have some edges, gratings, resonators or other subwavelength features), phonon polaritons may also be excited without external optical antennas. FIGS. 1A, 1B, and 2A (and also FIG. 3A to be described further below) illustrate some simple examples of a patterned device (single resonator). In unstructured devices, for example, infinite films, the phonon-polaritons may not be excited by a direct far-field illumination. It should further be appreciated that other methods for the excitation beyond the optical antennas, e.g., far- to near-field coupling through a prism placed above the SiC 202 at a small air gap distance, in the order of the free-space wavelength, may also be used.

[0062] In various embodiments, spectroscopic sensing may be done using the platform described herein without a tip. This may be applied to both: sensing of the semiconductor layer material change (e.g., Ge oxidation), and sensing of an external layer deposited on top of the resonators. For example, the external layer may be deposited on the Ge layer (e.g., 204, FIG. 2A) and/or the SiC (e.g., 202, FIG. 2A). Performing the sample scanning in real-space using a tip (e.g., tip 270), however, may provide a great advantage in spatial resolution over known spectroscopic sensing approaches: the data recorded locally by the tip may provide local

information of the material change at deep subwavelength scale (e.g., submicron in this disclosure, referred to as in-plane resolution), while the far-field spectroscopy would require making large-scale arrays of resonators and could not be performed locally.

[0063] For the near-field microscopy, a reflection-mode s-SNOM setup (e.g., by Neaspec) with custom thermally-tunable CO₂ laser (e.g., by Access Laser) may be used for performing infrared nano-imaging. Standard metal-coated tips, e.g., Arrow-NCpt (Nanoworld), with ~245 - 275 kHz oscillation frequency have been utilized as near-field probe in the imaging experiment. Vertically polarized component of the tip-scattered light may be selected using a polarizer. Pseudo-heterodyne detection scheme may be used for the optical data acquisition. The tip-scattered signal demodulated at the second (s2) and the third (s3) harmonics of the tip oscillation frequency may be analysed. Low contrast optical cross-sections may be averaged by several neighbouring lines to increase the signal-to-noise ratio.

[0064] As a non-limiting example, germanium structures may be fabricated on one or more silicon carbide substrates using electron beam lithography (EBL), followed by 7 nm Ge layer deposition and lift-off processes. In greater detail of the fabrication, AR-P 6200 resist and AR 600-546 developer (ALLRESIST), for example, may be used for EBL process on 6H-SiC wafers. EBL patterns may be written in, for example, Helios NanoLab 650 system (FEI). Germanium films may be thermally evaporated on the patterned substrates in high vacuum (10^{-7} - 10^{-6} mTorr) using, for example, Univex 250 system (Leybold). The lift-off process may be done in, for example, AR 600-71 remover.

[0065] Owing to its excellent adhesion, the germanium film forms a high-quality interface, which is as smooth as nearly atomically-flat substrate (see FIGS. 3A and 3B showing the topography of a 1000×500 nm germanium resonator 304 on silicon carbide 302). FIG. 3A shows an atomic-force microscopic image recorded in s-SNOM together with the optical data shown in FIG. 5A to be discussed later. Sporadic dot-like features resulted solely from contaminations in the EBL step and can be routinely eliminated in technology by optimizing the lithography process. FIG. 3B shows profiles of the resonator 304 taken along the same cross-section (marked with a dashed white line in FIG. 3A) at 1 and 16 days (after fabrication) respectively. As may be observed, there is little difference in the two profiles obtained at different days. Such feature of nanometric germanium films as described may provide a

substantial advantage as the polaritons propagation greatly benefits from high-quality interfaces.

[0066] Given an ideal Ge-SiC interface, highly-confined SPhPs can be described using rigorous or simplified dispersion relations for a three-layer system having a negative-permittivity substrate (e.g., SiC substrate 202, FIG. 2A), a positive-permittivity dielectric coating layer (e.g., elemental Ge material 206, FIG. 2A) of a deep subwavelength thickness, and air (e.g., 280, FIG. 2A). For a 7-nm Ge film on 6H-SiC used and described herein, the rigorously calculated SPhP wavelength at $\omega = 924.5 \text{ cm}^{-1}$ (the excitation frequency mainly used in the various techniques) is about 643 nm. To describe the actual Ge-SiC interface, however, it may be necessary to take into account an ultra-thin germanium oxide layer, which may be formed on Ge surface upon exposure to the ambient atmosphere. The dispersion of the resulting four-layer system (e.g., as schematically shown in the inset of FIG. 2A) may be numerically estimated by analyzing of the imaginary part (r'') of the interface reflection coefficient via transfer matrix method. At a fixed excitation frequency, this numerical calculation produces a value of the SPhP wavelength which depends on the thicknesses of the elemental germanium (d) 206 and oxide (h) 208 layers. The total thickness of a composite film ($T = h + d$) having germanium and oxide may be assumed to be fixed at 7 nm (for example, see FIGS. 3A and 3B) and the SPhP wavelength as a function of the oxide thickness for $\omega = 924.5 \text{ cm}^{-1}$ may be calculated. The corresponding results are plotted in FIG. 2B, which is a plot of the imaginary part of the interface reflection coefficient (r'') for p-polarization calculated at $\omega = 924.5 \text{ cm}^{-1}$. FIG. 2B shows curves 282, 284 depicting SPhP wavelength (λ_p) scaling versus the oxide thickness (h). The nearly-linear curve (dark solid curve) 282 highlights local maxima of r'' (max- r'') and represents the scaling law of the SPhP wavelength, $\lambda_p(h)$. The sensitivity of polaritons to the oxide thickness is represented by the slope $\Delta\lambda_p/\Delta h$, which may range as $9.1 \pm 0.7 \text{ nm per \AA}$ along the curve 282. This number is practically remarkable as it allows locally tracing the composition change of the film at the atomic scale. Indeed, s-SNOM can routinely resolve the spatial optical features of a few 10s nm (changes in the polariton wavelength for the techniques disclosed herein), which provides angstrom-level tomographic resolution for the oxide thickness estimation when divided by the slope value. Such resolution is in the range of materials lattice constant - the smallest (bottom-limited) scale of chemical interactions.

[0067] Simplified analysis of $\lambda_p(h)$ scaling may also be carried out analytically by assuming highly-confined nature of SPhP modes ($\lambda_p \ll \lambda_0$). This condition results in the following dispersion relation:

$$\alpha_1 e^{2k_p(h-d)} + \alpha_2 e^{2k_p h} + \alpha_3 e^{-2k_p d} \simeq \alpha_4 \quad \text{Equation (1),}$$

5 where $k(p)$ is the complex polariton wavevector,

$$\alpha_1(\omega) = (\varepsilon_h - \varepsilon_d) (1 - \varepsilon_h) (\varepsilon_s + \varepsilon_d),$$

$$\alpha_2(\omega) = (\varepsilon_h + \varepsilon_d) (1 - \varepsilon_h) (\varepsilon_d - \varepsilon_s),$$

$$\alpha_3(\omega) = (\varepsilon_h + \varepsilon_d) (1 + \varepsilon_h) (\varepsilon_s + \varepsilon_d),$$

$$\alpha_4(\omega) = (\varepsilon_h - \varepsilon_d) (1 + \varepsilon_h) (\varepsilon_s - \varepsilon_d), \text{ and}$$

10 ε_s , ε_d and ε_h are permittivities of the substrate (SiC), germanium and oxide layers, respectively.

[0068] Derivation and analysis of the SPhP wavelength scaling relation may be as follows. An approximate dispersion relation for a TM-polarized surface-polariton wave in the four-layer system (corresponding to Equation (1)) may be derived from Maxwell's equations assuming
15 highly-confined nature of the mode. For solving Maxwell's equations, the approach introduced for two- and three-layer systems may be expanded to the case of four-layer system (see, for example, the inset of FIG. 2A), with additionally applying simplifications to the mode fields before obtaining the final dispersion formula. Using the inset of FIG. 2A as a non-limiting example, the four-layer system includes a negative-permittivity (ε_s) substrate 202 and air (ε_a
20 = 1) 280 occupying semi-infinite spaces on the bottom and top of the system. Two intermediate bottom and top layers correspond to elemental germanium 206 and oxide 208 (thickness and permittivity are d , ε_d and h , ε_h correspondingly). T denotes a combined thickness of the intermediate layers 206, 208. The y-axis points inwards into the page.

[0069] Considering time-harmonic electromagnetic fields oscillating at frequency
25 ω ($\frac{\partial}{\partial t} = -i\omega$), a TM mode with only H_y magnetic field being nonzero will have the electric component E_x in the form of:

$$E_x = -i \frac{1}{\omega \varepsilon_0 \varepsilon} \frac{\partial H_y}{\partial z} \quad \text{Equation (2),}$$

which directly follows from Maxwell's equations for the media with dielectric permittivity ε ; ε_0 denotes dielectric permittivity of vacuum.

[0070] Considering Equation (2), the magnetic and electric field components of an interface-bound TM surface polariton wave can be written as a combination of exponentially decaying along z and propagating along x functions (expressions for E_z component are omitted as they are not required for the further derivation):

5 for $z > h$:

$$H_y = A e^{ik_p x} e^{-q_a z} \quad \text{Equation (3a),}$$

$$E_x = iA \frac{1}{\omega \varepsilon_0 \varepsilon_a} q_a e^{ik_p x} e^{-q_a z} \quad \text{Equation (3b),}$$

for $z < -d$:

$$H_y = B e^{ik_p x} e^{q_s z} \quad \text{Equation (4a),}$$

$$E_x = -iB \frac{1}{\omega \varepsilon_0 \varepsilon_s} q_s e^{ik_p x} e^{q_s z} \quad \text{Equation (4b),}$$

for $-d < z < 0$:

$$H_y = C_d e^{ik_p x} e^{q_d z} + D_d e^{ik_p x} e^{-q_d z} \quad \text{Equation (5a),}$$

$$E_x = -iC_d \frac{1}{\omega \varepsilon_0 \varepsilon_d} q_d e^{ik_p x} e^{q_d z} + iD_d \frac{1}{\omega \varepsilon_0 \varepsilon_d} q_d e^{ik_p x} e^{-q_d z} \quad \text{Equation (5b),}$$

for $0 < z < h$:

$$H_y = C_h e^{ik_p x} e^{q_h z} + D_h e^{ik_p x} e^{-q_h z} \quad \text{Equation (6a),}$$

$$E_x = -iC_h \frac{1}{\omega \varepsilon_0 \varepsilon_h} q_h e^{ik_p x} e^{q_h z} + iD_h \frac{1}{\omega \varepsilon_0 \varepsilon_h} q_h e^{ik_p x} e^{-q_h z} \quad \text{Equation (6b),}$$

where $q_i^2 = k_p^2 - k_0^2 \varepsilon_i$ Equation (7),

$i = a, h, d, s$ denote corresponding layers air 280, oxide 208, germanium 206, substrate 202 (see inset of FIG. 2A) of the interface (or system),

20 A, B, C_d, D_d, C_h, D_h are complex coefficients,

$k(p)$ is the complex polariton wavevector, and

k_0 is the wavevector in free space.

[0071] Continuity of H_y and E_x at interfaces $z = h$, $z = 0$, and $z = -d$ results in the following system of six linear equations:

25 for $z = h$:

$$A e^{-q_a h} = C_h e^{q_h h} + D_h e^{-q_h h} \quad \text{Equation (8a),}$$

$$A \frac{q_a}{\varepsilon_a} e^{-q_a h} = -C_h \frac{q_h}{\varepsilon_h} e^{q_h h} + D_h \frac{q_h}{\varepsilon_h} e^{-q_h h} \quad \text{Equation (8b),}$$

for $z = 0$:

$$C_h + D_h = C_d + D_d \quad \text{Equation (9a),}$$

$$-C_h \frac{q_h}{\varepsilon_h} + D_h \frac{q_h}{\varepsilon_h} = -C_d \frac{q_d}{\varepsilon_d} + D_d \frac{q_d}{\varepsilon_d} \quad \text{Equation (9b),}$$

5 for $z = -d$:

$$B e^{-q_s d} = C_d e^{-q_d d} + D_d e^{q_d d} \quad \text{Equation (10a),}$$

$$-B \frac{q_s}{\varepsilon_s} e^{-q_s d} = -C_d \frac{q_d}{\varepsilon_d} e^{-q_d d} + D_d \frac{q_d}{\varepsilon_d} e^{q_d d} \quad \text{Equation (10b).}$$

[0072] Assuming large-momentum solutions ($k_p \gg k_0 |\sqrt{\varepsilon_i}|$), Equation (7) may be reduced to $|q_i| \simeq |k_p|$ and $q_i \simeq -k_p$ chosen, which corresponds to the propagating negative-index mode.

10 Solving the system, Equations (8a) - (10b), using this assumption provides a simplified dispersion relation in the form:

$$\alpha_1 e^{2k_p(h-d)} + \alpha_2 e^{2k_p h} + \alpha_3 e^{-2k_p d} \simeq \alpha_4 \quad \text{Equation (11),}$$

where $\alpha_1(\omega) = (\varepsilon_h - \varepsilon_d)(\varepsilon_a - \varepsilon_h)(\varepsilon_s + \varepsilon_d)$,

$\alpha_2(\omega) = (\varepsilon_h + \varepsilon_d)(\varepsilon_a - \varepsilon_h)(\varepsilon_d - \varepsilon_s)$,

15 $\alpha_3(\omega) = (\varepsilon_h + \varepsilon_d)(\varepsilon_a + \varepsilon_h)(\varepsilon_s + \varepsilon_d)$, and

$\alpha_4(\omega) = (\varepsilon_h - \varepsilon_d)(\varepsilon_a + \varepsilon_h)(\varepsilon_s - \varepsilon_d)$.

Substituting the air-layer permittivity ε_a with 1 (i.e., $\varepsilon_a = 1$), Equation (11) leads to Equation (1).

[0073] The calculated $\lambda_p(h) = 2\pi/|Re(k_p)|$ solution of Equation (1) (at $\omega = 924.5 \text{ cm}^{-1}$ for $T = 7 \text{ nm}$) is plotted as the curve (white dashed curve) 284 in FIG. 2B, which closely merges with $\max-r''$ (see curve 282) at shorter SPhP wavelengths as expected from the asymptotic. The derived relation would allow direct analysis of the scaling and the dispersion of highly-confined SPhPs in nanometric composite films, providing a link between the interface composition change and the polariton wavelength.

25 **[0074]** For theoretical calculations, the dispersion and scaling relations for the four-layer system (see, for example, the inset of FIG. 2A) have been directly derived from Maxwell's equations. In calculations, the germanium and germanium oxide may be modelled as lossless

layers with refractive indexes of 4 and 1.5 correspondingly; silicon carbide permittivity may be “ $-1.73 + 0.21i$ ” (at frequency of 930 cm^{-1}), and “ $-2.10 + 0.23i$ ” (at frequency of 924.5 cm^{-1}).

[0075] To experimentally identify the wavelength of SPhPs, polaritons near the edge of an effectively semi-infinite germanium slab (with the size well exceeding SPhP propagation distance) fabricated on a SiC substrate together with nano-resonators (e.g., Ge-based structures on SiC substrate) may be mapped. As an example, FIG. 2C shows an s-SNOM image recorded at $\omega = 924.5 \text{ cm}^{-1}$ at the corner of the structure 1 day after the sample fabrication. In greater details, it is a near-field image (optical amplitude s_2) recorded at the corner of a 7-nm thick large ($10 \times 10 \text{ }\mu\text{m}$) germanium microstructure 204c on SiC substrate 202c at $\omega = 924.5 \text{ cm}^{-1}$. A typical deep sub-diffraction fringe pattern may be observed. The corresponding near-field profile (or near-field cross-section) along the white dashed line in FIG. 2C is plotted in FIG. 2D. It is noted that the global decrease of the near-field amplitude in the Ge area (204c, FIG. 2C) compared to bare SiC (202c, FIG. 2C) is a result of a strong change in tip-scattering efficiency between two regions arising from resonant light-matter interactions in s-SNOM tip-SiC system. The extracted SPhP wavelength is 400 nm, which is given by a double value of the fringe period (“ $\lambda_p/2$ ” model for fringes interpretation is used). By repeating s-SNOM mapping and extraction of λ_p at different times after the sample fabrication, SPhP wavelength dynamics may be obtained, which is schematically shown with arrows pointing to λ_p scaling curve in FIG. 2B. Calculations have been done with respect to the max- r'' curve 282. However, it should be noted that the results obtained by both methods, as represented by the curves 282, 284, are almost indistinguishable (i.e., closely match each other). At 1, 10 and 16 days after the fabrication, the polariton wavelength shrinks from about 400 nm to about 360 nm and then to about 345 nm, which corresponds to an increase in SPhP wavelength confinement (λ_0/λ_p) from about 27 to about 30 and then to about 31.4. By matching experimental and calculated values (max- r'') of λ_p , the oxide thickness may be extracted, which increases from about 3 nm to about 3.5 nm and then to about 3.7 nm accordingly.

[0076] Whether it may be preferable to have an oxide layer whose thickness changes (e.g., increases) with time depends on the applications. For example, if the oxidation of Ge is to be monitored locally, the device having Ge is to be characterized while oxidation process is ongoing (before saturation). In other applications, it may generally be preferable to have a fixed oxide thickness (e.g., as thin as possible), although there may be some exceptions as changes in

the oxide thickness may provide an additional degree of freedom in tuning the resonator performance. As a non-limiting example, the oxidation of Ge may be reduced by using alternative techniques for Ge coating, for example, by using sputtering instead of thermal deposition.

5 **[0077]** The oxidation of the germanium film has been additionally cross-analysed using X-ray photoelectron spectroscopy (XPS) and scanning transmission electron microscopy (STEM), which directly show the chemical presence of germanium oxide at the film surface and its development with time to the thickness of about 3.6 nm (after 16 days) in agreement with the model prediction as will be discussed below.

10 **[0078]** The XPS analysis may be performed using, for example, an AXIS Supra spectrometer (Kratos Analytical) equipped with a hemispherical analyzer and a monochromatic Al K-alpha source (1487 eV) operated at 5 mA and 15 kV. The XPS spectra may be acquired from an area of $700 \times 300 \mu\text{m}$. A 3.1-volt bias may be applied to the sample to neutralize charge build up on the sample surface. Pass energy 20 eV may be used for high-resolution scans acquisition.

15 **[0079]** For STEM imaging, the Ge-SiC sample cross-section for STEM imaging may be prepared in, for example, Crossbeam 540 FIBSEM (ZEISS) system. The sample may be protected with ~ 10 nm platinum (Pt) layer using sputtering prior to loading in the FIB, and may be additionally covered with 200-300 nm of e-beam induced Pt layer inside the FIB chamber before the cross-section milling. STEM imaging may be performed using, for example, 2100F
20 (JEOL) microscope operating in dark-field mode.

[0080] XPS analysis relating to oxidation of the germanium film directly indicates the chemical presence of both elemental semiconductor and its oxide, as well as the oxide time-dependent development during the sample exposure to the ambient atmosphere, as may be observed in FIG. 4A. FIG. 4A illustrates the normalized XPS spectra recorded after different times of the
25 sample exposure to the ambient atmosphere. The data marked as “fresh” corresponds to less than 5 min exposure time of the sample transferring from the evaporator to the XPS chamber. The data were recorded at 70° emission angle in the XPS system to maximize the photoelectron collection from the sample surface.

[0081] To obtain the information on the different chemical states of Ge in the sample, curve
30 fitting of the core-level Ge 3d peak may be performed using, for example, the ESCApe™ software (Kratos Analytical). Fitting of the XPS data, as shown in FIG. 4B for fitting of the 16-

days data from FIG. 4A, shows that the oxide is primarily composed by GeO_2 (i.e., Ge^{4+}) component with smaller presence of suboxides (Ge^{3+} , Ge^{2+} , Ge^{1+}). The spectra may be charged-corrected based on the fitted $\text{Ge } 3d_{5/2}$ peak at 29.3 eV. The primary signal from elemental Ge (Ge^0) may be fitted with two components, i.e., $\text{Ge } 3d_{5/2}$ (29.3 eV) and $\text{Ge } 3d_{3/2}$ with spin-orbit splitting of 0.58 eV and intensity ratio of 3:2. The Ge suboxide peaks (Ge^{1+} , Ge^{2+} and Ge^{3+}) may be assigned with even spacing of about 0.9 eV between the elemental Ge and Ge^{4+} peak. The Ge^{4+} (i.e., GeO_2) component may be left as a free parameter to obtain the best fit. A control measurement of the oxide layer thickness, performed by scanning transmission electron microscopy for the final state of oxidation (i.e., 16 days), gives a value of 3.6 nm (see inset in FIG. 4B showing dark-field STEM image of germanium film vertical cross-section, which includes (from left to right) SiC substrate, elemental Ge and oxide layers, and protective Pt cap. **[0082]** The extraction of the oxide thickness from measured phonon polariton wavelength is based on the permittivity of thick crystalline GeO_2 films, which has been considered: case (1) exactly at the position of the laser line, where the permittivity values of thick crystalline GeO_2 films used are: “-0.512530221614508+0.8155142237098446i” (at 930 cm^{-1} laser line), and “-0.6719954880630346+0.860195232389105i” (at 924.5 cm^{-1} laser line), and case (2) by taking an approximate lossless value in the broad transparency window (refractive index of ~ 1.5 (which corresponds to permittivity of “2.25”)), which nearly overlaps with the laser line and covers the blue part of the spectrum. While both approaches provide qualitatively comparable results, the approximate lossless permittivity model gives better agreement with control STEM measurement (oxide thickness extracted from 1-day, 10-days and 16-days near-field data are about 2.71 nm, about 3.17 nm and about 3.31 nm (based on the permittivity values provided above for case (1)), and about 2.99 nm, about 3.45 nm and about 3.66 nm (lossless model, corresponding to case (2) mentioned above). It is noted that the position and strength of germanium oxide infrared absorption peaks may depend on one or more of the crystal structure, chemical composition and morphology of the film. The possibility that the infrared properties of nanometric native amorphous oxide layer on germanium may deviate from known values is not excluded.

[0083] The discussed atomic-level thickness estimation via SPhPs may open up possibilities for nanometric film composition tomography, including semiconductor device local screening for the several nanometer technology node. At the same time, the discussed interactions may

provide additional degree of freedom in phonon-polariton nanophotonics, enabling continuous tuning of SPhPs wavelength at a fixed excitation frequency.

[0084] In various embodiments, there may be edge and sheet SPhP modes on the Ge-SiC nanoresonators. The sheet modes exist in the whole volume of the Ge-SiC resonator (similar to classical Fabry-Perot modes), while the edge modes can only be generated and exist on its edges. The edge modes carry higher momentum (i.e., smaller wavelength), which enables higher confinement of the optical field compared to the sheet modes. As a demonstration of potential phonon-polaritonic devices on a Ge-SiC platform, s-SNOM imaging of Ge rectangular nanoresonators with different sizes may be performed. The observed near-field distributions show deep sub-diffraction optical features, represented by a number of hot spots both at the inner part of the resonators and at its edges, as may be observed in FIGS. 5A to 5E relating to s-SNOM images for highly-confined surface polariton modes on 7-nm thick germanium nanoresonators. FIGS. 5A to 5E show s-SNOM images recorded at $\omega = 924.5 \text{ cm}^{-1}$ for, respectively, 1000×500 nm 504a, 300×500 nm 504b, 500×100 nm 504c, 300×100 nm 504d, and 500×500 nm 504e Ge structures, on SiC substrates 502a, 502b, 502c, 502d, 502e. The legend bar illustrated in FIG. 5A is the same for all images. Such spatial features are usually classified as sheet (s-) and edge (e-) modes correspondingly.

[0085] FIG. 5F shows optical cross-sections taken along dashed lines illustrated across the near-field image in FIG. 5E of the 500×500 nm square resonator 504e showing near-field amplitude (s3) distribution (s-mode (sheet mode) along the white dashed line and e-mode (edge mode) along the black dashed line). FIG. 5G shows an optical cross-section taken along the dashed line illustrated across the near-field image in FIG. 5D of the 300×100 nm rod resonator 504d showing near-field amplitude (s3) distribution. Corresponding estimates for the spatial confinement of the sheet mode at the center of the square resonator 504e and the edge mode at the corner of the rod resonator 504d are about 90 and about 235, respectively. These confinement values are defined as the excitation laser wavelength divided by the full width of the observed field distribution peaks at its half maximum. Such a large squeezing of light via SPhPs could enable on-chip optoelectronic devices with ultracompact footprints at the subwavelength scale. Furthermore, tighter spacing of the peaks distribution along the edge may be observed compared to the inner part of the resonator sheet (see FIG. 5F), which implies the higher-momentum nature of edge modes. While not necessarily needed to be considered in the

concept of tomography, edge modes, however, may provide advantages at extremely small-footprint devices due to its higher confinement. The higher confinement of edge modes has been reported in known plasmonic and hyperbolic material systems, while the results disclosed herein provide the first observation of the phenomenon in nearly isotropic media supporting surface phonon-polaritons.

[0086] Tunability of near-field patterns in the resonator may be provided for by changing one of or both the composition of the material and the laser excitation frequency. In order to demonstrate the former, the focus may be on the sheet modes as they may be better visible in the experiment or imaging. To achieve a higher accuracy of tracing the mode dynamics, measurements may be performed for the case of the resonator supporting several maximums in the field distribution (e.g., 1000×500 nm rectangular resonator shown previously in FIG. 5A).

[0087] FIGS. 6A to 6C show near-field optical images of 7-nm thick 1000×500 nm resonators 604a, 604b, 604c on SiC substrate 602a recorded at $\omega = 924.5 \text{ cm}^{-1}$ for different oxide thicknesses, illustrating images of the resonators 604a, 604b, 604c subsequently recorded three times : 1, 10 and 16 days after sample fabrication. FIGS. 6D to 6F show results of modelling of the modes (or simulated field distributions) at resonators 604d, 604e, 604f corresponding to the experimental images of FIGS. 6A to 6C respectively. FIGS. 6G to 6I show experimental and modelled near-field distributions along the central horizontal cross-section (highlighted with a white dashed line in FIG. 6A as an example) of the resonator modes in FIGS. 6A to 6F. The left-side figures (i.e., FIGS. 6A, 6D, 6G), the middle figures (i.e., FIGS. 6B, 6E, 6H) and the right-side figures (i.e., FIGS. 6C, 6F, 6I) correspond to the oxide thicknesses highlighted with arrows in FIG. 2B and respectively labelled in FIGS. 6G, 6H and 6I.

[0088] Comparison between FIG. 6G and FIGS. 6H and 6I shows that Ge oxidation as small as ~5Å in depth may lead to complete switching of the sheet mode from a lower order to a higher order. This is represented by the appearance of an additional maximum in the field distribution inside the resonator. The experimental results are supported by simulations carried out using the phenomenological model, which accounts for all possible reflections of a tip-launched wave in the resonator travelling with the measured polariton wavelength (as described below). Corresponding field profiles in FIGS. 6G to 6I match well with the experimental peaks in the inner part of the resonator 604a, 604b, 604c but deviate from the measured data at the edges

since the model is constructed for description of sheet modes only, which is the aim of the tracing in the experiment.

[0089] For the purpose of theoretical calculations, simulations of the resonator modes are based on ray-optics phenomenological model used for highly-confined surface polaritons modelling.

5 The tip-launched surface waves, here, propagate circularly outwards until they reach resonator edges, while only normally-incident surface waves can be reflected back to the tip position and contribute to the detected signal. The waves continue to oscillate between two pairs of opposite edges, until the energy is fully dissipated due to loss. The resulted complex electric field at each point inside the resonator can be treated as a superposition of four waves and calculated as the
10 summation of four geometric series:

$$E = \sum_{j=x_1, x_2, y_1, y_2} E_j \quad \text{Equation (12),}$$

where E_j represents the total complex electric fields of the mode travelling to and reflected from each edge in x and y directions from the tip position, and x_1, x_2, y_1, y_2 are coordinates of the four edges of a rectangular resonator correspondingly.

15 [0090] The field of each mode can be expressed as:

$$E_j = A(1 + re^{2i\beta d_j}) \sum_{m=0}^{\infty} (r^2 e^{2i\beta L_j})^m \quad \text{Equation (13),}$$

where A, r, β denote the amplitude of launched field along each direction, complex reflection coefficient of the mode at the germanium boundary and complex propagation constant of the surface mode respectively, d_j denotes a distance to four edges of the rectangular cavity, and L_j is
20 the cavity (or resonator) size in each direction. The real part of β is calculated from experimentally determined surface mode wavelength (λ_p) as $2\pi/\lambda_p$. The magnitudes of r and A are set equal to 1; d_j and L_j are inferred from the tip position inside the cavity and the cavity dimensions. The phase of reflection coefficient and the imaginary part of β are used as fitting parameters to reproduce the field distribution obtained in experiment.

25 [0091] Nanometric Ge-SiC interfaces may hold great potential for efficient spectral tunability of phononic devices as a result of strong dispersion in the polar crystal. Tuning of near-field patterns on the resonator by a very small adjustment of the excitation frequency is possible, as described below and experimentally demonstrated. As may be observed in FIGS. 7A and 7B showing the s-SNOM images recorded for 1000×500 nm resonator 704 (oxide thickness, h
30 = 3.7 nm) on SiC substrate 702 at $\omega = 924.5 \text{ cm}^{-1}$ and $\omega = 930 \text{ cm}^{-1}$ respectively, detuning of

the laser from $\omega = 924.5 \text{ cm}^{-1}$ to $\omega = 930 \text{ cm}^{-1}$ (which is $\sim 0.5 \%$ frequency shift) leads to the appearance of completely new sheet and edge optical field distributions in the $1000 \times 500 \text{ nm}$ structure 704.

[0092] FIG. 7C shows the normalized near-field cross-sections along horizontal dashed white lines in FIGS. 7A and 7B, highlighting sheet modes, where results 790a correspond to the dashed white line in FIG. 7A, and results 790b correspond to the dashed white line in FIG. 7B. FIG. 7D shows the normalized near-field cross-sections along vertical dotted white lines in FIGS. 7A and 7B, highlighting edge modes, where results 792a correspond to the dotted white line in FIG. 7A, and results 792b correspond to the dotted white line in FIG. 7B.

[0093] The corresponding cross-sections shown in FIG. 7C, normalized to the field at edges of the resonator 704 for both frequencies, show a transition from four peaks to two peaks in the inner part of the resonator 704. The edge near-field pattern demonstrates similar transition from a higher to a lower order, as may be observed in FIG. 7D.

[0094] As an additional study of the spectral tunability, calculations of the polariton wavelength dependence versus oxide thickness at $\omega = 930 \text{ cm}^{-1}$ may be performed. FIG. 8 shows SPhP wavelength scaling (versus the oxide thickness (h)) calculated for $\omega = 930 \text{ cm}^{-1}$. Result (dark solid) 882 shows the local maxima of r'' (max- r'') and result (white dashed) 884 shows the solution based on Equation (1). The solid white circle marks the oxide thickness (3.62 nm) estimated via Equation (1) based on a control near-field measurement (after 16 days) at this frequency, which is consistent with value obtained from $\omega = 924.5 \text{ cm}^{-1}$ data (i.e., 3.66 nm, as described above). The study shows an increase of the slope $\Delta\lambda_p/\Delta h$ to $14.2 \pm 1.2 \text{ nm per \AA}$ compared to $\omega = 924.5 \text{ cm}^{-1}$.

[0095] Using numerical simulations, an example of refractive index spectroscopic sensing on the Ge-SiC platform disclosed herein is also provided, which may show the potential performance of few-nm thick Ge-SiC resonators for refractive index spectroscopic sensing. The results are shown in Table 1 and FIGS. 9A to 9D.

[0096] Table 1 shows the comparison of FOM (figure of merit, $\text{FOM} = \Delta\lambda_{\text{res}}/(\Delta n \cdot \text{res_width})$, where " λ_{res} " represents the position of the resonance (i.e., minima of the curves in FIG. 9A, and maxima in FIGS. 9B, 9C and 9D), "res_width" represents the width of the corresponding resonance, and the parameter "n" refers to the refractive index of a virtual analyte coating

(defined as a lossless media having given value of “ n ”) used in simulations to assess the sensitivity of the metamaterial resonances to the change in this parameter; the higher the FOM, the better) on the Ge-SiC and known platforms. The Ge-SiC metamaterial used for the spectroscopic sensing simulations is based on 7-nm thick Ge resonators array. The resonator size used in the simulation is the same as in FIG. 5E (i.e., 500×500 nm) and the array period is 1 μ m. For all platforms, the simulations were done in equal conditions using 5 nm thick analyte coating of gradually increasing refractive index, n .

Table 1: Comparison of FOM on the Ge-SiC of various embodiments and known platforms

Sensing platform	Ge-SiC	Ref [1]	Ref [2]	
			split-ring resonator	coupled split-ring resonator
FOM, (RIU ⁻¹)	2.5	0.65	0.37	1.02

Ref [1] - Rodrigo, D. *et al.*, "Mid-infrared plasmonic biosensing with graphene", *Science* **349**, 165–168 (2015),

Ref [2] - Pryce, I. M., Kelaita, Y. A., Aydin, K. & Atwater, H. A., "Compliant metamaterials for resonantly enhanced infrared absorption spectroscopy and refractive index sensing", *ACS Nano* **5**, 8167–8174 (2011).

[0097] FIGS. 9A to 9D show results of numerical simulations supporting corresponding data in Table 1. The simulation parameters are the same as described above in relation to Table 1. FIG. 9A shows reflection spectrum shift for the Ge-SiC platform of various embodiments, FIG. 9B shows the extinction spectrum shift for the structure reported in Ref [1], while FIGS. 9C and 9D show reflection spectrum shift for the structure reported in Ref [2] for cases of split-ring and coupled split-ring based metamaterials respectively.

[0098] The results, as summarized in Table 1 and FIGS. 9A to 9D, show that the FOM for spectroscopic index sensing on the platform disclosed herein is as good as, if not better than, those of known mid-IR devices.

[0099] As described, nanometric interfaces between germanium and silicon carbide are capable of supporting highly-confined mid-IR surface phonon-polariton modes at the nanoscale. Owing to the surface nature of the polaritons, the architecture of various techniques disclosed herein displays good performance at several nanometer semiconductor thicknesses, adding new opportunities for “flatland” optoelectronics. The variety of deep sub-diffraction SPhP modes revealed in the Ge-SiC nanoresonators described herein shows the feasibility of potential device

footprint miniaturization. Considering high field confinement and the modes tunability, the platform disclosed herein may provide opportunities for integrated nanophotonics and sensing applications. In various embodiments, the surface phonon-polariton modes are the reference output, where sensing may be performed by monitoring changes in the modes.

5 **[0100]** The techniques disclosed herein may provide for potential applicability of the resonators or devices described herein to atomic-scale sensing. The devices of various embodiments may be used for sensing up to 1 atom scale.

[0101] While various embodiments have been described and experimentally demonstrated using a 7-nm germanium-based structure or layer as an example, it should be appreciated that
10 the thickness is not so limited and the techniques disclosed herein may be extended to cover a wide range of thicknesses (up to few tens of nm, for example, until where the SPhPs are no longer significantly confined, e.g., at about 70 nm thickness). The 7 nm thickness has been used as a representative illustrative example which enables demonstration of a combination of both:
15 good optical performance (i.e., highly confined and experimentally well resolvable modes) and high sensitivity. It should be appreciated that the thickness of the germanium-based structure or layer may, for example, be up to 50 nm. Depending on the applications, a thicker or a thinner version of the Ge layer in the mentioned thickness range can be potentially utilized. The mentioned extended thickness range may provide a plausible opportunity for supporting highly confined SPhPs (which is a necessary condition for driving similar-type devices). Such
20 interpolation of the current representative example of 7 nm thick Ge layers to higher thickness values is reasonable and within expectation and is supported based on the discussion and the results provided herein and the confined factor (about 30 for a 7-nm film) given.

[0102] The SiC substrate described herein is an example of a polar crystal or polar crystal substrate that can be used. Polar crystal substrates or polar crystals are built from polarizable
25 molecules, which enable excitation of dipole moments in the material yielding to SPhPs existence at the relevant frequencies. SPhPs are generated due to negative real part of dielectric permittivity. In polar crystals, permittivity generally becomes negative in the mid-IR/THz spectral range. However, it should be appreciated that some types of polar crystals may not be suitable. For example, crystals with a very high optical loss are not suitable. Further, layered
30 Van der Waals polar crystals supporting hyperbolic modes (e.g., BN (boron nitride)) are also not suitable.

[0103] While the device has been described in terms of a Ge layer on a SiC substrate (which are Group IV materials), it should be appreciated that other materials may be used, including other Group IV materials. Other materials, beyond Group IV, may be potentially used as the substrate, for example, crystals such as quartz and sapphire as well as w-AlN (wurtzite aluminum nitride), w-GaN (wurtzite gallium nitride), ZnO (zinc oxide), GaP (gallium phosphide), AlAs (aluminium arsenide), InP (indium phosphide), GaAs (gallium arsenide), InAs (indium arsenide), BaF₂ (barium fluoride), and InSb (indium antimonide). In general, the substrate should be a low optical loss crystalline substrate with negative real part of dielectric permittivity (which is generally caused by the existence of SPhPs and observed for most of the crystals in mid-IR/THz region; use of crystals with smaller losses would benefit for practical implementations). Layered Van der Waals materials such as BN are not suitable and, therefore, excluded as a material for the substrate.

[0104] For the layer (as part of the resonator), non-limiting examples may include Si (belonging to Group IV materials), GST (germanium-antimony-tellurium alloys), InP, PbTe (lead telluride), GaP, and ZnSe (zinc selenide) may potentially be used. In general, the material for the layer should have low optical loss in the IR and has high refractive index (some of the materials can be used both as a substrate and as a coating layer (i.e., slab) depending on the choice of the wavelength of operation). The material for the layer may optionally be oxidisable to form an oxide layer.

[0105] While the invention has been particularly shown and described with reference to specific embodiments, it should be understood by those skilled in the art that various changes in form and detail may be made therein without departing from the spirit and scope of the invention as defined by the appended claims. The scope of the invention is thus indicated by the appended claims and all changes which come within the meaning and range of equivalency of the claims are therefore intended to be embraced.

CLAIMS

1. A device for confining surface phonon-polaritons, comprising:
a polar crystal substrate configured to support the surface phonon-polaritons in the
5 device; and
a layer comprising elemental germanium, the layer being arranged on the polar crystal
substrate to confine the surface phonon-polaritons,
wherein the layer has a thickness of about 50 nm or less.

10 2. The device as claimed in claim 1, wherein the layer has a thickness of about 7 nm or
less.

3. The device as claimed in claim 1 or 2, wherein the layer further comprises germanium
oxide.

15 4. The device as claimed in claim 3, wherein the layer comprises a film comprising the
germanium oxide, wherein a thickness of the film is between about 2.5 nm and about 4 nm.

5. The device as claimed in any one of claims 1 to 4, wherein the polar crystal substrate
20 comprises silicon carbide.

6. The device as claimed in any one of claims 1 to 5, further comprising an optical antenna
configured to generate a near-field light for excitation of the surface phonon-polaritons in the
device.

25 7. The device as claimed in claim 6, wherein the optical antenna comprises a metal tip.

8. The device as claimed in claim 6 or 7, wherein the layer is patterned to define the
optical antenna.

30 9. The device as claimed in claim 8, wherein the layer comprises a grating to define the
optical antenna.

10. The device as claimed in any one of claims 1 to 9, wherein the layer comprises a shape of a rectangle, a square or a rod.

5 11. A method for forming a device for confining surface phonon-polaritons, comprising:
forming a layer comprising elemental germanium on a polar crystal substrate, the polar crystal substrate being configured to support the surface phonon-polaritons in the device, and the layer being configured to confine the surface phonon-polaritons,
wherein the layer has a thickness of about 50 nm or less.

10 12. The method as claimed in claim 11, wherein the layer has a thickness of about 7 nm or less.

13. The method as claimed in claim 11 or 12, wherein the layer further comprises
15 germanium oxide.

14. The method as claimed in claim 13, wherein the layer comprises a film comprising the germanium oxide, wherein a thickness of the film is between about 2.5 nm and about 4 nm.

20 15. The method as claimed in any one of claims 11 to 14, wherein the polar crystal substrate comprises silicon carbide.

16. The method as claimed in any one of claims 11 to 15, further comprising forming an optical antenna configured to generate a near-field light for excitation of the surface phonon-
25 polaritons in the device.

17. The method as claimed in claim 16, wherein forming an optical antenna comprises patterning the layer to define the optical antenna.

30 18. The method as claimed in claim 17, wherein patterning the layer comprises forming a grating in the layer to define the optical antenna.

19. The method as claimed in any one of claims 11 to 18, wherein the layer comprises a shape of a rectangle, a square or a rod.