Exploring Plasmonic Resonances Toward “Large-Scale” Flexible Optical Sensors with Deformation Stability

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The next generation of sensors requires a simple yet compact lab on chip-based precise optical detection mechanism where data interpretation can be achieved with minimum effort. Hereby, cost-efficient strategies of manufacturing both propagating surface plasmon polariton (SPP) and localized surface plasmon resonance (LSPR) sensors on flexible platforms are explored via mechanical instabilities and oblique-angled metal evaporation. Centimeter scaled dielectric grating structures produced by plasma oxidation of pre-stressed polydimethylsiloxane film have comprised the substrates, thus imparting inherent flexibility. Subsequently, both continuous and discontinuous 1D-metallic lattices are obtained via vapor deposition of gold at different angles. The optical isotropy (gold surface-grating) and anisotropy (gold edge-grating) are distinctly observed as a difference between forward and backward diffraction efficiencies, backed by analytical correlation to the observed orders. Supported with electromagnetic modeling, the SPP and LSPR excitations are experimentally characterized under reflectance and transmittance measurements, along with a demonstration of their sensing capabilities. The LSPR supported flexible sensor provides superiority in terms of sensitivity, which is investigated under mechanical deformations to exhibit consistency of the resonant wavelength. Such consistency is strategically unraveled via “finite element method” based approaches, thus providing a new paradigm of cost-efficient, large-scaled flexible sensors.

1. Introduction

Decoding the art of light manipulation[1] has been the topmost interest of researchers for the last few decades. The utilization of light-manipulation has been reflected in optoelectronic devices,[2] diffraction gratings,[3] flexible electronics,[4] as well as different kinds of bio-photonic sensors.[5] Typical surface plasmon resonance (SPR) sensors are popular in the field of bio-sensing[6] owing to their bulk sensitivity, significant penetration depth, and extended propagation distance.[7] These sensors operate on a well-known optical phenomenon satisfying the phase-matching conditions for the incoming light with the wave vector of the supported SPP modes for a metal-dielectric interface. Such light-matter coupling can be achieved through the propagation of evanescent surface waves generated by total internal reflection through prism,[8,9] waveguiding,[10,11] and fiber grating coupling,[12] as well as through diffraction grating.[13] However, a single nanometric chip-based biosensor[14] is always...
preferable compared to a bulky optical setup. Thus, the grating-coupled compact SPP sensors generated substantial interest for the “ready-to-test,” centimeter-sized, clinically approved sensors[35] fabricable through different lithographic means. These grating-coupled SPR sensors are designed by either a corrugated metal surface[16] or a dielectric grating in hybrid metal configurations[13,17] with sensitivities of the order of hundreds of nanometers per refractive index (RI) variation in wavelength-based interrogation.

In contrast, metallic grating structures with finite edges support localized surface plasmon resonance (LSPR)[38,19] that can be observed using similar wavelength-based detection methods. As a coupled grating effect, the resonant wavelengths suffer redshift from those of single nanowires, resulting in conversion from evanescent to radiative diffraction modes with broader linewidths[20]. These metallic nano-slit sub-wavelength structures[21,22] have been profoundly used in photovoltaics[23] and sensing applications under strong coupling schemes[24,25] for enhanced interactions. Compared to SPR sensing, LSPR exhibits improved surface sensitivities[26] preferable for sub-micron-sized biomolecule detections[27] as well as SERS-based measurements.[28] These LSPR supported metallic grating structures can further be utilized for efficient light concentration[29,30] and hot carrier extraction,[31–33] leading to a new class of effective nanophotonic devices. Whether SPP or LSPR, 1D nanopatterning via top-down approaches like electron beam lithography or direct laser writing[34] can limit the final patterned surface to micrometer scale, thus hindering the scalability and signal to noise ratio. Interference lithography imparts a practical approach toward attaining patterned surfaces in the range of tens of millimeters, depending on the expanded beam profile and accuracy of collimation. However, such processes can only be applied to photosensitive materials, and hence, require intermediate steps for pattern transferring onto other materials or surfaces.[13]

Interestingly, complex nanostructures achieved via wrinkling on a soft polymer substrate not only bypasses the multistep fabrication process but also enhances the uniformity in the range of centimeter square area. The privilege of using polymers like polydimethylsiloxane (PDMS) lies in achieving a sensing mechanism over a flexible platform, maintaining the current trend toward the development of wearable sensors.[35] This flexibility as the backbone of elastomeric electronics[36] is the utmost concern for the system of thin metal film compliant to a soft substrate. Previous PDMS-based sensors involving optical detection schemes[37,38] have already proved to be sensitive toward various external parameters; the advantage of incorporating direct sinusoidal patterning via wrinkling provides the freedom to choose different plasmonic resonances through ease alteration of deposition parameters. Most of the reported flexible sensors record change in pressure/strain through variation output optical or electrical signals,[39] where tracking of deformation acts as the primary sensing mechanism. However, for flexible optical devices working on principles of plasmonic resonances (photocatalysis, photodetection, RI sensing), deformation of the resonant nanostructures can result in unnecessary shifting of the resonant modes[40] away from the wavelength of interest, thus hindering targeted applicability. Hence, flexible devices with deformation-stable optical resonant modes are required to be explored for employing various plasmonic applications in real-life scenarios (deviation from ideal cases with flat substrates) toward monitoring of physical quantities other than pressure/strain.

In this present work, an approach toward the large-area fabrication of grating-based flexible plasmonic sensors with a periodicity of ~1 μm is established. The target of achieving actual large-scale devices (centimeter length) is accomplished by incorporating the wrinkling-assisted grating formation with the bottom-up physical vapor deposition processes. Oblique angle deposition (OAD)[41,42] based techniques to obtain two different plasmonic resonances viz the SPP and LSPR modes on a flexible PDMS platform are demonstrated, following a simple fabrication protocol. Starting with the basic diffraction properties of metallic surface-grating, the contrasting anisotropic diffractive behaviors of metallic strips deposited at the edges of a grating (edge-grating) are explored. Both normal, as well as the angled incidence of incoming light onto these patterned surfaces, result in the experimentally obtained grating diffraction curves for several orders (diffraction vs wavelength) that matches well with the theoretical calculations. The diffraction efficiencies studied under such observations, thus, can become handy for the implementation of such diffractive elements in real-life applications. Practical implementations, as targeted in this article, are demonstrated using the inherent resonant plasmonic modes through sensing of surrounding RI variation. Further, the structural change observed under the strain field with proper characterization using in situ scanning electron microscopy (SEM) and focused ion beam (FIB), in correlation with UV–Vis–NIR spectroscopy, are explained. Finite element method (FEM) based modeling has also been investigated for the first time to accurately estimate the structural change induced for the development of the flexible sensor to support our findings of deformation-stable resonant modes.

2. Results and Discussion

2.1. Fabrication of the Nanostructures by Wrinkling and Metal Vapor Deposition

The basic building block of our 1D-lattice structures is comprised of a dielectric PDMS grating fabricated through the wrinkling procedure described in the Experimental Section. This wrinkling procedure involves in situ oxygen plasma oxidation under a strain field, leading to a structural periodicity of 952.99 ± 1.04 nm with a grating amplitude of 258.40 ± 4.02 nm. A thin stiff film compliant to a soft substrate, like PDMS under a compressive stress field induces wrinkle structures, provided that the force field is above the critical strain. The compressive strain must be maintained above the borderline of the critical strain value to keep the periodic nature of the wrinkles. The value for the optimum periodicity can be attributed to the trade-off between the bending energy ($U_{b}$) of the skin and the stretching energy ($U_{s}$) of the foundation.[43] To attain a global energy minimum, the skin always prefers to have larger periodicity, whereas the foundation favors having a shorter period. Nanopatterning via the wrinkling technique holds a record of fabricating nanostructures over macroscopic length scales
ranging in meters. Details about the wrinkle fabrication technique and other related parameters can be found in Figure S1, Text T1, Supporting Information. In general, freestanding metal films are prone to rupture at the sites of strain concentration, called “necking,” unlike the elastomeric substrate. A freestanding film can rupture and move apart to accommodate the local elongation; however, the scenario changes when an elastomeric substrate is bonded to such films. The compliant elastomeric substrate delocalizes the applied strain further; thus, thin metal films can accommodate higher rupturing strain where the interphase layer plays a critical role. Once de-bonded from the elastomeric substrate, the metal film can again behave as a freestanding film. The appearance of a wrinkled surface amplifies the local stress concentration at the crest, unlike non-corrugated surfaces. As a consequence, the wrinkled substrate can have more pathways for the local stress decay when subjected to tensile strain.

To instigate plasmonic effects into these 1D-lattices formed by mechanical instabilities, the OAD technique has been implemented to generate both the gold (Au) surface-grating and edge-grating structures offering different resonant mechanisms of SPP and LSPR, respectively. Figure 1a describes the fabrication of these different resonant configurations through the variation of the single tuning parameter of deposition angle $\theta_{\text{dep}}$, ranging in between 0° and 90°. Fixing the angle $\theta_{\text{dep}}$ at 0° results in the uniform continuous metal film that can support the propagation of the SPP modes. In contrast, an oblique angle as high as 65° can result in the sharp-edged metallic strips to locally confine the plasmons. In the fabrication process, 5 nm of titanium (Ti) is evaporated, followed by 50 nm of gold (Au) in both normal and oblique orientations. For apparent observation, FIB-SEM imaging is used to visualize the cross-sections of these grating-based structures as presented in Figure 1b-i,b-ii. Au thickness of 50 nm can be confirmed for the surface-grating from Figure 1b-i, whereas for the edge-grating structure, the tooling factor (Text T1, Supporting Information) has been adapted to maintain an even thickness at the edges (Figure 1b-ii). Formation of such nanostraps through OAD has been reported previously; yet, for the first time, analyses in great depth has been carried out to explore and compare the different plasmonic resonances for suitable sensing applications through theoretical electromagnetic finite-difference time-domain (FDTD) modeling, further justified with mechanical simulations (FEM). To correlate the behavior of the thickness gradient between surface-grating and edge-grating, the case of $\theta_{\text{dep}} = 30°$ is also studied, schematic and FIB profiling of which can be found in Figure S2, Text T2, Supporting Information. The differences are clarified by considering one specific period that has been divided into two regions in Figure 1b-i,b-ii. As the metal thickness varies, being thinner at the crest, Ti has been specifically chosen to avoid Ti–Au inter-diffusion. Strong inter-diffusion of Cr–Au has been reported to influence chemical changes in a thin gold film. The confinement of the gold layer in one-half of the period introduces the anisotropic nature of the structure as well as sustainable LSPR modes that have been explored in the next sessions.

2.2. Exploring Optical Anisotropy by Angle-Dependent Spectroscopy

The basic diffraction-related studies of a grating structure coated differently with normal as well as an angled deposition are experimentally investigated in close conjunction with analytical diffraction calculations. Compared to a dielectric grating, a metallic grating provides enhanced reflectivity while maintaining the basic grating diffraction properties. This is directly
evident from Figure 1c, showing strong diffracted orders, in contrast to a bare PDMS grating. However, structural anisotropy led by angled deposition can tailor the reflectivity with the introduction of directionality that has been previously explored in passive parity-time symmetric thin-film waveguides.[51] Figure 2a depicts a schematic representation of the transverse electric (TE) (purple arrow) and transverse magnetic (TM) (blue arrow) polarization incidence, where the electric field vectors are aligned perpendicular and parallel to the plane of incidence, respectively. The TM polarization, in particular, is responsible for the generation of surface plasmon polaritons (SPP) at the metal (Au)-dielectric (air) interface of a uniformly coated metallic surface-grating structure.[13] The angle of incidence (θ_{inc}) for such structures is defined by the angle between the grating normal and the incident beam, as shown in the figure. The diffracted orders (±m; m = 0, 1, 2) corresponding to the broad source follow the basic wavelength-dependent grating equation (Text T3, Supporting Information) to produce the well-known grating intensity distribution in the far-field projection. Figure 2b exhibits such intensity distribution of the diffraction orders of three different metallic grating structures, fabricated at three deposition angles of 0°, 30°, and 65°, respectively. c,d) represents the diffraction color plot for metallic gratings with θ_{dep} at 0° and 65°, respectively. The color scale provides the normalized reflected intensity.

Figure 2. Diffraction studies exhibiting anisotropic behavior a) TE & TM polarization of an obliquely incident light on a generic 1D-grating structure, irrespective of the deposition angle. b) Diffraction intensity captured using a Bertrand lens setup using a broadband light source. The inset scale bar has a value of 20 µm. Three grating intensity distributions are captured from three different samples prepared with deposition angles of 0°, 30°, and 65°, respectively. c,d) represents the diffraction color plot for metallic gratings with θ_{dep} at 0° and 65°, respectively. The color scale provides the normalized reflected intensity.
due to instrumental constraints), and broadband scans (400–1500 nm) are collected for each of the discrete angles that represent the angle of diffractions. These spectra are then converted to angle scanned reflectance values as a function of a particular wavelength. The reflectance reveals quantitative anisotropy in the diffraction efficiencies for the positively and negatively diffracted orders in the case of Au edge-grating (Figure 2d) compared to the Au surface-grating (Figure 2c). Such anisotropy can be used for different device applications where redirection of diffraction orders only into a particular direction can be successfully achieved. Additionally, knowledge of the qualities of the diffracted modes can be useful for understanding the strength of the plasmon resonances instigated by such modes.

Next, the diffraction-related studies on these surface and edge-grating-based metallic 1D-lattices are extended for different configurations of incident angles. This is in line with the theoretically predicted analytical curves following the grating equation (details in Text T3, Supporting Information). The diffraction angles of our fabricated structures are now a function of wavelength as well as the incidence angle ($\theta_{\text{inc}}$), which strengthens the consistency of the diffraction properties. To observe the diffraction curves experimentally, both of these kinds of gratings are utilized and collected spectra in the positive quadrant (angle of diffraction, $\theta_{\text{dep}} = 10^\circ$ to $80^\circ$). Figure 3a,b shows measured diffraction efficiency calculations for these two cases, namely the surface and the edge-grating, respectively. The diffraction orders (both $+m$ and $-m$) as a function of angle of incidence are theoretically calculated using “grating order transmission analysis” scripting in Lumerical FDTD,[56] where the power of the different diffracted orders is plotted as a function of wavelength and presented in Figure S4, Text T3, Supporting Information. Such theoretical calculations for the “+$m$” orders are also plotted (solid lines) within Figure 3 for exact identification of the diffracted orders on incidence with different $\theta_{\text{inc}}$ (slight variation in the wavelength position due to difference in the period under comparison). Figure 3a-i,b-i displays the $\theta_{\text{inc}} = 0^\circ$ case where the data are collected for the diffracted beams except for the zeroth-order reflections (cannot be captured due to the requirement of the detector position at the source). It can be seen that in terms of order strength for $m = +1$ and $+2$, both surface-grating and edge-grating samples have almost equal performance. As $\theta_{\text{inc}}$ is increased (cases ii, iii, and iv), the edge-grating structure has better performance than the surface-grating for the $+m$ orders exhibiting higher diffraction efficiencies (for orders $m = 0$, $+1$), as depicted in Figure 3a,b-ii. Moreover, $m = +2$ can be observed contrastingly well in Figure 3b-ii when compared to Figure 3a-ii. The same goes for Figures 3a-iii,b-iii; however, edge-grating dominates for the orders $m = 0$, $+1$, without the presence of $m = +2$ in each of these plots. For Figure 3a-iv,b-iv, due to the very high incidence angle, one can also observe the order $m = -1$, which has higher efficiency for the surface-grating (Figure 3a-iv) than the edge-grating (Figure 3b-iv).

Thus, for the negative orders, the metallic contribution in reflection is not accounted due to the absence of metal at the opposite edges of the edge-grating structure. In contrast, the surface-grating succeeds for such orders with uniform metal distribution on both sides of the grating ridges. The experimentally obtained orders match with the analytical prediction for both TM (Figure 3) as well as TE polarization (Figure S5b–d, Text T3, Supporting Information). Such a study is important for the anisotropic edge-grating structures that can be used to generate LSPR excitations with higher excitation strengths.

![Figure 3](https://example.com/figure3.png)

**Figure 3.** Diffraction studies on wrinkled PDMS-Au grating backed by the theoretical investigation. Experimental observation of the grating-based diffraction for TM polarization with the diffracted angles of several orders plotted as a function of incident wavelength. The recorded diffracted intensities are normalized for cases (a-i,b-i) normal incidence, as well, a-(ii–iv), b-(ii–iv) oblique incidences at $-15^\circ$, $-30^\circ$, and $-45^\circ$, respectively. This accounts for uniform Au grating ($\theta_{\text{dep}} = 0^\circ$) and oblique Au grating ($\theta_{\text{dep}} = 65^\circ$). Diffracted efficiencies of several orders are thus evaluated, corresponding to the theoretical estimation (FDTD analysis) shown via lines for a range of $10^\circ$ to $80^\circ$.
The TM plot for $\theta_{\text{dep}} = 30^\circ$ has been documented in Figure S5a, Text T3, Supporting Information. More details on the quantitative analysis of the grating order can also be found in Figure S6 and Table T1, Text T3, Supporting Information.

2.3. Plasmonic Modes in Surface-Grating and Edge-Grating Nanostructures

To study the plasmonic behavior of the fabricated samples, optical characterization using both experimental as well as FDTD simulations are carried and discussed in this section. The sinusoidal continuous thin gold film backed by PDMS substrate thus has two different dielectric-metal interfaces: PDMS/Au and air/Au, which can give rise to the excitation of propagating SPP modes for incidence with TM polarization of light. Such excitation of SPP modes, although not possible in the case of a flat metal surface due to the lying of SPP dispersion curve outside the light-cone, can, however, be generated in corrugated metallic surfaces by bringing in additional in-plane momentum through the grating diffraction.\(^{[33]}\) Figure 4a schematically shows the fabricated surface-grating structures under reflectance measurements using normal and oblique angled probing. The angled illumination configuration is important for carrying out experimental measurements since normal incidence reflectance cannot be recorded by the detector in the current spectrometer system (due to the impossibility of the source and detector at the same position). Figure 4b-i shows the simulated reflectance spectra with TM polarization for the surface-grating structure, calculated using FDTD analysis. Two resonant dips are observed at 541 and 966 nm, which can be identified as $\text{SPP}_{2\pm}$ and $\text{SPP}_{2\pm}$, respectively. Such reflectance dips are signatures of mth-diffracted orders being evanescent toward excitation of $\text{SPP}_{\text{mm}}$, corresponding to a specific wavelength. The diffraction-oriented analysis behind the excitation of such modes is explained in Figure S7, Text T4, Supporting Information. Additionally, the effects of parametric alterations such as grating period, grating amplitude, and metal layer thickness are studied by parametric sweep conditions in FDTD simulations that are plotted and discussed in Figure S8, Text T4, Supporting Information. For oblique incidence, the degenerated modes ($\text{SPP}_{\text{mm}}$) can be split into non-degenerate $\text{SPP}_{\text{mn}}$ and $\text{SPP}_{\text{nm}}$ modes. Figure 4b-ii provides both simulation and experimental reflectance with $\theta_{\text{inc}} = 6^\circ$, where $\text{SPP}_{3\pm}$, $\text{SPP}_{3\pm}$, and $\text{SPP}_{3\pm}$ are currently visible within the range under observation. Figure 4c exhibits the magnitude of the electric field ($|\vec{E}|$) distributed on the metallic surface corresponding to normal incidence excitations at i) 541 nm and ii) 966 nm. The oscillating charge distribution on the gold surface (“+” and “−” denote the origin and termination of the field lines) represent the SPP generation with a color bar showing the field strength where the distance between the two charges represents the wavelength associated with such excitation. To obtain a dispersion curve, the angle of incidence is varied from $6^\circ$ to $30^\circ$ and the reflectance spectra observed both via simulation as well as experimentation are contour-plotted in Figure 4d. The exact nature of the mode splitting observed for both i) simulation and ii) experiment thus verifies the established electromagnetic model, along with confirmation of the modes at even normal incidence that are currently beyond the experimental detection limit.

For the edge-grating-based structures, TM polarized based normal incidence can cause excitation of dipolar localized plasmon modes depending on the shapes (thickness and width) of the OAD based resonating metal nanostrips. Such resonances are similar to the plasmonic nanobars or nanowires that can only be excited similarly in TM polarization, with charge accumulation at metal edges.\(^{[32,33]}\) On excitation at the shape-dependent resonant wavelength, these structures form oscillating dipoles that absorb incident radiation and re-emit the energy in terms of scattering. The optical characteristics can be explained by the Mie theory considering the scattering and absorption cross-sections resulting in optical extinction.\(^{[34]}\) These extinctions are often expressed as negative logarithmic of transmittances\(^{[35]}\) where significant extinction peaks indicating resonance can be correlated to their transmittance dips.\(^{[36]}\) Hence, for an easier mode of detection, these structures are experimentally operated in transmission modes, as shown in Figure 4e. Previous transmittance studies\(^{[37]}\) demonstrated redshift of the dipolar mode for an increased nano strip width (as well as periodicity) where due to this increment, additional multipolar modes\(^{[37]}\) are found to appear at lower wavelengths (blue shifted) as compared to the dipolar resonance. FDTD simulated transmittance of the edge-grating structure under TM polarized normal incidence is presented in Figure 4f with dipolar resonances occurring at 1455 nm and multipolar resonances observed at 942 and 806 nm. A good match is obtained in the experimental transmittance; the dipolar plasmonic mode being located at 1455 nm along with multipolar modes at 971 and 817 nm. However, compared to the simulation (806 nm), the higher-order multipolar mode at 817 nm is less prominent in the experimental transmittance that can be attributed to the structural differences between realized edge-grating and the simulation model. Hence for proper identification, separate Gaussian fits have been applied to these experimentally observed modes in Figure 4f that are separately presented in Figure S9 and Table T2, Text T5, Supporting Information. The electric field distribution (magnitude) corresponding to the prominent resonant dips at i) 942 nm and ii) 1445 nm are plotted in Figure 4g displaying the intensified plasmonic modes. Charge distribution at the grating edges are shown via current density plots provided in Figure S10, Text T5, Supporting Information, for all these plasmonic modes. Since the structure bears asymmetry, the angle of incidence scan for a range of $-45^\circ$ to $+45^\circ$ is carried out both in simulation as well as experimentally, to cover both sides of the grating. The dispersion relation obtained by the study is given in Figure 4h, showing both the i) simulation and ii) experimental dispersion relations which also have a good resemblance in terms of diffraction instigated “mode-splitting” positions as well as asymmetric distribution. The color bar in Figure 4h is inverted as compared to the one in Figure 4d to ensure the difference between reflection and transmission measurement. Whether SPP or LSPR, the fabricated structures characterized by TE polarization fails to provide any significant resonant dips.\(^{[38]}\) Figure S11, Text T6, Supporting Information, provides normal incidence spectra as well as the angle of incidence scan for study, thus proving the existence of such polarization-dependent resonant plasmonic modes in our fabricated structures.
2.4. Performance in RI Sensitivity

Once finished with the fabrication and in-depth optical characterization, both SPP and LSPR resonance properties of the respective surface-grating and edge-grating structures are tested for the targeted sensing application. For modulation of the analyte region, the cover index (previously air) is now replaced with deuterium oxide, commonly known as “heavy water (D₂O)”, to use as an analyte medium whose RI can be easily varied. The reason for choosing heavy water instead of commonly available...
deionized water (H₂O) is the presence of the molecular absorption bands in NIR that can hamper the detection of the SPP modes in the current window of spectroscopic interrogation. Since the SPP resonance mechanism operates in the reflection scheme, a minimum of 6° incidence is used for detection under oblique angle illumination of the incident probe beam. The two resonant modes SPP⁺₁ and SPP⁻₂, both splits due to the grating induced non-degeneracy. The black curve in Figure 5a-i shows such modes as reflectance dips, which can be identified in the following positions: SPP⁺₂ = 662 nm, SPP⁻₁ = 1102 nm, and SPP⁺₁ = 1356 nm. The cover index is modulated from pure heavy water to a mixture of heavy water and sodium chloride (D₂O + NaCl), and corresponding changes in the resonance positions are calculated for all the SPP modes. It is found that the shift in the resonant wavelengths for a constant change of the index is proportional to the resonant wavelength;[59] thus, the modes at higher wavelengths have undergone a larger shift (Δλ). To estimate an average sensitivity of such structure, the shift in resonant wavelength “Δλ” upon index variation is estimated at 15 nm corresponding to SPP⁻₁ mode at 1102 nm, resulting in a sensitivity of 349 nm RIU⁻¹. Details about the RI sensing have been documented in the Text T7, Supporting Information. The indices of the pure heavy water and its salt solution are calculated from Figure S12, Text T7, Supporting Information. The sensing performance of the surface-grating structure is also modeled using the FDTD based simulation, where a sensitivity of 886 nm RIU⁻¹ (details in the Table T3, Text T7, Supporting Information). Thus, the experimentally obtained sensitivity values seem to be reduced than those predicted by simulation theory, which can be attributed to two reasons. These are i) presence of defects like cracks within surface-grating, resulting in discontinuity of the propagating SPP modes, and ii) presence of all the experimentally observed resonant modes (Figure 5a-i) in blue-shifted positions compared to that of the FDTD simulation (Figure 5b-i). Similar sensing experiments are performed with the edge-grating structure supporting the LSPR modes.

Since such resonant modes are represented as transmittance dips, we have used the transmission mode of the spectrophotometer, unlike the sensitivity measurements with SPP modes of surface-grating structures. Thus, the LSPR modes can be visualized under normal incidence that gets further split as non-degenerate grating modes under oblique illumination of the probe beam. A similar variation of the surrounding index of the gold edge-grating caused the localized resonating mode corresponding to the TM polarizations to shift at higher wavelengths, as seen from Figure 5a-ii. The fundamental mode at lower energy (higher wavelength of 1327 nm) exhibits a “Δλ” value of 27 nm, resulting in a sensitivity of 628 nm RIU⁻¹. The corresponding FDTD simulation model in Figure 5b-ii records a sensitivity of 841 nm RIU⁻¹. Therefore, it can be concluded that the surface line defects within such grating structures have not affected the experimental sensitivity performance in such proportion as it has caused in the case of SPP-based sensing (experimental SPP sensitivity almost reduced to half, from the ideal simulation case). This is quite straightforward; since surface irregularities (defects/Y-branches or the cracks, discussed in Text T1, Supporting Information) are mostly oriented along with the grating line directions, the excitation of the LSPR modes via excitation with TM polarization remains unaffected as the isolated metal strips need to be excited rather than a continuous surface wave. In terms of practical sensing applications, the edge-grating-based LSPR sensors, thus prove to be beneficial as compared to the surface-grating-based SPP ones, even though the present SPP design may offer higher bulk sensitivity due to its longer evanescent tail.

Figure 5. Sensing performance study for the SPP (θdep = 0°) and LSPR (θdep = 65°) sensors. a-i) Spectral shift observed under variation of the surrounding refractive medium from D₂O to D₂O + NaCl solution for the SPP sensor. a-ii) Similar measurement using the LSPR sensor. b). Simulated sensing curve for both i) SPP and ii) LSPR sensors. c) The schematic shows the experimental setup with cavity formation for the analyte liquid.
In order to visualize the reproducibility of the current fabrication method as well as its direct impact on the sensitivity performance a comparative study has been performed with three sample for each of the SPP and LSPR supported RI sensors. Table T4, Text T7, Supporting Information, displays the fabricated sample parameters with Figure S13 and Table T5, Supporting Information, recording the repeatability in the sensing performance. A comparison with the current state-of-the-art plasmonic sensors has been provided in Table T6, Text T7, Supporting Information, keeping in focus of the current lithography-free mesoscale approach. The LSPR supported edge-grating structure draws further attention under deformable conditions like stretching, where it can also offer a consistent positioning (with tolerances) of the resonant mode that is explored in the upcoming section.

2.5. Deformation Stability of LSPR Modes under Stretching of the Edge-Grating

Due to the periodic patterning of the metallic gold strips, the edge-grating is expected to be aided by the flexibility of the underlying wrinkled-PDMS substrate, unlike the surface-grating structure. As an outcome, the edge grating shows fascinating behavior when subjected to uniaxial strain, perpendicular to the wrinkle direction. The optical responses can be well explored with UV–Vis–NIR spectroscopy, owing to the large area fabrication. The uniaxial strain is increased gradually from 0 to 50%, and the corresponding spectral change upon stretching has been documented in Figure 6a-i. The anisotropic nature of the edge-grating exhibits a critical role in the optical response under stretching, and the advantage can be demonstrated by altering the \( \theta_{\text{inc}} \) in between 0° and ±30°. For normal incidence, the anisotropic nature of the edge-grating is not prominent; the outcome appears to be the combined optical response of the wedge-shaped structuring. Upon stretching, the LSPR dip position shows a slight redshift; the shift in dip-position is negligible up to 20% stretching. As the uniaxial strain reaches the limit of 30%, the redshift becomes a little prominent that can be accounted for a minor increase in periodicity. The full width at half maximum (FWHM) value shows an increment from 172.24 to 252.35 nm (a detailed study of the relative dip positions can be found in Table T7, Text T8, Supporting Information). For the 30% to 50% stretching range, the multipolar LSPR dip again remains almost consistent, thus making it interesting to put more insight between the cases involving the change (20% to 30% strain) in the upcoming discussions. Due to the anisotropic nature of the edge-grating, it is worthy of observing such stretching effects in oblique incidence for plasmonic mode selective applications. For the oblique incidence cases of \( \theta_{\text{inc}} = \pm 30^\circ \) under 0% strain (Figure 6a-ii,iii), these spectra can be directly related to the dispersion plot of Figure 4h-ii. The FWHM in Figure 6a-ii improves due to the inclusion of dipolar LSPR modes, FWHM being 100.48 nm at \( \theta_{\text{inc}} = -30^\circ \) (dipolar) compared to 161.49 nm at \( \theta_{\text{inc}} = 0^\circ \) (multipolar). Additional modes ≈700 nm for the \( \theta_{\text{inc}} = +30^\circ \) in Figure 6a-iii can be assigned to the diffraction order of \( m = 2 \).

With an increment of strain (from 0 to 50%), the modes exhibit minute shifts as tabulated in Table T8, Text T8, Supporting Information.

**Figure 6.** a) Response of LSPR upon stretching of edge-grating at different \( \theta_{\text{inc}} \) of i) 0°, ii) \( \theta_{\text{inc}} = -30^\circ \), and iii) \( \theta_{\text{inc}} = +30^\circ \) in the inset graph depicts the change in FWHM as a function of applied strain. b) Optical stability at cyclic strain pattern for the edge grating under normal incidence. c) Bending gap behavior upon stretching. The dotted black line indicates a steady increase in size, while the solid black line corresponds to the shrinking of the gap through stress release.
An in-depth understanding of multipolar LSPR mode under stretching (θ_{inc} = 0°) is executed with an in situ stretching experiment employing SEM. This experiment is achieved with a custom-designed indigenous stretching device (the design can be found in Figure S14, Text T8, Supporting Information). The edge-grating sample is clamped with a fixed torque of 6 cN.m and subjected to strain at a 2 mm min^{-1} rate and further subjected to a cyclic forward and backward stroke in between 20% and 30% strain for 50 times to investigate the robustness and the dip shifting. The same pattern has been followed during in situ stretching at SEM (more about those can be found in Figure S15, Text T9, Supporting Information). In addition to the large-area and thus low-cost fabrication, reproducibility is another advantage of the wrinkling method. The mean dip position after 50 repetitive cycles do not alter that much; a standard deviation of 1.5, 2.48, and 3.71 is observed for the relaxed, 20% stretched, and 30% stretched sample, respectively. No adverse structural effect has been noticed during that cyclic strain pattern; the crack generated collapses back during backstroke and maintains the same after 50 cycles. A mild change in the crack gap for 20% strain can be attributed to the strain hysteresis of that material; likewise, the crack gap of 0.64 ± 0.03 and 0.70 ± 0.04 µm has been reported for the 20th and the 50th cycles at 20% strain, respectively (details has been documented in Table T9, Text T9, Supporting Information). In addition to that, the in situ FIB during stretching has been achieved with the above-mentioned specialized setup, and the relative changes in the periodicity and amplitude of the edge grating have been studied from the cross-sectional view (the relative changes can be found in Figure S16 and Table T10, Text T9, Supporting Information). Interestingly, from the current analysis, the gold film does not debond, leading to the nonrupturing of the gold film even at a higher strain. The periodicity shifts from 985.28 ± 30.27 nm (10% strain) to 1037.50 ± 38.16 nm (30% strain), whereas the amplitude shifts from 256.14 ± 1762 nm (10% strain) to 248 ± 18.37 nm (30% strain). The changes mentioned above are insignificant compared to the applied strain; however, the counterintuitive outcome has been spotted for 50% strain, exhibiting periodicity of 935.50 ± 35.35 nm and amplitude of 235.17 ± 20.37 nm. This effect can be attributed to the widened crack in the PDMS substrate, hampering the manifestation of the periodicity and the amplitude under uniaxial strain.

To establish a clear picture of the outcome, SEM micrographs at three different strains of 10%, 30%, and 50% are used to evaluate the changes. Two representative types of behavior, under strain, are summarized in Figure 6c, with a more detailed analysis in Figure S17, Text T9, Supporting Information. Generally, upon applying the strain, the wrinkle tends to bend, and the gap tends to increase until the wrinkle gets detached from one of the sides of the substrate, or additional cracks are introduced in the vicinity of no more than five wrinkles away from the initial one. Such fragmentation released the local strain, which allows the gap to collapse back into a more exposed bare PDMS area. The local-strain-diminishing effect is not sufficient to prevent the further widening of the bending gap. Thus, one can infer that upon moderate strain up to 30%, the gaps formed in between the wrinkles experience a steady increase in size, building up the local strain. In contrast, after crossing a certain threshold, lying below 50% of applied strain, multiple cracks occur due to an excess of the potential energy. Interestingly, such behavior is confirmed for several wrinkle lengths within the range of 10–25 µm, suggesting a persistence length along the wrinkling direction being less than 10 µm. Further, an in-depth study with finite element analysis (FEA) has been performed to connect the outcome.

2.6. FEA based on In Situ Stretching under SEM

Since the established system is fundamentally different from previously reported PDMS-based strain sensors (for example, where metal nanoparticles are embedded within PDMS matrix[40]), the deformation in these kinds of systems under the strain field is explored for the first time to date. To correlate the changes and the explanation, a unique numerical simulation setup has been portrayed in Figure 7. As evident from Figure 7a, the edge-grating under strain field is observed from SEM micrographs. To understand the behavior of this kind of system, additional atomic force microscopy (AFM) analyses of the wrinkled PDMS substrate are executed. A gradual increment of strain value has resulted in the decreased amplitude with an increment in the periodicity. As the critical strain is crossed, the direction of the wrinkle reverses along with the initial crack direction. The analysis of SEM images can be found in Figure S18 and Table T11, Text T10, Supporting Information. This expected outcome does not align with the previous in situ FIB-SEM analyses due to the partial rigidification of the edge-grating.

Now coming back to the deformation study of the edge-grating, the same spot scanning at Figure 7a-(i–iv) shows fragmentation at a higher strain value. An increment in the effective length containing ten wrinkles from 10.487 (b1) to 12.095 µm (b3), with a gap of 1.608 µm, in between the bunch of four and six wrinkles, has been observed. The wrinkled substrate has a crack density of 7.37%, the distance between two cracks has been calculated, and a substantial change has been spotted. The distance “a” decreases from 12.227 (a1) to 8.696 µm (a3). Due to the applied strain perpendicular to the wrinkled direction, bending of a single wrinkle has been observed; the bending gap shows an incremental value, marked as c(1, 3, 5) in Figure 7a, which ranges from 1.581 (c1) to 3.162 µm (c5) as given in Table T12, Text T10, Supporting information. Upon applying strain, the transverse compression along the y-axis at the junction or pre-cracks becomes more prominent; in support of that, the profiling in the y-direction has been done. The grayscale value increases from 59.28 ± 14.66 to 102.16 ± 34.62. (details can be found in Figure S19 and Table T13, Text T10, Supporting information). Whenever needed, the applied bias voltage in SEM has been toggled to ~50 V to capture the secondary electron, showing a distinct change in the contrast value over the region. In order to support this interesting phenomenon, a numerical simulation of the PDMS substrate is modeled as an elastic rectangular block of dimensions 20 µm × 6 µm × 20 µm and stretched axially by 30% using displacement boundary conditions. Setup details have been documented in the experimental section.
While the shell model is 2D, the layer thickness $h_{\text{layer}}$ appears to be a material parameter. This thickness parameter and the stiffness parameters $\mu_{\text{layer}}$ and $\lambda_{\text{layer}}$ of the Cosserat shell determine the elastic behavior of the thin oxidized PDMS layer. These parameters have been obtained from quantitative nanomechanical mapping (QNM) cross-section measurement (details can be found in Figure S20 and Table T14, Text T10, Supporting Information). For further implementation, the Mooney-Rivlin parameters assigned to the substrate during this analysis have been documented in Table T15, Text T10, Supporting Information. After releasing the axial component of the displacement boundary conditions at the right boundary, wrinkles form due to the stress mismatch. In order to determine the accuracy of the parameters implemented, a colored topographic map is generated, which reveals a periodicity and amplitude of $967.31 \pm 3.04$ and $223.42 \pm 2.90$ nm (details have been documented in Figure S21, Text T10, Supporting Information), respectively. This outcome aligns with the experimental topographic profile mentioned earlier; thus, the same parameters can further be used. The gold grating is then modeled by attaching another Cosserat shell exactly on the parts of slopes (the region in between the crest and valley) facing in the positive $x$-direction, as can be seen from the inset of Figure 7b-i marked as Au. Here, we chose a grating thickness parameter $h_{\text{gold}}$ and stiffness parameters $\mu_{\text{gold}}$ and $\lambda_{\text{gold}}$ characteristic for the gold layer (parameters have been documented in Table T16, Text T10, Supporting Information). After this, the PDMS substrate with the two Cosserat shells on top is stretched again by 10%, 30%, and 50% using axial displacement boundary conditions. The parts with gold grating layer stretch out much lesser than the parts without gold. The simulated stretching behavior has been documented in Figure 7b; the color scale at the right depicts the stress distribution of the underlying PDMS substrate, that is, the Frobenius norm of the first Piola–Kirchhoff stress-tensor. With the increment of the uniaxial stress pattern, the region of high-stress shifts toward the valleys of the original wrinkle pattern. This high stress indicates a potential location for crack formation, as evident from the location of each crack observed in the experiment.

3. Conclusion

In summary, we have successfully exhibited the potential use of a cost-effective, flexible plasmonic grating involving wrinkling instability and OAD as a fabrication protocol over a large area, which is proven to be up-scalable further. In contrast to the uniformity, non-uniform wedge structuring of the plasmonic grating involving LSPR claims its excellence over optical anisotropy. Owing to its unique topographic feature, which in turn proves to be an asset for circumnavigating the limited sensing behavior of the SPP sensors and the alternating rigidified pattern further widens an exciting field of numerical stress analysis closing the gap between plasmonic and numerical stress simulation community. The alternating gold layer in the edge-grating limits the degrees of freedom under uniaxial strain field; therefore, stress localization is released via transient cracks in the polymeric substrate in contrast to the materials reported so far, a “new class” of material analysis being reported. The use of LSPR sensors hold great potential for their ability to detect small amounts of functional biopolymer species; this is especially true for viral detection,\cite{62} which is of intense focus in the current pandemic situation. Developing new LSPR materials that can enhance our capabilities in this field is therefore highly desirable, which is a longer-term application that we envisage for our materials. Thus, boosted with the established theoretical analysis and easily approachable fabrication means, one can successfully design an advanced class of functional materials to set a new paradigm of flexible and large-scale plasmonic and optoelectronic devices with applications in energy harvesting.\cite{33}
4. Experimental Section

PDMS Preparation and Wrinkle Fabrication: A thin sheet of PDMS was prepared by mixing the pre-polymer and the curing agent (Sylgard 184 kit, Dow Corning), maintaining a ratio of 10:1 (w/w) in between the dimethylsiloxane oligomer and crosslinking agent. The curing process was executed in two steps starting with room-temperature curing for 24 h, followed by 4 h of heat treatment at an elevated temperature of 80 °C. The 24-h curing was carried out by placing the PDMS slab on a leveled plate to maintain a uniform thickness. Afterward, the PDMS sheets inserted into molds of 4.5 cm × 1.0 cm dimension. These pieces of PDMS were clamped into a custom-designed stretching device at 30% applied strain and subjected to a low-frequency oxygen plasma treatment (Flecto 10 USB, 80 watts, Plasma Technology, Germany) for 1800 s while maintaining 0.3 mbar chamber pressure. More information on the fabrication procedure and the wrinkled topography can be found in Figure S1, Text T1, Supporting Information. A faster strain removal rate was maintained to avoid excess crack formation, though a longer oxidation time eliminates the reduction of crack density.

Thin-Film Deposition: OAD was achieved using a specially designed homemade setup where the deposition device had been semi-modified for the current purpose. A Hel-X modular thin film deposition system (Korvos Technology) teamed with a Telemark e-beam source was utilized for both oblique angle and normal deposition without any stage rotation during the process. The Telemark e-beam source was equipped with four rotatable pocket sources. Ti layer of 5 nm was deposited, followed by a 50 nm Au layer at a constant deposition rate of 1 Å s⁻¹ and a chamber pressure of 1.5 × 10⁻⁶ mbar. The thin film thickness was monitored using a calibrated quartz crystal thickness monitor; for better accuracy, the tooling factor was optimized for each layer material.

UV–Vis–NIR Spectroscopy: UV–Vis–NIR spectroscopy was executed at reflection geometry and transmission geometry depending on the demand, using a Cary 5000 spectrometer (Agilent Technologies, USA) coupled with the universal measurement accessory to capture the optical spectra reported in this article. The beam spot size was fixed to 5 × 5 mm² for UV–vis and NIR detectors. All the dispersion spectra were captured by rotating the sample plane with a constant plane of incidence and polarization direction defined with respect to the wrinkle PDMS. The measured data was corrected from the spectra of the blank PDMS. The polarization angle of 0° and 90° comply with the configuration where the light was polarized along with the wrinkles (TE) and perpendicular to the wrinkles (TM), respectively.

Bright-Field Imaging: A bright-field reflection microscopy setup was used to capture surface images of formed wrinkles at the Nikon ECLIPSE LV100ND microscope. A halogen light source (12 V, 50 W) focused on a 50x objective lens was deployed for unpolarized illumination. A Nikon DS-Fi2 5.24 megapixel charged-coupled device camera coupled with the computer was used to capture the images, further analyzed with Fiji[64] and Igor Pro (WaveMetrics) software. Bertrand lens setup was used with a 50x objective for capturing the diffraction pattern of the grating samples.

FDTD Simulations: FDTD method was used (FDTD: 3D Electromagnetic Simulator) to perform the numerical calculations (Lumerical Inc.).[52] The structures were represented by the rectangular shapes, with the dimensions matching the ones determined by the SEM imaging. A plane wave source (λ = 400–1400 nm) was used to simulate the optical response under normal incidence illumination along the z-axis; for dispersion diagrams, angle incidences were imparted considering BFAST techniques. Periodic boundary conditions were set along X and Y directions, with perfectly matching layers along Z-axis. To obtain the optical responses, reflection and transmission monitors with frequency matching the wavelength span of the source were used. For the dielectric properties of gold, the data from Johnson and Christy[46] was fitted using six coefficients, with a root-mean-square error of 0.25. All simulations were set to reach an auto-shut-off of at least 10⁻⁵ before reaching 300 fs of the simulation time. For the best simulation stability, the mesh step size was set at 1 nm in all three principal directions covering the metal-dielectric interface.

AFM: For evaluating the topography of wrinkled PDMS, AFM height images were measured using a Dimension Series Fastscan (Bruker-Nano, Santa Barbara, USA) operated in tapping mode with Nanoscope 9.7 using stiff cantilevers TESP A (40 N m⁻¹, 300 kHz, Taps300, Budget Sensors, Bulgaria). More information can be located in Figure S1, Text T1, Supporting Information.

QNM: Evaluation of the mechanical properties were executed by overcasting a peryleneetetracarboxylic dihydride doped PDMS[80] onto plasma modified PDMS. This embedded system was used to prepare the cross-section, further subject to scanning in the QNM mode. Before casting the colored PDMS, a gas-phase silanization (30 min in low atmospheric pressure) was performed using vinyltrimethoxysilane 98% to increase the adhesion in-between the plasma modified PDMS and the colored PDMS. The colored conditions were kept similar to the wrinkling stage, except that the PDMS is not subjected to any strain field. A ratio of 10:1 (w/w) was upheld in between the dimethylsiloxane oligomer and the crosslinking agent for the over-casted PDMS, cured at the room temperature for 24 h. The layered structure was cut into 0.5 × 1.0 cm² pieces, followed by a smoothing process using a Cryo-microtome (EM UC6/FC6, Leica, Austria) on a section of 200 × 600 μm² perpendicular to the interface of colored PDMS and oxidized PDMS. The QNM measurements were performed using the Dimension Series Fastscan (Bruker-Nano, Santa Barbara, USA) operated in ScanAsyst mode with Nanoscope 9.7. A Fluid+ cantilever (tip radius 5 nm, spring constant 0.7 N m⁻¹) was used to capture images of size 1 × 1 μm² with resolution kept at 312 × 512 pixels.

SEM: SEM micrographs were captured using a NEON 40 FIB-SEM workstation (Carl Zeiss Microscopy GmbH, Oberkochen, Germany), operating under accelerated voltage (electron high tension) of 3.5 kV. The platinum precursor used for “FIB-cut” was trimethyl(methylcyclopentadienyl) platinum (IV) (CAS Nr.: 94442-22-5). The molecules were cracked by the ion beam, where the platinum (a mixture of platinum and carbon in practice) remained on the surface. The energy selective backscattered voltage was toggled between 300 and ~50 V, whenever needed, to understand the change in morphology during the in situ stretching experiment. Milling of the samples were executed at two steps, “deposition mode” and “mill for depth,” consecutively. The area of interest was chosen to be of 20 μm × 2.5 μm rectangular area. A constant current of 100 pA was maintained during the “deposition mode,” lasting for 300 s. During the “mill for depth,” an area of 15 μm × 1.5 μm was exposed with a slightly higher milling current of 500 pA, compared to the previous step. Specifically, the beam currents of 100 and 500 pA were chosen due to their near-perfect gaussian shape.

RI Sensing: A cavity system (with a dimension of 1.2 x 0.6 x 0.15 cm³) was prepared with enough cavity volume to contain 2 mL of liquid analyte (both of the solutions). The surrounding medium was altered to monitor the sensitivity of the structures. Initially, deuterium oxide (D₂O, 99.9% pure) was used to revamp the RI of the surrounding medium, followed by a (0.3 g mL⁻¹) solution of sodium chloride (NaCl) and D₂O. The cavity was repeatedly rinsed between measurements to avoid any possible error margin in the RI variation. For determining the RI of D₂O and NaCl solution, a digital multiple wavelength refractometer DSL-R (Schmidt + Haensch) was used to measure data at five frequency points that were extrapolated and used for the sensitivity calculation of the LSPR and SPP modes.

FEA Simulation: Mooney-Rivlin material[60] (Syrlgard 184, mixing ratio 10:1) with parameters derived from uniaxial tensile tests. On the deformed upper surface, a stiffener material layer was attached, modeled by a geometrically exact Cosserat shell.[69] The model was discretized using second-order (27-nodes) Lagrange finite elements for the substrate and second-order (9-nodes) geodesic finite elements for the shell,[69] no locking occurs for this type of shell discretization.[70] The grid for the substrate was manually graded, with a high resolution in the vicinity of the shell, resulting in a substrate grid of 16012 vertices. The attached shell model was discretized on the 2D restriction of the substrate grid to the upper boundary, which has 375 vertices. The calculations were done using the DUNE libraries for C++ for solving partial differential equations with grid-based methods.[71]
Supporting Information

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

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Conflict of Interest

The authors declare no conflict of interest.

Data Availability Statement

Research data are not shared.

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