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Metasurfaces for label-free biosensing mid-infrared optics and active photonic devices

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Abstract

Novel two-dimensional metamaterials, known as metasurfaces, have emerged as a breakthrough platform for controlling electromagnetic wave properties at the nanoscale. These metasurfaces consist of subwavelength nanoantennas or so-called meta-atoms, which can be engineered at will to obtain the desired optical functionalities. The doctoral thesis aims to advance the current state-of-the-art metasurface technology for mid-infrared (mid-IR) applications and photonic devices, including label-free biochemical sensing, large-scale fabrication of various highly efficient all-dielectric and plasmonic mid-IR metasurfaces as well as active nanophotonic components with incorporated phase-change materials.

The first part of the thesis focuses on surface-enhanced infrared absorption spectroscopy with dielectric metasurfaces supporting high-quality (high-Q) resonances. Specifically, it introduces an imaging-based nanophotonic method for detecting mid-infrared molecular fingerprints and its' implementation in chemical identification and compositional analysis of surface-bound analytes. This technique features a two-dimensional pixelated dielectric metasurface with a range of spectrally selective resonances, each tuned to a discrete frequency. The method enables a molecular absorption signature read-out at multiple spectral points and the translation of resulting information into a barcode-like spatial absorption map for imaging. Furthermore, the thesis demonstrates high-Q angle-multiplexed metasurfaces, which deliver a large number of on-demand resonances in the mid-IR. The angle-multiplexed method combines chemically specific broadband IR detection with device-level simplicity and spectrometer-less operation of angle-scanning refractometry. We used this technique to detect distinct absorption signatures of different interacting analytes, including proteins, DNA aptamers, and biodegradable polymers. Strikingly, these novel metasurface-based chemical detection methods are capable of resolving absorption fingerprints without the need for spectrometry, thereby paving the way towards sensitive and versatile miniaturized mid-IR spectroscopy devices.

Yet another major contribution of the thesis includes a universal method for wafer-scale nanofabrication of various mid-IR nanophotonic metasurfaces. The core of the approach is based on CMOS-compatible processes where the metasurfaces are fabricated on free-standing metal-oxide membranes. The ultra-thin membranes provide excellent optical properties, notably high transparency over the whole mid-IR spectral range and effective refractive index close to unity, which are crucial in realizing highly efficient metasurfaces. To demonstrate the versatility of our method, we realized metasurfaces for a diverse range of applications in the mid-IR, ranging from highly efficient optical wavefront and polarization control to plasmonic metasurfaces for label-free biochemical detection in aqueous solutions. The membrane-based metasurface concept overcomes the limitations of currently used materials in the mid-IR, therefore enabling mass-production of diverse photonic devices with applications in key areas such as biosensing, optical communications, thermal imaging, and spectroscopy. Therefore, the introduced nanofabrication method has the potential to accelerate the adoption of mid-IR metasurfaces for commercial applications.

The last chapter of the doctoral thesis demonstrates programmable all-dielectric Huygens' metasurfaces consisting of multi-layer germanium disk meta-atoms with strategically incorporated non-volatile phase change material Ge₃Sb₂Te₆. Switching the phase-change material between its' amorphous and crystalline structural states enables nearly full dynamic light phase control with high transmittance in the mid-IR spectrum. The metasurface is realized experimentally, showing post-fabrication tuning of the light phase within a range of 81% of the full 2π phase shift. The versatility of the tunable Huygens' metasurfaces is demonstrated by optically programming the spatial light phase distribution of the metasurface with single meta-unit precision and retrieving high-resolution phase-encoded images using hyperspectral measurements. The programmable metasurface concept overcomes the static limitations of previous dielectric metasurfaces and moves the metasurface-based technology one step closer to ultracompact active optical elements encompassing tunable lenses, dynamic holograms, and solid-state spatial light modulators, amongst others.

Keywords:

Metasurfaces, Metamaterials, Surface-enhanced Infrared Absorption Spectroscopy, Nanophotonics, Biosensing, Tunable metasurfaces, Optical Programming, Meta-optics, High-throughput Nanofabrication, Phase-change Materials

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Résumé

Les métasurfaces se sont révélées comme plateforme révolutionnaire permettant de contrôler les propriétés des ondes électromagnétiques à l'échelle nanométrique. Ces métasurfaces sont constituées de nano-antennes sub-longueur d'onde, aussi appelées méta-atomes, qui peuvent être conçues avec précision afin d'obtenir les fonctionnalités optiques souhaitées. Cette thèse de doctorat a pour but de faire progresser la technologie de métasurface de pointe actuelle pour les applications dans l'infrarouge moyen, comme la détection biochimique sans étiquette, ou la programmation active de phase optique. De plus, cette thèse contribue à l'avancé de la fabrication à grande échelle de diverses métasurfaces entièrement diélectriques ou plasmoniques, fonctionnants très efficacement dans l'infrarouge moyen.

La première partie de la thèse se concentre sur la spectroscopie d'absorption infrarouge exaltée de surface avec des métasurfaces diélectriques supportant des résonances de haute qualité (facteur Q élevé). Plus précisément, elle introduit une méthode nanophotonique basée sur l'imagerie pour détecter les signatures moléculaires dans l'infrarouge moyen et sa réalisation pour l'identification chimique et l'analyse de la composition des analytes liés à la surface. Cette technique comporte une métasurface diélectrique pixellisée bidimensionnelle avec une gamme de résonances spectralement sélectives, chacune ajustée à une fréquence discrète. Le procédé permet la lecture d'une signature d'absorption moléculaire en plusieurs points spectraux et la traduction des informations résultantes en une carte spatiale d'absorption de type code-barres pour l'imagerie. En outre, la thèse démontre des métasurfaces multiplexées en angle et à facteur Q élevé, qui fournissent un grand nombre de résonances à la demande dans l'infrarouge moyen. La méthode de multiplexage angulaire combine la détection infrarouge chimiquement spécifique et à large bande, avec la simplicité au niveau du dispositif et le fonctionnement sans spectromètre de la réfractométrie à balayage angulaire. Nous avons utilisé cette technique pour détecter des signatures d'absorption distinctes de différents analytes en interaction, y compris des protéines, des aptamères d'ADN et des polymères biodégradables. Remarquablement, ces nouvelles méthodes de détection chimique basées sur les métasurfaces sont capables de résoudre les signatures digitales d'absorption sans avoir besoin de spectrométrie. Cela ouvre ainsi la voie à des dispositifs de spectroscopie pour l'infrarouge moyen qui sont miniaturisés, sensibles et polyvalents.

Une autre contribution majeure de cette thèse comprend une méthode universelle pour la nanofabrication à grande échelle de diverses métasurfaces nanophotoniques pour l'infrarouge moyen. Le cœur de l'approche est basé sur des processus compatibles CMOS où les métasurfaces sont fabriquées sur des membranes en oxyde de métal autoportantes. Les membranes minces offrent d'excellentes propriétés optiques telles qu'une transparence élevée sur toute la bande spectrale de l'infrarouge moyen et un faible indice de réfraction effectif, qui sont tous deux cruciaux pour la réalisation de métasurfaces hautement efficaces. Pour démontrer la polyvalence de notre méthode, nous avons réalisé des métasurfaces pour une large gamme d'applications dans le milieu infrarouge, allant du contrôle très efficace de front d'onde optique et de polarisation, aux métasurfaces plasmoniques pour la détection biochimique sans étiquette dans les solutions aqueuses. Le concept de métasurface à base de membrane surmonte les limites des matériaux actuellement utilisés dans le milieu infrarouge, permettant ainsi la production en masse de divers dispositifs photoniques avec des applications dans des domaines clés tels que la biodétection, les communications optiques, l'imagerie thermique et la spectroscopie. Par conséquent, le processus de nanofabrication introduit a le potentiel d'accélérer l'adoption de métasurfaces infrarouge moyen pour des applications commerciales

Le dernier chapitre de cette thèse de doctorat présente des métasurfaces de Huygens entièrement diélectriques et programmables constituées de méta-unités à disques Ge multicouches incluant le matériau Ge₃Sb₂Te₆, qui est un matériau à changement de phase non volatil. La commutation du matériau par changement de phase entre ses états structurels amorphe et cristallin permet un contrôle de phase de la lumière presque entièrement dynamique avec une transmittance élevée dans le spectre infrarouge moyen. La métasurface est réalisée expérimentalement, montrant le réglage post-fabrication de la phase de la lumière dans une plage de 81% du déphasage complet de 2π . La polyvalence des métasurfaces accordables de Huygens est démontrée en programmant optiquement la distribution spatiale de la phase de la lumière de la métasurface avec une précision allant jusqu'à la méta-unité individuelle, et en récupérant des images haute résolution codées en phase à l'aide de mesures hyperspectrales. Le concept de métasurface programmable surmonte les limitations statiques des métasurfaces diélectriques précédentes et rapproche la technologie basée sur la métasurface vers des éléments optiques

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actifs ultra-compacts tels que les lentilles accordables, les hologrammes dynamiques et les modulateurs spatiaux de lumière.

Mots-clés

Spectroscopie d'absorption infrarouge à surface améliorée, nanophotonique, métasurfaces accordables, programmation optique, méta-optique, nanofabrication

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Abbreviations

AI	artificial intelligence
ALD	atomic layer deposition
AFR	angle-multiplexed fingerprint retrieval
BIC	bound states in the continuum
CRP	C-reactive protein
DLW	direct laser writing
DNN	deep neural networks
DRIE	deep reactive ion etching
DUV	deep ultraviolet
EBL	electron beam lithography
ED	electric dipole
EV	extracellular vesicles
FTIR	Fourier transorm infrared
FWHM	full width at half maximum
high-Q	high-quality
IR	infrared
LIDAR	light detection and ranging
LSPR	localized surface plasmon resonance
MCT	mercury cadmium telluride
MD	magnetic dipole
MEMS	microelectromechanical systems
PhC	photonic crystal
PR	photoresist
SEIRAS	surface-enhanced infrared absorption spectroscopy
SEM	scanning electron micrograph
SPR	surface plasmon resonance
SPP	surface plasmon polariton
QCL	quantum cascade laser
Q-factor	resonance quality factor

Chapter 1 Introduction and motivation

1.1 Nanophotonics

Photonics is a branch of physics that studies light generation and its' interaction with matter. It is a very active field of research, which is constantly growing from year to year. Photonics has brought revolutionary inventions and technologies that have changed our daily lives. For instance, since the invention of the laser and optical fibers, the communications industry has been completely transformed, enabling the modern-day internet. Advanced imaging systems can achieve super-resolution capabilities in live cells, which is paradigm-shifting for biological and pharmaceutical studies. The solid-state light sources have considerably reduced the energy consumption for light generation. Last but not least, solar cells have been adopted across the globe with high efficiency, matching the price for energy production from conventional fossil fuelbased electricity generators.

Interestingly, photonics has even more potential and could provide a plethora of new applications and technologies considering the vast opportunities at the nanoscale. The state-of-the-art nanofabrication techniques have revolutionized the field of photonics, enabling nanoscale optical structures for advanced manipulation of light. In a broader perspective, nanophotonics allows the designing of optical materials at will to provide the desired functionalities [1]. The subwavelength structures of nanophotonic devices can be tailored to confine light into nanoscale volumes, which can drastically improve light-matter interactions enabling highly efficient light generation, ultra-sensitive optical sensors, and complete control of electromagnetic wave properties.

1.1.1 Photonic crystals

One of the first examples for on-chip miniaturized photonic systems is photonic crystals (PhC), which are periodic structures with alternating regions of high and low refractive index. Of note, the periodic modulation of the refractive index in PhCs scatter and modulate light, forming band gaps in a similar way as the ions in a crystal lattice affect the electrons in semiconductor

materials. The formation of the band gaps in the PhCs can be explained by destructive interference of the multiple reflections from the high and low refractive index boundaries. Therefore, the photonic crystals can be tailored to allow only certain wavelengths to propagate through them. Notably, PhCs can be observed in nature expressed as structural coloration in animals. For instance, the bright color reflection from the butterfly wings and the iridescent colors of peacock feathers are by virtue of PhCs.

The simplest form of a photonic crystal is a one-dimensional periodic slab, which can be realized by depositing a stack of dielectric layers (**Figure 1.1a**). Notably, PhCs can be observed in nature expressed as structural coloration in animals. For instance, the bright color reflection from the butterfly wings is an effect of 1D PhC structures (**Figure 1.1b**). The first one-dimensional photonic crystal was described and experimentally realized by Lord Rayleigh in 1887. Since then, the material deposition techniques have greatly improved, allowing deposition of various materials, which can be finely tuned to efficiently transmit or reflect specific wavelengths. Nowadays, the one-dimensional PhCs are commonly used in optics, light sources, and laser systems as Bragg gratings, efficient mirrors, and anti-reflection coatings. A scanning electron micrograph of an experimentally realized 1D PhC is displayed in **Figure 1.1c**.

The PhC can also be realized in two dimensions (2D) by periodically alternating the local refractive index in two directions (**Figure 1.1d**). One of the examples of naturally occurring 2D photonic crystals is the nanostructure in peacock feathers that provide bright and iridescent color reflection (**Figure 1.1e**). The first 2D photonic crystal was described by Eli Yablonovich and John Sajeev in 1987 [2]. The 2D PhCs usually are fabricated by etching highly periodic and subwavelength holes into slabs consisting of high refractive index material. In this manner, one can engineer photonic dispersion in the 2D corrugated slab. By introducing defects into the PhC, light can be strongly confined or spatially guided through the PhC slab with diffraction-limited accuracy (**Figure 1.1f**). Such 2D photonic crystals with precisely introduced defects can be used for ultrafast lasers [3], highly efficient optical memories [4], and for light guiding [5].

Furthermore, the PhC can be extended to three-dimensional (3D) structures with varying refractive index (**Figure 1.1g**). Such structures have also been observed in nature, specifically as quasi ordered 3D PhCs in the scales of various species of beetles, reflecting specific wavelengths of light (**Figure 1.1h**). Experimentally such structures can be realized with multi-step lithography methods. An example of a nanofabricated 3D PhC is illustrated in **Figure 1.1i**. Although the photonic crystals provide a powerful platform for light manipulation, the miniaturization of photonic devices with PhCs is very challenging due to the diffraction limit and the low dielectric constant in dielectric materials.



Figure 1.1: Examples of photonic crystals in nature and photonics. (a) Schematic drawing of one dimensitonal photonic crystal. Figure adapted from ref. [6] (b) Example of 1D photonic crystals in butterfly wings, reflecting bright blue light. Figure adapted from ref. [7]. (c) 1D photonic crystal realized with multi-step thin layer deposition methods. Figure adapted from ref. [7]. (d) Schematic drawing of a 2D photonic crystal. Figure adapted from ref. [6]. (e) example of a 2D crystal in the feathers of peacocks, where the planar periodic structures provide light reflection with bright and iridescent colors. Figure adapted from ref. [7]. (f) Nanofabricated photonic crystal for light guiding applications. Figure adapted from ref. [8]. (g) Sketch of a 3D photonic crystal. Figure adapted from ref. [6]. (h) Quasi-ordered photonic crystals in

the scales of various beetles reflect the light at specific wavelengths. Figure adapted from ref. [7]. (i) 3D photonic crystal realized with a multi-step lithography process, where the refractive index periodically varies in all three directions. Figure adapted from ref. [7].

1.1.2 Plasmonics

Confining light into nanoscale volumes requires new strategies. In principle, there is only one core parameter to manipulate the light in a material, that is the dielectric constant ε . For a lossless material, dielectric permittivity can be calculated as $\varepsilon = n^2$, where n is the material's refractive index. The common dielectric materials in the visible and infrared spectral range have refractive indices spanning from 1 to 4. As the wavelength of light in the medium is inversely proportional to the material's refractive index, it is very challenging to confine the light into subwavelength volumes using the conventional low-loss dielectrics. However, other types of materials, such as metals, can have negative electric permittivities by orders of magnitude larger than those of the dielectric materials. This characteristic of metals arises from a large number of electrons in the conduction band, which can freely move within the crystal lattice. When an alternating electric field is applied to the metal-dielectric interface, a hybrid wave of photon and electric charge oscillations can be excited, which is called the surface plasmon polariton (SPP), see Figure 1.2a and b. Due to the high dielectric constant of the metals, these waves can be confined to deeply subwavelength volumes, drastically improving the light-matter interaction. The first SPPs were observed back in 1902 in reflective metal gratings as pronounced fluctuations in the intensity of specific narrow spectral bands. This phenomenon was named after R. W. Wood as Wood's anomaly because it was not possible to explain it with the conventional diffraction grating theory. Only in the year 1957 was Wood's anomaly explained as the surface plasmon polariton propagating in the metal gratings. However, it took another four decades until the field of plasmonics fully emerged. The SPP first found applications in the field of biosensing, where the surface plasmon resonance (SPR) was used to detect minuscule changes of the local refractive index induced by antibody binding at the metal-dielectric interface [9]. In SPR sensors, the local refractive index changes upon antibody binding are detected as resonance shifts of the reflected light (Figure 1.2c and d). Due to the high sensitivity and reproducibility, the SPR detection method has now become the gold standard in label-free and real-time monitoring of biochemical interaction [10].

Interestingly, the surface plasmon resonances can also be excited in individual metallic nanoparticles, where the incident electric field of the incoming light induces coherent oscillations of electrons within the metal conduction band (**Figure 1.2e**). This phenomenon is known as localized surface plasmon resonance (LSPR). When the LSPR is excited, it strongly enhanced the electric fields close to the surface of the individual nanoparticles and drastically improving the light-matter interactions (**Figure 1.2f**). The modern nanofabrication techniques propelled the field of plasmonic, enabling reproducible and precise fabrication of the desired geometrical shapes of individual nanoparticles. Owing to the capabilities of strongly confining the electromagnetic fields, the field of plasmonics holds great potential for realizing subwavelength waveguides [11], [12], and nanoscale interconnections between photonics and electronics, therefore improving the performance of current state of the art computation devices by orders of magnitude. Furthermore, plasmonic nanoparticles have the potential for applications in energy generation [13], photocatalysis and photodetection [14], water desalination [15], [16], thermal therapy for targeted cancer therapy [17]. Furthermore, plasmonic nanoparticles have found a use for biosensing in pregnancy tests and in enhanced fluorescence microscopy and spectroscopy [18].



Figure 1.2: Surface plasmon polaritons and localized surface plasmons. (a) The electric field of the surface plasmon polariton at the metal-dielectric interface. Figure adapted from ref. [19] (b) Surface plasmon polariton propagation and the electric field decay. Figure adapted from ref. [19] (c) SPR sensor schematics for biosensing applications. Figure adapted from ref. [20] (d) SPR sensorgram showing resonance shift $\Delta\theta$ after antibody binding. (e) Schematics of localized surface plasmon resonance in metal nanoparticles. Figure adapted from ref. [21] (f)

Schematics for extremely high field confinement into nanoscale volumes with plasmonic nanoparticles. Figure adapted from ref. [22].

1.2 Metasurfaces

Metasurfaces or so-called zeroth-order gratings are the 2D counterparts of the metamaterials that consist of subwavelength periodic structures providing on-demand functionalities and complete control of electromagnetic wave properties. The great advantage of the metasurfaces over the 3D metamaterials is the ease of nanofabrication. The metasurfaces can be realized in a thin, subwavelength slab consisting of dielectric or plasmonic materials with a single-step lithography nanofabrication process. Due to this reason, metasurfaces are now emerging as a breakthrough platform for manipulating light at the nanoscale, leading to advanced nanophotonic device architectures for lasing, ultrathin optics, active wavefront control, and sensing.

The first metasurfaces were realized with metal-based materials supporting localized surface plasma resonances. Various plasmonic metasurface designs for a diverse range of applications are illustrated in **Figure 1.3a**. The collective nature of the precisely reproduced nanoparticles strongly enhances the light-matter interactions and provides distinct resonant features, which can be applied for enhanced sensing [23] and light generation [24]. Furthermore, the ultracompact device footprints and straightforward integration in miniaturized photonic devices enable their use for point-of-care applications [25]. Additionally, the precise periodic arrangement of the nanostructures allows to spatially control optical phase [26], amplitude [27], and polarization [28], [29] with subwavelength resolution enabling ultra-flat optical elements such as lenses, holograms, and beam steering devices. An achromatic plasmonic metalens showing diffraction-limited focusing capabilities in reflection mode is displayed in **Figure 1.3b**. Besides the sensing and optical phase control, the plasmonic materials give the flexibility to obtain zero or even negative effective refractive index, which can provide exotic functionalities such as superlensing [30] and optical cloaking [31]–[33].



Figure 1.3: Plasmonic metasurfaces for light-matter interactions, sensing, and optical wavefront control. (a) SEMs of various plasmonic metasurface designs for sensing, chiroptical effects, and wavefront shaping. Figure adapted from ref. [34]. (b) Left: Schematic of an achromatic plasmonic metalens operating in reflection mode. Right: SEM of the fabricated plasmonic metalens and its focal length at different wavelengths. Figure adapted from ref. [35].

1.2.1 Dielectric Metasurfaces

Although plasmonic metasurfaces provide exciting applications in optical wavefront control and sensing, they are fundamentally limited by the intrinsic Ohmic losses of the plasmonic materials. In the past decade, an alternative platform for realizing metasurfaces based on lowloss dielectric has emerged. The physics of optical resonances in dielectric metasurfaces is mostly associated with the Mie scattering of subwavelength resonators [36], see Figure 1.4a. As the effective wavelength of the incident light is close to the feature size of a high-index nanoparticle, optical resonances arising from the oscillating displacement currents can be excited. Notably, plasmonic nanoparticles generally show strong electric dipole resonance, and their responses to the magnetic field of light are weak. Due to the different resonance mechanisms, dielectric nanoparticles can show strong responses to both electric and magnetic fields. This property enables many novel light manipulation techniques that are challenging to achieve using plasmonic metasurfaces, such as complete forward scattering with Huygens metasurfaces [37], [38] and enhanced chiral sensing [39]. The electrical and magnetic dipoles and quadrupoles are the first and second Mie-type modes, which are the most common resonances observed in the spectra of dielectric resonators (Figure 1.4a). The dependence of the resonance wavelength and the dimension of a spherical dielectric nanoparticle can be described as $g(\lambda/n)=2\pi r$, where g is a positive integer, λ is the resonance wavelength, r is the radius and n is the refractive index [40], [41]. Mie-type resonances can be precisely tuned for different target wavelengths ranging from ultraviolet (UV), visible [42], to infrared (IR) [43] by geometrical tailoring of the metasurfaces and the choice of the material. This scalability provides a great degree of freedom in designing metasurfaces for a diverse set of applications, such as sensing, diffraction-limited light focusing [44], [45], polarization control [45], miniaturized spectroscopy [46] as well as holography [45], [47]. An example of ultra-flat all-dielectric metalenses operating in transmission mode with high efficiency is shown in Figures 1.4c and d. Another example showing dielectric metasurfaces consisting of tall TiO₂ pillars sitting on SiO₂ substrates for controlling the amplitude and wavelength of the transmitted light is illustrated in Figure 1.4d. By precisely arranging the dielectric resonators, the authors demonstrated a nanopainting operating with white light in transmission mode [48].



Figure 1.4: Mie resonances and dielectric metasurfaces. (a) Mie resonances in dielectric resonators. Figure adapted from ref. [36]. (b) Scanning electron micrograph of SiO₂ nanopillars un fused silica substrates. Figure adapted from ref. [49]. (c) Arrays of metalenses patterned on a 4-inch fused silica wafer. Figure adapted from ref. [49]. (d) Photorealistic full-color nanopainting enabled by a low-loss all-dielectric metasurface. Figure adapted from ref. [48].

1.2.2 Active Metasurfaces

Originally metasurfaces were designed to provide only static functionalities [50]. However, recently, these concepts have been extended towards active optical devices enabling multi-functional and reconfigurable photonic devices. There are various approaches for obtaining active metasurfaces, where one of the simplest forms is mechanical tunability with elastic and stretchable substrates [51], microelectromechanical systems (MEMS) [52],[53], and also angle-multiplexing [54], [55]. Additionally, the metasurfaces can be reconfigurably switched with electrical, thermal, and optical stimuli, using 2D materials [56], liquid crystals [57], and phase change materials [58], [59]. Interestingly, these approaches allow to extend the functionalities of metasurfaces and enable new applications, such as tunable beam steering devices [57] and atomically thin lenses [60], as well as tunable, perfect absorbers for advanced imaging

detectors [59]. Although tunable metasurfaces offer novel functionalities with exciting potential applications, most of the realized active metasurfaces suffer from low efficiencies, or are still limited to specific functionalities. To unleash the full power of reconfigurable metasurfaces, there is a need for efficient and universal metasurfaces that can be spatially tuned with high resolution, therefore enabling universal devices with on demand functionalities.

1.3 Infrared spectral range

Infrared light is electromagnetic radiation with wavelengths spanning from 800 nm up to 1 mm, divided into three regions, namely, near-infrared (0.8 µm to 2.5 µm), mid-infrared (2.5 µm to 25 µm) and far-infrared or terahertz wavelength range (25 µm to 1000 µm), see Figure 1.5a. The infrared range is technologically important, as it is crucial for many applications ranging from telecommunications with optical fibers and chemical analysis to thermal imaging and remote sensing. Regarding telecommunications, the modern-day internet would not be possible without infrared fiber-based communication systems (Figure 1.5b). Furthermore, the mid-infrared (mid-IR) spectral range is particularly interesting for nondestructive chemical analysis as intrinsic rotation and vibrational bands of a wide range of molecules lie in this spectral region (Figure 1.5c). These atom vibrational frequencies within the molecule are determined by the chemical bonds between them, and the vibrational absorption bands are unique for each molecule. Therefore, the mid-IR spectral range is often called the chemical fingerprint region. The mid-IR spectral range also contains two broad atmospheric windows, which enable remote sensing, free-space telecommunications, and applications in astronomy. Furthermore, it is well known that any heated object emits electromagnetic radiation in the form of black body radiation. Of particular interest, objects with temperatures near the room temperature have emission peaks in the mid-IR wavelength range rendering the mid-IR particularly important for remote thermal sensing and imaging (Figure 1.5d).

Although the infrared spectral range offers many exciting applications, it also brings its' challenges and limitations. Most of the applications in the mid-IR require cumbersome and expensive equipment, like Fourier transform infrared spectrometers, liquid nitrogen cooled detectors, or expensive quantum cascade laser sources. Additionally, the mid-IR optics require nonconventional materials and demanding fabrication techniques. Last but not least, due to the large mismatch between the molecule size and the infrared wavelength, the light-matter interactions are inherently low, hindering the sensitivity of mid-IR-based chemical sensors.



Figure 1.5: Infrared spectral range and IR applications. (a) Electromagnetic radiation spectral ranges. Bottom: Subclasses of the infrared spectral range. Figure adapted from ref. [36]. (b) Example of an optical fiber bundle for optical telecommunications. Figure adapted from ref. [61]. (c) Molecular vibrational absorption bands in the mid-IR spectral range. Figure adapted from ref.[62]. (d) Thermal image of a golden retriever showing high contrast of the temperature between its' nose and rest of the body. Figure adapted from ref. [63].

1.4 Motivation and outline

The metasurfaces have emerged as a breakthrough platform for manipulating light with ultracompact photonic device architectures. The metasurface unit-cell geometry can be tailored to obtain on-demand optical functionalities. Although metasurfaces have already demonstrated various functionalities, a lot of effort is still needed to bring the metasurface technology closer to widespread use and commercial applications. This doctoral thesis spans the development of novel metasurfaces and their fabrication techniques for applications in the infrared spectral range. It places emphasis on label-free biosensing in the mid-IR fingerprint region with dielectric metasurfaces for the detection of proteins, lipids, and DNA, as well as other chemical species. Here, the metasurfaces can provide the much-needed near-field enhancements, improving the absorbance signals of molecules by orders of magnitude. Therefore, metasurface-based detection systems enable chemically specific detection of analytes with low concentrations and studies of sub-monolayer systems. Besides, the novel dielectric metasurfaces can be tailored to express multiple functionalities such as spectral filtering, resonance tenability, and high sensitivity of surface-bound molecules. Therefore, metasurfaces have the potential to miniaturize infrared spectroscopy devices providing a platform for point-of-care and highly sensitive chemical sensors.

Additionally, dielectric metasurfaces have shown high efficiency for optical wavefront shaping and light focusing. Besides, the subwavelength scale of the resonators and abilities to strongly confine the light at nanoscale volumes offer many opportunities to realize actively tunable and reconfigurable photonic devices with a compact footprint. The active metasurfaces hold numerous potential applications such as light detection and ranging (LIDAR) for autonomous vehicles, adaptive optics, and optical free-space communications. Recently there has been a lot of effort channeled into the research of tunable metasurfaces. Nevertheless, highly efficient and tunable metasurfaces having subwavelength spatial resolution are still missing. This doctoral thesis demonstrates tunable dielectric metasurfaces with incorporated phase change materials, which enable high transmission efficiencies and nearly complete control of optical phase properties with subwavelength spatial resolution.

The metasurfaces also have a great potential in the mid-IR range to replace the bulky and expensive conventional optical components. However, due to the limited choice of suitable materials, it is very challenging to realize such nanophotonic devices with large-scale nanofabrication methods. So far, the mid-IR metasurfaces have been produced with nanofabrication processes that are not scalable, rendering the high costs of metasurface manufacturing. As such, a universal and CMOS-compatible process flow of mid-IR metasurfaces is needed to accelerate the adoption of the mid-IR metasurface technology for commercial applications. The thesis has a strong emphasis on metasurface nanofabrication and introduces a method for wafer-scale functional metasurface production for mid-IR photonics and biosensing.

Overall, the thesis has nine chapters where the first chapter introduces the field of nanophotonics and metasurfaces while the second chapter covers the state of the art of surface-enhanced infrared absorption spectroscopy, dielectric high-Q, and wavefront shaping metasurfaces, as well as metasurface nanofabrication techniques.

The third chapter demonstrates novel high-Q metasurfaces providing spectrally sharp and background-free resonances. The all-dielectric metasurfaces are utilized to form pixelated metasurfaces, where each 'metapixel' resonates at a specific frequency allowing to probe molecular absorption bands over a wide spectral range. The pixelated metasurface concept enables direct translation between the spectral and spatial information and direct molecular fingerprint readout with imaging-based detection methods, overcoming the need for bulky and expensive IR spectroscopy systems. Therefore, the pixelated high-Q metasurfaces pave the way towards miniaturized label-free chemical sensor devices.

Chapter 4 addresses the long-standing challenge of water absorption in mid-IR-based biosensing by using a unique 'Tidal microfluidic" concept that enables rapid shift cycles between aqueous and dry conditions. Therefore the "Tidal microfluidic" method allows obtaining spectroscopic data without any perturbation of water while maintaining the structural stability of the sensitive bioanalytes. The dielectric metasurfaces were integrated into microfluidic cells, and the operation of "Tidal microfluidic" method was successfully demonstrated by various multi-step bioassays for capture and detection of liposomes and inflammation biomarker C reactive protein. The presented method brings the metasurface-based mid-IR biosensors markedly closer to biomedical applications.

Chapter 5 introduces high-Q angle-multiplexed metasurfaces which allow to continuously tune the resonances over an extensive wavelength range with a very high spectral resolution. The angle-multiplexed method combines chemically specific broadband IR detection with devicelevel simplicity and spectrometer-less operation of angle-scanning refractometry. The method was successfully demonstrated with germanium-based metasurfaces by detecting minute quantities of polymers, single-stranded DNA, and submonolayers of proteins.

Building upon the angle-multiplexed metasurface concept, chapter 6 presents a hyperspectral vibrational imaging method that enables the acquisition of more than 10⁵ spectra per measurement. The large set of spectral data improves the signal-to-noise ratio and enables ultra-sensitive detection of proteins and their secondary structure analysis. Furthermore, a spatial surface functionalization method is demonstrated, which allows patterning of the surface with a high spatial resolution for simultaneous detection of multiple analytess. In addition, the fast acquisition of large amounts of data opens up opportunities for advanced spectral analysis with artificial intelligence for augmented detection of various biomarkers.

The subsequent Chapter 7 addresses the long-standing challenge of high-throughput metasurface fabrication in the mid-IR by establishing a novel wafer-scale CMOS compatible process flow of both dielectric and plasmonic metasurfaces for applications, ranging from label-free biosensing and spectral filtering to electromagnetic wave polarization and wavefront control. The superior optical properties of the realized metasurfaces enable record-high 96% transmission efficiency in the mid-IR without any additional anti-reflection coatings. The introduced nanofabrication method enables low-cost production of highly efficient metasurfaces and has the potential to accelerate the adoption of metasurfaces for real-world applications in the mid-IR.

The penultimate Chapter 8 introduces tunable metasurfaces consisting of hybrid germanium and Ge₃Sb₂Te₆ disk meta-units. The meta-atom geometry and thicknesses of the layers are tailored to obtain electric and magnetic resonant modes in close spectral proximity, where they can interfere constructively in the transmission mode. Switching the Ge₃Sb₂Te₆ between its structural states enables dynamic light phase control with high transmittance. The versatility of the active Huygens' metasurfaces is demonstrated by optically programming spatial light phase distributions with single meta-atom precision and retrieving high-resolution phase-encoded images over large areas. The programmable metasurface concept overcomes the static limitations of previous dielectric metasurfaces, paving the way for "universal" metasurfaces and highly efficient, ultra-compact active optical elements like tunable lenses, dynamic holograms, and spatial light modulators.

The concluding chapter 9 summarizes the main results of the doctoral thesis and their potential impact. Chapter 9 also describes the potential further directions of the demonstrated mid-IR metasurfaces and their associated challenges.

Chapter 2 State of the art

2.1 Surface-enhanced infrared absorption spectroscopy

The mid-infrared (mid-IR) spectrum is essential for sensing because of the presence of characteristic molecular absorption fingerprints originating from the intrinsic vibrational modes of chemical bonds. Mid-IR spectroscopy allows direct characterization of molecular structures with chemical specificity unique to this spectral range and is therefore widely recognized as the gold standard for chemical analysis. It is also a powerful nondestructive and label-free technique for identifying biochemical building blocks, including proteins, lipids, and DNA. However, because of the mismatch between mid-IR wavelengths and dimensions of molecules, the sensitivity of mid-IR spectroscopy is limited when detecting signals from nanometer-scale samples [64], biological membranes [65], or low numbers of surface-bound molecules [66].

Nanophotonics can overcome this limitation by exploiting the strong near-field enhancement of subwavelength nanoantennas. When the resonance is spectrally overlapped with the absorption fingerprints, the enhanced molecule-resonator coupling can lead to a change in either the frequency or the strength of the resonance, from which the molecular fingerprints can be extracted. This concept, surface-enhanced infrared absorption (SEIRA), has been realized using various plasmonic platforms, where one of the simplest for is with rod type of antennas [67]–[69].

Such antenna geometries focus the incident light into hot spots of the electromagnetic fields, providing strong light-matter interaction and therefore enabling the detection of otherwise weak absorption signatures down to, e.g., monolayers of proteins [70], [71] (**Figure 2.1a**). Surface-enhanced infrared absorption spectroscopy (SEIRAS) techniques have enabled a wide range of sensing applications across diverse fields, such as chemical engineering, pharmaceutical research, materials science, environmental monitoring, and personal health [67]. SEIRAS has been particularly impactful for biosensing, where detecting and differentiating the absorption signatures of the basic building blocks of life, including lipids, proteins, and nucleic acids (**Figure 2.1b**) with high sensitivity, is essential. In addition, the non-invasive and label-free

nature of infrared spectroscopy enables the real-time and in situ detection of molecular interaction kinetics in complex bioassays or processes involving biological membranes. The sensitivity and consequently the limit of detection of SEIRAS approaches are crucially determined by the geometry, material choice, and spatial arrangement of the nanostructured antenna elements. The following section highlights some of the central design paradigms for highly surface-sensitive resonators and their applications [72].



Figure 2.1: Surface-enhanced infrared absorption spectroscopy (SEIRAS). (a), Infrared absorption spectroscopy optically detects the characteristic vibrational bands of molecules associated with their chemical bonds. Resonant nanoantennas can enhance these signatures and access chemical and compositional information from monolayers and few-molecule systems, providing strong enhancements of the absorption signals. (b), SEIRAS techniques are crucial for understanding complex biological systems such as cells and membrane interaction processes because they can differentiate between a multitude of fundamental biological building blocks, including lipids, proteins, sugars, and nucleic acids. The figure is adapted from ref. [73].

So far, the metasurfaces for SEIRAS have been realized with plasmonic materials such as gold, aluminum, and silver. One of the simplest and most commonly used resonator geometries for SEIRA sensing is the rod-type nanoantenna design which provides strong dipole moments and tightly confines the electromagnetic fields. The enhanced light-matter interaction at the tips of

the antennas improves the absorbance signals by orders of magnitude [67]. Additionally, the signal improvement can be further boosted by carefully optimizing the unit cell periodicities of the plasmonic metasurfaces [74]. One such example is depicted in **Figure 2.2a** left, where the authors realized gold nanorod metasurfaces with nanoantenna length of 2.2 μ m [75]. The authors further demonstrated chemically specific protein detection with submonolayer sensitivity **Figure 2.2a** right.

The metasurface sensitivity can be further improved by utilizing more complex resonator designs, such as nano-gap nanoantennas [68], [76] or resonant geometries that provide higher resonance quality factors (Q-factor) [77]. The work by L.Dong et al. demonstrates near-field enhancements up to 10^{7} , allowing to detection of as few as 500 molecules of 4-NTP [68]. Another nanogap antenna design is depicted in **Figure 2.2b**, where the authors demonstrate coaxial metasurface designs. Interestingly, the nanogaps with sizes as small as 7 nm were reproducibly realized with common laser lithography nanofabrication methods and atomic layer deposition of Al₂O₃. Such metasurfaces provide more than an order of magnitude higher signals of thin layers of proteins when compared to the regular nanorod designs [78].

Besides surface sensitivity, it is important to have the near-field enhancement over a wide spectral range, which is necessary to target multiple chemical species simultaneously. For instance, the main absorption bands of proteins lie in the spectral range from 1450 cm⁻¹ to 1750 cm⁻¹, while for the lipids, the strongest absorption bands are close to 3000 cm⁻¹. Therefore it is not possible to target both molecular species with a single resonant metasurface. Recently multiresonant nanoantennas were introduced for monitoring the real-time protein and lipid interactions [79]. The authors demonstrated detection of lipid vesicles which were loaded with cargo molecules, and subsequent liposome puncturing with melittin peptide, which resulted in the release of the cargo analytes **Figure 2.2c**. Strikingly, such label-free metasurface-based detection mechanism has the potential to be used for biological studies of protein and cell membrane interactions and various classes of lipid vesicles such as exosomes, synaptic vesicles, and liposomes, spanning the research of cancer diagnostics and treatment, pharmaceutical research, and neurodegenerative diseases [79].

Interestingly the infrared spectroscopy not only allows to distinguish between various biological building blocks, such as proteins, DNA, and lipids, but it can also provide information about the protein's secondary structure and conformation. Their native conformation The protein secondary structure is maintained by the hydrogen bonds between adjacent amino acid residues in polypeptide chains. The major components of the secondary structure are protein secondary alpha helixes and beta sheets. The protein secondary structure is particularly important of protein because it determines if the protein is functional or not and how the proteins interact with other biological macromolecules. Changes in protein secondary structure are believed to be the primary cause of Parkinson's disease, Alzheimer's disease, Huntington's disease, and many other degenerative and neurodegenerative disorders [80]. Therefore it is of high importance to monitor the protein states with label-free methods and high sensitivity. Dordaneh et al. has demonstrated that SEIRA can be a viable option to monitor the protein misfolding and secondary structure of low amounts of analytes. The authors show dynamic monitoring of β -sheet to disordered conformation transitions in a monolayer of disease-related α -synuclein protein **Figure 2.2d**.

Additionally, SEIRAS can also be utilized for sensing small molecules such as gases and volatile organic compounds. H. Zhou et al. have demonstrated gold-based metasurfaces with a metal-organic framework for simultaneous detection of various gas species. Here the metalorganic framework is needed to concentrate the small gas molecules to the surface near the tips of the plasmonic antennas, where electromagnetic fields are localized most strongly. Additionally, the plasmonic metasurfaces can be realized with alternative materials, such as highly doped semiconductors[81] and two-dimensional materials like graphene [56]. The 2D materials are particularly interesting for gas sensing because their optical response is significantly perturbed upon molecule adsorption. H. Hu et al. utilized graphene nanoribbon metasurfaces to probe the SO₂ NO₂ N₂O and NO rovibrational modes [82]. The experimental gas cell with integrated metasurface is shown in **Figure 2.2e.** The demonstrated devices show fast response times (<1min) and sensitivity of 800 zeptomoles per 1 μ m². Such devices could potentially be used for breath analysis and monitoring of volatile organic compounds.

The plasmonic-based SEIRAS provide strong amplification of the chemical absorption signals in a broad spectral range, where the resonance bandwidth of the nanoantennas is much larger than the full width at half maximum (FWHM) of the molecular absorption bands, see **Figure 2.2a-c**. . In the operation of techniques such as surface-enhanced infrared absorption spectroscopy (SEIRA) and vibrational circular dichroism spectroscopy, it requires that the resonance
bandwidth covers the spectral band of the molecular absorption. Therefore, a relatively broadband resonance can be useful in this regard. On the other hand, wide spectral resonance bandwidth means that still complex and expensive equipment such as Fourier transform infrared spectrometers, and tunable quantum cascade laser sources are needed to read out the chemical fingerprints of the target analytes. Metasurfaces supporting spectrally selective resonances, in principle, could overcome these limitations, simultaneously providing both absorption signal amplification and additional spectral information of the chemical absorption bands.



Figure 2.2: Plasmonic antennas for surface-enhanced spectroscopies. (a) Rod type gold nanoantennas and the corresponding absorbance signals of surface-bound streptavidin monolayer. Adapted from ref. [75]. (b) Coaxial nanogap antennas for increased SEIRA signals. Adapted from ref. [78]. (c) Multi-resonant gold nanoantennas for simultaneous detection of lipid bilayers and proteins. Adapted from ref. [83]. (d) Detection of protein secondary structure and transitions of conformation states. Adapted from ref. [84]. (e) Gas sensing with graphene nanoribbon metasurfaces Adapted from ref. [82].

2.2 All-dielectric metasurfaces supporting high-Q resonances

The spectrally sharp or high-quality factor (high-Q) resonances are crucial for enhancing lightmatter interactions. The resonance quality factor (Q-factor) can be calculated as the resonance frequency over the FWHM of the resonance, and it describes how fast the energy is dissipated from the resonator. For optical resonators, the Q-factor shows for how many oscillation cycles the photon is trapped within the resonator. The Q-factor is highly dependent on loss mechanisms, mainly the absorption and scattering losses of the resonators. The Q-factor is a measure of field enhancement. In principle, the field enhancement of a metasurface is proportional to $\gamma_{rad} (Q^2/V)$, where γ_{rad} is the radiative decay ratio of the metasurface unit-cell (called meta-atom), Q is the quality factor of the resonance mode, and V is the mode volume. Therefore, metasurfaces with a high-quality factor (high-Q) resonance can generate stronger field enhancement, which is a key for most optical sensing techniques.

In order to obtain high-Q resonances, the constituent materials of the metasurfaces need to have low intrinsic losses. Therefore it is highly challenging to realize spectrally selective metasurfaces with plasmonic-based materials. Recently, an alternative approach based on all-dielectric materials have emerged, which enables strong field enhancements and spectrally selective resonances. The high refractive index materials such as Si and Ge have near-zero absorption losses over large spectral windows. For those reasons, they are often used to realize high-Q metasurfaces. To achieve spectrally sharp resonances, it is also crucial to minimize the nanoantenna scattering losses. The most simple resonances in dielectric materials are the electric and magnetic dipole modes which strongly scatter the light and are observed as broad reflection peaks in the spectrum. The scattering of the nanoantenna can be minimized by tailoring the geometry of the metasurface unit cell.

Several state-of-art works on novel dielectric metasurfaces with high-Q factor resonances are presented in **Figure 2.3**. As mentioned, dielectric nanoparticles can show low optical losses and strong magnetic dipole resonance. Yang *et al.* reported a Fano-resonant dielectric metasurface by taking advantage of these features [85]. A scanning electron microscopic (SEM) image of the metasurface is presented in **Figure 2.3**a. The metasurface has been designed for operation at the telecommunication wavelength band so that the material loss of Si is minimized to further increase the resonance quality. The unit cell consists of two nanoresonators, amorphous silicon (a-Si) bar, and a-Si disk. The electric dipole mode of the bar resonator serves as the bright mode, while the out-of-plane magnetic dipole mode of the ring resonator is dark in nature. The coupling of the bright and dark modes suppresses the far-field radiation and results in a sharp spectral feature. The transmission spectrum of the metasurface reveals a sharp resonance peak at 1371 nm with a Q factor of 483 [85]. Another alternative approach for designing high-Q factor metasurfaces is to introduce a mode interference inside the individual resonators [86]. Semmlinger *et al.* demonstrate excitation of an anapole resonance, which results from destructive interference between the electric and toroidal dipoles in a metasurface. (**Figure**

2.3b). The unit cell of the metasurface is a nanodisk, as can be seen in the left panel of Figure 2b. To achieve a proper resonance property in the anapole metasurface, amorphous TiO_2 is used as the constituent material because of its low loss in the visible regime. The anapole resonance produced a sharp dip in the transmission spectrum, as can be observed in the right panel of **Figure 2.3b**. Notably, the simulation results for both of the metasurfaces (the inserts in **Figure 2.3a** and **b**) illustrate that electromagnetic energy is strongly confined around their surfaces at the resonance condition. This characteristic is very useful to boost the light-matter interactions at the nanoscale for many applications, including several biosensing applications.

More recently, a new approach for achieving high-Q resonant metasurfaces based on the quasibound state in the continuum (quasi-BIC) has attracted significant attention [87]-[89]. BICs are the optical modes that remain ideally confined even though they are compatible with freespace radiation. A true BIC is a mathematical object with an infinite Q factor and a vanishing resonance [90]. Within the concept of metasurfaces, in BIC conditions, the resonance feature in the transmission spectrum collapses due to the transformation of the resonance mode to a dark mode. Symmetry-protected BIC can become quasi-BIC by breaking the in-plane symmetry of the unit cell with a controllable asymmetry parameter. This provides so-called supercavity modes[87] with finite but high-Q factors. Absorption influences the total Q-factor of a quasi-BIC resonance, yet the radiative Q-factor for all quasi-BIC supporting metasurfaces has an inverse quadratic relation with the asymmetry parameter of the unit cell. This quadratic correlation, along with the linear scalability of Maxwell's equations, can be employed to engineer metasurfaces with desired properties. BIC modes have been previously observed in plasmonic metasurfaces by Lovera et al. [91]. They proposed a possible link between Fano resonances and BIC modes in their work. Later, the theory of quasi-BIC has been developed and systematically explained by Koshelev et al. within the context of dielectric metasurfaces [89]. An example of a dielectric metasurface based on the physics of BIC is presented in Figure 2.3c. The metasurface consists of pairs of Si nanoellipses as resonant unit cells. The middle panel of Figure 2c represents that when the nanoellipses are parallel, a pure BIC mode is excited with an infinite Q factor in the spectra and spectrally vanishes. By breaking the in-plane symmetry with a gradual tilt of the ellipses, a radiation channel is created, and the BIC is turned into a quasi-BIC mode having a finite and tunable Q factor. A resonance dip can be seen in the spectra, and their quality factor varies with the rotation angle. Simulation results of the electric

field distribution for the symmetric and asymmetric nanoellipse pair at the resonance wavelength are presented in the bottom part of **Figure 2.3c**. It displays similar field patterns, a characteristic of the transition between the pure BIC mode to the quasi-BIC mode. More recently, a silicon-based metasurface with a record-high-Q factor has been realized (**Figure 2d**). The authors introduce an in-plane inversion symmetry breaking by cutting out part of the edges [92]. The metasurface provides an experimentally measured resonance Q factor up to 18'511 for operation in the telecommunication wavelength with the resonance wavelengths ranging from 1487 nm to 1557 nm. These recent works show that the type of optical resonances, functionalities, and the working wavelengths can be effectively tuned by changing the material, geometry, and arrangement of the unit cell. Therefore dielectric metasurfaces can provide an attractive platform for sensing applications, like SEIRAS. Although the presented high-Q metasurfaces in **Figure 2** allow to probe only a specific narrow spectral band of the targeted molecular absorption spectrum, there are several approaches how to circumvent this restriction, which will be introduced in the following chapters.



Figure 2.3: Examples of high-Q factor dielectric metasurfaces. (a) Fano-resonant metasurface [85]. Left panel: SEM image of the metasurface consisting of Si bars and disks. Insert: the electric field pattern at the resonance wavelength. Right panel: simulation (purple curve) and experiment (red) transmission spectrum of the metasurface. (b) Anapole metasurface [43]. Left panel: SEM image of the metasurface consisting of TiO₂ disks. Insert: the electric field pattern at the resonance wavelength. Right panel: Transmission spectrum of the metasurface. (c) Quasi-BIC metasurfaces with different symmetry breakings [89]. Top panel: Schematic of the metasurface consisting of asymmetric Si asymmetric nano ellipse pairs. Middle panel: Dependence of the transmission spectra versus the rotational angle θ (indicated in the top panel). Bottom panel: Comparison of the electric field patterns for the BIC and quasi-BIC mode, respectively. (d) Ultrahigh-Q factor quasi-BIC metasurface [92]. Left panel: SEM image of the metasurface consisting of Si nanoresonators. Insert: the electric field pattern at the resonance wavelength. Right panel: Transmission spectra with different cut-out sizes. The polarization of the excitation for the metasurface shown in this figure is along the x-axis shown in (d). Figure 2.3 is adapted from ref. [93].

2.3 Dielectric metasurfaces for optical wavefront control

The low losses and the strong electric and magnetic resonances make the dielectric metasurfaces very attractive for the manipulation of light optical phase, amplitude, and polarization. The near-zero absorption losses in dielectric materials allow to significantly improve the operating efficiency of the metasurfaces, especially when compared to plasmonic counterparts. For those reasons, the field of wavefront shaping dielectric metasurfaces has gained a lot of attention.

One of the first dielectric metasurfaces capable of light focusing with diffraction-limited spot sizes was realized with TiO₂ metasurfaces with fin-based unit cell geometry **Figure 2.4a**. The working principle of the demonstrated metalens is based on the geometric phase, also known as the Pancharatnam–Berry (PB) phase. In the PB phase metasurfaces, each meta-atom operates as half waveplates with spatially varying optical axis [94], [95]. The PB phase metasurfaces modulate the optical phase by spatially varying anisotropy instead of accumulating the optical path difference [96], [97]. This method enables gradual spatial tunability of the optical phase and enables highly efficient optical elements. Another example of PB phase metasurfaces is demonstrated in **Figure 2.4b**, where the authors realized gradient metasurfaces with Silicon nanobeam nanoantenna geometries. The authors demonstrated various functionalities of such metasurfaces, like Bessel beam generation, light focusing, and beam deflection with high transmission efficiency. Although the PB phase metasurfaces can achieve high efficiencies in transmission mode, they are functional only for circularly polarized light. Therefore for practical applications, the PB phase metasurfaces have low efficiencies because the polarization state of the incoming light first has to be converted to a circular polarization state.

To overcome the limitations of the PB phase-based metasurfaces, Arbabi et al. introduced polarization-insensitive metasurfaces for light wavefront shaping applications. The meta unit cell consists of circularly shaped a-Si posts with a height of approximately 3 λ/n , where λ is the operation wavelength, and n is the refractive index of a-Si [98]. Here the optical phase is directly related to the diameter of the posts instead of their orientation, making the metasurface operate with arbitrary polarization states. Later, A. Arbabi et al. demonstrated how the geometry, particularly the ellipticity of the meta-atom design, can be tailored to obtain full control of both the optical phase and polarization [45]. The metasurface unit cell is demonstrated in **Figure 2.4c** left. The authors demonstrated various applications, such as polarization-dependent beam splitting and light focusing. Furthermore, to validate the versatility and multifunctionality of these metasurfaces, the authors demonstrated spatially encoded holograms, where the metasurface would display the Caltech logo when illuminated with one polarization and «Caltech» letters when illuminated with the orthogonal polarization state (**Figure 2.4c** right).

Another approach for realizing highly efficient metasurfaces for wavefront shaping is by combining electric and magnetic resonant modes. Usually, the electric and magnetic dipole modes are observed as broad reflection peaks in the spectrum, giving a π optical phase shift over the resonance. Interestingly, the dielectric resonator geometry can be shaped in a way to spectrally overlap these two resonances, where they can interfere constructively in the transmission mode, which is known as the Kerker's effect [99]. When Kerker's condition is met, the metasurface scatters the light forward. In addition, the contribution of both electric and magnetic resonances enable obtaining a 2π phase shift which is needed for full control of the optical phase.

Decker et al. demonstrated the Kerker's effect with silicon disk nanoantennas in the near-infrared spectral range [37]. The disk geometrical shape allows controlling the spectral positions of the electric and magnetic dipole resonances, where the electric dipole resonance is more dependent on the disk radius while the magnetic resonance is dependent on the resonator height. The electric dipole resonance is induced by the incident electric field, which creates a collective polarization of the dielectric nanoantenna at the resonance frequency [100]. The magnetic dipole mode is characterized by an oscillating displacement current loop, which creates an associated strong magnetic dipole. The magnetic dipole mode in the resonator can be excited when the resonator height is bigger than the half wavelength in the resonator (λ /2n). An example of Huygens metasurface-based lens is demonstrated in **Figure 2.4d**, where the unit cell geometry consists of a 2 rectangular component design [101]. The metasurface was realized on IR transparent CaF₂ substrates, using high refractive index led telluride alloy (PbTe). The specific materials allow achieving full optical phase control with ultra-thin metasurface dimensions (λ /8). The metasurfaces show transmission efficiencies up to 75% and diffractionlimited focusing in the mid-IR (**Figure 2.4d**).

Recently the wavefront shaping metasurfaces have been extended to incorporate also strong near-field enhancements and high resonance Q-factors [102], [103]. Such devices combine

both spectral selectivity and capabilities of controlling the direction of light propagation. Besides, the strong electromagnetic field enhancement can provide additional advantages for realizing active and tunable metasurfaces. Metasurfaces supporting resonances with quality factors up to 2500 and capable of steering light beams are shown in **Figure 2.4e**. The metasurface consists of the sapphire substrate and Si bars, where the Si bars have induced subtle perturbations which allow exciting a high-Q resonant mode. An SEM image of the high-Q metasurface is displayed in the bottom part of **Figure 2.4e**.



Figure 2.4: Metasurfaces for wavefront shaping (a) TiO_2 Fin-based metalens based on geometric phase for light focusing with diffraction-limited spot sizes Adapted from ref. [95]. (b) Dielectric PB phase nanobeam metasurfaces for nondispersive Bessel beam generation. Adapted from ref. [94]. (c) Left: a-Si nanopillar-based metasurfaces enabling complete control

of optical phase and polarization in transmission mode. Right: Simulation and experimental results of spatially encoded holograms for each polarization state. Adapted from ref. [45] (d) Mid-IR Huygens metasurfaces made from PbTe with two rectangular component unit cell. Adapted from Ref. [101]. (e) Spectrally selective Si metasurfaces for beam steering applications in the near-IR spectral range. Adapted from Ref. [103].

Overall dielectric metasurfaces are a very promising approach to obtain complete control of electromagnetic wave properties with high efficiency and ultra-low device footprint. So far, most of the metasurfaces have been realized in the near-infrared and visible spectral ranges, where they have the potential to be integrated directly in smartphones as optics for imaging cameras and also potential use in many other optical systems. In addition, metasurfaces have a great untapped potential for mid-infrared photonics, where they could replace the bulky and expensive conventional optical elements in optical sensors and imaging devices. Highly efficient mid-IR metasurfaces for wavefront shaping and polarization control will be introduced in Chapter 7, while actively tunable metasurfaces for wavefront shaping applications will be introduced in Chapter 8.

2.4 Methods for dielectric metasurface nanofabrication

The performance of dielectric metasurfaces is highly dependent on the precise reproduction of the desired meta-atom shape, size, and constituent material optical properties. Usually, the metasurface nanofabrication process begins with a selection of a proper substrate material, which should be transparent with near-zero absorption losses and with a low refractive index. The low refractive index is needed to increase the refractive index contrast between the metasurface nanoantennas and the substrate, which is needed to confine the electromagnetic fields within the resonators and avoid the resonant mode leaking [100], [104]. In the visible spectral range, the typical substrate materials are SiO₂ and Al₂O₃, which have a relatively low refractive index, near-zero absorption losses, and good mechanical durability to support the metasurfaces.

The Second main step of the metasurface nanofabrication process is the selection and deposition of the metasurface material. In order to obtain high efficiency of the metasurface, the dielectric material needs to have a high refractive index and low absorption losses. **Figure 2.5** provides an overview of low-loss dielectric materials (k < 0.001), which are suitable candidates for metasurface sensors in the UV–visible and IR regimes. Some of the suggested materials have already been implemented, such as TiO₂ in the visible regime and Si in the IR regime. On the other hand, the utilization of many other materials for metasurfaces is yet to be explored, and they can be investigated to open up new applications in the field of dielectric metasurfaces. For example, as shown in **Figure 2.5a**, by using high bandgap materials, such as diamond, AlN, and HfO₂, the working wavelength of dielectric metasurface sensors can be extended into the UV regime. It will be useful for sensing technologies such as resonance Raman spectroscopy [105] and UV circular dichroism spectroscopy [106]. By using active materials, such as GaAs and GaN, multifunctional metasurfaces capable of not only generating near-field enhancements but also working as on-chip light sources for ultra-compact sensor integration. In addition, some unconventional materials, including high-index chalcogenides [107], [108], multiple quantum wells [109], [110], phase-change media [111], [112], and perovskites [113], [114] have been recently used for metasurfaces to obtain new functionalities. Further investigation of the unconventional materials for metasurfaces could lead to high-performance optical biosensors and active wavefront shaping devices.



Figure 2.5: Refractive index (*n***) of low-loss dielectric materials for metasurfaces at (a) the UV-Visible regime and (b) the IR regime.** The double arrow lines indicate the wavelength range where the related materials have a near-zero extinction coefficient. The height of the double-headed arrows corresponds to the average value of the refractive index in the wavelength ranges. Possible sensing techniques of dielectric metasurfaces at different regimes are labeled on the top of the figure.

After the material deposition, the precise resonator shape needs to be reproduced, which is usually done with lithography techniques. So for most of the metasurfaces have been realized using electron beam lithography (EBL) methods. In the EBL process, a focused beam of electrons is scanned to write custom shapes into electron-sensitive polymer film (photoresist),

which is coated on the metasurface material. The electrons that interact with the photoresist (PR) induce the polymer crosslinking, changing its solubility in the photoresist developer. Therefore, after the exposure, the resist can be selectively removed, leaving the desired PR patterns on the metasurface material. In order to translate the patterns into the metasurface material, a dry plasma etching process is needed, followed by oxygen plasma treatment for remaining photoresist removal. The advantage of EBL is that it can achieve sub 10 nm spatial resolution without the need for lithography masks. Therefore it is a great method for rapid prototyping of the metasurfaces and is the standard method for realizing nanophotonic devices for research purposes. A wavefront shaping metasurface realized with EBL is demonstrated in Figure 2.6a, which operates down to the deep-ultraviolet spectral (DUV) region [115]. Here, the EBL method allows to reproducibly fabricate nanoantennas of sizes ranging from 50 nm to 160 nm. Figure 2.6b shows another example of EBL realized nanoantennas which consist of Si dimer resonators with a gap size of 20 nm. The Si-dimer structures confine the light in the nanogap and provide strong signal amplification for surface-enhanced Raman spectroscopy applications. The EBL is a powerful method for realizing advanced metasurfaces with nanometer-scale resolution. However, it is limited by its' writing speed which is approximately 1mm² per hour, depending on the spatial resolution and the electron beam size. Moreover, it is not possible to upscale the nanofabrication speed with the EBL methods. Therefore electron beam lithography is not a viable option for large-area nanofabrication and mass production of metasurfaces.

The throughput of metasurface fabrication can be improved by orders of magnitude with direct laser writing (DLW) methods. Direct laser writing still gives the flexibility to produce various metasurface shapes without the need for lithography masks. The DLW can achieve reproducible shapes with ~0.5 μ m spatial resolution. Bagheri et al. utilized the direct laser writing method to realize square centimeter-sized plasmonic nanoantenna arrays for SEIRAS applications [74]. More recent work from Ren et al. demonstrates wavefront shaping metasurfaces realized with two-photon lithography [47]. Here, instead of using the photoresist as a mask, the resist serves as the metasurface material. The realized metasurface is shown in **Figure 2.6c** bottom, consisting of ~4 μ m tall pillars as unit cells. Interestingly, the two-photon lithography enables direct writing of 3D nanostructures by photoinduced polymerisation of the liquid resist, which is coated on a SiO₂ substrate. By controlling both the nanoantenna height and the orien-

tation, the authors demonstrated complete control of the complex amplitude and showed metasurfaces for angular momentum holography capable of multiplexing up to 200 independent orbital angular momentum channels. The direct laser writing has been shown to be an effective complementary lithography method to EBL for metasurface fabrication. Although it is possible to realize centimeter-scale metasurfaces with the DLW, the thourghput is still to low to realize wafer-scale metasurfaces in a cost-efficient manner.

The gold-standard lithography method for large-area nanofabrication with a high spatial resolution is the DUV lithography method. The operating laser wavelength in the DUV wavelength range effectively improves the resolution and enables reliable reproduction of nanostructures with sizes of 100 nm. The DUV and other high-throughput nanofabrication techniques require a lithography mask of the desired patterns, which are then projected on the wafers using complex optical systems containing up to 30 lenses. These lithography masks are usually fabricated using high-resolution EBL or DLW methods. Recently the DUV lithography was used to realize large-area SiO₂ metalenses for light focusing and imaging [49]. The corresponding process flow is illustrated in **Figure 2.6d**, where the resonant structures were directly etched in the SiO₂ substrate. Using this method, the authors demonstrated the cost-effective realization of centimeter-scale metalenses on standard 4-inch SiO₂ wafers. The main advantages of the DUV lithography method are the high resolution, high fabrication throughput, and contactless operation. The contactless operation is crucial to preserve the lithography Mask (reticle), and it ensures that the lithography mask can be in principle used indefinitely. This is in strong contrast to other large area nanofabrication techniques such as nanoimprint and nanostencil lithography.

The nanoimprint lithography relies on direct contact between the imprint mask and the photoresist. There are two main nanoimprint techniques, namely, thermal nanoimprint without any light exposure and UV nanoimprint, where the imprint mask is pressed against the photoresist with subsequent UV light exposure. The nanoimprint lithography can achieve even higher spatial resolution than the DUV lithography, with repeatable reproduction of metasurfaces with critical dimensions below 20nm [116]. A schematic of the nanoimprint process is shown in **Figure 2.6e**, where a single-step nanofabrication method of TiO₂-based optical wavefront shaping metasurfaces is demonstrated [117]. The authors suspended TiO₂ nanoparticles in the photoresist, which enabled to increase in the effective refractive index of the material, therefore providing a platform for straightforward metasurfaces with a resolution comparable to the EBL. However, due to the direct contact between the nanoimprint lithography mask and the photoresist, the nanoimprint masks deteriorate over time and induces defects on the manufactured devices. As the occurrence of the defects is completely random, it is very challenging to detect when the defects appear, and the nanoimprint mask has to be changed.

Another approach for realizing large area metasurfaces is based on stencil technology, where a shadow mask is used to evaporate the target metasurface material in specific patterns. The stencil mask is realized on thin free-standing Si_3N_4 membranes. An illustration of nanostencil lithography is demonstrated in **Figure 2.6f**, where the stencil maki s placed in close proximity of the wafer, and the metasurface material is evaporated with high directionality through the stencil mask apertures. Aksu et al. realized highly reproducible plasmonic metasurfaces with gold nanorod antennas with optical performance nearly identical to the EBL fabricated metasurfaces [118]. The great advantage of nanostencil lithography is that it is single-step nanofabrication, where the metasurface patterns are directly deposited on the substrate material. However, this method is prone to occurring defects in the lithography mask, and also, the attainable spatial resolution is lower when compared to the nanoimprint lithography.

Although various wafer-scale nanofabrication methods have been used to realize various metasurfaces, due to the lack of materials with suitable optical properties in the infrared, it remains highly challenging to realize metasurfaces with high-throughput for mid-infrared spectral range. For these reasons, there is a need for a cost-effective and high-throughput nanofabrication method of efficient mid-IR metasurfaces.



Figure 2.6: Metasurface nanofabrication methods. (a) SEM image of EBL fabricated metasurfaces operating in the UV spectral range. Adapted from ref. [115]. (b) SEM images of EBL fabricated Si meta-atoms with a gap size of 20nm. Scale bar, 100nm. Adapted from ref. [119]. (c) Two-photon direct laser writing of dielectric metasurfaces for complete control of complex amplitude. Adapted from ref. [47]. (d) Dielectric metasurface nanofabrication method using DUV lithography method. Adapted from ref. [49]. (e) Illustration of the nanoimprint process flow and an SEM of the soft imprint mask. Scale bar for the SEM, 1µm. Adapted from ref. [117]. (f) Illustration of the nanostencil process and direct metasurface material evaporation. Bottom: an SEM of the realized gold nanoantennas with a length of 1100nm. Adapted from ref. [118].

Chapter 3 Imaging-based molecular barcoding with all-dielectric pixelated metasurfaces

3.1 Introduction

The previous chapter showed the powerful technique of SEIRAS for label-free and chemically specific detection of minute quantities of various analytes. So far, most of the metasurfaces for SEIRAS applications have been realized with plasmonic-based materials. In this chapter high-Q all-dielectric metasurfaces for chemical fingerprint detection are introduced. A crucial aspect of the dielectric metasurfaces is the electromagnetic field enhancement and the localization of the near-fields. For sensing applications, it is important to have the highest electric near-field intensity outside of the resonator volume, where the surface-bound molecules can interact with the electromagnetic fields. Most of the realized high-Q dielectric metasurfaces strongly confine the fields within the meta-atom volumes (see Figures 2.3a, b, and d), and it is challenging to realize efficient metasurfaces that can strongly amplify the absorption signals of the molecules. The low-loss dielectric metasurfaces offer the opportunities to achieve high-Q resonances, which not only enhance the electromagnetic fields but also provide spectral selectivity. Therefore high-Q metasurfaces combine multiple functionalities, namely signal enhancement and spectral filtering, which can be used for novel SEIRAS techniques enabling compact footprint and spectrometer-less operation. Strikingly, these novel high-Q metasurfaces address the sensitivity and equipment limitations of the mid-IR spectroscopy and open up possibilities for miniaturized mid-IR biochemical sensors.

3.2 High–Q metasurface Meta-atom design

In this doctoral thesis, a metasurface design based on zig-zag arrays of elliptical dielectric metaatoms was developed, where the collective resonance is formed by the electric dipole modes polarized along the long axis of each individual meta-atom. For a lossless system, the linewidth of the resonance depends on the scattering loss, which is determined by the overlapping of the mode profile and the field polarization of the scattering channels. For the periodic zig-zag metasurface studied here, the scattering channels are the zeroth-order plane waves propagating in the normal direction; the overlapping of the mode profile and the plane wave is determined by the net-electric dipole moment in each unit cell. The zig-zag design allows to precisely control this overlap by fine-tuning the unit cell geometry, including the orientation angle θ of the meta-atoms. When the collective mode is excited, the dominant component of the dipole moments of the meta-atoms (*py*) is actually perpendicular to the incident field polarization Ex^i as shown in **Figure 3.1a**. However, due to the antisymmetric distribution of the components ($p_{1,y} = -p_{2,y}$), the out-coupling with the plane wave of *Ey* polarization is forbidden, and thus the overall scattering loss of the collective mode is suppressed significantly. In fact, only the *px* component is nonzero ($p_{1,x} = p_{2,x}$) and therefore contributes to the scattering loss. For simplicity, we assume that the zig-zag array is lossless and positioned in a homogenous background. The forward and backward scattered fields are contributed by the collective dipole resonance with nonzero net dipole moment px, which can be expressed as

$$E^f = E^i_x + \frac{i\omega\eta}{2A} p_x, \tag{1a}$$

$$E^{b} = \frac{i\omega\eta}{2A}p_{x},$$
 (1b)

where η is the wave impedance of the surroundings and *A* is the area of the unit cell. The net dipole moment within a unit cell can be further expressed as

$$p_x = i2Iu\frac{\sin\theta}{\omega},\tag{2}$$

where u is the normalized dipole moment of a single meta-atom. I is the corresponding frequency-dependent current amplitude that captures the resonant behavior, which can be calculated via

$$I = \frac{E_x^i u \sin \theta}{Z},\tag{3}$$

with Z being the effective impedance of the meta-atom under the collective resonance, taking into account all the mutual interaction. Generally, the effective impedance around a single resonance can be approximated with an RLC circuit:

$$Z = -i\omega L - \frac{1}{i\omega c} + R, \tag{4}$$

where R is the effective resistance and is contributed solely by the radiative loss in a lossless system. From energy conservation, it requires that

$$\left|E_{x}^{i}\right|^{2} = \left|E^{f}\right|^{2} + |E^{b}|^{2}.$$
(5)

Substituting Eqs. (1a) to (4) into Eq. (5), and using the identity: $\operatorname{Re}(1/Z) = \operatorname{Re}(Z *)/|Z| 2 = R/|Z| 2$, we obtain the following relation between the effective resistance R and the orientation angle θ :

$$R = \frac{2\eta u^2 \sin^2 \theta}{A}.$$
 (6)

Since the quality factor $Q = R^{-1}\sqrt{L/C}$ and the effective inductance L and capacitance C do not change significantly when θ is small. It is expected that the quality factor $Q \propto 1/\sin 2\theta$, which grows dramatically as the orientation angle θ decreases. To confirm the effect, we simulate the resonance behavior using the geometrical parameters $A = 1.96 \mu m$, $B = 0.96 \mu m$, Px =3.92 μ m, and $Py = 2.26 \mu$ m, where A and B are the long and short axis of the ellipse and Px and Py are the unit cell periodicities along the x and y axis. In the simulations, the structure height was fixed to 0.7 µm. By changing the orientation angle while keeping other parameters unchanged, we clearly observe the asymptotic behavior of the quality factor as θ decreases (Figure 3.1b). In practice, the Q-factor achievable is limited by various factors, including material loss and finite sample size. Our zig-zag concept provides a straightforward way to control the Q-factor and can be easily applied to meta-atom designs other than ellipses. In general, the higher Q-factors associated with lower orientation angles increase the sensitivity of the resonators to changes in the environment, leading to improved fingerprint detection performance. On the other hand, this increased sensitivity also makes the system more susceptible to small variations in structure size associated with nanofabrication inhomogeneity. In experiments, an orientation angle of $\theta = 20^{\circ}$ was chosen to provide a trade-off between these two factors by delivering experimental Q-factors above 100 within our fabrication tolerances. Unlike many geometries based on leaky guiding modes where the electric field is mostly confined within the high-index material, this particle-based collective dipole resonance allows strong near-field enhancement at the surface of the meta-atom, which is a desirable feature for surface-based molecular sensing. Figure 3.1c shows the enhancement of the electric near-field intensity on two different cut-planes: one is a horizontal cut-plane 2.5 nm away from the substrate, the other is a vertical cut-plane across the long-axis of the meta-atom. We find strongly enhanced electric near-fields in between the meta-atoms, with electric near-field intensity enhancement values of up to 1500. This enhancement value is which is within the $10^3 - 10^4$ enhancement range of many widely studied metal-based antenna geometries for use in practical applications [67]. In general, high field confinement is easier to achieve in metallic resonators due to the strong contrast between the dielectric functions of the metal and the non-metallic environment. However, this field localization comes at the expense of the resonance Q-factor due to the intrinsic damping of the metal. Even though higher field enhancements values of 10⁷ can be achieved using metallic nanogap antennas with interelement spacings below 10 nm [68], they are difficult to fabricate with the reliability and reproducibility needed for practical sensing devices. Figure 3.1d again highlights the near-field intensity on the meta-atom surface, where we plot the amplitude distribution along the three line-cuts shown in Figure 3.1c. Note that z = 0 nm and z = 700 nm represent the surface of the substrate and the top surface of the meta-atoms, respectively; we choose z = 2.5 nm and z = 702.5 nm to match the thickness of the molecule layer. Significantly, the enhanced near-fields are localized in distinct hot-spots on the surface of the meta-atoms, which is a characteristic feature of many nanophotonic systems based on localized resonators. During sensing experiments, the target analytes interact with both the low and high intensity regions of the electric field around the meta-atom. Therefore, the effective enhancement of the molecular absorption signature is determined by the averaged electric near-field intensities around the meta-atom. We estimate this effect by averaging the simulated electric near-field intensities over a 2.5 nm thick layer around the meta-atoms and obtain an effective enhancement factor of 320 for a scaling factor of S=1.0. The reduced effective enhancement compared to the hot-spot values is common to all localized resonance geometries and is similarly found in plasmonic platforms [66]. These performance considerations are valid as long as the analyte presented to the surface exhibits sufficient spatial uniformity, which is fulfilled in a multitude of analyte systems of interest such as molecular monolayers, biological species (lipids, proteins, DNA, etc.) suspended in buffer solutions, or layers of solid analytes deposited by, e.g., evaporation. Low numbers of molecules can be resolved as long as a statistical distribution over the meta-atom surface is ensured, or additional surface functionalization is employed to selectively attach the molecules in the hot-spot regions.



Figure 3.1: Theoretical analysis of high-Q collective resonance based on zig-zag arrays. (a) Schematic of the collective dipole mode of the array when excited with E_x^i polarization. (b) Simulated Q-factors and resonance wavenumbers under different orientation angle θ . (c) Simulated electric near-field intensity enhancement $|E/E_0|^2$ at the resonance frequency with orientation angle $\theta = 20^\circ$, where $|E_0|$ denotes the incident field amplitude. (d) Near-field intensity enhancement $|E/E_0|^2$ along three line cuts, shown as dashed-lines in panel (c). Inset magnifies the part around the boundary between the silicon meta-atom and the surroundings.

3.3 Pixelated metasurface concept

Here we adopt the zig-zag metasurface design and employ it to realize a mid-IR nanophotonic sensor and demonstrate its capability for enhancing, detecting, and differentiating the absorption fingerprints of various molecules. Traditionally, high-*Q* resonances in metasurfaces are generated via the interference of superradiant and subradiant modes [120]–[122]. In contrast, our design exploits the collective behavior of Mie resonances, which can be recognized as supercavity modes driven by the physics of bound states in the continuum [87]. Furthermore, the high-*Q* resonances of our design are spectrally clean without additional resonance background, which is particularly attractive because it allows for the highly spectrally selective

enhancement of spectroscopically rich molecular fingerprint information. Specifically, we implement a two-dimensional (2D) array of high-*Q* metasurface pixels, where the resonance positions of individual metapixels are linearly varied over a target mid-IR fingerprint range. This configuration allows us to assign each resonance position to a specific pixel of the metasurface, establishing a one-to-one mapping between spectral and spatial information (**Figure 3.2a**). By comparing the imaging-based readout of this spatially encoded vibrational information before and after the coating of target analyte molecules, we demonstrate chemically specific molecular barcodes suitable for chemical identification and compositional analysis.

Individual metapixels contain the previously described zig-zag resonator arrays of anisotropic hydrogenated amorphous silicon (a-Si:H) resonators, which provide high-Q resonances when excited with linearly polarized light and allow for straightforward resonance tuning via scaling of the unit cell geometry by a factor S (Figure 3.2b). Numerically simulated reflectance spectra of an exemplary 5×5 metasurface pixel array with a scaling factor variation from S = 1.0to S = 1.3 show sharp resonance peaks (average Q > 200) with near-unity reflectance intensity and linear tunability of the resonance positions covering the spectral range from 1350 to 1750 cm⁻¹ (Figure 3.2c). Our metapixel design also provides enhancement of the local electric nearfield intensity confined to the resonator surface by more than three orders of magnitude, which is ideal for the sensitive detection of analyte molecular vibrations (Figure 3.2d). The target spectral range from 1350 to 1750 cm⁻¹ contains characteristic molecular stretching and bending vibrations found in hydrocarbons and amino acids, making it crucial for detecting and differentiating the absorption signatures of biomolecules, environmental pollutants, and polymeric species, among others. We first focus on a biosensing application by showing chemical-specific protein detection, where the distinct protein absorption fingerprint is governed by the amide I and II vibrational bands located near 1660 cm⁻¹ and 1550 cm⁻¹, respectively.

A sub–5-nm conformal protein layer covering the pixelated metasurface causes a pronounced modulation of the individual metapixel reflectance spectra due to the coupling between the molecular vibrations and the enhanced electric near-fields around the dielectric resonators. This reflectance modulation manifests primarily as attenuation and broadening of the metapixel resonance, which is correlated with the strength of the amide I and II molecular vibrations (**Figure 3.2e**). The envelope of the metapixel reflectance spectra unambiguously reproduces the protein absorption signature, confirming efficient molecular fingerprint detection. The metapixel res-

onances provide linewidths much narrower than the spectral feature size of the individual amide I and II absorption bands near 60 cm⁻¹. This is in strong contrast to metal-based antennas used in plasmonic SEIRA approaches, which typically exhibit linewidths above 200 cm⁻¹ limited by the intrinsic damping of the metal [67]. This advantage allows us to read out the protein absorption signature at multiple discrete frequency points and to translate this spectrally resolved absorption information into a barcode-like spatial map of the individual metapixel absorption signals (**Figure 3.2f**).



Figure 3.2: Molecular fingerprint detection with pixelated dielectric metasurfaces. (a) Pixelated metasurface composed of a two-dimensional array of high-Q resonant metapixels with resonance frequencies tuned over a target molecular fingerprint range. (b) Spectrally clean high-Q (Q > 200) resonances are provided by zig-zag arrays of anisotropic a-Si:H resonators.

Resonance frequencies are controlled by scaling the unit cell lateral dimensions by a factor S. Geometrical parameters are $A = 1.96 \ \mu\text{m}$, $B = 0.96 \ \mu\text{m}$, $Px = 3.92 \ \mu\text{m}$, and $Py = 2.26 \ \mu\text{m}$, with a fixed structure height of $H = 0.7 \ \mu\text{m}$ and an orientation angle of $\theta = 20^{\circ}$. (c) Numerically simulated metapixel reflectance spectra for different values of the scaling parameter S, chosen to cover the amide band spectral region around 1600 cm–1. (d) Simulated electric near-field intensity enhancement |E/E0|2 for S = 1, where |E0| denotes the incident field amplitude. (e) The envelope of metapixel reflectance amplitudes reproduces the absorption fingerprint of an adjacent model protein layer (top inset). (f) Conceptual sketch of a molecule-specific barcode produced by imaging-based readout of the metasurface's reflectance response. Image regions 1 and 2 indicate the spatially encoded vibrational information from the corresponding metapixel resonances in (e)

3.4 Experimental realization and optical characterization

A pixelated dielectric metasurface design consisting of an array of 10×10 metapixels was fabricated using electron-beam lithography and reactive ion beam etching. Ellipse axes and unit cell periodicities were identical to the values given for the numerical simulations in Figure 3.2, and the unit cell was linearly scaled between S = 1.00 and S = 1.34 in 100 steps. A fixed metapixel size of 100 µm × 100 µm was chosen to provide a trade-off between metapixel signal-to-noise ratio and the number of pixels (**Figure 3.3a**). Analysis of scanning electron microscopy (SEM) images captured for multiple metapixels confirmed the accurate reproduction of the resonator design as well as the linear scaling of the unit cell geometry over the entire metasurface area (**Figure 3.3b**).

The metasurface was characterized in reflection using a quantum cascade laser-based mid-IR microscope equipped with a 480 × 480 pixel array-based imaging detector (Daylight Solutions, Spero). We used a refractive 4× objective with a 2-mm field of view to acquire the optical response of all metasurface pixels simultaneously (**Figure 3.3c**). Reflectance images captured for different wavenumbers of the incident mid-IR radiation are shown in **Figure 3.3d**. At each incident wavenumber, high reflectance intensity indicates the excitation of a metapixel with matching resonance frequency in a specific spatial location on the metasurface. Reflectance spectra are obtained by combining reflectance images for a range of incident wavenumbers and integrating the resulting spectrally resolved data over the individual metapixel areas. The spectra of 21 exemplary metapixels and extracted resonance positions of all 100 metasurface pixels are shown in **Figure 3.3e** and **f**. The fabricated pixelated metasurface delivers resonances with a low average full width at half maximum (FWHM) of 13.7 cm⁻¹ and uniform tuning of the resonance frequency over the amide band range from 1370 to 1770 cm⁻¹. This corresponds to

a spectral resolution of 4 cm⁻¹ and an average Q of 115, which is an improvement of more than one order of magnitude over metallic antenna geometries [77], [123]. Besides, our design can easily be extended to cover a larger spectral region by increasing the range of geometrical scaling parameters.



Figure 3.3: Experimental realization of the pixelated metasurfaces. (a) Optical images of the fabricated 100-pixel metasurface. (b) SEM micrographs confirm the linear relationship between scaling factor and ellipse feature size. (c) Sketch of the imaging-based mid-IR microscopy system. (d) Reflectance images of the pixelated metasurface recorded at four specific wavenumbers in the mid-IR spectral range. (e) Normalized reflectance spectra for 21 of the 100 metapixels. Resonance positions of the colored curves correspond to the respective reflectance images in (d). (f) Extracted resonance positions for all metapixels.

3.5 Optical performance and SEIRA measurements with the dielectric metasurfaces

We demonstrated molecular fingerprint detection by interrogating a physisorbed monolayer of recombinant protein A/G. Metapixel reflectance spectra before and after the protein A/G physisorption are shown in **Figures 3.4a** and **b**, respectively. All spectra are normalized to the



Figure 3.4: Molecular fingerprint retrieval. (a) Normalized metapixel reflectance spectra before physisorption of a protein A/G monolayer. R_0 indicates the envelope of peak reflectance amplitudes (dashed line). (b) Normalized spectra after protein physisorption, including reflectance envelope $R_{\rm S}$ (dashed line). (c) Protein absorption fingerprint calculated from the reflectance envelopes R_0 and R_S compared to an independent IRRAS measurement (dashed line, scaled and offset for clarity). (d) Absorbance variation curves derived from 5 metasurface measurements without the presence of any analytes. We obtain a root mean square noise value of Arms = 1.8 mOD and a corresponding 3σ noise level of 5.4 mOD.

peak reflectance values of the reference measurement without the analyte. The absorbance signal calculated from the peak reflectance envelopes before (R_0) and after physisorption (R_s) reveals the characteristic amide I and II absorption signature of the protein A/G molecules, which is in good agreement with an independent infrared reflection-absorption spectroscopy (IRRAS) measurement (**Figure 3.4c**). Furthermore, the high absorbance signal of up to A = 140 mOD (milli–optical density units) extracted from a protein mono-

layer demonstrates the strong vibrational enhancement of our metasurface design, which exceeds the performance of widely used metal antenna geometries [74] by more than one order of magnitude.

We estimate the limit of detection of our sensor metasurface by considering the absorbance value of 140 mOD obtained from a protein monolayer (**Figure 3.4d**) together with the noise level of our experiments. The experimental noise level (which is determined by factors such as detector noise, source stability, and optical alignment) can be estimated by capturing a total of

n = 5 reference metasurface measurements without the presence of any analytes. For all data sets, the envelopes of the peak reflectance values Ri ($i = 1, \dots, n$) are derived as shown in the manuscript, and the average value of these envelopes is calculated via $R_{avg} = (R_1 + \dots + R_n)/n$. This allows us to determine the absorbance variation

$$\Delta A_i = -\log(R_i/R_{avg}) \tag{7}$$

for each measurement as shown in. Each absorbance variation curve consists of p = 100 points consistent with the 100 pixels of the metasurface design, where $\Delta Ai(k)$ denotes the curve value at a specific pixel position with $k = 1, \dots, p$. The total noise level can be quantified by calculating and averaging the root mean square (RMS) value for all curves, which results in an experimental noise level value of

$$A_{rms} = \frac{1}{n} \sum_{i}^{n} \sqrt{\frac{1}{p} \sum_{k=1}^{p} (\Delta A_{i}^{k})^{2}} = 1.8 \ mOD$$
(8)

In general, sensors are assumed to reliably detect signals exceeding three times the noise, which is often referred to as the 3σ noise level. In our experiments, we observed an absorbance signal of around Aexp = 140 mOD for a protein A/G monolayer, which corresponds to 55220 molecules per µm2 when assuming densely-packed spherical protein A/G molecules with a diameter of 4.8 nm calculated from their molecular mass. A comparison of the signal and noise levels results in a detection limit of 2130 molecules per μ m2 for protein A/G detection, assuming a linear relationship between molecular coverage and the sensor signal. Signal-to-noise ratio considerations also play an important role in the broadband operation of our metasurface-based approach, specifically when moving from illumination with a tunable but narrow-band quantum-cascade laser (QCL) to an intrinsically broadband globar source. In general, this transition is associated with a decrease in the available light intensity. However, due to the narrow-band nature of QCLs, the acquisition of the sensor metasurface response in a specific frequency range requires a large number of sequential measurements determined by the desired frequency resolution. For instance, covering the wavenumber range from 1300 cm⁻¹ to 1800 cm⁻¹ with 4 cm⁻¹ resolution requires 125 sequential measurements. In broadband operation, only one single measurement is needed to capture the same information. This advantage enables an increase of the acquisition time by the same factor of 125, greatly improving the signal-to-noise ratio and compensating, in part, the decrease in the intensity of the incident light. If additional gains are needed for a target application, high sensitivity pixelated detectors such as mercury cadmium

telluride focal-plane arrays can be utilized in place microbolometer arrays. Combined with an experimental noise level of 1.8 mOD, this value corresponds to a detection limit of 2130 mole-cules/ μ m².

3.6 Imaging-based molecular barcoding using all-dielectric metasurfaces

Miniaturization of IR sensor devices has traditionally been challenging because of the need for scaled-down Fourier-transform IR (FTIR) spectrometers or frequency scanning laser sources. Recent sensor-on-chip approaches based on thin-film optical waveguides have made progress with monolithic integration, in which the light source, sensing element, and detector are fabricated on a single chip [124], [125]. In comparison, our technique enables a complementary integration scheme in which the pixelated metasurface sensor can be combined with an IR imaging detector such as a high-resolution microbolometer or a mercury cadmium telluride (MCT) focal plane array. When illuminated with an external broadband light source, this arrangement can overcome the need for a mid-IR spectrometer in a compact footprint [126], [127]. Furthermore, our scheme addresses several constraints of complete monolithic integration, such as the limited operating range of chip-based light sources and detectors [128], as well as sensitivity limitations caused by the low near-field enhancement factors of conventional waveguides [124].

The demonstrated metasurfaces show spectrally sharp and background-free resonances, and after analyte coating, the resonances attenuate accordingly to the absorption surface-bound molecule absorption bands (**Figure 3.5a** and **b**). We assessed the capability of our metasurface sensor for imaging-based spectrometerless fingerprint detection by calculating the integrated reflectance signal from the spectral data of each metapixel. These integrated signals are analogous to a readout of the metasurface's optical response with a broadband detector before (I_0) and after (I_s) addition of the protein layer (**Figure 3.5d**) and are used to calculate metapixel absorbance signals via $A = -\log(I_s/I_0)$, which are then rescaled from 0 to 100 for presentation (**Figure 3.5e**). The resulting barcode-like spatial absorption map of the protein A/G monolayer clearly shows the spectral location and relative intensity distribution of the characteristic amide I and II absorption bands as two distinct high-signal regions of the image providing chemically specific fingerprint detection in a miniaturized design and without the need for spectrometry.

This functionality is enabled by the spectrally clean high-Q resonances of the dielectric metapixels and cannot be achieved with metapixels based on conventional metal antennas as a result of linewidth limitations.



Figure 3.5: Molecular fingerprint retrieval and spatial absorption mapping. (a) Normalized metapixel reflectance spectra before physisorption of a protein A/G monolayer. R₀ indicates the envelope of peak reflectance amplitudes (dashed line). (b) Normalized spectra after protein physisorption, including reflectance envelope RS (dashed line). (c) Broadband spectrometerless operation of the metasurface can be emulated by integrating the reflectance signal of all pixels. (d) Spectral integration translates the absorption signature in (c) into a 2D spatial absorption map, which represents the molecular barcode of the protein (a.u., arbitrary units).

3.7 Imaging-based compositional analysis

In addition to protein A/G, we also tested a polymer mixture composed of polymethyl methacrylate (PMMA) and polyethylene (PE). The molecular barcodes feature mutually distinct high-intensity image regions unique to the vibrational signature of the investigated analytes, underscoring the chemical identification capability (**Figure 3.6**).

Our barcoding technique offers the potential for identifying molecular species in arbitrary analyte compositions through pattern recognition based on a library of multiple molecular barcode signatures. To illustrate this approach, we detected a series of predefined mixtures of PMMA and PE polymer molecules deposited on the metasurface by thermal evaporation. Figure 3.6: Molecular barcodes of a mixture of PMMA and PE polymers. Barcode matrices for PMMA/PE polymer mixtures with several mixing ratios. Linear decomposition analysis of all mixing states Ymix with respect to the pure PMMA and PE barcode matrices confirms accurate readout of the deposited polymer ratios. **Figure 3.6** shows molecular barcodes for pure PMMA and PE as well as PMMA/PE mixing ratios of 0.25, 0.50, and 0.75. The characteristic molecular signatures of PMMA and PE appear as distinct image features in the top and bottom halves of the barcode matrix, respectively. When increasing the relative amount of PE in the mixture, we observed a substantial increase of the PE signal versus mixing ratio combined with an associated decrease of the PMMA signal.

We carried out further image-based analysis by decomposing the barcode matrices of all mixing states *Y*mix into a linear combination of the PMMA and PE molecular barcodes according to $YY_{mix} = (\beta_{PMMA} \cdot X_{PMMA}) + (\beta_{PE} \cdot X_{PE})$, where X_{PMMA} and X_{PE} are the input barcodes of the pure materials, and β_{PMMA} and β_{PE} are the output coefficients associated with the analyte content on the surface. The PMMA and PE polymer amounts obtained from our image decomposition analysis accurately captured the linear variation of the polymer composition, highlighting the rich chemical and compositional information available from such absorption maps. Although simple linear decomposition is implemented in this demonstration, nonlinear processes (such as those in biomolecular interactions involving multiple analytes and kinetics) are foreseen to make use of more sophisticated neural network–based image recognition methods and machine learning.



Figure 3.6: Molecular barcodes of a mixture of PMMA and PE polymers. Barcode matrices for PMMA/PE polymer mixtures with several mixing ratios. Linear decomposition analysis of all mixing states Ymix with respect to the pure PMMA and PE barcode matrices confirms accurate readout of the deposited polymer ratios.

3.8 Extended spectral working range

Our dielectric resonator design allows for the straightforward extension of the operating spectral range by increasing the span of scaling factors S. **Figure 3.7a** shows simulated reflectance spectra for scaling factors between S = 0.56 and S = 2.0, linearly interpolated in 21 steps. The geometrical parameters before scaling are identical to the design described in the manuscript with $Px = 3.92 \mu m$, $Py = 2.26 \mu m$ for the unit cell periodicities, and $A = 1.96 \mu m$, $B = 0.96 \mu m$ for the ellipse long and short axes, and an orientation angle of $\theta = 20^{\circ}$. We find high Q-factor

resonances covering the mid-IR molecular absorption band region from 2.5 μ m to 10 μ m together with a linear relationship between scaling factor and resonance position (**Figure 3.7b**), which facilitates the design of suitable metapixels for arbitrary target absorption bands. The decrease in performance at a wavelength of around 5 μ m is due to the intrinsic absorption of a-Si:H in this range, and can be overcome by moving to a different resonator material such as germanium. With the exception of the aSi:H absorption region, high resonance sharpness (Q > 100) is maintained over the full target wavelength range (**Figure 3.7c**), and Q-factors above 600 can be achieved in the long wavelength region around 10 μ m.



Figure 3.7: Extended metasurface design working range. (a) Simulated reflectance spectra for scaling factors ranging from S = 0.56 to S = 2.0. For each spectrum, only the dominant reflectance peak is shown. (b) Resonance position varies linearly with scaling factor over a wide range. (c) Q-factors remain above 100 over the entire wavelength range, with peak values above 600 in the long wavelength region around 10 μ m.

3.9 Molecular fingerprint detection performance comparison.

We assess the performance of our dielectric metapixel design by numerically comparing it to a widely used traditional SEIRA approach based on metallic nanostructures. Specifically, we follow the guidelines for periodicity optimized gold nanoantenna SEIRA substrates outlined in Ref. [74] to obtain resonant metallic metapixel designs in our target spectral range. The reflectance spectrum of an exemplary gold metapixel displays a pronounced peak centered at 1560 cm⁻¹ and a FWHM of 565 cm⁻¹ (Figure 3.8a). The antenna geometry is defined as antenna length 2.1 µm, antenna width 0.14 µm, and antenna height 0.1 µm. The distance between antennas is 1 µm in x-direction and 2 µm in y-direction. Even though gold nanoantennas are used for the following numerical comparison in accordance with Ref. [74], comparable performance is obtained for other metals such as silver and copper in the infrared. To gauge the molecular fingerprint detection performance, the metallic metapixel surface is covered with a 2.5 nm thick conformal model protein layer analogous to the simulations for the dielectric metapixels presented in Figure 3.2. Even though the addition of the protein layer produces a clear change of the resonance lineshape (R_S) compared to the reference spectrum (R_0) , the protein-induced reflectance modulation is much lower compared to the dielectric metapixel case (Figure 3.8a). To quantify the performance difference between the metallic and dielectric metapixel designs, we calculate the absorbance signal from the reflectance curves R_0 and R_s via $A = -\log(R_s/R_0)$. We find maximum absorbance signals of around 275 mOD for the dielectric case compared to around 16 mOD for the metallic case, demonstrating that our dielectric metapixel concept can deliver performance improvements of more than one order of magnitude over such metal-based designs (Figure 3.8b).



Figure 3.8: Molecular fingerprint detection performance comparison. (a) Simulated reflectance spectra for metallic antennas with three different materials. Comparison of simulated reflectance spectra for gold nanoantennas and our dielectric resonators before (R_0) and after (R_s) addition of a conformal model protein layer. (b) Absorbance signal calculated from the reflectance curves R_0 and R_s from panel (a). The dielectric metapixel design provides an absorption signal improvement of over one order of magnitude.

The key differentiating factor of our imaging-based dielectric metapixel concept is its ability to extract molecular fingerprint information from the integrated reflectance signal, which corresponds to the usage of a broadband light source and detector (see Figure 3.5). To check whether such performance is possible using the previously discussed metallic metapixels, we tune the length of the gold nanoantennas to produce a series of metallic metapixels with resonance frequencies covering the target fingerprint range (Figure 3.9a). More specifically, the antenna length is linearly interpolated from 2.1 µm to 3.1 µm in 21 steps while keeping the other geometrical parameters the same. A direct comparison between the metallic and dielectric metapixel cases is performed by integrating the reflectance spectra in the range from 1340 to 1840 cm⁻¹ before (I₀) and after (I_S) addition of the model protein layer. The integrated absorbance signal for both cases is then obtained via $A = -\log(I_S/I_0)$. We find that the integrated signal from the dielectric metapixels clearly reproduces the protein amide I and II absorption signature (Figure 3.9b). In strong contrast, the integrated signal from the metallic metapixels is unable to resolve the protein signature, even though a slight variation of the reflectance envelope R_s is still visible in Figure 3.8. Such comparatively poor performance is due to the broad linewidth of the gold nanoantenna resonances and the associated large integrated reflectance signal. Consequently, small protein-induced modulations of the reflectance signal have only a negligible influence on the total integrated signal, making broadband fingerprint detection with such metallic metapixels challenging at realistic signal-to-noise levels.



Figure 3.9: Performance comparison of imaging-based detection via integrated signals. (a) Simulated reflectance spectra for gold and dielectric metapixels designed to exhibit resonances covering the amide I and II spectral range. (b) Integrated absorbance signal obtained by integrating the reflectance data in panel (a) from 1340 to 1840 cm⁻¹. A pixelated metallic

metasurface is unable to resolve the amide I and II absorption signature due to the high associated resonance linewidths.

3.10 Discussion and outlook

The demonstrated all-dielectric metasurfaces show spectrally selective and background-free resonances that can be tuned by scaling the meta-atom unit cell from one metapixel to another. This novel high-Q metasurface design has a great potential for ultra-sensitive and label-free chemical fingerprint detection of various analytes. Interestingly, the pixelated metasurface concept combined with imaging-based detection enables direct translation between spectral and spatial information. Additionally, the imaging-based method can be used to directly read out the molecular absorption fingerprints from the total reflectance signals of the metasurface. Therefore this novel technique opens up new avenues for miniaturized point-of-care devices for biochemical detection. Moreover, novel advanced data processing toolkits could be implemented to further improve the sensor performance. The metasurface-based chemical sensor miniaturization, advanced sampling techniques, and potential advanced data analysis are further discussed below.

3.10.1 Metasurfaces for on-chip integration and SEIRAS miniaturization

Our molecular fingerprint detection concept allows direct integration between sensor and imaging detector by placing the pixelated dielectric metasurface directly on a pixelated broadband IR detector such as a microbolometer or an array based on mercury cadmium telluride (MCT) elements (**Figure 3.10a**). Such an integrated configuration requires the operation of the dielectric metasurface in transmission. In this case, the integrated absorbance from individual metapixels needs to be calculated via $A = -\log((I_S - I_B) / (I_0 - I_B))$, where I_0 and I_S denote the broadband readouts of the sensor metasurface before and after the addition of the analyte molecules, and I_B represents the resonance-free background. We perform molecular detection simulations similar to the ones in **Figure 3.2** with a design optimized for operation in transmission. This optimization yields geometrical parameters of $Px = 3.51 \ \mu m$, $Py = 2.03 \ \mu m$ for the unit cell periodicities, and $A = 1.76 \ \mu m$, $B = 1.29 \ \mu m$ for the ellipse long and short axes, with an orientation angle of $\theta = 20^{\circ}$. Simulated transmittance spectra for scaling factors between S = 1.00 and S = 1.36 (linearly interpolated in 25 steps) are shown in **Figure 3.10b**. Importantly, we find that the envelope of metapixel transmittance spectra still unambiguously reproduces the target molecular absorption fingerprint, with signal modulations up to 30%



Figure 3.10: Towards miniaturized sensor devices. (a) Sketch of a possible configuration for compact imaging-based molecular fingerprint detection. The pixelated metasurface sensor is placed directly on top of a broadband IR detector array. (b) Fingerprint detection performance of the metasurface design in transmission.

3.10.2 Advanced sampling techniques

One of the central features of our pixelated metasurface approach is the spatial encoding and separation of spectral information. Therefore, the metasurface's performance is determined by the number and size of individual metapixels for a given detector field of view. In general, a single metapixel covering the detector field of view will provide the best performance in terms of signal-to-noise ratio since the analyte absorption signature is amplified and detected over the full area, but will provide spectral information only for a single frequency point. For higher numbers of metapixels p, the spectral resolution increases, but only a reduced fraction of the metasurface area (in general 1/p) will provide resonant enhancement. In experiments, metapixel sizes of 100 µm x 100 µm were chosen to provide a trade-off between sufficiently high signalto-noise ratios and the number of pixels required for 4 cm⁻¹ spectral resolution. Due to the flexibility of our metasurface design, a variety of advanced sampling techniques can be applied to further tailor signal-to-noise ratio and spectral coverage. To illustrate two such concepts, we consider an artificial molecular fingerprint with two features (absorption bands I and II), which exhibit large spectral separation and strongly dissimilar absorption magnitudes (Figure 3.11). First, the retrieval of absorption signatures from weak molecular vibrations can be improved by utilizing metapixels with increased sizes for these frequency points [129], which results in higher signal-to-noise ratios as outlined above. Likewise, metapixel size can be decreased for spectral regions of strong molecular absorption, maximizing the total number of metapixels in the detector field of view. Second, the spectral resolution of the absorption bands of interest can be increased by implementing non-uniform frequency sampling. With this approach, denser frequency sampling is employed in spectral regions with fine fingerprint features, whereas the molecular signature is sampled more broadly otherwise. This technique allows increasing the spectral fidelity of the fingerprint reproduction while keeping the total number of metapixels constant.



Figure 3.11: Advanced sampling techniques. (**a**, **b**) Challenging molecular absorption signatures with large spectral separation and strongly dissimilar absorption magnitudes can be resolved by employing metapixels with tailored sizes as well as non-uniform frequency sampling.

3.10.3 Improved sensing with advanced data processing

The imaging-based detection method allows to gather of a large amount of data, and in principle, it can be used to train artificial neural networks to recognize certain chemical species. Although deep learning has already shown great potential in the field of biosensing, in which deep neural networks have previously been used for herpes simplex virus detection from holographic images [130], it has not yet been fully explored for spectral-based biosensing. In this context, we envision that molecular barcodes are the ideal candidates to enable, in conjunction with DNNs, the identification and kinetic characterization of complex biological entities in realistic environments, such as the dynamic interactions between cells and extracellular vesicles (EVs), which include exosomes and synaptic vesicles. Specifically, a dataset containing the molecular barcodes of extracellular vesicles under various biological and/or physiological conditions would be used to train a neural network to identify, categorize, and quantify them in real-time, enabling the recording of the intricate dynamics of these complex entities (**Figure 3.12**). While challenges remain in populating the training dataset with enough correctly labeled


barcodes related to extracellular vesicles, the successful union of these two cutting-edge technologies will create a new and unprecedented window into the behavior of such processes, enabling a deeper understanding of biological systems from the single-molecule level towards the complexity of living cells

Figure 3.12: Machine learning for nanophotonics and sensing. Neural networks trained from molecular barcodes of biological entities in different biological/physiological environments have the potential to identify, quantify, and track individual components in complex systems.

Chapter 4 Mid-IR dielectric metasurface integration into microfluidic systems

4.1 Introduction

The previous chapter demonstrated how dielectric metasurfaces could be used for SEIRASbased label-free biochemical sensing. In order to move this novel technology closer to practical biosensing applications, the dielectric metasurfaces need to be integrated with microfluidic devices. Microfluidics is a field of research for controlling and guiding the flow of liquids and gasses at the microscale level. Microfluidics is crucial to enable operation with minute quantities of bioanalytes, therefore significantly improving the sensitivity of optical and electrochemical sensors [131]–[133]. Besides, microfluidic devices have the capabilities to mix various analytes, sort different particles, and form droplets of specific sizes [134], [135]. Additionally, microfluidic systems are highly desired for their user-friendly operation principles, which are relevant for real-world applications.

The microfluidic integration of metasurfaces operating at visible and near-IR spectral ranges has been successfully demonstrated before [131]. However, microfluidic integration of mid-IR metasurfaces brings its own challenges, which are primary associated with the strong absorption of mid-IR light by water molecules and the constituent materials of microfluidic cells. In the mid-IR, the strong water absorption bands can obscure the molecular fingerprint signals of the target analytes. Moreover, the high absorption losses of water can completely quench the high-Q resonances of the dielectric metasurfaces rendering the operation with aqueous solutions in mid-IR highly challenging.

In order to address this long-lasting problem of mid-IR-based biosensing systems, this chapter introduces a unique "Tidal microfluidic" system that enables rapid cycles of metasurface drying and incubation steps. Therefore the sensitive bioanalytes are exposed to air only for a brief moment during the measurement and remain their structural stability until the next incubation phase of the bioassay. Furthermore, for the successful detection of specific target analytes, there is a need for robust and diverse surface functionalization methods. It is of high

importance for biosensing applications to form stable protein or other functional biomolecule layers that can selectively capture target biomarkers. This chapter shows a successful integration of functionalized germanium metasurfaces into the "Tidal microfluidic" system for detection of lipid vesicles and C reactive protein, which is a biomarker of sepsis and inflammation processes. Therefore tidal microfluidics can open up an avenue for biomedical diagnostic applications with mid-IR-based photonic sensors.

4.2 Water absorption and high-Q resonances

The previously demonstrated spectrally selective metasurfaces provide high sensitivity and can detect submonolayers of biological analytes. However, all the measurements were performed in dry conditions. For real-world biological applications, the sensors need to operate with aqueous solutions because biomolecules like proteins tend to denature when exposed to air for long times. The metasurface simulated reflectance for various unit-cell scaling factors is displayed in Figure 4.1a, showing gradually tuned resonances with reflectance close to unity. The top part of Figure 4.1b shows the unit cell of the metasurface when immersed in 1.5 µm thick layer of water. The corresponding reflectance spectra and the water extinction spectrum are shown in the bottom part of Figure 4.1b. The resonance peak reflectance is reduced from 1.0 to 0.155, and the resonance is completely quenched when it spectrally overlaps with the absorption peak of water. These results show that the high sensitivity of these metasurfaces can be detrimental when operating in the water medium. Besides, the water absorption peak significantly overlaps with the main absorption bands of proteins. In principle, the water could be replaced with heavy water (D_2O) , which has the main absorption peak of water shifted from 1640 cm⁻¹ to 1200cm⁻¹. However, exposure to heavy water perturbs the native states of proteins and can denature them [136].



Figure 4.1: High-Q metasurface performance in water medium (a) Top: A sketch of the unit-cell. Bottom: The corresponding reflectance spectra for various scaling factors. The scaling factor is color-coded, where blue is the largest scaling factor and red is the smallest scaling factor. (b) Top: a sketch of the metasurface unit cell immersed in water with a depth of 1.5 μ m. Bottom: reflectance spectra of metasurfaces when immersed in water. The corresponding water extinction coefficient over the targe spectral range is plotted on top of the metasurface reflectance spectra.

4.3 Tide microfluidics

The numerical simulation data in **Figure 4.1** shows that it is highly challenging to work with mid-IR high-Q metasurfaces in the water medium. This limitation can be addressed with a "Ti-dal microfluidic" system which minimizes the target biomolecule exposure to air while allowing quasi-real-time measurements of the binding. The Specific microfluidic cell consists of three different laser-cut PMMA parts, which are glued together. Here the direct laser cutting and low-cost PMMA material bring cost advantages when compared to the commonly used PDMS microfluidic devices. The PMMA-based microfluidic device is designed to have one

main inlet and outlet. From the inlet, the analyte is guided directly to the center of the main microfluidic chamber, while the two exit ports of the main chamber allow rapid retraction of the analyte to the outlet, see **Figure 4.2** (1-2). The sensor chip is placed on top of the microfluidic cell with the metasurface nanoantennas facing down into the microfluidic chamber, where they can interact with the target analytes. To ensure zero water leakage from the PMMA and metasurface chip interface, an additional thin PDMS layer is introduced between the microfluidic chamber and the metasurface chip, which allows to hermetically insulate the microfluidic cell.

The working principle of the tidal microfluidics begins with the analyte introduction through the inlet, see **Figure 4.2** (1). The metasurface is then exposed to the target analyte for a certain amount of incubation time. After the incubation, the analyte is retracted through the outlet for the next cycle of incubation (**Figure 4.2** (2)). The analyte retraction allows to preservation of the precious biological samples for subsequent incubation steps. In such a way, the tidal microfluidic system enables operation with minute quantities of analytes. Step (3) includes a thorough wash with phosphine buffer saline (PBS) solution to flush away any unbound molecules. A subsequent wash step with ultra-pure H₂O is introduced to remove any remaining salts from the metasurface. Right after the washing steps, the metasurface is rapidly dried with compressed air, see **Figure 4.2** (4). The final step of the cycle is the IR measurement of the surfacebound biomolecules (**Figure 4.2** (5)). After the measurement, the cycle starts again from step one. Interestingly, the tidal microfluidics method enables signal readout after each step of surface functionalization while minimizing the biomolecule exposure to air. Furthermore, the system can be expanded to perform quasi-real-time monitoring of molecular binding kinetics.



Figure 4.2: Microfluidic chamber design and tidal microfluidic working principle. (1) The analyte is introduced through the inlet of the microfluidic channel and incubated on the metasurface. (2) After the incubation, the analyte is retracted. (3) The sensor chip is thoroughly washed with PBS and water. (4) stream of compressed air ensures a quick drying process of the metasurface. (5) After the removal of water, the spectroscopic measurements are performed.

4.4 Metasurface design and nanofabrication

The previously demonstrated amorphous silicon metasurfaces on MgF₂ substrates provide spectrally sharp and background-free resonances. However, their operation range and fabrication yield could be improved by introducing new materials both for substrate and the nanoantennas of the metasurfaces. Regarding the substrate, MgF₂ is lossless in the spectral range from the UV wavelengths to 1250 cm⁻¹ (0.2 μ m to 8 μ m). Therefore using MgF₂ as a substrate, only

a small part of the vibration absorption bands can be accessed. For instance, the main absorption bands of nucleic acids and carbohydrates lie beyond the transparency window of MgF₂ ($\lambda_{DNA} \sim 1200 \text{ cm}^{-1} - 1300 \text{ cm}^{-1}$, $\lambda_{CHO} \sim 1000 \text{ cm}^{-1}$). An alternative material to MgF₂ with a low refractive index, near-zero absorption losses, and high chemical stability is CaF₂. The calcium diflouride is transparent up to 1000 cm⁻¹ (10 µm), allowing to capture the absorption signals from the main vibrational bands of nucleic acids and carbohydrates.

Similarly, a-Si has various absorption bands throughout the mid-IR and is opaque beyond 1000 cm⁻¹ (10 µm). Besides, due to the large difference in thermal expansion coefficient and the stress between Si and CaF₂, it is very challenging to deposit high-quality and defect-free a-Si thin films on MgF₂ and CaF₂ substrates. In order to overcome the limitations of the previously demonstrated a-Si metasurfaces, a new fabrication process flow of germanium-based metasurfaces on CaF₂ substrates is introduced (Figure 4.3a). The process starts with a thorough CaF2 substrate cleaning with H₂O₂: NH₄OH : H₂O in dilution of 1:1:5 (RCA1 cleaning step). Right after, a 5 nm thick SiO₂ layer is deposited with the magnetron sputtering method as an adhesion layer for further germanium deposition. Step (3) involves a 700 nm thick germanium layer sputtering on the substrate with magnetron sputtering. Subsequently, a 400nm PMMA with a molecular weight of 495 kDa is spin-coated on the substrate. The metasurface patterns are generated with electron beam lithography. After the development of the exposed photoresist, a 20nm Al₂O₃ is evaporated as a hard mask, and the remaining photoresist is removed in a liftoff process (immersion in a photoresist solvent for 6h). The metasurface pattern is translated in the germanium thin film by inductively coupled plasma (ICP) reactive ion etching. The germanium forms a thin native oxide layer when exposed to the atmosphere, which is soluble in water. Therefore the metasurface needs to be coated with a protective layer that would prevent the germanium oxide interaction with water. In the final step, the germanium metasurface is coated with a 5 nm thick Al₂O₃ protection layer with atomic layer deposition.

Figure 4.3b shows the unit-cell of the Ge-based high-Q metasurface consisting of two elliptical resonators tilted by 20° from the y axis. Using this meta-atom geometry a 12 x 8 pixelated metasurface was realized with metapixel size of 100 um and scaling factors from 1 to 1.3 Figure 4.3c. In order to probe the absorption fingerprints homogeneously over the large area metasurface, we randomly assigned the scaling from one metapixel to another. As it is often difficult to coat the target analytes completely uniformly over all metapixels, it can induce false absorption signals. The randomization of scaling factors allows improving the detection of the

analytes when the surface coating is not uniform. An optical micrograph showing the fabricated metasurface with 12x8 metapixels is shown in **Figure 4.3d**. Here to demonstrate the often observed nonuniform distribution of the analytes over large areas, the metasurface is coated with polystyrene beads. The SEM of the corresponding metasurface is shown in **Figure 4.3e**, confirming the precise resonator shape, size, and straight side-wall profile.





mensions at the scaling factors of the unit-cell 1.0. (c) The layout of 12 x 8 pixelated metasurface with randomized scaling factors from one metapixel to another ranging from 1 to 1.30. (d) Optical micrograph of the realized metasurface before, showing metasurface dimensions of 1.0 x 1.5 mm. (e) SEM of the Ge metasurface on CaF_2 substrate confirms the desired meta-atom size and shape.

4.5 Surface functionalization and protein layer stability

For biosensing applications, it is crucial to develop proper surface functionalization protocols that enable selective capture of the target analytes. Besides, it is important to have high stability of the coated layers over time and repeated washing steps. Here, the dielectric metasurface integration into a microfluidic device and a three-step surface functionalization protocol is demonstrated. First, the metasurface is coated with a hexamethyldisilazane (HMDS) monolayer, which makes the surface hydrophobic. Then the metasurface is integrated into the microfluidic device, after which the surface is functionalized with biotinylated bovine serum albumin (BSA) with 500 nM concentration for 1h at 4 °C. Here the coated HMDS layer improves the hydrophobic-hydrophobic interactions between the protein molecules and the surface, therefore enhancing the protein physisorption on the surface and ensuring a continuous coating of a monolayer Figure 4.4a. The measured molecular fingerprints of BSA is displayed as a barcode which shows the absorbance wavenumber in color and the absorption strength as the intensity of the color. Here two-dimensional color plot allows to simultaneously illustrate the absorption strength, wavenumber, and the spatial location Figure 4.4 center. The molecular barcode in Figure 4.4a shows strong absorption near 1660 cm⁻¹ and 1530 cm⁻¹, corresponding to the Amide I and amide II bands of the proteins. After the BSA physisorption, repeated washing steps with PBS and ultrapure water are performed 5 times. Figure 4.4b shows the absorption signal modulation after five washing steps. The measurement data demonstrates that the BSA layer is stable over time and consecutive washing steps.

The biotinylated BSA has on average 11 biotin functional groups per molecule, ensuring that after the physisorption, there are available biotin functional groups. The biotin protein has a strong affinity to streptavidin, and the biotin-streptavidin bond is amongst the strongest nonco-valent bonds between biological macromolecules. Therefore biotin-streptavidin binding process ensures a robust surface functionalization and is often used in immunoassays. Additionally, most of the biological macromolecules can be functionalized with biotin groups making the functionalization method adaptable for a wide range of applications.

After the five washing steps, the surface functionalization continued with streptavidin binding (200nM) for an hour at room temperature. **Figure 4.4c** shows the molecular absorption barcode of the surface-bound streptavidin. The absorption of streptavidin was calculated as the $A_S=A_{S+BSA}-A_{BSA}$, where A_{S+BSA} is the total absorbance of BSA and streptavidin, and A_{BSA} is the absorbance of BSA. The molecular barcode shows strong absorption near 1660 cm⁻¹ and 1550 cm⁻¹. After the streptavidin binding, a thorough 5 step washing procedure with PBS and ultrapure water was repeated. The molecular barcode after the washing steps shows only minute changes in the absorption signal for a couple of metapixels, see **Figure 4.4d**. The measurement data confirm the high stability of the BSA and streptavidin layers.



Figure 4.4: Surface functionalization and protein layer stability. (a) Physisorption of biotinylated bovine serum albumin and the corresponding molecular barcode after the incubation. (b) Change in the absorption signal represented as molecular barcode after five thorough wash steps with PBS and water. (c) Binding of streptavidin and the corresponding molecular barcode of streptavidin. (d) The absorption signal change after five consecutive washing steps with PBS and water.

The "Tidal microfluidic" concept allows not only to detect the endpoints of the analyte binding but also the monitor the binding kinetics. A bioassay demonstrated in **Figure 4.4** was repeated with consecutive incubation time steps of BSA (18s, 28s, 43s, 1min3s, 1min38s, 2min30s, 3min55s, 5min50s, 9min4s, 13min55s, 5x PBS, and H₂O wash steps). The absorption data for each time step is displayed in **Figure 4.5**, where the dark blue color indicates the beginning of the surface functionalization, while the dark red color corresponds to the absorbance after streptavidin binding and five washing steps. The measurement data shows that the BSA signal reaches 0.05 mOD at the Amide I band (1660cm⁻¹) after only 18s of incubation and reaches 0.09 mOD after the total incubation time of ~40 minutes. Right after the washing steps, streptavidin was bound to the surface with the same incubation time steps (18s, 28s, 43s, 1min3s, 1min38s, 2min30s, 3min55s, 5min50s, 9min4s, 13min55s, 5x PBS, and H₂O wash steps). The absorbance after 18s of streptavidin incubation increases from 0.09 mOD to 0.16 mOD in the amide I band absorption region (1660 cm⁻¹). The signal saturates after ~40 min of incubation and shows total absorbance signal from BSA and streptavidin protein at 0.27 mOD and stays stable after five consecutive wash steps with PBS and ultra-pure water.



Figure 4.5: Real-time binding kinetics of BSA and streptavidin. The BSA physisorption is monitored over time, followed by five consecutive washing steps. After BSA coating follows streptavidin binding, which increases the absorption signal to 0.27 mOD. The stable signal profile after the washing steps confirms high protein layer stability.

4.6 Liposome capture and biosensing

The tidal microfluidics was further used to demonstrate lipid vesicle (liposome) capturing and detection with dielectric metasurfaces. The lipid vesicles consist of at least one lipid bilayer and are often used for drug delivery as well as carriers for nucleic acids in mRNA and DNA vaccines. For instance, the mRNA vaccines are used for COVID-19 by "Pfizer". Additionally,

the native exosomes could potentially be used as biomarkers for cancer detection [137]. Therefore, successful binding and detection of liposomes can open up many potential applications in pharmacology and biomedical diagnostics.

A bioassay for lipid vesicle capturing is introduced in **Figure 4.6a**, where the surface is first coated with a monolayer of HMDS, after which follows biotinylated BSA is physisorption for 1h and subsequent streptavidin binding for 1h. After a monolayer of streptavidin is formed on the surface, biotinylated tethers (Biotin-TTCACT-Cholesterol-TEG from (*IDT*)) were bound to streptavidin with 15 min incubation time. In the last step, the liposomes were captured by the surface-bound tethers. The protocol for preparing the liposomes was taken from ref. [138].

Figure 4.6b shows the corresponding molecular absorption barcodes after each binding step. The BSA and streptavidin show absorption signatures in the spectral range from 1500 -1700 cm⁻¹ (Amide I and Amide II region), while the liposomes show chemical fingerprints near 1450cm⁻¹ and 1750 cm⁻¹ associated with the CH₂ bending and the C=O (lipid ester) vibrational bands. The extracted spectral data from the molecular barcodes over time is displayed in **Figure 4.6c**, showing lipid signal saturation after 2min 30s.



Figure 4.6: Liposome binding and detection with pixelated metasurfaces. (a) Surface functionalization steps, starting with a coating of HMDS monolayer, BSA physisorption, streptavidin binding, and capturing of liposomes. (b) The measured molecular barcodes after each functionalization step show distinct absorption signals of the lipid vesicles in the spectral ranges near 1450 cm⁻¹ and 1740 cm⁻¹. (c) The extracted spectra after each measurement step showing the binding kinetics of the liposomes.

4.7 C reactive protein detection

In order to show that the proteins remain in their right conformation and remain functional after the repeated exposure to air, we performed a bioassay for selective C reactive protein (CRP) detection. The CRP is a pentameric protein circulating in the blood plasma which concentration increases upon inflammation in a human body. The CRP protein is a relevant biomarker for inflammation [139], early sepsis detection [25], and cardiovascular diseases [140].

The surface functionalization steps are displayed in **Figure 4.7a**, where the first step starts with HMDS layer coating. The second step includes recombinant protein A\G physisorption (500 μ g/mL) on the surface for 2h at room temperature. In order to avoid nonspecific binding, the surface was blocked by incubating BSA (1% w/w) for 1h at room temperature. Step number 4 includes CRP antibody binding. Here the protein A\G helps to bind the antibodies and orienteer them in a way that their functional sites are accessible for subsequent protein binding. After the surface functionalization with antibodies the CRP protein is introduced into the microfluidic chamber for 2h at room temperature with 1.75 μ M concentration.

To confirm successful surface functionalization, after each binding step, spectral measurements were performed. The corresponding molecular barcodes of steps 2-5 are displayed in **Figure 4.7b**, which shows a gradual increase of the absorption signals in the spectral range of the main protein absorption bands. The protein A\G coating induces strong absorption near 1660 cm⁻¹ and 1550cm⁻¹ (Amide I color-coded in yellow-orange, and Amide II in blue-teal). The blocking of the surface with BSA further increases the absorption signal in the protein absorption range. The molecular barcode in **Figure 4.7b** panel (4) confirms anti-CRP antibody binding. While panel (5) in **Figure 4.7b** demonstrates the successful capturing of C reactive protein. The measurement data of the protein CRP capture shows that the antibodies still remain functional after brief exposure to air while performing measurements. Therefore, the "Tidal microfluidic" concept could also be extended for the SEIRAS with plasmonic nanoantennas, which could improve the signal-to-noise ratio and the detection limits of low concentration analytes.



Figure 4.7: Protein CRP detection. (a) Schematic of the bioassay steps for selective protein CRP binding to the all-dielectric metasurfaces. (1) Surface modification by HMDS coating. (2) Recombinant protein A\G physisorption to the metasurface. (3) Surface blocking with BSA to minimize nonspecific protein binding to the surface. (4) antibody (anti-CRP) binding for selective capture of CRP protein. (5) Protein CRP capturing and detection. (b) Bioanalyte molecular fingerprint barcodes with displayed absorbance, spectral and spatial positions. (2) Recombinant protein A\G absorption map. (3) BSA absorption map. (4) antibody (anti-CRP) molecular absorption map. (5) Protein CRP molecular barcode.

4.8 Discussion and outlook

The numerical simulation results show that the high-Q metasurface resonances are completely quenched, where they spectrally overlap with the water absorption bands. Therefore direct detection of biological analytes in water medium is not possible with the high-Q metasurfaces. In this chapter, all-dielectric metasurface integration with "Tidal microfluidics" was demonstrated, enabling real-time binding measurements of various proteins, antibodies, and lipid vesicles. Multiple bioassays were introduced for stable protein layer formation and subsequent capture of target analytes.

Interestingly, the proteins and antibodies remained functional and active after the brief exposure times to air when performing the IR measurements. Therefore, showing the great potential of all-dielectric metasurfaces for real-world applications in biosensing and medical diagnostics. Moreover, the "Tidal microfluidics" eliminates the undesired quenching of SEIRAS signal induced by the absorption of water while maintaining the functionalities of the surface-bound proteins and antibodies. In addition "Tidal microfluidic" concept could be extended and would improve the signals for plasmonic-based SEIRAS as well as refractometric-based sensors.

The bioassays of lipid vesicles could be further improved by loading them with cargo analytes such as DNA, carbohydrates, and pharmaceuticals. In this case, studies of the drug delivery and cargo release could be performed by simultaneously tracking the signals of the different classes of the biomolecules. In order to move closer to real biomedical diagnostics of human C reactive protein with all-dielectric metasurfaces, studies of direct CRP capture and detection from human serum are needed. Additionally, the demonstrated surface functionalization methods can be further improved by replacing the physisorption-based functionalization step with covalent binding-based functionalization steps, therefore ensuring conformal and even more stable protein monolayers.

Overall, the "Tidal microfluidics" enables the integration of all-dielectric metasurfaces in microfluidic devices for SEIRAS-based sensing of complex bioassays with various classes of bioanalytes. Therefore "Tidal microfluidic" concept paves the way towards miniaturized biochemical sensors and medical diagnostic devices operating in the attractive chemical fingerprint spectral range.

Chapter 5 Angle-multiplexed metasurfaces for label-free biosensing

5.1 Introduction

The pixelated dielectric metasurfaces have shown great capabilities to detect various biomolecules with high sensitivity, where the spectral resolution of the pixelated metasurfaces is directly proportional to the amount of the 'metapixels' in the metasurface. Therefore, to ensure fine spectral resolution, the pixelated metasurfaces need to cover millimeter-scale areas. Additionally, to measure the absorption spectrum of the biomolecules accurately, the target analytes have to be coated uniformly across the whole metasurface. As the absorption signal is proportional to the amount of surface-bound molecules on the nanoantennas, here, a nonuniform coating can potentially induce noise or false absorption signatures. In this chapter, a novel anglemultiplexed molecular fingerprint detection method is introduced, which utilizes the light incidence angle to gradually tune the resonance frequency over a broad spectrum. Therefore with the angle-multiplexed metasurfaces, the chemical fingerprints can be detected from a single spatial location, overcoming the noise limitations associated with non-uniform analyte binding.

As demonstrated in Chapter 1, the control of light incidence angle as a parameter for excitation of resonances has been previously used in SPR biosensors. The SPR biosensors are established as the gold standard for label-free bioanalyte detection, both in laboratory settings and commercial applications [10], [141]. SPR techniques are based on the resonant excitation of electromagnetic surface waves at a metal-dielectric interface, which provides a resonance that is highly sensitive to the refractive index of the surrounding analyte. One of the most common SPR device implementations is angle-scanning, where momentum conservation is utilized to retrieve the resonance lineshape using a single wavelength source and a broadband detector. This approach provides low device-level complexity and, importantly, does not require the use of a bulky and expensive spectrometer for accessing the refractometric response of the resonance. Even though such refractometric methods can detect the presence of specific molecules in combination with suitable surface functionalization, they lack the capability of ab-initio

chemical identification. Chemically specific optical detection is enabled by the distinct absorption signatures of chemical and biological analytes at infrared (IR) frequencies [142], [143].

In this chapter, a germanium-based metasurface sensor is introduced, which combines chemically specific broadband IR detection with the device-level simplicity and spectrometer-less operation of angle-scanning refractometric approaches. As a resonator material, germanium offers opportunities for improving the performance of dielectric sensors due to its higher refractive index and lower absorption losses in the mid-IR compared to silicon [144]. Specifically, we implement a nanophotonic resonator design that provides a highly surface-sensitive and spectrally sharp resonance, where the spectral position can be controlled with the incidence angle of the mid-IR light. This angle-multiplexed approach delivers a large number of on-demand resonances in the mid-infrared from a single metasurface chip, only limited by the range of light incidence angles. For angular positions in which the resonances match the vibrational modes of analyte molecules, a strong modulation of the far-field optical response occurs due to highly accessible surface-enhanced electric near-fields. By retrieving the angle-resolved reflectance signal from such metasurface before and after coating with the analyte molecules, the full spectral content of the molecular absorption fingerprint can be retrieved. We experimentally realize a metasurface capable of providing more than 200 resonances when illuminated with incidence angles ranging from 13° to 60° and utilize the resulting wide spectral coverage between 1100 cm⁻¹ and 1800 cm⁻¹ with 1.4 cm⁻¹ resonance step size to demonstrate chemically specific detection of different molecular analytes such as polymers, proteins, and DNA. Specifically, we implemented a multi-analyte bioassay to detect human odontogenic ameloblastassociated protein (ODAM) by using single-stranded DNA aptamers, which has strong implications for diagnosing periodontal diseases. Finally, we show that our method is capable of retrieving spectrally resolved molecular fingerprint information even when used with incoherent broadband light sources and detectors, paving the way towards compact and low-cost mid-IR sensors.

5.2 Angle-multiplexing

Angle multiplexing is a powerful concept that allows encoding different values of optical parameters such as polarization or phase on a single metasurface [55], unlocking additional degrees of freedom in realizing versatile nanophotonic devices. However, so far, this flexibility has not been leveraged for sensing or spectroscopy applications. Our angle-multiplexed device

is designed to resonantly reflect in a narrow spectral range around a frequency v at each incidence angle θ when illuminated with a broadband source (**Figure 5.1a**). This optical response is provided by a dielectric metasurface consisting of an anisotropic zig-zag array of germanium resonators on a calcium fluoride (CaF₂) substrate, which interacts collectively to generate ultrasharp resonances in reflection. Crucially, the metasurface provides a monotonic relationship between the resonance frequency and the incidence angle, allowing us to uniquely associate every angular position with a specific target frequency in the spectral working range (**Figure 5.1a** bottom).

The high-Q metasurface design not only provides angle-multiplexing capabilities but also supports strongly enhanced electric near-fields in the vicinity of the resonators, leading to high surface sensitivity. Near-field coupling to adsorbed analyte molecules causes a pronounced attenuation of the resonance lineshape dependent on the strength of the absorption bands (**Figure 5.1b**). The high surface sensitivity combined with the spectrally selective resonant reflection for specific incidence angles enables the implementation of a compact sensor device consisting of a broadband source, two mirrors on co-axially rotating arms, and a broadband detector (**Figure 5.1c**).

Our angle-multiplexed fingerprint retrieval (AFR) method detects samples on the sensor surface by measuring the analyte-induced light intensity change at each incidence angle. By combining signal measurements at all angular steps, the absorption spectrum of the analyte is recovered. The output of such an AFR device is uniquely determined by the magnitude and spectral location of the vibrational bands of the analyte, which are correlated with the imaginary part k of the complex refractive index $\tilde{n} = n + ik$ (Figure 5.1d).



Figure 5.1: Angle-multiplexed broadband fingerprint retrieval. (a) A germanium-based high-Q all-dielectric metasurface delivers ultra-sharp on-demand resonances with specific resonance frequency v for every incidence angle θ with broad spectral coverage. Continuous scanning of the incidence angle produces a multitude of resonances over a target fingerprint range, realizing an angle-multiplexed configuration ideally suited for surface-enhanced mid-IR molecular absorption spectroscopy. (b) Strong near-field coupling between the dielectric resonators and the molecular vibrations of the analyte induces a pronounced attenuation of the resonance lineshape correlated with the vibrational absorption bands. (c) Angle-multiplexing combined with the spectral selectivity of high-Q resonances allows for broadband operation and straightforward device implementation. (d) Chemically specific output signal of the device scheme from panel c, which is determined by the imaginary part k of the analyte's complex refractive index \tilde{n} .

5.3 Resonance tunability

The fundamental building block of our metasurface design is a rectangular unit cell featuring two elliptical germanium resonators on top of a CaF₂ substrate, where the main ellipse axes are tilted asymmetrically with respect to each other to produce a zig-zag array (**Figure 5.2a**). The structure height is 800 nm, while the short ellipse axis and long axes are 900 nm and 2250 nm, respectively, with an orientation angle of 10 degrees against the y-axis. When excited with light polarized along the x-axis at normal incidence, this metasurface based on symmetry-broken elements is capable of delivering an ultra-sharp resonance (Q > 200) with low spectral background (**Figure 5.2b**), originating from the physics of *bound states in the continuum* (BIC)

[87], [89]. This type of interference-governed resonant states were originally introduced in quantum mechanics but have since been extended to other branches of wave physics such as acoustics and optics [87], [90], [145]. On a fundamental level, a BIC can be considered as a localized state with vanishing fields within a continuous spectrum of radiating waves. Consequently, an ideal BIC would exhibit an infinite Q-factor and would be inaccessible for electromagnetic probes from the far-field. To access and exploit these states in metasurface optics, quasi-BICs can be realized by breaking the symmetry of the underlying resonant structure [89] as shown in Fig 2A. In addition, germanium provides negligible intrinsic material losses over the full mid-IR range, further supporting the formation of high-Q resonant modes.

The metasurface resonance can be excited as long as the incident light provides a non-zero electric field component along the x-axis. Therefore, we can scan the light incidence angle in two different planes (y-z and x-z) of the unit cell while maintaining efficient metasurface operation. These two ways of exciting the system will be designated as "modes" from now on. Specifically, the first mode (TE_y) describes light with *k* vector in the y-z plane and light polarisation along the x-axis. The second mode (TM_x) refers to *k* vector and polarisation along the x-z plane. Numerical simulations of the metsurface confirm the formation of an ultra-sharp resonance lineshape in reflection with a Q-factor of 270 at normal light incidence (**Figure 5.2**b). In addition, the numerical data demonstrates a spectrally clean resonance with a low background reflectance. Strikingly, the resonance can be shifted towards either higher or lower wavenumbers for increasing incidence angles depending on which mode is used.

To further quantify the resonance tuning behavior, we calculate and plot the full angular dispersion of the metasurface reflectance spectra. The use of both the TE_y and TM_x resonance modes enables an extremely wide and continuous spectral tuning range from 1080 cm⁻¹ to 1820 cm⁻¹ for incidence angles between 0 and 60 degrees (**Figure 5.2c**). Notably, the resonance remains spectrally clean with low background reflectance over the full tuning range and provides a monotonous relationship between resonance frequency and light incidence angle. In addition to the angular tunability, the high-Q dielectric metasurface strongly amplifies the electric near-fields around the resonators with intensity enhancement factors I/I_0 of up to 6000 (**Figure 5.2d**). Advantageously, the highly enhanced near-fields are mostly located on the outer surface of the resonators, making our nanophotonic design very attractive for sensing applications.

The remarkable resonance frequency angular sensitivity can be explained by the collective nature of the quasi-BIC, where the retardation among meta-atoms plays a crucial role in determining the resonant properties of the collective mode. We can develop a deeper understanding of this behavior by modeling the system as an effective medium and considering its impedance $Z_{eff} = -i\omega L_{eff} + i/(\omega C_{eff}) + R_{eff}$, which is calculated from the effective inductance L_{eff} , capacitance C_{eff} and resistance R_{eff} of the quasi-BIC. These effective parameters can be derived from the lattice sum of the complex electromagnetic interaction of the array with retardation taken into account [146]. Since the scattered field from an in-plane electric dipole is intrinsically anisotropic in the plane of the metasurface, the electromagnetic interaction of the meta-atoms is also anisotropic. As a result, the lattice sum of the electromagnetic interaction provides different responses when retardation is increased along either the x- or y-axis of the unit cell under oblique excitation. This effect can lead to an opposite resonance shift of the guasi-BIC when the plane of incidence changes from x-z (TM_x mode) to y-z (TE_y mode). Our analysis reveals that this behavior is a general feature of zig-zag dipole arrays made from different materials, which can be observed even in a simple zig-zag array of line-dipoles embedded in an isotropic medium with refractive index n=1 (Figure 5.2e). The calculated effective impedance of the line dipoles is shown in (Figure 5.2f), where the circles mark the zeros of the imaginary part of the effective impedance $Im(Z_{eff}) = 0$, which determine the angle-dependent resonance frequencies of the quasi-BIC.



Figure 5.2: Working principle of the angle-multiplexed metasurface. (a) The dielectric metasurface design consists of a zig-zag array of elliptical germanium resonators on a calcium fluoride substrate. When varying the incidence angle, we consider both the TMx (red plane) and the TEy (blue plane) modes. (b) Simulated reflectance spectra for normal incidence and for an incidence angle of $\Theta = 55^{\circ}$ in both TMx and TEy modes. Strikingly, the two modes show similar spectral shifts of around 300 cm⁻¹, but in opposite shift directions, enabling wide spectral coverage with a single metasurface design. (c) Full resonance dispersion curves (color-coded reflectance) vs. incidence angle illustrate the continuous tunability of ultra-sharp resonances over the target wavenumber range together with the spectrally opposite behavior of the TMx and TEy modes. (d) Due to the highly accessible and strongly enhanced electromagnetic near-fields around the resonators, our design is ideally suited for amplifying and detecting the molecular vibrations of adsorbed analytes. (e) A zig-zag array of line-dipoles embedded in a homogenous environment with a unity refractive index. The length and the orientation angle of the dipoles are 2.7 µm and $\alpha = \pm 10$ degrees, respectively. (f) The effective reactance $Im(Z_{eff})$ of the quasi-BICs as a function of the incident angle under different excitation

modes. The circles mark the positions where the reactance is equal to zero, which determine the angle-dependent resonance frequencies of the quasi-BICs.

5.4 Effective impedance model of the quasi-BICs

In order to obtain a deeper understanding of the resonance shift of the quasi-BICs supported by the zig-zag dipole array, we developed a semi-analytical model based on the effective impedance of the array [146]. Assuming the collective mode of the array is built on the electric dipole mode of the meta-atom, the interaction of the zig-zag array and incident wave can be expressed as

$$\vec{Z}\mathbf{I} = \mathbf{V},\tag{1}$$

where

$$\vec{Z} = \begin{bmatrix} Z_{self} & Z_{mut} \\ Z_{mut} & Z_{self} \end{bmatrix},$$
(2)

is the effective impedance of the collective mode; $\mathbf{I} = [I_1, I_2]^T$ is the corresponding current amplitude of the dipoles, and $\mathbf{V} = [V_1, V_2]^T$ is the effective electromotive force, with subscripts "1" and "2" denoting the two different orientation angles of the dipoles.

We are interested in the angle-dependent resonance shift, which can be understood by analyzing the behavior of the impedance. The expressions

$$Z_{self} = \sum_{m=-\infty}^{\infty} \sum_{n=-\infty}^{\infty} Z_s^{(m,n)} e^{i(m\beta_x P_x + n\beta_y P_y)}, \qquad (3)$$

and

$$Z_{mut} = \sum_{m=-\infty}^{\infty} \sum_{n=-\infty}^{\infty} Z_M^{(m,n)} e^{i\beta_x P_x/2} e^{i(m\beta_x P_x + n\beta_y P_y)}$$
(4)

describe the lattice sum of the complex electromagnetic interaction of the meta-atoms, where the subscript "self" ("mut") denotes that the lattice sum is performed over meta-atoms with the same (different) orientation angles, and $Z_S^{(m,n)}$ and $Z_M^{(m,n)}$ are the impedance elements that describe the interaction between the meta-atoms located at the lattice sites (0,0) and (*m*,*n*). β_x and β_y are the transverse wave-vectors of the collective mode along the x and y directions, respectively.

Typically, a system described by Eq. (1) can support two normal modes: a symmetric mode ($I_1 = I_2$) and an antisymmetric mode ($I_1 = -I_2$). The qusi-BICs correspond to the antisymmetric mode, and the effective impedance of this mode can be described by

$$Z_{eff} = Z_{self} - Z_{mut} = \sum_{m,n} (Z_S^{(m,n)} - e^{i\beta_x P_x/2} Z_M^{(m,n)}) e^{i(m\beta_x P_x + n\beta_y P_y)}.$$
 (5)

For loss-less meta-atoms positioned in a homogenous environment, the impedance elements $Z_S^{(m,n)}$ and $Z_M^{(m,n)}$ can be calculated deterministically from the normalized current $\mathbf{j}(\mathbf{r})$ and charge $q(\mathbf{r})$ distributions of the meta-atoms:

$$Z_{S}^{(m,n)} = \frac{i}{4\pi} \iint_{V_{1}V_{1}} \left(-\omega\mu \mathbf{j}_{1}^{(0,0)} \cdot \mathbf{j}_{1}^{(m,n)} + \frac{q_{1}^{(0,0)}q_{1}^{(m,n)}}{\omega\varepsilon} \right) \frac{e^{ik|\mathbf{r}_{1}^{(0,0)} - \mathbf{r}_{1}^{(m,n)}|}}{|\mathbf{r}_{1}^{(0,0)} - \mathbf{r}_{1}^{(m,n)}|} d^{3}\mathbf{r}_{1}^{(0,0)} d^{3}\mathbf{r}_{1}^{(m,n)} , \qquad (6)$$

$$Z_{M}^{(m,n)} = \frac{i}{4\pi} \iint_{V_{1}V_{2}} \left(-\omega\mu \mathbf{j}_{1}^{(0,0)} \cdot \mathbf{j}_{2}^{(m,n)} + \frac{q_{1}^{(0,0)}q_{2}^{(m,n)}}{\omega\varepsilon} \right) \frac{e^{ik|\mathbf{r}_{1}^{(0,0)} - \mathbf{r}_{2}^{(m,n)}|}}{|\mathbf{r}_{1}^{(0,0)} - \mathbf{r}_{2}^{(m,n)}|} d^{3}\mathbf{r}_{1}^{(0,0)} d^{3}\mathbf{r}_{2}^{(m,n)}.$$
(7)

The subscripts "1" and "2" denote the two orientation angles of the meta-atoms, and the superscript (m,n) denotes the lattice site.

The terms for interacting currents $\mathbf{j}^{(0,0)} \cdot \mathbf{j}^{(m,n)}$ correspond to the complex magnetic interaction power, while the terms for interacting charges $q^{(0,0)}q^{(m,n)}$ correspond to the complex electric interaction power [147], which can be further denoted as the inductance, capacitance, and resistance:

$$L_{S}^{(m,n)} = \operatorname{Re}\left[\frac{1}{4\pi} \iint_{V_{1}V_{1}} \mu \mathbf{j}_{1}^{(0,0)} \cdot \mathbf{j}_{1}^{(m,n)} \frac{e^{ik|\mathbf{r}_{1}^{(0,0)} - \mathbf{r}_{1}^{(m,n)}|}}{|\mathbf{r}_{1}^{(0,0)} - \mathbf{r}_{1}^{(m,n)}|} d^{3}\mathbf{r}_{1}^{(0,0)} d^{3}\mathbf{r}_{1}^{(m,n)}\right],$$
(8)

$$L_{M}^{(m,n)} = \operatorname{Re}\left[\frac{1}{4\pi} \int_{V_{1}V_{2}} \mu \mathbf{j}_{1}^{(0,0)} \cdot \mathbf{j}_{2}^{(m,n)} \frac{e^{ik|\mathbf{r}_{1}^{(0,0)} - \mathbf{r}_{2}^{(m,n)}|}}{|\mathbf{r}_{1}^{(0,0)} - \mathbf{r}_{2}^{(m,n)}|} d^{3}\mathbf{r}_{1}^{(0,0)} d^{3}\mathbf{r}_{2}^{(m,n)}\right],\tag{9}$$

$$1/C_{S}^{(m,n)} = \operatorname{Re}\left[\frac{1}{4\pi\varepsilon} \iint_{V_{1}V_{1}} q_{1}^{(0,0)} q_{1}^{(m,n)} \frac{e^{ik|\mathbf{r}_{1}^{(0,0)} - \mathbf{r}_{1}^{(m,n)}|}}{|\mathbf{r}_{1}^{(0,0)} - \mathbf{r}_{1}^{(m,n)}|} d^{3}\mathbf{r}_{1}^{(0,0)} d^{3}\mathbf{r}_{1}^{(m,n)}\right],$$
(10)

$$1/C_{M}^{(m,n)} = \operatorname{Re}\left[\frac{1}{4\pi\varepsilon} \iint_{V_{1}V_{2}} q_{1}^{(0,0)} q_{2}^{(m,n)} \frac{e^{ik|\mathbf{r}_{1}^{(0,0)} - \mathbf{r}_{2}^{(m,n)}|}}{|\mathbf{r}_{1}^{(0,0)} - \mathbf{r}_{2}^{(m,n)}|} d^{3}\mathbf{r}_{1}^{(0,0)} d^{3}\mathbf{r}_{2}^{(m,n)}\right],$$
(11)

$$R_{S}^{(m,n)} = \operatorname{Re}\left[Z_{S}^{(m,n)}\right],\tag{12}$$

$$R_M^{(m,n)} = \operatorname{Re}\left[Z_M^{(m,n)}\right].$$
(13)

Therefore, the effective impedance of the quasi-BIC can be re-expressed as

$$Z_{eff} = -i\omega L_{eff} + i/(\omega C_{eff}) + R_{eff}, \qquad (14)$$

where

$$L_{eff} = \sum_{m,n} (L_S^{(m,n)} - e^{i\beta_x P_x/2} L_M^{(m,n)}) e^{i(m\beta_x P_x + n\beta_y P_y)}, \qquad (15)$$

$$1/C_{eff} = \sum_{m,n} (1/C_S^{(m,n)} - e^{i\beta_x P_x/2} 1/C_M^{(m,n)}) e^{i(m\beta_x P_x + n\beta_y P_y)},$$
(16)

$$R_{eff} = \sum_{m,n} (R_S^{(m,n)} - e^{i\beta_x P_x/2} R_M^{(m,n)}) e^{i(m\beta_x P_x + n\beta_y P_y)}, \qquad (17)$$

are the effective inductance, elastance (inverse of capacitance), and resistance due to radiative loss, respectively.

For the plot shown in **Figure 5.2**, we calculate an array of line dipoles embedded in a homogeneous environment with a refractive index of one. The current distribution **j** of the line dipoles is approximated by a sinusoidal function. The zeros of the reactance, i.e. $Im(Z_{eff}) = -\omega L_{eff} + 1/(\omega C_{eff}) = 0$, mark the resonant frequencies. We find that the angle-dependent resonant shift shown in **Figure 5.2c** can be reproduced very well even with a simplified line-dipole model.

Due to the anisotropy of the interaction among the in-plane dipoles, the spatial distribution of the impedance elements $Z_s^{(m,n)}$ and $Z_M^{(m,n)}$ are also anisotropic, as shown in **Figure 5.3**. As a

result, when retardation is increased along the x or y-direction, the lattice sum changes in different ways. Further analysis shows that for the TM_x mode, the effective elastance $1/C_{eff}$ decreases while the effective inductance L_{eff} increases with the incident angle, leading to a decreased effective reactance and a red-shift of the resonance. In contrast, a reverse trend is observed for TE_y mode, which results in a resonance blue-shift, as shown in **Figure 5.4**.



Figure 5.3: The lattice distribution of the impedance element $Z_S^{(m,n)}$ and $Z_M^{(m,n)}$



Figure 5.4: The change of the ef-fective inductance and elastanceunder different incident angles. To avoid the complexity introduced by the first order diffraction, the effective inductance and elastance are evaluated at 1100 cm⁻¹.

5.5 Fourier transform infrared spectroscopy measurements

The germanium-based sensor metasurface was fabricated via top-down electron-beam lithography on calcium fluoride (CaF₂) substrates, which have low absorption losses and low refractive index in the mid-IR spectral range. A magnesium oxide (MgO) layer of 5 nm thickness was sputtered as an adhesion layer for increased germanium layer stability on CaF₂ substrates. On top of the MgO layer, an 800 nm thick germanium layer was deposited by DC magnetron sputtering. The resonator pattern was defined using electron beam lithography in spin-coated double-layer polymethyl methacrylate (PMMA 495K and PMMA 950K) films. An Al₂O₃ hard mask of 20 nm thickness was deposited via electron beam evaporation and wet-chemical lift-off process. The resonator pattern was subsequently transferred into the underlying germanium layer by fluorine-based dry plasma etching. To passivate the germanium surface, the resonators were uniformly coated with 10 nm Al₂O₃ by atomic layer deposition. For compatibility with open beam angle-scanning measurements, a large-area metasurface with an approximate diameter of 4 mm was realized to fully cover the incident light beam (**Figure 5.5a**). Scanning electron microscopy images show excellent uniformity of the resonator structure sizes over such a large area together with the accurate reproduction of the individual resonator geometry (**Figure 5.5b**). The minimum gap size between adjacent resonators is above 200 nm, which is suitable for high-throughput fabrication methods such as soft-imprint lithography (**Figure 5.5c**).

The metasurface optical performance was characterized with a Fourier transform infrared spectrometer (Bruker Vertex 70V) equipped with a variable angle reflection accessory (Bruker A519/Q). We chose an angular range between 13 to 60 degrees with 0.2-degree angular resolution, which resulted in a total of 236 acquired reflectance spectra per angle scan. The minimum scan angle of 13 degrees is due to the mechanical limitations related to the size of the mirrors in the variable angle accessory.

Normalized reflectance spectra for both TE_y and TM_x excitations are shown in (**Figure 5.5d**). For presentation, a subset of all spectra with an average peak position separation of 15 cm⁻¹ is chosen to improve clarity. The high-Q resonant behavior with low background reflection is in good agreement with the simulated results. In addition, the experiments confirm the wide resonance frequency tunability from 1120 to 1805 cm⁻¹ with an average resonance step size of 1.45 cm⁻¹. Importantly, the resonance quality factor remains high for all incidence angles with an average Q factor of 121, enabling high sensitivity and spectral selectivity throughout a broad spectrum covering a multitude of distinct molecular fingerprints. The resonance step resolution could be improved further by using commercially available rotation stages with angular resolution below $3 \cdot 10^{-4}$ degrees, which would increase the number of resonances by more than two orders of magnitude compared to our experiments.

To assess the surface sensitivity of the dielectric metasurface, we spin-coated a thin film of PMMA onto the chip. The normalized reflectance spectra after PMMA deposition show strong attenuation of the reflectance peaks correlated with the vibrational bands of the polymer (**Figure 5.5e**). To further quantify the retrieved absorption signature of the PMMA, we calculated the absorbance $A(\theta)$ from the peak reflectance amplitudes R_0 and R_A at each incidence angle before and after polymer coating following $A(\theta) = -\log_{10}(R_A/R_0)$ (**Figure 5.5f**).

For comparison, a standard infrared reflection absorption spectroscopy (IRRAS) measurement was performed with a PMMA layer on a gold surface, spin-coated using the same parameters as in the previous experiments. We find that the presence and spectral position of the PMMA vibrational bands are in good agreement between our angle-multiplexed approach and the IR-RAS measurement. Moreover, our metasurface delivers a more than 50 times higher absorption signal due to the strongly enhanced near-field vibrational coupling.



Figure 5.5: Angle-multiplexed molecular fingerprint detection. (a) Photograph of a fabricated large-area all-dielectric metasurface used for reflection experiments. (b, c) SEM micrographs of the metasurface confirm the homogeneity of the nanofabrication. (d) Normalized reflectance spectra of the metasurface before analyte coating. The angular range is from $\Theta =$

13° to $\Theta = 60^{\circ}$, which corresponds to a wide spectral tuning range of 1120 to 1800 cm⁻¹. (e) Normalized reflectance spectra after deposition of a spin-coated PMMA thin film. Multiple molecular absorption bands of the PMMA are clearly visible as a distinct modulation of the reflectance spectra. (f) Absorbance spectrum calculated from the reflectance envelopes before and after analyte coating. Agreement with independent IRRAS measurements is excellent, and a signal enhancement factor of around 50 is observed.

5.6 Angle-multiplexed vibrational fingerprint retrieval

The wide applicability of traditional angle-scanning SPR approaches originates from their high sensitivity and capability for spectrometer-less operation. To show that our metasurface-based concept can be implemented with similar device-level simplicity, we examine the spectral distribution of reflected light intensity in our measurements before and after PMMA deposition in more detail (**Figure 5.6a**). We find that due to the low resonance background signal, the majority of the analyte-induced optical modulation occurs as reflectance changes close to the resonance peak itself (**Figure 5.6b**).

Therefore, when illuminating the sensor metasurface with a broadband light source, the total reflectance signal for any given incidence angle is strongly correlated with the strength of the molecular absorption band at the corresponding resonance frequency. By recording the total reflectance intensity for all incidence angle steps, the full absorption signature of the molecular analyte can be retrieved over the spectral operating range of the metasurface. Importantly, this detection method can be implemented using a broadband detector and light source, enabling spectrometer-less operation. In this total reflectance configuration, the final spectral resolution of the approach is determined by both the resonance step size introduced above and the Q-factor of the resonances. In our experiments, we chose a resonance step size of around 1.5 cm⁻¹ together with Q-factors of around 200, which yields an effective spectral resolution below 5 cm⁻¹. This resolution value is up to one order of magnitude narrower than the spectral feature size of the target samples' vibrational bands, such as those from proteins. In fact, commonly used FTIR spectroscopy typically operates at a resolution of 8 cm⁻¹ to 4 cm⁻¹ for protein studies. By moderately increasing the angular resolution and the resonance Q-factor [121], highly competitive spectral resolutions below 2 cm⁻¹ could be achieved.

To demonstrate the viability of this approach, we evaluated the total reflectance intensities I_0 and I_A before and after PMMA deposition using spectral integration. The angle-dependent sensor signal of our AFR method was then calculated via $S_{AFR} = -\log_{10}(I_A/I_0)$. Since there is a one-to-one correspondence between the incidence angle and the metasurface resonance frequency, the AFR signal is represented as a function of wavenumber.

The AFR signal for the PMMA layer clearly captures the multiple characteristic absorption features of the deposited polymer molecules (**Figure 5.6c**). Strikingly, efficient fingerprint retrieval is maintained even for spectrometer-less operation, and the AFR signal provides results similar to the previous spectroscopic evaluation of the peak reflectance attenuation (**Figure 5.5f**). The disagreement in the spectral region around 1600 cm⁻¹ arises due to a slight redshift of the resonance after the analyte coating and the uneven spectral intensity profile of the used light source. This discrepancy can be minimized by using a light source with a more even spectral power distribution. It is important to note that the resonance redshift and uneven illumination do not affect the response in spectroscopic operation, as can be seen in **Figure 5.5f**.

To highlight the capabilities of broad spectral coverage of our sensor to chemically detect a wide range of different analytes, we performed a bioassay for the detection of human odontogenic ameloblast-associated protein (ODAM) by using single-stranded DNA aptamers which can specifically bind to ODAM [148]. Since ODAM plays a key role in odontogenesis, it has been considered as a strong biomarker protein for diagnosing periodontal diseases [149], [150]. Based on a high correlation between the level of ODAM in gingival crevicular fluid and the severity of periodontal diseases, the facile and fast detection of ODAM is expected to give adequate treatment to patients in a timely manner and enable the early diagnosis of periodontal disorders. In addition, the majority of current detection methods still need expert skills and laborious procedures for their clinical diagnosis. Therefore, applying a bioassay based on ODAM-specific binding aptamer on our device could address the needs for an early, simple, and rapid diagnosis of periodontal diseases and their progression.

During the course of the bioassay, we first physisorbed polylysine molecules onto the sensor surface, which produced strong absorption signal increases at multiple spectral positions of 1150 cm⁻¹, 1530 cm⁻¹, and 1640 cm⁻¹, which are connected to the backbone, amide II, and amide I absorption bands of the molecules, respectively (**Figure 5.6d**). After polylysine deposition and rinsing with deionized water, single-stranded DNA molecules were incubated on the metasurface. Due to the negative net charge of DNA and the positively charged polylysine, the DNA aptamers bind to the surface through electrostatic interaction. The bound aptamer molecules produce distinct absorption signal increases at 1235 cm⁻¹ and 1650 cm⁻¹, which are well

correlated with literature data of single-stranded DNA absorbance [151]. The final step of the bioassay was the binding of ODAM protein to the single-stranded DNA aptamers, which could be detected by the strong signal increases at the characteristic amide I and amide II absorption bands at 1540 cm⁻¹ and 1660 cm⁻¹ (**Figure 5.6d**). The high signal-to-noise ratio of our angle-multiplexed detection approach allows us to resolve sub-monolayer analyte molecule amounts with a limit of detection of 3000 molecules per μ m², which would correspond to 0.27 pg/mm² surface mass sensitivity. Importantly, this level of sensitivity can be achieved in the spectrometer-less operation mode of our angle-scanning method, highlighting the potential of AFR-based sensors for realizing compact absorption fingerprint detectors.



Figure 5.6: Spectrometer-less angle-scanning molecular fingerprint detection and application to a multi-step bioassay. (a, b) The high resonance sharpness and low reflectance background of our metasurface design over a broad tuning range enable the retrieval of vibrational fingerprint information from the total reflectance signals I_0 and I_A . (c) The AFR signal clearly reproduces the PMMA absorption fingerprint over 600 cm⁻¹, confirming the spectrometer-less detection capability of our approach. (d) The broad spectral coverage of the angle-multiplexed

method enables chemically specific fingerprint detection of a wide range of analytes in a bioassay involving interactions of polylysine, DNA, and ODAM protein molecules. Multiple distinct absorption bands of these biomolecules are well resolved.

5.7 Measurement noise evaluation and limit of detection

The experimental noise was evaluated by two consecutive measurements of an empty chip for all 236 light incidence angles, where the first measurement was taken as a reference measurement and the second as a noise measurement. The noise of the absorbance was calculated from the total reflectance signal with integration range from 1050 cm⁻¹ to 1830 cm⁻¹ via

$$AFR_N = -\log(I_N/I_R), \qquad (22)$$

where AFR_N is noise signal, I_N is the total reflectance signal of noise measurement and I_R is the total reflectance signal from the reference measurement. The absorbance noise values were calculated for all 236 angle steps and are displayed in **Figure 5.7a**. The total noise level was quantified by calculating the standard deviation of the noise signal, which results in an experimental noise level value of

$$AFR_{\rm Nrms} = \sqrt{\frac{1}{p} \sum_{k=1}^{p} \left(AFR_{Ni}^{(k)} \right)^2} = 1.57, \qquad (23)$$

where $AFR_N^{(k)}$ denotes the noise value at a specific angular position with $k = 1, \dots, p$, and p = 236, consistent with the angular steps.

The sensors can reliably detect signals that are three times above the noise level. To evaluate the limit of detection of our AFR method, we measured the AFR signal from physisorbed streptavidin monolayer, see **Figure 5.7b**. The peak signal value is $AFR_{strep} = 86.5$ (*a. u.*) whereas the noise $3\sigma = 4.7$ (*a. u.*), this shows that we could detect 18.4 times fewer molecules per unit area. To calculate the minimum amount of molecules that we could detect with the AFR method, we need to calculate how many streptavidin molecules are needed to uniformly cover $1 \ \mu m^2$ area. The molecular weight of the streptavidin molecule is 55 kDa, which would correspond to 4.8 nm diameter considering the densest packing of the atoms. This results in 55200 molecules per 1 μm^2 , assuming a monolayer coverage of the streptavidin molecules. Knowing that the absorption signal from a monolayer of streptavidin is 18.4 times above the 3σ noise



floor, the limit of detection is 3000 molecules per μ m² area which would correspond to 0.27 pg/mm² surface mass sensitivity.

Figure 5.7: Noise and limit of detection. (a) measured AFR signal noise from two consecutive measurements of all angle steps (b) The AFR 3σ comparison with the AFR signal from monolayer of streptavidin.

5.8 Effective spectral resolution for total reflectance operation

In the total reflectance operation scheme, which utilizes the spectrally integrated signal from the metasurface, the effective spectral resolution is influenced by both the resonance step size and the Q-factor of the resonances. We implemented a temporal coupled-mode theory (TCMT) approach to model the influence of two narrow vibrational bands on the line shape of a high-Q resonance. Specifically, the high-Q nanophotonic resonators were described using their resonance frequency ω_R and damping rate γ_R . The two narrow vibrational bands were modeled using identical damping rates $\gamma_V^{(1)} = \gamma_V^{(2)} = \gamma_V = 0.1 \text{ cm}^{-1}$ and were assumed to be spaced equally around a center frequency of $\omega_c = 1600 \text{ cm}^{-1}$ with spectral separation $\Delta \omega$, which yields the individual spectral positions of the bands as $\omega_V^{(1,2)} = \omega_c \pm \Delta \omega/2$. The coupling constants between the two non-radiative vibrational modes and the radiative resonator mode are fixed as $\mu^{(1)} = \mu^{(2)} = \mu = 0.05 \text{ cm}^{-1}$.

The reflection amplitude of the resonator coupled to the two vibrational bands is then given as

$$r = \gamma_R / [i(\omega - \omega_A - \omega_\mu) + \gamma_R + \gamma_\mu], \qquad (18)$$

where

$$\omega_{\mu} = \sum_{i=1}^{2} \frac{\mu^{2} \left(\omega - \omega_{V}^{(i)} \right)}{\left(\omega - \omega_{V}^{(i)} \right)^{2} + \gamma_{V}^{2}}$$
(19)

and

$$\gamma_{\mu} = \sum_{i=1}^{2} \frac{\mu^{2} \gamma_{V}}{\left(\omega - \omega_{V}^{(i)}\right)^{2} + \gamma_{V}^{2}}.$$
(20)

To assess the spectral resolution, we calculated reflectance spectra for different values of the resonance Q-factor and spectral separation of the bands over a wide parameter range. For every



Figure 5.8: Spectral resolution as a function of Q-factor for different values of the resonance step size.

point in this parameter space, we then evaluated whether the two narrow bands could still be identified from the integrated reflectance signals. The resulting plot of the spectral resolution (i.e., the lowest spectral band separation that can still be identified for a given Q-factor) is shown in **Figure 5.8**. The numerical modeling shows that the maximum achievable resolution of our metasurface-based approach is

around 4 cm⁻¹ using a resonance step size of 0.5 cm⁻¹. Since our experiments target vibrational bands with spectral feature sizes much larger than this value (see, e.g., **Figure 5.6c**), we chose a resonance step size of 1.5 cm⁻¹, which results in an effective spectral resolution of around 5 cm⁻¹. Importantly, highly competitive spectral resolutions below 2 cm⁻¹ can be achieved by using a metasurface with increased but still experimentally feasible quality factors.

5.9 Discussion and outlook



Figure 5.9: miniaturized sensor device. (a) Optical design with a high Na objective and microbolometer imaging detector. (b) schematic drawing of the optical frequencies imaged on the microbolometer detector showing simultaneous acquisition of full spectrum without any moving mechanical parts

A novel metasurface-based mid-IR sensor approach was demonstrated, which simultaneously provides strong enhancement of the electromagnetic nearfields and external tuning of the resonance frequency by controlling the incidence angle of light. By using straightforward angle-scanning reflectance measurements, we have obtained a multitude of ultra-sharp (Q > 100) and highly surface-sensitive resonances over a wide spectral range from 1100 cm⁻¹ to 1800 cm⁻¹ with a spectral tunability step size smaller than 1.5 cm⁻¹. We used this all-dielectric sensor metasurface to detect the characteristic mid-IR absorption fingerprints of surface-adsorbed molecules by correlating the reflectance signal at each incidence angle with the strength of the molecular absorption at the corresponding resonance frequency. Importantly, we have shown that our method can be implemented using a broadband incoherent light source and detector to enable the spectrometer-less retrieval of spectrally resolved molecular fingerprints. In comparison to other angle-scanning techniques such as SPR, our method provides not only high sensitivity but also chemical specificity, unlocking new opportunities in label-free biosensing. We have leveraged our angle-multiplexed fingerprint retrieval technique to detect the absorption signatures of polylysine, DNA aptamer, and ODAM protein molecules relevant for periodontal disease detection in a multi-step bioassay over a broad spectral range, allowing to detect their association with a highly
competitive surface mass sensitivity of 0.27 pg/mm2. Because our approach is capable of extracting absorption fingerprints without the need for bulky spectrometers or tunable lasers, it holds the potential for enabling a new toolkit of sensitive, cost-effective, and field-deployable sensors for a wide range of applications. Moreover, such a device could be implemented without any moving mechanical parts, with an imaging detector and high NA optics (**Figure 5.9a**). With the depicted system, both TE and TM modes and all the resonances corresponding to the light incidence angles could be imaged simultaneously on the microbolometer detector array (**Figure 5.9b**). Such an imaging system with integrated high-Q metasurfaces would pave the way towards rapid and ultra-sensitive detection of various chemicals finding applications in medical diagnostics, drug testing as well as food quality control.

Chapter 6 Hyperspectral vibrational imaging with angle-multiplexed metasurfaces

6.1 Introduction

The angle-multiplexing is a powerful method that enables encoding multiple functionalities on a single metasurface [54], [55]. Chapter 5 of the thesis shows how the angle-multiplexed metasurfaces can be used to precisely tune the resonances over a broad spectral range and detected molecular absorption fingerprints with ultra-high sensitivity. However, the previously demonstrated angle-multiplexed method in Chapter 5 was limited to a single spectrum acquisition per measurement, therefore limiting its capabilities of multiple biomarker detection. To overcome this limitation, a vibrational hyperspectral imaging method with all-dielectric metasurfaces is introduced. The Chapter demonstrates the integration of angle multiplexed metasurfaces with a microbolometer-based imaging system enabling the acquisition of more than 10⁵ spectra per measurement. The large amounts of data can be used to significantly improve the signal-to-noise ratio enabling the analysis of protein secondary structure. Furthermore, the chapter demonstrates spatial surface functionalization and subsequent detection of spatial protein distribution. The hyperspectral vibrational imaging method opens up possibilities for simultaneous detection and screening of hundreds of biomarkers. Furthermore, large amounts of data have a high potential for advanced data processing with machine learning or deep neural network (DNN) algorithms.

6.2 Hyperspectral vibrational imaging with high-Q angle-multiplexed metasurfaces

The hyperspectral imaging schematics are displayed in **Figure 6.1a.** Here, contrary to the previous chapter, the metasurface operates in the transmission mode. The incoming linearly polarized IR light comes from the bottom side of the metasurface. The metasurface is placed on a rotation stage that allows to gradually tilt the metasurface and subsequently tune the resonance frequency with fine spectral resolution. The absorption fingerprints of the spatially functionalized metasurface for each tilt angle are captured with a microbolometer-based imaging detector operating at room temperature. The imaging setup covers 2 x 2 mm field of view with an imaging detector containing 480 x 480 pixels. When combining the images of all the metasurface tilt angles, a hyperspectral imaging data cube with more than 230,000 spectra is retrieved with spatial and spectral information, which can be used to train neural networks to recognize the target analytes such as proteins, nucleic acids, and other chemical species such as polymers and microplastics (**Figure 6.1b**).



Figure 6.1: Hyperspectral imaging with angle-multiplexed high-Q metasurfaces. (a) Schematic drawing of all-dielectric metasurfaces for hyperspectral imaging. Bottom: the metasurface is gradually tilted, which results in the continuous tuning of the resonance wavelength. Top: The light passing through the metasurface is captured with an imaging detector for each angular step. (b) Each measurement allows collecting $\sim 10^5$ spectra which can potentially be used to train DNN to recognize the major classes of biomolecules and other analytes such as microplastics.

6.3 Numerical simulations and operation in cross-polarization mode

The metasurface design for hyperspectral vibrational imaging is based on the metasurfaces presented in chapter 5. The meta-atoms of the metasurface consist of two elliptically shaped germanium resonators with a height of 700 nm sitting on a CaF₂ substrate. (**Figure 6.2a**). The unit cell periodicity along x-axis is 3800 nm, while along the y axis is 2250nm. The elliptical resonator short axis and long axes are 860 nm and 2160 nm, respectively, with an orientation angle of 10 degrees against the y-axis. The high-Q resonance is excited with a linearly polarized light with the polarization axis tilted by angle φ , see **Figure 6.2b**. The rotated polarization enables to obtain a sharp transmission peak when operating in a cross-polarization setup [77], [152]. Finite difference time domain numerical simulations were performed with the polarization enables to obtain a sharp transmission peak when operating from 0 to 45° for both transverse electric (TE) and transverse magnetic (TM) polarization states (**Figure 6.2c**). The numerical simulations show that it is possible to cover the spectral range from 1200 cm⁻¹ up to 1700cm⁻¹, which is broad enough to target most of the major absorption bands of the biological building blocks like lipids proteins and nucleic acids. The operation in transmission mode gives various advantages for metasurface' integration into optical setups and device miniaturization.



Figure 6.2: Numerical simulations of angle-multiplexed metasurfaces in a cross-polarization setup. (a) The meta-atom design of the angle-multiplexed metasurface for hyperspectral

vibrational imaging setup. (b) Polarization axis of the electric field in the xy plane for the operation in cross-polarization mode. (c) Numerical simulations showing gradually tuned transmission peaks for different metasurface tilt angles.

6.4 Experimental realization and optical characterization

The previously described metasurfaces were realized on 1cm wide and 1mm thick CaF₂ substrates with the nanofabrication process flow of germanium-based metasurfaces shown in chapter 4. The realized metasurface with a size of 2 x 2 mm is shown in **Figure 6.3a**, where the metasurface size is matched with the FOV of the imaging system. The scanning electron micrographs confirm the meta-atom uniformity and replication of precise shapes and size **Figure 6.3b**. The optical measurements were performed with a laser-based infrared spectrometer (Spero, *DRS Daylight Solutions*). Here, the tunable quantum cascade lasers emit linearly polarized light. Therefore, no additional polarizers before the metasurface were needed. The metasurfaces were integrated into a miniaturized rotation stage with additional custom 3D printed holders, see **Figure 6.3c**. In order to operate in a cross-polarization mode, an additional polarized was introduced into the optical setup after the metasurface. The measurement data for different metasurface tilt angles confirm low broad spectral tunability and low background of the resonances **Figure 6.3d**. Here to switch between the TE and TM polarization state, the rotation stage was rotated by 90°.



Figure 6.3: Experimental realization of the metasurfaces and their optical characterization. (a) Optical image of the 1cm wide CaF_2 chip containing a 2 x 2 mm large high-Q germanium metasurface. (b) SEM of the metasurface confirming the precise shape and size as well as uniformity of the germanium resonators. (c) Integration of the metasurface with a miniaturized rotation stage in a cross-polarization setup. (d) Measurement data for various tilt angles and both polarization modes (TE and TM) confirm high-Q resonances with low background in transmission.

6.5 Protein secondary structure analysis and spectral measurements of surface-bound proteins

In the previous chapters, the proteins were detected by targeting the amide I and amide II absorption bands, where the absorption signals were used to retrieve the information of the protein's primary structure. However, this information does not give any additional information about the protein state or structure. The proteins have a structured hierarchy where the higherorder structures define the protein active states and functionalities **Figure 6.4a**. The protein's primary structure consists of long amino acid chains that are held together with covalent peptide bonds **Figure 6.4a.** The secondary structures, such as α -helices and β -sheets, are formed by hydrogen bonds, while the tertiary structure is formed with disulfate bonds. The highest level of protein hierarchy is the quarternary structure, which is formed by several protein subunits connected into a closely packed system (**Figure 6.4a**). In order to access the information of protein higher-order structures with IR spectroscopy, a high signal-to-noise ratio of the protein IR spectral absorption measurements is required. Here, the demonstrated measurement method in **Figure 5.3** allows acquiring thousands of spectra simultaneously, which can be averaged to significantly improve the signal-to-noise ratio.

The low noise spectral data can be used to perform second derivative spectroscopy, which is a method for spectral separation of two or more overlapping absorption peaks. The second derivative spectroscopy is often used for the analysis of the protein secondary structure **Figure 6.4b**. As mentioned in chapter 2, the precise analysis of protein secondary structure can give information if the proteins are correctly folded and if the protein macromolecule functions properly. The misfolding and aggregation of proteins are often related to various diseases such as Alzheimer's and Parkinson's diseases. Therefore second derivative spectroscopy could potentially be used for early diagnostics of the disorders induced by protein misfolding [84].



Figure 6.4: Protein structure hierarchy and protein secondary structure analysis with IR spectroscopy. (a) Protein structure hierarchy showing primary secondary tertiary and quaternary structures. Figure adapted from ref. [153]. (b) Protein second derivative spectrum of amide I band and the secondary structure compositional analysis using IR spectroscopy. Figure adapted from ref. [154].

In order to test the sensing performance of the metasurface, the surface was first coated with a monolayer of HMDS, which improves the adsorption of proteins. Subsequently, apoferritin protein was physisorbed for one hour at room temperature with a concentration of 40 μ g/mL in PBS. The adsorbed protein molecules induce pronounced attenuation of the resonances in specific spectral locations near 1660 cm⁻¹ and 1530 cm⁻¹ which correlates well with the Amide I and amide II absorption bands of proteins, see **Figure 6.5a**. The inset of **Figure 6.5a** illustrates the apoferritin molecule, which is 400 kDa in size, and its' secondary structure contains mostly alpha-helices. The inset of **Figure 6.5a** is adapted from ref. [155]. Measurements having finer steps of metasurface tilt angles were performed to analyze the amide I band in detail. The angular steps were chosen to linearly tune the resonance wavelength from 1600 cm⁻¹ to 1700 cm⁻¹ with a resolution of 1 cm⁻¹. **Figure 6.5b** shows the absorbance of apoferritin in the amide I spectral region, reaching up to 0.32 mOD. The plotted data is an average of spectra from 24x24 pixels corresponding to 100 x 100 μ m area of the metasurface. The absorption data

were smoothed with the Savitzky-Golay filtering algorithm for further secondary-derivative analysis.

Figure 6.5c displays the second derivative spectrum of the smoothed data from **Figure 6.5b**, showing a pronounced dip near 1655 cm⁻¹ and a secondary dip near 1680 cm⁻¹. These spectral positions of the dips reveal the contributions to the overall spectrum of the underlying absorption peaks of the protein secondary structures such as alpha-helices, beta-sheets, beta-turns, and random coils. The dip in the second derivative spectrum near 1655 cm⁻¹ is associated with alpha-helixes, while the spectral dip at 1680 cm⁻¹ is associated with the underlying absorption peak of beta-turns [156]. The presented second derivative spectrum agrees well with the literature data of the apoferritin composition, showing that 82% of the apoferritin molecule consists of alpha helixes and 13% of beta turns while the rest of random coils [157]. Therefore the angle-multiplexed metasurfaces provide high enough sensitivity for protein secondary structure analysis and could be further implemented to detect the misfolding of proteins.



Figure 6.5: protein absorption spectrum and secondary structure analysis of apoferritin. (a) Normalized transmittance of the metasurface after physisorption of apoferritin. The inset shows a schematic of the apoferritin molecule. Inset: adapted from ref. [155]. (b) Measured

absorbance of apoferritin in the spectral region from 1600 cm⁻¹ to 1700 cm⁻¹ a single cm⁻¹ spectral resolution. (c) Second derivative spectrum revealing the secondary structure of apoferritin containing mostly alpha-helices and beta-turns.

6.6 Spatial functionalization of the angle-multiplexed metasurfaces

In order to demonstrate hyperspectral vibrational imaging capabilities, a spatial surface functionalization method had to be established. The spatial functionalization allows capturing of multiple target analytes and their simultaneous detection within one measurement. There are two main approaches for spatial surface functionalization, where one is spotting the analytes with high precision on the sensor area. And the second most commonly used method is lithography, which allows obtaining very high spatial resolution of the surface functionalization.

In this chapter, a surface functionalization method using lithography techniques is demonstrated. **Figure 6.6a** shows the spatial surface functionalization steps, where, first, the sensor chip is coated with a monolayer of HMDS (**Figure 6.6a**). Right after, the metasurface is coated with a photoresist with a height that exceeds the resonator height (700 nm). The following lithography and development steps define the spatial pattern where the surface needs to be functionalized. Subsequently, a dry etching process with O_2 plasma is performed to remove the uncovered HMDS layer. The second to last step involves photoresist removal with acetone. In the final step, the empty surface without HMDS is blocked with reagents that selectively bind to metal-oxide surfaces (ALD coating in this case), which hinders nonspecific binding in further functionalization steps with biomolecules.

With the surface functionalization protocol, the metasurfaces can be functionalized in arbitrary patterns with high resolution. And when assisted with spatial spotting, it can enable the detection of various target molecules simultaneously (**Figure 6.6b**).



Figure 6.6: Spatial surface functionalization. (a) Surface functionalization steps. First, the metasurface is coated with an oxide layer (Al_2O_3 or SiO_2). Second, the surface is coated with a monolayer of HMDS. Right after follows photoresist spin-coating and lithography steps. Oxygen plasma is used to remove the exposed HMDS layer. The acetone wash is performed for photoresist removal. The exposed metasurface without HMDS is blocked with chemical reagents, such as PEG-silane, that covalently binds to the metal-oxide surface (**b**) Schematic a surface functionalized with an arbitrary pattern.

6.7 Hyperspectral vibrational imaging with dielectric metasurfaces

To demonstrate the hyperspectral vibrational imaging concept, first, the metasurface was spatially functionalized with an HMDS layer having an arbitrary pattern with a floral shape (**Figure 6.7a**). Here, the exposed surface without HMDS layer was kept as is without any further surface blocking. The proteins such as BSA and streptavidin have a higher binding affinity to HMDS than the oxide layer when PBS buffer solution with a pH of 7.2 is used. After the patterning, biotinylated BSA was physisorbed for one hour at room temperature (40 μ g/ml in PBS). After the BSA coating, the streptavidin was bound to the surface for one hour at room temperature (4 μ g /ml in PBS). The measured normalized transmittance of the metasurface containing an HMDS layer is displayed in **Figure 6.7b**. The measurement data shows pronounce signal attenuation in the spectral regions of protein absorption peaks (1530 cm⁻¹ and 1660 cm⁻¹).

The acquired images at the specific spectral locations, color-coded in **Figure 6.7b**, are displayed in **Figure 6.7c**. The image for the resonance wavenumber of 1560 shows high contrast of the pattern, showing that the proteins did not bind well to the areas without an HMDS layer. The second image shows lower contrast because, near 1600 cm⁻¹, the proteins absorb less of the IR light. While high contrast is obtained again at the peak of the amide, I band (1650 cm⁻¹). The observation of the increased contrast at 1650 cm⁻¹ correlates well with the spectroscopic data in **Figure 6.7b**. The contrast of the pattern is gradually lost when moving out of the protein absorption bands towards higher wavenumbers. Therefore, the measurement data confirms the hyperspectral vibrational imaging capabilities of low quantities of bioanalytes with the angle-multiplexed high-Q metasurfaces.



Figure 6.7: Hyperspectral imaging of spatially functionalized metasurface. (a) Pattern for the spatial surface functionalization. (b) Metasurface transmittance signal measured from the HMDS coated part of the metasurface. (c) Images acquired for various metasurface tilt angles, corresponding to resonance frequencies indicated in Figure 6.7b.

6.8 Discussion and outlook

The chapter demonstrates all-dielectric metasurfaces for vibrational hyperspectral imaging of low quantities of analytes. The metasurface operation with cross-polarization mode allows obtaining a spectrally distinct transmission peak at the resonance. The operation in transmission mode is particularly attractive because it can facilitate the integration of such metasurfaces into miniaturized optical sensor systems. The presented hyperspectral imaging setup with all-dielectric metasurfaces allows acquiring more than 230,000 spectra per measurement which can be subsequently used for advanced image analysis assisted by artificial intelligence methods,

such as machine learning and DNNs. It has been shown that hyperspectral imaging data analysis with DNNs improves the overall performance for identifying various crops and plants from hyperspectral satellite and aerial images [158]–[160]. Such methods could also be applied for improved recognition of various biological analytes when using the presented hyperspectral vibration imaging method. Moreover, the DNN-based data processing could further improve the analysis of the protein secondary structure [161], which would be a key for successful and reliable detection of protein misfolding.

To reliable protein secondary structure analysis, the measurement system needs to be further improved with additional coating steps that would prevent the protein denaturation after exposure to air during the prolonged measurements. The preservation of protein secondary structure would enable detection of misfolded proteins and the use of all-dielectric metasurfaces for detection of diseases related to protein structural changes. Therefore, the successful implementation of these protective coatings will accelerate the adoption of all-dielectric metasurfaces for medical diagnostics. One of the potential coating materials is sucrose, which improves the stability of proteins during freeze-drying processes [162]. Sugar trehalose has also been found effective for the preservation of protein coatings that are exposed to air [163]. Additionally, solutes such as ectoine and hydroxyectoine can be added to the buffer solution. The solutes help to retain a thin layer of water around the protein molecules, therefore preventing the unfolding of the proteins [164].

The imaging concept allows multiplexing the detection of various analytes. **Figure 6.5** shows data acquired from an area of 100 x 100 μ m², which is 1/400 of the total metasurface area. Therefore the metasurface could be used for simultaneous detection of 400 different analytes, which is orders of magnitude more than what is possible with the pixelated metasurfaces demonstrated in chapters 3-4. Therefore the angle-multiplexed hyperspectral imaging method could be used for screening of multiple bioanalytes and diseases.

The experimental results show that metasurfaces can be functionalized in arbitrary patterns. In principle, spatial surface functionalization can be used to improve the signal-to-noise ratio and sensitivity of point-of-care devices by implementing light interference effects. For instance, the metasurface can be functionalized in a concentric ring pattern, which can operate as a Fresnel lens. In this case, analyte binding to the surface would induce pronounced constructive light interference and focusing effect, which would change the signal values near the focal spot by

orders of magnitude. With such a method, planar high-Q metasurfaces could be used as both sensors and optical wavefront control devices.

In general, the hyperspectral vibration imaging method allows acquiring a large amount of data with a single measurement, which can be used for data analysis aided by artificial intelligence. Furthermore, the presented detection method can open new possibilities for protein secondary structure analysis, multiplexed detection of various biomarkers, and advanced sensors with spatial surface functionalization methods.

Chapter 7 Wafer-scale nanofabrication of functional mid-IR metasurfaces

7.1 Introduction

Metasurfaces have emerged as a breakthrough platform for manipulating light at the nanoscale and enabling on-demand optical functionalities for next-generation biosensing, imaging, and light-generating photonic devices. However, translating this technology to practical applications requires low-cost and high-throughput fabrication methods. Due to the limited choice of materials with suitable optical properties, it is particularly challenging to produce metasurfaces for the technologically relevant mid-infrared spectral range. These constraints are alleviated by realizing functional metasurfaces on almost completely transparent free-standing metal-oxide membranes. In this chapter, a universal nanofabrication process is implemented for highly efficient dielectric and plasmonic mid-infrared metasurfaces with wafer-scale and CMOS-compatible manufacturing techniques. Superior characteristics are revealed of the highly uniform metasurfaces by demonstrating fine spectral selectivity and flexible wavefront and polarization control with record-high 96% transmission efficiency. The last section of the chapter demonstrates aluminum plasmonic devices and their integration into microfluidics for real-time and label-free mid-infrared biosensing of proteins and lipid vesicles. The versatility of the nanofabrication process flow and its compatibility with mass-production processes bring infrared metasurfaces markedly closer to commercial applications, such as thermal imaging, spectroscopy, and biosensing.

7.2 Metasurface fabrication methods and the associated challenges

Recently a lot of effort has been channeled into realizing metasurfaces and photonic devices for the visible and near-IR spectral ranges with high-throughput methods such as nanoimprint,[116], [117] laser interference[165], and deep ultraviolet (DUV) lithography.[49], [166] Most of these nanophotonic components are realized on fused silica substrates, which serve as excellent substrates for metasurfaces in the visible and near-IR wavelength ranges, where fused silica has a near-zero absorption coefficient, a low refractive index, and sufficient mechanical

durability. However, fused silica presents significant absorption losses in the mid-IR, therefore limiting its use in this spectral location. Although the operating range of metasurfaces can be extended with sapphire [167] and fluoride-based [101], [168] substrates, those materials are still opaque throughout most of the mid-IR wavelength bands. Moreover, IR transparent fluoride crystals are highly brittle and therefore pose a challenge for wafer-scale fabrication. Amongst commonly used substrate materials, the high refractive index Si and Ge are prone to reflection losses, and they do not provide the much-needed refractive index contrasts between the meta-atoms and surrounding medium. Therefore, innovative fabrication approaches are needed to overcome the current limitations for producing metasurfaces with low-cost techniques for the technologically important mid-IR spectral range.

In this thesis, this long-standing challenge is addressed by introducing a universal method for wafer-scale and cost-effective fabrication of nanophotonic metasurfaces. Our method is based on CMOS-compatible processes in which the metasurfaces are fabricated in a high-throughput manner on silicon wafers supporting optically transparent free-standing Al₂O₃ membranes with DUV lithography. The nanoscale membranes with a thickness of ~100 nm show high transmission and effective refractive index close to unity across a broadband range, i.e., from 2 to 20 µm, thus serving as almost optically invisible substrates for metasurfaces. The versatility of our membrane-based fabrication method and its compatibility with a wide choice of all-dielectric and plasmonic materials is demonstrated by realizing mid-IR metasurfaces for a diverse range of applications. First, the fabrication precision and uniformity are validated by producing spectrally selective metasurfaces with a variance of the spectral response of less than 0.22% across the entire wafer and comparable optical performance (e.g., resonance quality factor >100) to the counterparts fabricated with high-end electron beam lithography (EBL) methods. Additionally, this Chapter shows functional dielectric metasurfaces for light wavefront and polarization control, reaching diffraction-limited focusing capabilities and polarization conversion efficiency up to 96%. Furthermore, large-area plasmonic metasurfaces composed of CMOS-compatible multiresonant aluminum (Al) nanoantennas are presented. By integrating the Al-based metasurfaces into an opto-microfluidic device and taking advantage of the ideal mechanical and optical properties of the membranes, we perform real-time and label-free mid-IR biosensing of the interaction between proteins and lipid vesicles. Our high-throughput fabrication method based on Al₂O₃ free-standing membranes can open a path for low-cost and

mass-production of metasurfaces to enable their widespread use in mid-IR device technologies and the relevant photonic applications.

7.3 High-throughput fabrication process flow for mid-IR metasurfaces

The reported process flow is depicted in Figure 7.1a, which starts with an atomic layer deposition (ALD) of a 100 nm thick Al₂O₃ film onto a 4-inch silicon wafer. The Al₂O₃ is selected as the membrane material due to its compelling optical[169], [170], and robust mechanical properties.[171] The second step involves the deposition of a thin Al or Ge film as the plasmonic and dielectric optical material for the metasurfaces, respectively. In order to create largearea metasurfaces in a high-throughput manner, DUV lithography processes are employed by using a stepper (KrF laser source, λ =248nm) to print the patterns of metasurfaces. The patterns are transferred into the metasurface material (Al or Ge) by a dry etching process. Then the metasurface layer is coated with a photoresist (PR) layer from both sides, where the front side PR serves as a protective layer for the remaining steps, and the back-side coated PR is exposed during a UV lithography step assisted with a back-side alignment procedure. The UV lithography step defines the position and size of the free-standing membrane on the 4-inch wafer. The membrane-based metasurfaces are formed by removing the Si wafer material below the Al₂O₃ thin film by a deep reactive ion etching (DRIE) process. The final step involves wafer cleaning and PR removal by using oxygen plasma. The details of the fabrication method can be found in the methods section.

Figure 7.1b displays a photograph of a fully processed 4-inch wafer consisting of multiple dielectric metasurfaces. To verify the optical properties of the free-standing membrane, the transmittance of a 100 nm thick Al₂O₃ membrane over a wide spectral range was measured using a Fourier transform infrared (FTIR) spectrometer. As shown in **Figure 7.1c**, the results indicate that the membrane has a near-unity transmittance over an ultra-wide bandwidth spanning from 2.5 μ m (5000 cm⁻¹) to 10 μ m (1000 cm⁻¹) and maintains above 85% transmittance from 10 μ m (1000 cm⁻¹) until 20 μ m (500 cm⁻¹). Notably, the ultra-thin thickness of the membrane reduces the effective refractive index of the surrounding medium down to 1.04, which allows achieving close to ideal metasurface performance. In general, the presence of substrate breaks the symmetry of the dielectric environment surrounding the meta-atoms, creating undesirable side effects such as resonance shift and broadening,[100] reduced efficiencies of the designed functionalities,[37], [104], [111], [172], [173] and unwanted interference phenomena

[100], [173]. In contrast, the remarkably low effective refractive index of the Al₂O₃ membranes significantly suppresses such undesired effects from conventional substrates and enables optically "free-floating" metasurface films in the air. Based on this unique configuration, one can improve the overall performance of metasurfaces (depicted in **Figure 7.1d**) for lightwave control and biosensing.



Figure 7.1: Wafer-scale fabrication of membrane-based-metasurfaces. (a) Fabrication steps of the membrane-based metasurfaces. (1) Atomic layer deposition of a 100 nm thick Al₂O₃ film. (2) deposition of metasurface material. (3) Deep UV lithography for high-through-put pattern generation. (4) Dry plasma etching. (5) Photoresist coating. (6) UV laser writing for defining membrane openings. (7) Deep reactive ion etching through the wafer. (8) Oxygen plasma for resist removal. (b), Photography of a fully processed 4-inch silicon wafer consisting of large-area metasurfaces. (c), Low refractive index¹⁷ and high transmittance throughout an ultra-wide spectrum covering from 2 μ m and 20 μ m make the Al₂O₃ membrane an attractive substrate material for Mid-IR metasurfaces and nanophotonics. (d) Illustration of various types of metasurfaces that can be fabricated with the reported method, including tilted Ge ellipses supporting high-Q resonances, Ge nanopillars enabling wavefront and polarization control and Al-based multiresonant plasmonic nanord antennas.

7.3.1 Numerical simulations of High-Q metasurfaces

High-Q metasurfaces were realized on the thin Al_2O_3 membranes. The precise meta-atom geometry is displayed in **Figure 7.2a**. The metapixel consists of meta-atoms that are arranged in an array over an area of 100 x 100 μ m (**Figure 7.2a** bottom). The unit cell size is scaled from one metapixel to another while keeping the height of the nano-antennas constant, which allows to gradually tune the resonance frequencies of the metapixels, see **Figure 7.2b**. The metapixels are randomly shuffled with different scaling factors to create 10 x 10 pixelated metasurface where the distance between the metapixels is 50 μ m (**Figure 7.2c**). With this pixelated metasurface approach, we can perform direct translation between spectral to spatial information [174]. The numerical simulations of the metasurface optical response were performed using CST Microwave Studio software. The Ge material is assumed to be lossless and has a refractive index of 4.0 in the spectral range from 5.5 μ m to 8.5 μ m, and for Al₂O₃, the optical properties were taken from Kischkat et al. [169].



Figure 7.2: Numerical simulations of membrane-based all-dielectric high-Q metasurfaces. (a) a sketch of the meta-atom and a single metapixel. (b) The simulated reflectance

spectra of a representative 22 different high-Q metapixels on a free-standing Al_2O_3 membrane at different scaling factors. (c) Resonance wavenumber map of the 10 x 10 pixelated metasurface.

7.3.2 Effective refractive index calculations

An essential aspect of the metasurfaces is the effective refractive index of the surrounding medium. A lower and more uniform refractive index of the surrounding medium leads to improved metasurface efficiencies [37], [173]. Here we demonstrate that the thin free-standing membranes can lower the effective refractive index when compared to bulk substrates. **Figure 7.3a** shows the elliptical nano-antennas in a uniform medium with refractive index n_{medium}. The meta-atom design is based on two elliptically shaped germanium nano-antennas that are slightly tilted compared to the x and y-axis by 20°, see **Figure 7.3a**. The germanium has nearzero absorption losses in the mid-IR wavelength range, while the specific asymmetric resonator shape reduces the scattering losses. Such a design supports bound states in continuum[89], therefore providing high-Q resonances. The transmittance spectra for different refractive indexes of the surrounding medium is displayed in **Figure 7.3b**. The resonance frequencies for different refractive indexes are shown in **Figure 7.3c**. When the nano-antennas are placed on a 100 nm thick Al₂O₃ membrane, the resonance is shifted from 5.85 µm to 6.01 µm wavelength, which corresponds to an effective refractive index of 1.039.



Figure 7.3 effective refractive index. (a) Metasurface unit-cell in a uniform medium. (b) Transmittance spectra of the metasurface for different refractive indexes of the medium. (c) Resonance wavelength for the different refractive indexes of the surrounding medium and when a metasurface is placed on a 100 nm thick Al_2O_3 membrane.

7.3.3 Increased sensitivity with membrane-based metasurfaces

Interestingly, the low effective refractive index makes the metasurfaces more sensitive to the variations in the surrounding refractive index when compared to the metasurfaces sitting on

bulk substrates. This can be explained by the fact that the membrane-based metasurfaces experience a larger relative change of the refractive index compared to the metasurfaces on bulk substrates. To demonstrate higher sensitivity of the membrane-based metasurfaces, we performed numerical simulations of the metasurfaces sitting on both bulk substrates and free-standing Al_2O_3 membranes (**Figure 7.4a**). Additionally, we change the refractive index of the surrounding medium on the top side of the metasurface. The simulation data shows that the membrane-based metasurfaces experience up to 36% larger spectral shifts when compared to the regular bulk substrate metasurfaces (**Figure 7.4b**), which gives a clear advantage for refractometric sensing[131], [175], and active light wavefront control applications[57], [111]. Particularly for the metasurfaces of dynamic wavefront shaping capabilities, an increase of optical phase tunability from 0.64 of 2π to full 2π phase shift can be critical for the device to operate successfully.



Figure 7.4: Improved refractive index sensitivity. (a) Cross-section of both regular and membrane-based metasurfaces immersed in a surrounding medium with a varying refractive index n_{medium} . (b) Transmittance spectra of both metasurfaces when the n_{medium} is varied from 1 to 1.6.

7.4 Detailed nanofabrication process flow

7.4.1 Lithography mask fabrication

The reticle (DUV lithography mask) was realized on a 6-inch low thermal expansion quartz plate, which was coated with a 90 nm-thick layer of chromium and a 500 nm-thick PR layer (AZ1512 from MicroChemicals GmbH). The various metasurface geometries were patterned into the PR with direct UV laser writing (VPG200 from Heidelberg Instruments Mikrotechnik GmbH). Due to the DUV stepper machine demagnification of 4x, the nanoantenna shapes on

the reticle are 4x enlarged compared to the desired pattern size on the wafer. After exposure, PR is developed and, subsequently, Cr is etched. The final step includes PR stripping and rinsing with deionized water.

7.4.2 Sample preparation

The sample preparation started with RCA cleaning of the 4-inch Si wafers. The second step involves Al₂O₃ thin film deposition by ALD at 200 °C. Then follows metasurface material deposition (700 nm Ge evaporation for high-Q metasurfaces, 3500 nm Ge sputtering for wave-front control metasurfaces, and 100 nm evaporation of Al for plasmonic metasurfaces). Right after follows DUV lithography steps (anti-reflective layer and PR coating, exposure, and development). After the development, the patterned PR is used as a hard mask for the dry etching process. Then, the metasurface is coated with an 8 µm thick PR (AZ 10XT-60) layer from both sides. A UV lithography step with back-side alignment is performed using a direct laser writing lithography tool (MLA150 from Heidelberg Instruments Mikrotechnik GmbH), after which follows the development step. In order to increase the durability and etch selectivity during the DRIE process, PR is cured at 85 °C for at least 8 hours. The thin free-standing membranes are formed by removing the Si wafer material using a DRIE process until it reaches the Al₂O₃ layer. The final step involves the remaining PR removal with O₂ plasma.

7.5 Experimental realization of High-Q metasurfaces and fabrication uniformity

Metasurfaces that support high-quality factor (high-Q) resonances provide strong electromagnetic fields, spectral selectivity, and enhancement of light-matter interactions for fluorescent spectroscopy [176], differentiation of chiral molecules [177], and nonlinear light generation [92]. A number of mechanisms have been adopted for the designs of high-Q metasurfaces, which include lattice [178], [179] and Fano [120], [180] resonances as well as bound states in the continuum (BIC) [54], [92], [174]. Among them, the quasi-bound states in the continuum (quasi-BIC) have attracted significant attention recently. The utilization of quasi-BIC modes allows great flexibility for tailoring the resonance bandwidth, spectral locations, quality factor (Q-factor), and the distribution of the electric and magnetic fields across the meta-atoms[89]. For instance, meta-atoms that confine the fields within the resonator volume that can reach Qfactors up to tens of thousands are attractive for developing devices such as nanoscale light sources [88], [181], [182], and beam steerers [103]. Whereas metasurfaces providing strong field enhancements outside the resonator with Q-factors of a few hundred are compelling for sensing applications [54], [93], [174]. Achieving quasi-BIC modes in metasurfaces rely strongly on the precise control of the geometric parameters that can be achieved by breaking the in-plane symmetry of their meta-atoms [89]. Notably, the resonance quality and the associated field enhancements of high-Q metasurfaces can be affected significantly by the imperfections introduced during the fabrication processes. As a result, the high-Q metasurfaces have been realized primarily by low-throughput and expensive methods such as EBL [54], [92], [174].

We showcase the high-throughput fabrication of all-dielectric metasurfaces supporting quasi-BIC modes on 4-inch Si wafers containing 37 chips of the 'pixelated' metasurfaces (**Figure 7.5a**). We analyze the fabrication uniformity and spectral response of the highlighted region in **Figure 7.5b**, which consists of 100 metapixels. Here, each metapixel is 100 x 100 μ m and contains an array of elliptically shaped Ge meta-atoms in which the symmetry of the unit-cell is broken through their in-plane rotations. Additionally, the unit-cell size of each metapixel is scaled differently by a scaling factor (from 1 to 1.45 in 100 steps), therefore providing a broadband spectral range with high spectral resolution. Scanning electron micrographs (SEM) show pixelated metasurface and confirm the high uniformity of the meta-atoms (**Figure 7.5c, d**). The high magnification SEM demonstrates the precise meta-atom geometry with the specific rotation angle $\alpha = 15^{\circ}$, which breaks the in-plane symmetry of the unit-cell and controls the resonance Q-factor (**Figure 7.5e**). The cross-sectional SEM of the metasurface validates accurate meta-atom placement on the thin Al₂O₃ membrane (**Figure 7.5f**).

We characterized the optical performance of the pixelated metasurfaces with our tunable laserbased large-area mid-IR microscope having a hyper-spectral imaging function, see methods section. The measurement data show sharp and spectrally clean resonances that are precisely tuned from one metapixel to another over a wide wavelength range (**Figure 7.5g**). Notably, the achieved resonance Q-factors (Q~100) are comparable to the similar metasurfaces made by high-resolution EBL. Besides the precise replication of the meta-atom geometry, one of the important parameters of high-throughput fabrication is the uniformity of the device performance across the wafer. We measured the resonance positions of the pixelated metasurfaces over nine chips, as indicated in **Figure 7.5a**. The resonance spectral location maps of the nine chips show near-identical performance. We further focused on individual metapixels of each chip with a scaling factor of 1.29, which shows an average resonance wavenumber of 1423 cm⁻ (**Figure 7.5h**). Based on the spectroscopic data, the chip-to-chip spectral variance is less than 3 cm⁻¹, corresponding to less than 0.22 % variation in the resonance spectral position (**Figure 7.5h**). These results confirm the high reproducibility and robustness of our fabrication process, which could be implemented towards mass production of mid-IR metasurfaces.



Figure 7.5: All-dielectric high-Q resonant metasurfaces. (a), A nanopatterned standard 4inch silicon wafer consisting of 37 pixelated dielectric metasurface chips. (b) A single chip containing multiple metasurfaces. (c) color-coded SEM of high-Q pixelated dielectric metasurfaces. (d), SEM of a single metapixel. Insert: Zoom-in image of the metasurface. (e), High magnification SEM of the metasurface unit cell. (f), Side view shows thin Al₂O₃ membrane (in blue) and Ge resonators (in orange). (g), Normalized reflectance spectra of a representative single chip (from a region highlighted with black dashed lines in **b** for every 5th metapixel out of 100, demonstrating spectrally selective resonances tuned across a wide spectrum. (h) Resonance spectral position maps of the highlighted region for the nine different chips (with locations indicated in **a**) demonstrate repeatability and high uniformity with a chip-to-chip spectral variance of less than 0.22%.

7.5.1 Comparison with electron beam lithography

In order to compare the fabricated metasurface uniformity and resonance quality factor, we realized a slightly modified design of the elliptical resonators compared to the ones shown in **Figure 7.5**. Here the meta-atom geometry parameters match the ones from the work of Leitis et al.[54], where such germanium-based metasurfaces were realized on CaF₂ substrates using EBL. The dimensions of the experimentally characterized meta-atom are displayed in **Figure 7.6a**, where the elliptical resonator is 950nm wide and 2370 nm long with 4080 nm periodicity along the x-axis and 2380 nm along with a 10-degree tilt angle. The precise shape and uniformity of the fabricated metasurface are confirmed with an SEM image (**Figure 7.6b**). It shows not only the high-resolution DUV lithography but also illustrates that we can reliably produce metasurfaces with small gap sizes (<150nm) between the nano-antennas, which is crucial for improved near field enhancements. The measured reflectance spectra of the fabricated are displayed in **Figure 7.6c**. The achieved resonance quality factor at normal light incidence angle reaches up to 125, which is comparable to the quality factors of EBL fabricated metasurfaces reported by Leitis et al. [54].



Figure 7.6: All-dielectric High-Q metasurfaces. (a) High-Q metasurface resonator design parameters. (b) Scanning electron micrograph of the DUV fabricated metasurface. (c) Measured optical response confirms high-quality resonance with Q-factor of 125.

7.5.2 Silicon-based metasurfaces

The demonstrated fabrication process flow enables the incorporation of a wide variety of materials in the metasurface design. Here, we demonstrate Si-based metasurface on free-standing HfO₂ membranes. The fabrication process flows starts with 60nm HfO₂ deposition on Si wafer using the ALD method. Then a 700 nm thick polysilicon is deposited by low-pressure chemical vapor deposition (LPCVD) at 625 °C. The rest of the process remains the same, as described in **Figure 7.1**. The SEM of the fabricated metasurface is displayed in **Figure 7.7a**, while the cross-section of the thin membrane-based metasurface is displayed in **Figure 7.7b**. The highquality resonances are confirmed with mid-IR laser-based microscopy measurements **Figure 7.7c**. The average quality factor of the metasurfaces in the spectral range from 1400 cm⁻¹ to 1800 cm⁻¹ is 130. Therefore we show that the reported fabrication process flow is compatible with a variety of dielectric materials.



Figure 7.7: Silicon-based metasurfaces. (a) SEM of polysilicon metasurface on free-standing HfO_2 membranes. (b) Cross-section scanning electron micrograph of the DUV fabricated metasurface. (c) Measured optical response of Si metasurfaces confirms background-free and high-quality resonance with Q-factor of up to 130.

7.6 Highly efficient meta-optical elements

Meta-optics has shown a great promise for realizing photonic elements with on-demand functionalities, compact footprints, and seamless device integration for operation in transmission mode. In particular, meta-optical elements have significant potential in the infrared spectral range where they could replace the conventional bulky optical components that are usually made from delicate and unconventional materials such as CaF₂, ZnSe, and Ge by using costly fabrication techniques. However, achieving efficient and highly transmissive infrared metaoptical elements for light polarization and wavefront control is still challenging due to the limited choice of substrate materials. We tackle this problem by leveraging the unique advantages of the Al₂O₃ membranes and demonstrate two highly sought-after components, namely a metalens and a polarization controlling metasurface, with high transmission efficiencies. Such meta-optical components have the potential to replace the bulky and costly conventional mid-IR lenses and polarizers and could be readily used for miniaturized optical sensors, spectrometers, and integrated compact photonic devices.

In the metalens design, the meta-atoms are assigned as circular posts with a height of 3500 nm (**Figure 7.8a**) arranged in a hexagonal lattice. The symmetric shape and arrangement of the meta-atoms ensure that the resulting metalens will be insensitive to the polarization of the incident light, which is beneficial for not losing light in many practical applications. The simulation results of the transmittance and phase modulation versus the post diameter show a full 2π phase coverage with an average transmittance above 90% at the targeted working wavelength of 6.5 µm (**Figure 7.8a**, bottom). The results confirm that full wavefront control can be obtained while keeping the resulting device highly transmissive. The phase profile of the metalens is designed by considering the following equation:

$$\varphi(r) = \frac{2\pi}{\lambda} (\sqrt{f^2 + r^2} - f),$$

where $\varphi(r)$ is the required local phase at the radial distance of *r* from the center of the metalens, *f* is the focal length, and λ is the operational wavelength. The metalens consists of posts with different diameters that are arranged on the surface according to the calculated phase profile. The lens has a diameter of 700 µm and a designed numerical aperture (NA) of 0.4. SEM images of the metalens are presented in **Figure 7.8b**, and **c**. Zoom-in SEM images confirm that uniform posts with a high aspect ratio were successfully produced on the free-standing membrane after the etching process. We characterized the light focusing by the metalens using our tunable laser-based mid-IR microscope at a fixed wavelength of 6.5 μ m. The cross-sections of the output beam profile were recorded at different positions along the z-axis to analyze the threedimensional propagation of the focused Mid-IR beam (**Figure 7.8d**). Notably, we observed a diffraction-limited spot size of 19.8 μ m for the metalens having a numerical aperture (NA) of 0.39, which verifies the designed functionalities and the performance of the metalens.



Figure 7.8: Highly efficient metasurfaces for wavefront shaping. (a) Metasurface unit cell and numerical simulation data of the phase and transmittance for different post diameters at the operating wavelength of 6.5 μ m. (b) SEM images of the metalens, where the constituent materials Si, Al₂O₃, and Ge are color-coded in green, blue, and orange, respectively. (c) Crosssection of the metalens with highlighted thin Al₂O₃ membrane in blue and high-aspect-ratio Ge posts in orange. (d) The metalens (NA=0.4) shows strong focusing efficiency with a diffraction-limited spot size at λ =6.5 μ m.

We characterized the metalenses using a quantum cascade laser-based mid-IR microscope (DRS Daylight solutions Spero). The tunable laser sources enabled measurements of the metalens spectral response, while the high precision microscope stage allowed to characterize the focusing profile along the light propagation axis with high spatial resolution. In order to avoid overexposing the sensitive microbolometer detector, we inserted a neutral density filter in the light path. The measured focusing profile at a fixed laser wavelength of 6.5 μ m along the propagation axis is displayed in **Figure 7.9a**. The beam profile at the focal plane shows strong focusing and completely circularly symmetric intensity distribution (**Figure 7.9b**). The precise analysis of the beam profile confirms a diffraction-limited spot size of 9.9 μ m at the operation wavelength of 6.5 μ m (**Figure 7.9c**).



Figure 7.9: **Metalens characterization.** (a) Focusing profile of a metalens with 0.4 NA. (b) Beam profile at the focal plane. (c) The measured spot size confirms diffraction-limited focusing.

7.7 Birefringent mid-IR metasurfaces

In order to induce birefringence properties into the metasurface, we broke the rotational symmetry of the Ge posts. Specifically, we chose elliptical posts as the meta-atoms and carefully tuned the ratio between its long and short axes. This symmetry breaking enables the control of the light polarization states. **Figure 7.10** demonstrates the numerical simulation data of the optical phase delay when the light passes through the metasurface for different meta-atom post ellipticities at the operation wavenumber of 1360 cm^{-1} corresponding to $7.35 \,\mu\text{m}$. Specifically, the top part of **Figure 7.10a** shows the optical phase when the light is polarized along the y-axis, while the bottom panel shows the case when the light is polarized along the x-axis. The transmittance properties of the metasurface with different post ellipticities are displayed in **Figure 7.10b**, with light polarization along the y-axis at the top and polarization along the x-axis at the bottom. The optical phase difference between the two polarization states is shown in **Figure 7.10c**, while the average transmittance of both polarization states is displayed in **Figure 7.10d**.

Interestingly, in the phase difference map, we can find specific locations where the optical phase difference is 0.5 of the full 2π phase, meaning that it would turn the polarization by 90°. Therefore, the metasurface would perform as a $\lambda/2$ plate. The optical phase difference between the two polarization states can be obtained if the initial polarization of the light is 45° tilted compared to the x- and y-axis. The light that passes through the metasurface has orthogonal polarization. We characterized the metasurface by using the mid-IR laser-based microscope and an additional polarizer (analyzer) right after the metasurface (**Figure 7.10e**). If the analyzer

is parallel to the initial polarization state, then there is almost no light going through the system (**Figure 7.10f**). However, if the analyzer is turned perpendicular to the initial light polarization, then we obtain more than 96% of light transmittance (**Figure 7.10f** right panel). The measured optical response of the birefringent metasurface is in excellent agreement with the simulation data.



Figure 7.10: Birefringent metasurfaces. (a) Optical phase for different post radiuses and polarization states. (b) Birefringent metasurface transmittance for different post radiuses and polarization states. (c) Phase difference between the two polarization states for different post radiuses. (d) Average transmittance of the two polarization states. (e) A sketch of the experimental setup and the birefringent metasurface unit cell. (f) The transmittance of the metasurface for two orthogonal analyzer states.

The experimentally realized birefringent metasurface consists of elliptical posts with the meta unit design parameters shown in **Figure 7.11a**. An SEM image of the birefringent metasurface is presented in **Figure 7.11b**. We characterized the birefringent metasurface using our tunable laser-based mid-IR microscope with an additional polarizer (analyzer) placed below the metasurface. Here, the polarization of the incoming laser light is linear and aligned to be at -

45° with respect to the x-axis, see **Figure 7.11a**. The measurement data show that the metasurface performs as a $\lambda/2$ plate at 1360 cm⁻¹ (7.35 µm) and rotates the polarization by 90 degrees with more than 96% efficiency (**Figure 7.11c**) which is in excellent agreement with the simulation data. Additionally, at 1440 cm⁻¹ (6.95 µm), the birefringent metasurface induces a $\pi/2$ phase difference between the components and serves as a $\lambda/4$ plate. The results further point out that our method enables highly efficient metasurfaces for generating arbitrary polarization states at the targeted spectral positions. Overall, the realized meta-optical components operate with an average transmittance beyond 90%, without any anti-reflection coatings, showing that our membrane-based method is capable of producing highly efficient transmissive metasurfaces for wavefront and polarization control in the mid-IR range.



Figure 7.11: Experimentally realized mid-IR birefringent metasurfaces. (a) Schematic drawing of the birefringent metasurface unit cell and the optical setup. (b) SEM of the fabricated birefringent metasurface. (c) Optical measurements of the birefringent metasurface demonstrate $\lambda/2$ plate efficiency of more than 96% at 1360 cm⁻¹ wavenumber (λ =7.35µm).

7.8 Plasmonic CMOS compatible metasurfaces for mid-IR biosensing

In addition to dielectric metasurfaces, the reported wafer-scale method can be used for producing plasmonic metasurfaces, making it highly versatile for a diverse set of nanophotonic device applications, including biosensing.[183] A particularly interesting plasmonic material is aluminum, because, unlike the typically used Au and Ag, it is a CMOS-compatible metal capable of supporting resonances over an ultrabroad spectrum ranging from the UV to the IR.[69], [184]–[187] Furthermore, Al is a low-cost and the third most abundant element on Earth.[188] Al rapidly forms a 3-5 nm-thick Al₂O₃ oxide layer in air, acting as a protecting layer, which can also be functionalized conveniently for biosensing applications.[189] This property of Al provides an exceeding advantage for binding bio-analytes and dynamic monitoring of their complex interplay, which has not been investigated thoroughly yet. Here, we designed a plasmonic metasurface consisting of Al nanoantennas, where the unit-cell is based on the recently introduced self-similar multiresonant design to perform broadband biosensing using surfaceenhanced IR absorption spectroscopy (SEIRA).[190] This powerful technique provides high sensitivity to detect molecules at the monolayer level via the intense electric field enhancements at the nanoantenna hotspots, which boost light-matter interaction. Operation in the mid-IR provides access to absorption 'fingerprints' for chemically specific and label-free molecular detection. Our nanoantennas are precisely tuned to simultaneously provide strong electric field intensity enhancements in two spectrally separate mid-IR ranges, i.e., around 1600 and 2900 cm⁻¹ (Figure 7.12a), to enhance overlapping absorption bands of both proteins and lipids, respectively.[83] Thus, the designed metasurface offers sensitive and label-free monitoring of interactions between proteins and lipid vesicles in real-time. We successfully fabricate these plasmonic metasurfaces on our Al₂O₃ membranes (Figure 7.12b), which are suitable as optical windows for in-flow experiments due to their highly transmissive and robust properties. Thereby, we can reverse the chip and mount it in a custom-built microfluidic device below a micro-FTIR objective so that the incident IR light excites the nanoantennas through the transparent membrane back-side and reflects the SEIRA signal to the detector (Figure 7.12c). In this configuration, the incident IR light does not travel directly through the water, and only the evanescent electric field senses the water molecules, which leads to two dips in the far-field resonances without completely quenching them [75]. The measured spectral response is in very good agreement with numerical simulation data (Figure 7.12c).



Figure 7.12: High-throughput and CMOS-compatible aluminum plasmonic metasurfaces for real-time optofluidic mid-IR biosensing. (a) Numerical simulation of the electric field enhancement at the two targeted resonance positions. (b) SEM images of multiresonant plasmonic nanoantenna arrays. (c), The simulated and experimentally measured reflectance of the metasurface when immersed in water.

The metasurface response in air and water is displayed in Figure 7.13a, while the schematics of metasurface integration into a microfluidic cell are depicted in Figure 7.13b. We used our membrane-supported plasmonic metasurface to perform in-situ real-time SEIRA measurements to observe the capturing of liposomes. These are important biomolecular entities, which are constituted of lipid molecules forming spherical-shaped vesicles, and they can encapsulate molecules, e.g., for cellular communication in physiology or for drug delivery in engineered systems. Our SEIRA experiment consists of the subsequent injections of an EDC/NHS activation solution, streptavidin proteins, and finally biotinylated liposomes onto the chip surface, which was first functionalized ex-situ with a carboxyl-terminated phosphonic acid, whose phosphate anchor groups have a strong binding affinity to various metal and metal oxide surfaces including Al₂O₃.[189] Using reference absorption spectra for these three different analytes (Figure 7.13c), multiple linear regression resolves the biomolecular events on the sensor surface by tracking each analyte signal separately against time (Figure 7.13d).[83] In these real-time data, first, the EDC/NHS signal peaked (t = 45 min) before eventually dropping back to the baseline level. Next, the streptavidin signal started to rise (t = 50 min) as the proteins covalently bind to the freshly activated carboxyl end groups of the phosphonic acid molecules that formed the monolayer. After protein signal stabilization, the lipid signal increased (t = 130 min) with the liposomes binding to streptavidin via their displayed biotin groups. This experiment confirms the suitability of our Al-based plasmonic membrane chips for real-time, chemically specific biosensing in water. Furthermore, our metasurface sensor also offers the exciting perspective of augmenting it with deep learning algorithms to resolve even more complex biological samples.[138] Previously, EBL-fabricated Au nanoantennas on CaF₂ substrates were used for *in-situ* surface-enhanced infrared absorption spectroscopy measurements.[67], [73] However, switching to a wafer-scale fabrication process flow with a CMOS-compatible plasmonic metal such as aluminum offers the prospect of mass-producible biosensor chips, which could eventually be used for disposable diagnostic devices.



Figure 7.13: real-time optofluidic mid-IR biosensing of protein and lipid vesicle interaction. (a) The optical responses of the plasmonic metasurface in dry (dashed curve) and water medium (solid curve) show two strong resonances indicated by red and blue shades for simultaneous sensing of proteins and liposomes. (b) Illustration of the microfluidic integration with the membrane metasurface chip. (c) Measured absorbance of the EDC/NHS surface activation molecules, streptavidin protein, and liposomes. (d) Real-time regression signals of the streptavidin binding and liposome capturing events on a metasurface functionalized with phosphonic acids whose carboxyl groups were activated with an initial EDC/NHS solution. The inset schematics provide a chronological depiction of the biomolecular events where the monolayer of bound phosphonic acids on the nanoantennas is represented with three colors, i.e., red for the phosphate group moieties binding to the surface, black for the alkyl chain, and orange for the carboxyl group.

7.9 Discussion and outlook

The long-term limitations for mass-producing large-area highly efficient mid-IR metasurfaces are addressed by introducing a novel approach for a CMOS-compatible fabrication method that utilizes free-standing Al₂O₃ membranes. Due to the deeply subwavelength thickness (~2% of the operating wavelength), the membrane-based metasurfaces are optically transparent over a wide spectral range, and they have a remarkably low effective refractive index, which makes them a nearly ideal nanophotonic supporting layer and an optical window for various applications. The versatility of the method has been proven by realizing various types of large-area dielectric and plasmonic metasurfaces on 4-inch wafers for mid-IR photonics and biomedical spectroscopy. This chapter demonstrates high-Q resonant dielectric metasurfaces, highly efficient metalenses, and birefringent polarization-selective metasurfaces with record-high 96% transmission efficiencies. Additionally, aluminum-based plasmonic metasurfaces are incorporated into microfluidic devices for real-time, label-free biosensing, which could be used for dispensable medical devices. Considering the superior optical properties of the membranes and their compatibility with a diverse set of materials, they can be implemented in various compact and efficient photonic and micro-optical elements in a wide spectral range. Notably, although we realized the nanofabrication of large-are metasurfaces on 4-inch wafers in this work, the reported method can be seamlessly adopted for throughput of nanophotonic devices on the commonly used 12-inch wafers in the most advanced semiconductor foundries. Therefore, we believe our high-throughput and cost-effective fabrication method could accelerate the adoption of metasurface photonics to the semiconductor industry and provide cutting-edge optical devices and systems for mid-IR applications.
Chapter 8 All-dielectric programmable Huygens' metasurfaces

8.1 Introduction

Chapters 1 and 2 explain and illustrate how low-loss nanostructured dielectric metasurfaces have emerged as a breakthrough platform for ultrathin optics and cutting-edge photonic applications, including beam shaping, focusing, and holography [45], [174], [191]-[194]. However, the static nature of their constituent materials has traditionally limited them to fixed functionalities. In this chapter, tunable all-dielectric infrared Huygens' metasurfaces consisting of multi-layer Ge disk meta-units with strategically incorporated non-volatile phase change material Ge₃Sb₂Te₆ are introduced. Switching the phase change material between its amorphous and crystalline structural state enables nearly full dynamic light phase control with high transmittance in the Mid-IR spectrum. The metasurface is realized experimentally, showing postfabrication tuning of the light phase within a range of 81% of the full 2π phase shift. Additionally, the versatility of our tunable Huygen's metasurfaces is demonstrated by optically programming the spatial light phase distribution of the metasurface with single meta-unit precision and retrieving high-resolution phase-encoded images using hyperspectral measurements. The programmable metasurface concept overcomes the static limitations of previous dielectric metasurfaces, paving the way for "universal" metasurfaces and highly efficient, ultra-compact active optical elements like tunable lenses, dynamic holograms, and spatial light modulators.

8.2 Actively tunable metasurface design

Metasurfaces have emerged as one of the most exciting research directions in optics, where light scattering properties of materials can be controlled at will by designing subwavelength structures ("meta-units") that strongly interact with the incident light.[45], [174], [191]–[194] While originally only enabling static functionality [50], these concepts have recently been extended towards active optical devices by employing tunable metasurfaces for sensing and light focusing applications, where the optical response can be controlled using light inclination [54],

[55], [195], stretchable substrates [52], electrostatic biasing of 2D materials such as graphene [56], [196], and phase change materials [197]–[199].

Phase change materials such as Germanium Antimony Telluride compounds ((GeTe)_x-(Sb₂Te₃), short GST, are especially promising for tunable applications [200] because their nonvolatile phases (amorphous and crystalline) at room temperature enable high optical contrast with fast switching speeds [201]. This pronounced contrast between the phases originates from a unique bonding mechanism, referred to as "meta-valent bonding" [202]–[204]. In particular, GST layers can be switched from the amorphous to the crystalline state by increased temperature, optical or electrical pulses [205]. They can be re-amorphized using a melt-quench process, where the crystalline GST is heated over the melting point and then rapidly cooled down on nanosecond time scales [200]. Intermediate crystallization states of phase transition can also be accessed, enabling continuous tuning of the material properties [206].

So far, most tunable metasurface approaches were realized by placing plasmonic resonators on top of thin phase change material films with a thickness of 10 to 100 nm. Several plasmonicsbased reconfigurable metasurface applications have already been demonstrated, including beam steerers [207], bifocal cylindrical lenses [208], tunable antennas [209], perfect absorbers [59], and circular dichroism [210]. Even more complex electromagnetic wave phase coding has been demonstrated in the GHz spectral range with metal-based antennas in reflection mode [211], [212]. However, the high Ohmic losses of metals constrain plasmonic metasurfaces to low transmission efficiencies [213], limiting the realization of practical optical elements such as lenses and phase plates.

To overcome the losses associated with plasmonic geometries, new types of metasurfaces based on all-dielectric particles have emerged, where the strong optical response is provided by displacement currents rather than Ohmic currents [214], therefore significantly reducing the intrinsic losses of the resonators. Furthermore, the oscillating displacement current loops in dielectric resonators can provide a stronger magnetic response compared to the plasmonics [215], allowing to combine both electric and magnetic modes to create so-called Huygens' metasurfaces with unprecedented near-unity transmission and full optical phase control.[216] This in turn, enables imparting arbitrary phase patterns onto these metasurfaces, leading to the generation of freely designable holograms.[194]

Even though tunable resonators composed solely out of GST have been proposed,[112], [217], [218], their large sizes make such bulk GST structures challenging to switch between amorphous and crystalline phases. In an alternative approach, localized high refractive index regions

can be embedded within a thin GST film using laser writing, enabling the realization of functionalities like greyscale holograms, reconfigurable Fresnel zone plates and super-oscillatory lenses at visible and near-infrared wavelength ranges.[58], [219] In combination with polar crystal substrates, this was also employed to produce erasable ultra-confined surface phonon polariton resonators in the infrared wavelength range.[219] However, the low layer thicknesses required for efficient GST switching prevent such geometries from sustaining simultaneously magnetic and electric dipole modes, therefore these approaches suffer from low optical phase tunability and transmission efficiency when compared to Huygens' metasurfaces.[37]

Because of all these constraints, tunable and highly transmissive metasurfaces with complete control over the phase of light for practical optical applications are still missing. Here, we present an all-dielectric optically programmable Huygens' metasurface with high transmission efficiency and nearly complete 2π light phase control for wavefront manipulation applications. We first describe the design principle of the multi-layer and multi-material dielectric meta-units with the overlapping of the magnetic and electric dipole resonances. Next, we experimentally show how these two fundamental resonances can be tuned optically by switching individual meta-units with a pulsed laser, featuring an average transmission of more than 50% and an optical phase tuning range approaching 2π . Finally, we demonstrate the versatility of our method by optically programming the spatial light phase distribution of the metasurface with single meta-unit precision and retrieving high-resolution phase-encoded images using hyperspectral measurements.

8.3 Metasurface working principle

Our programmable metasurface design consists of meta-units formed by a multi-layer dielectric disk resonator incorporating two layers of the phase-change material Ge₃Sb₂Te₆ (GST) around germanium (Ge) core, which is chosen for its near-zero absorption losses and high refractive index in the mid-IR spectral range (**Figure 8.1a**). GST exhibits strong refractive index contrast when switched between the amorphous and crystalline phases [209] as well as low absorption losses in the mid-IR range, making it well-suited for the realization of high-efficiency optical elements and devices.[209] Due to the non-volatile nature of the GST phases, intermediate crystallization states can be accessed and maintained, allowing for fine-tuning of the meta-atoms' optical properties.[217] The meta-unit shape and height are specifically designed to sustain both electric dipole (ED) and magnetic dipole (MD) resonances in close spectral proximity (**Figure 8.1b**). The electric dipole mode is induced by the incident electric field, which creates a collective polarization of the dielectric meta-unit at the resonance frequency [220]. The magnetic dipole mode is characterized by an oscillating displacement current loop, which creates an associated strong magnetic dipole.

Due to the strategic GST layer placement on the top and bottom side of the meta-unit, the magnetic mode (high fields at the sides) is influenced more by the refractive index change of the GST upon crystallization than the electric mode (high fields at the center), resulting in a comparatively larger spectral shift λ_{MD} (Figure 8.1c). During the crystallization, the Kerker condition[221] is satisfied, where the spectral and spatial overlap of both resonances provides constructive interference in the transmission direction and results in near-perfect transmittance at the operating wavelength (λ_0 , Figure 8.1c). The combination of the respective optical phase shifts of π associated with each resonance enables nearly full 2π phase modulation across the spectral position of resonance overlap (Figure 8.1d). In addition, intermediate crystallization states enable the encoding of different values of the light phase in the whole accessible phase range while maintaining high average transmittance at the operating wavelength (grey region in Figure 8.1c, d). Crucially, by optically switching individual meta-units of the metasurface, it is possible to write an arbitrary optical phase profile onto the surface, which enables the realization of versatile optical devices like tunable lenses and spatial light modulators[222] (Figure 8.1e).



Figure 8.1: All-dielectric programmable Huygens' metasurfaces. (a) A multi-layer dielectric meta-unit design incorporating the switchable phase-change material GST in a sandwich-like structure enables mid-IR optical phase modulation. (b) The disk-shaped meta-units sustain magnetic (MD) and electric dipole (ED) resonances, where the spectral positions can be dynamically reconfigured by changing the crystallinity of the GST layers. (c) The sketched optical response of the metasurface shows high transmittance at the ED and MD overlap position,

where the Kerker's condition is fulfilled. (d) Due to contributions from both the ED and MD resonances, the sketched optical phase profile exhibits nearly a 2π phase shift across the resonance overlap position, providing full control over the propagation phase of transmitted light. (e) Using ultrashort laser pulses, arbitrary spatial phase profiles can be encoded on the metasurface, enabling the realization of a multitude of programmable optical elements.

8.3.1 GST optical properties

The GST complex permittivity ($\varepsilon = \varepsilon' + i\varepsilon''$) experiences large contrast when switched from amorphous to crystalline states [209]. For clarity, due to the nanofabrication induced perturbation and oxidation at the edges of the GST films, we assume higher absorption losses compared to the uniform thin films in the ref [209]. The GST optical properties of the intermediate crystallization states were calculated using linear interpolation of the complex permittivity:

$$\varepsilon'_{i} = \varepsilon'_{a} + s(\varepsilon'_{c} - \varepsilon'_{a}), \tag{1}$$

$$\varepsilon''_{i} = \varepsilon''_{a} + s(\varepsilon''_{c} - \varepsilon''_{a}), \qquad (2)$$

where *s* is the crystallization state (from 0 to 1) and indexes *a*, *c*, and *i* stand for amorphous, crystalline, and intermediate states. The real part *n* and imaginary part *k* of the complex refractive index ($\tilde{n} = n + ik$) can be calculated using the following equations:

$$n = \sqrt{\frac{1}{2} \left(\sqrt{\varepsilon'^2 + \varepsilon''^2} + \varepsilon' \right)}, \qquad (3)$$

$$k = \sqrt{\frac{1}{2} \left(\sqrt{\varepsilon^{\prime 2} + \varepsilon^{\prime \prime 2}} - \varepsilon^{\prime} \right)}, \qquad (4)$$

The real part of refractive index n for different intermediate crystallization states is displayed in **Figure 8.2a**, while the imaginary part k is displayed in **Figure 8.2b**.



Figure 8.2: GST optical properties. (a) The real part of the complex refractive index of the GST alloy for different crystallization states. (b) The imaginary part of the complex refractive index of GST alloy.

8.4 Numerical simulations of programmable dielectric metasurfaces

The optimized meta-unit consists of a disk with a radius of 640 nm and a unit cell periodicity of 2000 nm (**Figure 8.3a**). Its core is made of germanium (thickness $H_{Ge} = 330$ nm), which is surrounded by the top and bottom layers of GST ($H_{GST} = 90$ nm) in a multi-layer configuration. To protect the GST from oxidation and prevent inter-atomic diffusion between the GST and Ge, additional ZnS:SiO₂ buffer layers of 10 nm thickness are introduced at the layer interfaces. CaF₂ is chosen as substrate material because of its low refractive index and near-zero absorption in the near- and mid-IR spectral region.

The metasurface optical performance was simulated using the finite-difference time-domain software CST microwave studio. The CaF₂ substrate was assumed to be lossless and with a non-dispersive refractive index n = 1.4. The ZnS:SiO₂ buffer layers were assumed to be lossless with a refractive index $n_{ZnS:SiO2} = 1.6$, while the germanium was assumed to be lossless with an average refractive index of $n_{Ge} = 4.03$. The GST was simulated with the real part of the complex permittivity, as displayed in **Figure 8.2**.

Numerical simulations show that at the resonance frequency of the ED mode, the displacement field D is confined in the central part of the meta-unit (**Figure 8.3b**). In contrast, the displacement field for the MD resonance is also located in the bottom and the top GST layers of the meta-unit, resulting in a higher sensitivity to the GST refractive index changes during the phase transition (**Figure 8.3c**).



Figure 8.3: Huygens' meta-unit design simulations. (a) Sketch of the multi-layer meta-unit design, showing the CaF₂ substrate, Ge and GST resonator materials, and the ZnS:SiO₂ buffer layers. (b, c) Simulated displacement field profile at the ED and MD resonance wavelengths, showing that the MD resonance confines the displacement field strongly in the GST layers, therefore making it more sensitive to the refractive index changes associated with the GST phase transition. (d) Simulated transmittance (color-coded) of the Huygens' metasurface when the GST layers are gradually tuned from the amorphous to the crystalline state. e) Simulated transmission optical phase profiles (color-coded) for the same GST crystallization states from panel (d). (f) Transmittance (solid) and light phase (dashed) values at the operating wavelength of 3.75 μ m (dashed black line in (d),(e)) for all intermediate GST crystallization states.

The numerical simulations of the metasurface's optical response were performed for different intermediate GST layer crystallization states, where a linear interpolation of the GST complex

permittivity between the amorphous and crystalline states was assumed. The layer thickness and the disk radius are tailored to produce ED and MD modes in close spectral proximity when the GST is amorphous, with the MD mode at a slightly lower wavelength to ensure spectral overlap when the GST layer crystallizes.

As can be seen from the plot of transmittance over crystallization state and wavelength in Figure 8.3d, there is a strong spectral overlap of the ED (white curve) and MD (pink curve) modes at a wavelength of around 3.75 µm (dashed black line), which results in high transmittance values in this spectral region. Since the pink curve has a steeper slope than the white curve, the simulated data confirms that the MD mode is more sensitive to the changes in the GST crystallization state than the ED mode and therefore experiences larger spectral shifts. The extracted light phase spectrum from each crystallization state shows that a phase shift of nearly 2π is accessible in the operating wavelength range (Figure 8.3e). Finally, we specifically compare the transmittance and light phase values at the operating wavelength of 3.75 µm for each crystallization state (Figure 8.3f). We calculate a total light phase shift of $\Delta \phi = 0.86$. 2π with an average transmittance of 0.62. This optical phase profile can be used for implementation of optical devices such as beam deflectors using programmable Huygens' metasurfaces. Here, we also show that our dielectric disk at the electric and magnetic dipole resonances confines the electric near fields mainly inside its volume. This confinement mitigates the coupling between the neighboring meta-units, which is a useful property for controlling the phase profile in a straightforward manner. Furthermore, the transmission efficiency can be further improved to surpass 70% by embedding the resonators in a medium with a refractive index that matches the substrate material.

8.4.1 Resonator coupling and metasurface phase profile design

The resonator coupling is an important aspect when designing metasurface-based wavefront shaping devices, such as beam steerers, lenses, and holograms. The resonator near-field coupling can complicate the design of the metasurface. Thus the interactions with the adjacent meta-units should be taken into account.

We have performed simulations in order to investigate the near-field coupling for our design. As shown in **Figure 8.4a**, **b**, the dielectric disk at the electric and magnetic dipole resonances confines the electric near fields mainly inside its volume, indicating that the coupling between the neighboring meta-units is weak. In order to demonstrate that the near-field coupling does not significantly perturb the metasurface performance, we formed a supercell consisting of 5

resonators with different GST crystallization states. The specific GST crystallization states are chosen to create a linear phase profile across the supercell with a step size of 0.2 of full 2π phase shift (**Figure 8.4c**, **d**). The electric field intensity plot shows that the incoming beam is deflected at an angle θ (**Figure 8.4d**). A more detailed far-field analysis considering a metasurface consisting of a 50x50 resonator array (10x50 supercell array) shows that the beam is deflected at θ =22.6° deflection angle with angular FWHM of 2.1° (**Figure 8.4e**).





produces a linear optical phase gradient and deflects the incoming beam. (e) Detailed far-field analysis of a metasurface consisting of a 50 x 50 resonator array confirms beam deflection at an angle θ =22.6°.

8.4.2 Dielectric medium for increased transmission efficiency.

The transmission efficiency of the Huygens' metasurfaces depends on the ED and MD mode spectral overlap as well as the matching of the resonance linewidth. The spectral overlap of the two resonances can be tuned either by adjusting the disk geometry or by changing the GST crystallization phase. Due to the slight absorption losses of GST material, the MD resonance has higher FWHM compared to ED mode. The resonance linewidth matching between ED and MD resonances can be improved by optimizing the refractive index contrast between the resonance and surrounding medium, which determines the mode confinement of the ED and MD resonances. Such embedding can be realized by spin coating a thick layer of polymer on top of the metasurface.

Figure 8.5a shows the resonator geometry of the embedded metasurface. The refractive index of the surrounding medium is made to match with the CaF₂ refractive index is as reported in the methods section. In order to match with the operating wavelength in **Figure 8.3f**, the resonator diameter was reduced to 1200nm while the resonated layer stack height remained as described in **Figure 8.3a**. The numerical simulation data shows improved transmission efficiencies of the metasurface with an average transmission of more than 70% (**Figure 8.5b**).



Figure 8.5: Embedded resonators. (a) Metasurface meta-unit geometry in dielectric medium (b) Metasurface transmittance for all the GST crystallization states.

8.5 Experimental realization of the active Huygens metasurfaces

To tailor and study the mode overlap, multiple programmable metasurfaces consisting of metaunits with varying disk radius from 500 nm to 790 nm and a constant periodicity of 2000 nm were fabricated. The GST and Ge layers were sputtered with direct current magnetron sputtering, while ZnS:SiO₂ buffer layers were deposited by radio frequency magnetron sputtering. The resonator pattern was written by electron beam lithography in double-layer polymethyl methacrylate (PMMA) photoresist with different molecular weights (500 nm 495 K PMMA and 70 nm 950 K PMMA). A hard mask of 100 nm Al₂O₃ was deposited by electron beam evaporation. Subsequently, a lift-off process was performed to obtain the hard mask pattern. The disk patterns were transferred into the underlying layer stack by ICP plasma etching with Ar/CF₄ gas mixture ratio 50/10 sccm, RF power of 300W, and a chamber pressure of 50 mTorr. In order not to damage the GST layers and as the hard mask only slightly perturbs the overall performance, the remaining hard mask was not removed.

The transmittance of each array was characterized using a Fourier transform IR (FTIR) spectrometer in combination with an infrared microscope equipped with custom-made apertures that reduce the polar and azimuthal angular spread.

The plot of measured transmittance over disk radius and wavelength reveals that the spectral positions of the two main modes of the system are strongly modified by the radius of the disks (Figure 8.6a). Specifically, we find an increased sensitivity of the ED mode (dashed white line) to the disk radius compared to the MD mode (dashed pink line), therefore allowing for the fine adjustment of the individual mode positions. Figure 8.6b displays a scanning electron microscopy (SEM) image of part of the metasurface with R = 630 nm. Additionally, we performed atomic force microscopy (AFM) measurements of the height and sidewall profile of a meta-unit with R = 650 nm, which agreed well with the expected structure height of $H \approx 500$ nm (Figure 8.6c). The corresponding numerically simulated transmittance spectra of the metasurface are in very good agreement with the FTIR measurements (Figure 8.6d), assuming a slightly thinner GST layer thickness of 70 nm, Ge central core thickness of 325 nm and sidewall tapering angle of 10°. Here, the slightly lower layer thickness could arise from deposition rate uncertainties in the sputtering process. Exemplary spectra for three different radii from both the experimental measurements and numerical simulations are displayed in Figure 8.6e and f, highlighting the good agreement. Interestingly, both the experimental and numerical data reveal the presence of an additional dipole mode at higher wavelengths (> 4 μ m) which results



from the non-normal light incidence. It is associated with a displacement current loop parallel to the layer stack and the magnetic dipole pointing along with the normal of the layer stack.

Figure 8.6: Geometrical tuning of mode overlap. (a) Experimentally measured metasurface transmittance for meta-unit arrays with different disk radius, where the dashed lines indicate the spectral location of the ED and MD resonant modes. (b) SEM micrograph of nanostructured meta-units with R = 630 nm. (c) AFM scan of meta-units with R = 650 nm confirms the expected disk height. d) Numerically simulated transmittance spectra plot for different disk radii. (e, f) Comparison of individual spectra for the experiments and simulations from panels (a) and (d), shifted in the y-direction by 1.

8.6 Focusing optics and polarization states

The IR microscope is equipped with a Cassegrain reflective objective, which focuses the light with a polar angular spread from 10° to 24° (**Figure 8.7a**). In order to decrease the polar and azimuthal angular spread, we introduce a custom-made aperture in the beam path between the objective and the metasurface (**Figure 8.7b**). Due to the reduced azimuthal angular spread,

using a polarizer, we can control the light polarization between the s- and p-states (**Figure 8.7c**). The metasurface transmittance for different crystallization states while operating with the s-polarization mode is displayed in **Figure 8.7d**. In comparison, **Figure 8.7e** shows the optical performance when the metasurface is illuminated with the p-polarized light. Here, the metasurface was assumed to work with the light incidence angle of 18° . The metasurface, when operating with the s-polarization state, has considerably higher transmission efficiency at the target wavelength of $3.75 \,\mu\text{m}$ (**Figure 8.7f**). Therefore, all the optical measurements presented in the chapter were made with s-polarized light illumination.



Figure 8.7: Focusing optics and polarization states. (a) Sketch of focusing optics of the IR microscope. (b) Custom-made aperture for reducing the light incidence and azimuthal angular spread. (c) schematic drawing of the two polarization states. (d,e) The metasurface transmittance for the s- (d) and p-polarization (e) states when GST layers are gradually crystallized. (f) The transmittance values at the operating wavelength for s- and p-polarization states.

8.7 Active tuning and optical programming for optical phase control

Spatially selective GST crystallization was performed by means of optical switching with a pulsed laser ($\lambda_{\text{laser}} = 660 \text{ nm} \ll \lambda_0$), enabling precise control of the location and crystallization state, where increasing laser pulse powers were leveraged to obtain higher levels of GST layer crystallization (**Figure 8.8a**). Optical switching of the phase change material GST was realized by a custom-made laser setup[219], [222]. The light from a red, pulsed laser diode was focused through a 10x objective with a numerical aperture of 0.5 onto the sample surface. The sample

was placed on a Thorlabs NanoMax-TS (Max311/M) stage, which is movable in *x*-, *y*- and *z*direction and connected to a Thorlabs closed-loop piezo controller (BPC303). A custom program allows for the automated positioning of pulsed laser shots on the sample surface with 5 nm accuracy. In order to switch the GST to different crystallization states, the pulse duration of the laser diode was kept constant at 500 ns while the pulse power was varied between 0 and 35 mW. Each targeted meta-unit was switched by a single light pulse.

With the experimental setup individual meta-units can be switched to different crystallization states, enabling true optical programming of the metasurface [209]. Accordingly, individual subarrays of the disk array with R = 650 nm were optically switched and then characterized with a 2D focal plane array imaging detector attached to the FTIR spectrometer (Bruker Vertex 70), allowing to measure the spectral response of multiple neighboring subarrays and different material states simultaneously with micrometer pixel resolution. The spectra extracted from hyperspectral imaging data show that the resonance position exhibits a pronounced spectral shift with increased laser pulse power (Figure 8.8b). The numerical simulations with intermediate crystallization states are in good agreement with the measurement data and confirm the ED and MD mode overlap at about 3.75 µm. The sidewall tapering and inclined light incident angle perturb the ED and MD modes, reducing the metasurface transmission efficiency at the ED and MD resonance overlap. Nevertheless, the average transmittance for all crystallization states at the operation wavelength $\lambda_0 = 3.75 \ \mu m$ still remains over 53%, while the extracted light phase from the numerical data demonstrates a modulation of 81% of the full 2π phase shift (Figure 8.8c). Moreover, the transmittance minimum in Figure 8.8b shifts in total by about $\Delta \lambda = 360$ nm, resulting in a tuning figure of merit of TFOM = $\Delta \lambda$ /FWHM = 1.8, where the full-width-half-maximum (FWHM) of the amorphous state was taken as the reference. Thus, the transmittance can be tuned from in-resonance to completely out-of-resonance, enabling transmittance modulations of up to 60%. Additionally, we show reversible switching of the GST multi-layer system by a re-amorphization and re-crystallization process.

In order to demonstrate the optical programming of our Huygens' metasurface, we encoded images of the letters "G", "S" and "T" into the metasurface with R = 680 nm by switching the individual meta-units to different crystallization states. The change in the resonant properties is confirmed with data from the hyperspectral imaging measurements, which allow to directly correlate the spectral information with the simulated light phase. The metasurface-induced light phase shift is displayed pixel by pixel in a color-coded spatial light phase map (**Figure 8.8d**).

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The spectrally imaged light phase is overlaid on top of an optical micrograph of the metasurface, confirming the accurate addressing of single meta-units by our laser switching method. We further demonstrate that not only the optical phase can be tuned, but also the transmission properties of the metasurface can be controlled in a broad spectral range (**Figure 8.8e**), where the transmittance data is displayed over the optical micrograph of the metasurface. The hyperspectral imaging data shows that the transmission properties can be gradually tuned, and high contrast can be obtained at different spectral locations. Therefore, our multi-layered dielectric meta-unit design provides nearly complete control of light phase and transmission properties, which can be arbitrarily programmed with single meta-unit precision, making this method ideally suited for diverse applications like tunable lenses or dynamic beam shaping.



Figure 8.8: All-optical metasurface programming. (a) The crystallization states of individual meta-units are controlled by illumination with ultrashort laser pulses with a pulsed laser $(\lambda_{laser} = 660 \text{ nm} \ll \lambda_0)$, enabling spatial control over the transmission phase profile. (b) Experimental and simulated metasurface transmission for different crystallization states of the GST

(experimentally achieved with the denoted laser powers), where grey data shows simulated intermediate crystallization states. A clear shift of the resonance across the operating wavelength $\lambda_0 = 3.75 \ \mu m$ is observed (grey line). (c) Simulations of the light phase spectra for the crystallization states in (b). Extracted phase values at $\lambda_0 = 3.75 \ \mu m$ (grey line) confirm nearly complete 2π phase control. (d) Programming of arbitrary spatial light phase distributions is demonstrated by encoding the letters "G", "S", and "T" into our metasurface with different crystallization states, i.e. light phase (color-coded). The image is overlaid over a light micrograph of the metasurface. (e) Color-coded transmittance images for different resonance positions, highlighting the spatial light modulation capabilities of our programmable metasurface, where T_{max} defines the maximum transmittance value at the specific wavelength.

8.8 Reversible switching

We investigated the general ability to reversibly switch our metasurface on a sample that has the same layer stack (within layer thickness tolerances of the sputtering) as the sample described in our manuscript. Because this sample was not etched, it has a laterally continuous layer stack. This allows for more dedicated switching experiments because the switching results can immediately be seen from light micrographs. This is not possible on the patterned layer stack due to strong light scattering by the disk meta-units.

In **Figure 8.9**, we show a sketch of three switching locations, ordered in a row. Below, the switching results can be inspected in a light micrograph. The left spot is crystallized with a power of 8 mW and a pulse duration of 500 ns. A bright spot (crystalline GST) within the grey background (amorphous GST) is distinctly visible. The center spot was first crystallized with the same parameters but then re-amorphized with a power of 376 mW and a pulse duration of only 17 ns. The re-amorphized spot does not show any contrast against the background with amorphous GST, verifying the amorphization. The right spot was crystallized and re-amorphized like the center spot and then again crystallized like the left spot. It looks very similar to the left spot, proving that re-crystallization after re-amorphization is possible. These experiments illustrate the foundation for reversible switching. In our current work, we show proof-of-principle demonstrations for the realization of programmable dielectric Huygens' metasurfaces. Our design can be further optimized for reversible switching. For this, the materials in the layer stack have to be carefully chosen. Improvements could, for example, be gained by embedding the resonators in a transparent dielectric with high thermal conductivity.



Figure 8.9: Reversible layer stack switching. Top: Sketch of the switching events from left to right: crystallization, crystallization followed by re-amorphization, crystallization, and re-amorphization followed by re-crystallization. Bottom: Light micrograph of the corresponding switching results. The scale bar is 2 μ m.

8.9 Discussion and outlook

We have demonstrated a novel metasurface-based concept for nearly full light phase control with high transmission efficiency. Specifically, we incorporated the phase change material Ge₃Sb₂Te₆ in the all-dielectric multi-layer meta-unit design, which enables dynamic control of the spectral overlap between ED and MD modes. Thus, each meta-unit acts as a Huygens' source with variable light phase. The numerical simulations show near 2π phase shift upon GST layer crystallization with average transmittance above 50%. We experimentally realized such a metasurface by nanofabrication and characterized its performance with FTIR spectral measurements, which showed very good agreement with the numerical simulations. In order to demonstrate the versatility of our method, we optically programmed a light phase profile into the metasurface with single meta-unit precision and a maximum light phase tunability of 81% of full 2π . The encoded images were extracted with hyperspectral measurements. Our method targets the important mid-IR spectral window where it could enable applications in key areas like adaptive optics in astronomy, infrared imaging for defense and security, free-space optical communication, and remote sensing. Moreover, with emerging low-loss phase change materials at near-infrared and visible frequencies, the operational spectral window of the active metasurfaces can be further expanded.[223], [224] Therefore, our method provides an attractive platform for programmable and efficient wavefront manipulation for a wide range of applications, from tunable lenses and beam shapers to dynamic holograms and active image correction.

8.9.1 Beam focusing and manipulations with Huygens' metasurfaces

In order to demonstrate various functionalities of the programmable Huygens' metasurfaces we assign specific phase profiles along the metasurface plane. Here we assume that each resonator acts as a Huygens' point source with different optical phase values φ and strength *T* which corresponds to the transmittance properties of the metasurface at the specific operating wavelength (**Figure 8.8**):

$$E = \frac{\sqrt{T}e^{i(kr+\varphi)}}{r},\tag{5}$$

$$r = \sqrt{x^2 + z^2},\tag{6}$$

Where *E* is the electric field, x is the resonator position on the metasurface, and z is the light propagation axis. We applied a parabolic phase profile using the available phase and transmittance values from **Figure 8.8**. The wrapped phase and transmittance profile along the metasurface are displayed in **Figure 8.10a**. The specific metasurface optical phase profile concentrates light at a focal spot around 68 μ m away from the metasurface (**Figure 8.10b**). The focal plane cross-section confirms strong light focusing with the spot size having a full width at half maximum (FWHM) of 4 μ m (**Figure 8.10c**). In addition, we demonstrate the flexibility of the programmable Huygens' metasurface method by applying a cubic phase profile on top of the parabolic one to generate Airy beams (**Figure 8.10d**).



Figure 8.10: Applications of programmable Huygens' metasurfaces. (a) Parabolic metasurface optical phase profile and the corresponding transmittance for light beam focusing. (b) The light intensity map shows clear light focusing around $68\mu m$ away from the metasurface. (c) The cross-section at the focal plane shows a spot size FWHM of 4 μm . (d) Demonstration of Airy beam generation by inducing cubic phase profile on the metasurface.

Additionally, the Huygens metasurface can be extended further to high-Q, as demonstrated by M. Liu et al. in ref. [38]. The high field enhancements of high-Q resonators would allow to further reduce the thickness of the phase change materials, where the lower thickness would facilitate the reconfigurable switching of the phase change materials. Moreover, the recent efforts in the research area of phase change materials have resulted in new, nearly lossless alloys, which provide significant refractive index contrast between the amorphous and crystalline states of the tunable materials. These novel materials include SbSe [225], SbS [224], and GeSbSTe alloys [226]. The high-Q resonators in combination with the new phase change materials would enable electrical switching of the phase change materials with incorporated microheater elements. Such microheaters could be, in principle, made from conductive transparent oxides, such as ITO. The electrical switching concept of the metasurfaces would enable

universal metasurfaces that can be conveniently and rapidly switched to obtain a specific functionality. It would allow realizing ultra-fast solid-state spatial light modulators, tunable lenses, beam steerers, and adaptive optics.

Chapter 9 Conclusions and outlook

The thesis demonstrates major advancements in the field of mid-IR metasurfaces and their nanofabrication methods for applications ranging from label-free biosensing and active optical phase programming to wavefront and polarization control. The first two chapters of the doctoral thesis introduce the concept of metasurfaces and review the state-of-the-art metasurfaces for surface-enhanced infrared absorption spectroscopy and optical wavefront control. Additionally, Chapter 2 covers the latest progress on metasurfaces supporting high-quality resonances and nanofabrication methods for all-dielectric and plasmonic metasurfaces with emphasis on high-throughput nanofabrication methods. The doctoral thesis strongly focuses on the chemical fingerprint detection of biomolecules with all-dielectric metasurfaces and their potential integration in point-of-care sensor devices. Chapters 3 to 6 show the obtained results on all-dielectric high-Q metasurfaces and their implementation in label-free biochemical sensors. Chapter 7 presents a novel wafer-scale nanofabrication method of highly efficient functional metasurfaces for mid-IR optical wavefront control and biosensing. The doctoral thesis also introduces tunable dielectric metasurfaces for optical wavefront control and phase programming in Chapter 8. The main achievements of the research work covered in this doctoral thesis are described in more detail below.

9.1 High-Q metasurfaces for label-free biosensing

Chapters 3 and 4 introduce all-dielectric metasurfaces tailored to detect minute quantities of analytes in the IR region. The demonstrated metasurfaces support spectrally selective and background-free resonances, which can be gradually tuned across a broad spectral range. The combined functionalities of the metasurfaces were utilized to realize a pixelated metasurface, where each metapixel was tuned to a specific resonance frequency. The pixelated metasurface concept allows direct translation between spectral to spatial information. This, in fact, enables direct chemical fingerprint detection by measuring the total reflectance from each metapixel before and after analyte coating with imaging-based methods. The analyte binding attenuates the total reflectance of specific metapixels whose resonance frequencies overlap with the molecular absorption bands. The combined signal from all the metapixels forms a chemically specific "molecular barcode". Strikingly, sub-monolayer sensitivity of proteins can potentially be achieved with a single image and without the need for spectrometry or any moving mechanical parts. Therefore, the demonstrated high-Q metasurfaces enable the operation of miniaturized and highly sensitive biochemical sensors using low-cost broadband light sources and detectors.

Additionally, high-Q metasurface integration into a novel "Tide microfluidic" system was demonstrated in Chapter 4. The "Tide microfluidics" addresses the long-standing challenge of the interference of water absorption, which limits the sensitivity of IR measurements in aqueous solutions. The demonstrated microfluidic system enables biological analyte detection without the interference of water absorption in the IR spectral range while preserving the structural stability of the sensitive biological macromolecules. Furthermore, multiple surface functionalization protocols of all-dielectric metasurfaces were introduced for the successful binding of a diverse range of analytes. Measurements of successful capture of lipid vesicles using multistep binding assay were demonstrated. Detection of human C reactive protein was also demonstrated using a multi-step surface functionalization with antibodies against C reactive protein.

Chapter 5 introduces angle-multiplexed high-Q metasurfaces, which allow the continuous tuning of resonances with a very high spectral resolution over a wide spectral range while maintaining high surface sensitivity. When compared to the pixelated metasurface concept, the angle-multiplexed metasurfaces show significant improvement in terms of the achievable signal, spectral resolution, and operation range. Here, a single array of the high-Q resonators can achieve the same spectral resolution and operation range that would require hundreds of metapixels for the pixelated high-Q metasurfaces. The improved sensing mechanism was used to characterize the secondary structure of proteins from the faint features of curvature in the absorption spectra. Angle-multiplexed metasurfaces upscale the acquisition of absorption signals by five orders of magnitude, as shown with the hyperspectral vibrational imaging method described in Chapter 6. It allows the acquisition of large data cubes with more than a hundred thousand spectra per measurement, which can subsequently be used to train neural networks to recognize various analytes. Furthermore, the hyperspectral vibration imaging concept allows the spatial multiplex detection of various analytes, which could be used for screening hundreds of biomarkers simultaneously with the same sensor device. Regarding the surface functionalization and "Tide microfluidics" concept, both can be further improved, which would allow advancement towards implementable biomedical diagnostic applications. "Tide microfluidics" relies on alternating incubation in aqueous solutions and a rapid measurement when the metasurface is exposed to air. The exposed bioanalytes, such as proteins, could be protected from drying-induced denaturation with additional solutes in the buffer solution [164] or additional surface coatings that prevent protein from unfolding when exposed to air [163]. These mechanisms would allow for longer acquisition times which are needed to detect low concentrations of target analytes and for the analysis of the protein secondary structure. Furthermore, the recent advancements in microfluidic designs can be implemented to further improve the sensitivity and automation of measurements with "Tidal microfluidic" devices. Besides, smaller and more compact microfluidic systems would decrease the required volumes of analytes for target biomolecule detection. Additionally, surface functionalization can be optimized based on covalent binding, which would ensure improved layer homogeneity over the large pixelated metasurfaces.

The demonstrated bioassays in Chapters 3 to 6 contained just a few, well-defined analytes. When moving to biosensing of more complex biological systems such as extracellular vesicles, cargo-loaded liposomes or human serum, more advanced data processing algorithms could be implemented for successful target analyte detection. Specifically, deep neural network algorithms could be implemented for augmented detection and recognition of the biological molecules [73], [138].

Chapters 3 to 6 of the thesis mainly elaborate on biosensing applications of high-Q dielectric metasurfaces. Nevertheless, it is important to note that the demonstrated sensors are not limited only to sensing of biological analytes. The metasurface-based sensors might have even higher potential for other applications in fields of environmental monitoring, food quality control, pharmaceutics, chemical, and automotive industries. For instance, the widespread pollution of microplastics is a growing global environmental problem affecting the whole food chain with potential health hazards [227]. In principle, the membrane-based metasurface sensors demonstrated in Chapter 7 could be adapted to have submicrometer pores etched into the thin membranes, which would allow the filtration and capture of microplastics from the water. The proposed metasurface-based sensor would not only allow quantifying the microplastics but also determine the chemical species of the respective microplastic polymers. This would facilitate the evaluation of plastic contaminant levels in bodies of water and drinking sources.

Overall, the demonstrated technology of high-Q metasurfaces addresses two long-standing challenges of IR spectroscopy, namely, the low sensitivity and the need for cumbersome and expensive equipment. The high-Q metasurfaces enable new design architectures that will omit the need for spectrometers such as FTIRs with liquid nitrogen-cooled detectors or tunable quantum cascade laser sources. Furthermore, perfect absorption schemes could allow integrating light sources and sensors as a single unit, enabling further miniaturization of SEIRAS-based chemical detectors [228].

9.2 High throughput mid-IR metasurface nanofabrication

Chapter 7 of the thesis introduces a novel wafer-scale nanofabrication method of functional metasurfaces for mid-IR photonics and label-free biosensing. The presented method addresses the long-standing challenge of large-scale nanofabrication of highly efficient metasurfaces in the infrared spectral range. The core of the reported approach is based on CMOS-compatible processes where the metasurfaces are fabricated on free-standing aluminum oxide (Al₂O₃) membranes with Deep UV lithography. The thin Al₂O₃ membranes, with a thickness of ~100 nm, provide excellent optical properties over the entire mid-IR spectral range for realizing highly efficient metasurfaces. To demonstrate the versatility of our method, we realized large area metasurfaces for a diverse range of on-demand applications on 4-inch wafers. More specifically, the thin Al₂O₃ membranes show average transmission efficiency above 90% over an impressively broad spectral window spanning from 2 μ m to 20 μ m. Remarkably, they are found to have an ultra-low effective refractive index down to 1.04, which results in optically "free-floating" metasurface films in the air. These unique optical properties of the membranes eliminate the undesired effects from conventional substrates and enable efficient mid-IR metasurfaces.

The demonstrated method is compatible with CMOS processes and different types of plasmonic and dielectric materials. Therefore, the reported nanofabrication process can be adapted to produce a wide range of nanophotonic devices with high uniformity over large areas (0.22% variation of the resonance wavenumber). Diverse metasurfaces with a high-throughput fabrication method were realized, showing spectral filtering, focusing, and polarization control functionalities. The superior optical properties of the membranes and well-tailored metasurface designs allow the accomplishment of total mid-IR metasurface efficiencies to record high 96% without any additional anti-reflection coatings. To illustrate the versatility of the method, Chapter 7 also introduces CMOS-compatible plasmonic metasurfaces based on aluminum and integrated with microfluidics to perform real-time and label-free biosensing of protein and lipid interactions in aqueous solutions. Here, the optical properties of the Al₂O₃ membranes make them ideally suited as IR optical windows for microfluidic in-flow experiments.

The membrane-based metasurface concept overcomes the limitations of currently used materials in the mid-IR range, therefore enabling mass-production of a diverse set of efficient photonic devices. The reported method can be seamlessly used in current semiconductor foundries and has the potential to accelerate the adoption of metasurface technology on a commercial scale.

Moreover, the nanofabrication method can be further improved where the deep reactive ionetching processes can be replaced with wet etching processes of Si in KOH-based etchants. It would allow the simultaneous etching of multiple wafers, therefore further upscaling the nanofabrication. Additionally, the thin membranes demonstrated in Chapter 7 can have only a finite size (~1mm) before they become too fragile to support the large structures of IR metasurfaces. The membrane stability could be further improved by implementing thin Si-based supporting grids that would allow expansion of the membrane-based metasurface size to centimeter-scale photonic components while keeping the scattering losses low. Additionally, multilayer membranes could be used to improve the structural integrity of the membranes. This would allow the growth of the membrane-based metasurface application range to centimeterscale mid-IR optics. Such metasurfaces could replace many of the bulky and expensive mid-IR optical components

9.3 Active metasurfaces for optical wavefront control

Chapter 8 of the doctoral thesis introduces tunable all-dielectric Huygens' metasurfaces that enable dynamic and spatial control over the phase of propagating light in an ultrathin device, thereby providing a compact platform for highly efficient active optics in the mid-IR. The metasurface consists of specifically designed Ge disk resonators incorporating the non-volatile phase change material Ge₃Sb₂Te₆, where the resonator shape and placement of the GST layers is engineered to obtain full control over the optical phase with high transmission. All-optical switching of the phase change material is leveraged to realize active and external control over the optical properties, enabling the programming of arbitrary spatial phase profiles down to the single resonator level. In detail, unique all-dielectric Huygens' metasurfaces were designed, where the multi-layer disk resonator geometry is specifically tailored to meet the conditions for the Kerker effect in the mid-IRspectral region, therefore ensuring an overlap of magnetic and electric dipole resonant modes that interfere constructively, enabling full 2π optical phase shift and high transmission efficiency.

The metasurfaces avoid absorption losses and enable proper switching performance by strategically placing the low-loss phase change material only at the top and bottom surfaces of the disk meta-atom. The tunability of the metasurface optical properties was demonstrated by means of optical switching of the phase change material. The experimental results show resonance shifts of 370 nm, which correspond to optical phase tuneability of 81% of the full 2π optical phase shift. The versatility of our method was displayed by spatially encoding several transmission amplitudes and optical phase profiles in the metasurface. Thus, "post-fabrication optical programming" with a single meta-unit resolution was achieved, which was confirmed and visualized via hyperspectral imaging measurements.

The multi-layer and multi-material resonator concept overcomes the static limitations of previous dielectric metasurfaces and paves the way for high efficiency ultra-compact active optical elements, including tunable lenses, dynamic holograms, and spatial light modulators, which would find applications in key areas like adaptive optics in astronomy, free-space optical communication and remote sensing.

As mentioned above, the demonstrated metasurfaces show a step towards ultra-flat active optics and photonic devices. The optical programming process shown in Chapter 8 requires additional lasers and proper high-end optics to realize the described functionalities. Therefore, such metasurfaces yet to be well suited for practical applications and miniaturized tunable optics. In order to unleash the full potential of the tunable metasurfaces, a step towards electrically tunable metasurfaces is needed. Electrically tunable metasurfaces would give the flexibility to actively control the optical properties with single resonator precision and without the need for additional optics or high-power light sources. Therefore, electrically tunable metasurfaces with incorporated phase change materials would enable the realization of miniaturized and ultra-fast active optical elements.

The novel high-Q resonator designs [38], [88], [229] in combination with nearly lossless phase change materials [224]–[226] have the potential to propel the progress in achieving electrically

switchable metasurfaces. The high-Q metasurfaces Huygens' metasurfaces would allow reducing the minimum required thickness of the phase change material for obtaining full optical phase control. Here, the lower thickness of the phase change materials alleviates restrictions such as rapid heating and cooling for switching the phase change material between its amorphous and crystalline states.

The next major step for tunable metasurfaces would be the realization of highly efficient electrically switchable metasurfaces operating in the transmission mode. Indium tin oxide (ITO) is a promising material for microheater elements for switching phase change materials. The ITO is a conductive and transparent material in the visible and near-IR spectral ranges. It can be incorporated successfully into metasurfaces while keeping the absorption losses low [230], [231].

Additionally, novel deposition methods of phase change materials and electrodes have the potential to assist the progress of electrically tunable metasurfaces. Recently, there has been a lot of effort put into the realization of non-volatile random-access memories (nvRAM), which in contrast to dynamic RAM retains data without applied power. In order to develop these electronic devices, novel atomic layer deposition methods of phase change materials such as GeSbTe, GeSbSeTe and SbSeS were established [232]–[234]. Additionally, transparent metal oxides, like ITO [235] and aluminum-zinc-oxide [236], can be deposited with atomic layer deposition methods. In principle, these material deposition methods could be applied for metasurface nanofabrication processes. It would allow the integration of the phase change materials not only as flat layers but also vertically along the side walls or within the resonators, where it gives more flexibility of meta-atom design for ensuring near-field overlap with the phase change materials and high performance of the tunable metasurfaces.

9.4 Outlook

The metasurfaces have shown to be a breakthrough platform for controlling the light at the nanoscale. Over the last two decades, the research in this field has grown considerably, and the published results on metasurfaces show great potential for various photonic applications, including sensing, optical wavefront control, and light generation.

The metasurfaces are very promising for the development of mid-IR optics and photonics, which so far have been limited by the expensive optical components, detector systems, and

light sources. The advancements in metasurface technology are expected to propel the progress of novel mid-IR detectors and light sources, which will further assist the metasurface-based sensors and optical components demonstrated in this doctoral thesis. For instance, the broad-band IR light sources usually consist of heated SiC bars (globar sources). Due to their elongated shape, it is very challenging to collimate the light without major losses. The metasurface-based IR light sources could be tailored to have a specific emission wavelength without angular dispersion [237]. Moreover, the metasurface-based technology has the potential to realize IR emitters where the emission direction can be controlled at will with high efficiency. Moreover, the perfect absorber metasurfaces could also improve the microbolometer-based infrared light detector performance [59]. Therefore the metasurface-based light sources and detectors could further aid in miniaturization, and improved sensitivity of the proposed chemical sensor devices demonstrated in Chapters 3-6.

The metasurface technologies demonstrated in this doctoral thesis can potentially be combined to further miniaturize the sensors and obtain improved performance. For example, the high-Q pixelated metasurfaces can be integrated with ultra-thin metalens arrays, which would allow the focusing of the light from each metapixel on the microbolometer detectors. The metalenses would give the flexibility to tailor them for operation at specific wavelengths that match with the high-Q pixelated metasurface resonance frequencies. Furthermore, the metalenses would allow minimizing the optical path length from the high-Q sensor metasurface to detector. Potentially, novel high-Q metasurfaces could combine the functionalities of the sensing and wavefront shaping metasurfaces.

Individual high-Q resonators have also shown great promise for light generation [88], in addition to improving metasurface-based sensing systems. The demonstrated high-Q metasurfaces in this doctoral thesis rely on collective resonances which are prone to angular dispersion and inter-resonator coupling. The recently demonstrated individual subwavelength high-Q resonators overcome these limitations and are very promising for further miniaturization of optical sensors where they could reduce the sensor sizes by orders of magnitude when compared to metasurface-based sensors [87], [88]. In addition, due to the low coupling effects, the individual high-Q resonators provide an attractive platform for spectrally selective wavefront shaping devices. The reduced coupling between the resonators would allow the obtention of steep phase profiles across the resonator arrays. Moreover, high-Q resonators with large field enhancements can be advantageous for the realization of actively tunable and reconfigurable photonic devices.

Interestingly, the metasurface-based sensors could also be implemented together with electrophoresis systems. Here the electrophoresis would allow separating the bioanalytes such as proteins and DNA based on their charge and molecular weight, while the metasurfaces would enhance the chemically specific absorption fingerprints of the bioalaytes. Such a hybrid system would allow the separation of various proteins that have similar absorption fingerprints and obtain chemically specific data of their molecular conformation.

Over recent years, artificial intelligence (AI) has become an integral part of research and technology. The field of metasurfaces is no exception, where AI has shown great potential for designing metasurfaces with the desired functionalities [73], [238]. The successful realization of such algorithms will markedly accelerate the progress in the research of metasurfaces and their successful implementation for practical applications. Additionally, data processing with deepneural networks and machine learning algorithms is expected to improve the detection capabilities of the demonstrated metasurfaces for biochemical sensing [239].

The progress in supporting technologies such as mid-IR light sources and detectors is predicted to further facilitate the adoption of mid-IR metasurfaces for photonic applications. The overall cost of microbolometer imaging detectors has decreased over the years, and new light sources such as mid-IR light-emitting diodes [240], miniaturized supercontinuum sources [241], and low-cost quantum cascade lasers [242] have emerged. The metasurface-based biosensors will also benefit from novel surface functionalization methods, which will improve the attainable detection limits of the biomolecules and allow targeting of a wider range of biomarkers with higher specificity. Spatial surface functionalization methods of high-Q metasurfaces also provide interesting approaches for biochemical sensing, where the biological analyte binding can induce optical wavefront shaping effects resulting in increased sensitivity. For instance, the metasurface could be functionalized in concentric ring shapes forming a Fresnel lens, whereby after analyte binding would induce strong focusing effects. Additionally, the field of metasurfaces will greatly benefit from the advancements in material science and nanofabrication methods.

Overall, the thesis demonstrates that mid-IR metasurfaces are an exciting and growing field of research with a high potential for real-world photonic applications. The overall flexibility of metasurfaces in controlling light properties with ultra-low device footprint enables completely new and multifunctional optical components, sensors, light sources, and active photonic devices. In validation of this novel technology, we now see the first steps of the metasurface-based technology transfer from research to industry. Furthermore, there are a myriad of ways through which the demonstrated metasurfaces can further be improved, namely with new meta-atom designs, novel lossless materials, electrical switching mechanisms of phase change materials, and advanced surface functionalization methods. Therefore, this thesis provides a robust platform for more exciting advancements in the field of metasurfaces that are yet to come both in fundamental research as well as industry-oriented devices with real-world applications.

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Curriculum Vitae

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Profile

I am a dedicated and highly motivated researcher with diverse knowledge in the fields of optics, photonics, nanofabrication, and data analysis. I am particularly interested in nanophotonics and its' implementation for ultra-compact optical elements, novel biosensors, and active photonic devices.

Education

PhD in Photonics | 2016- 2021 | EPFL

• Nanophotonics, metasurfaces, nanofabrication, spectroscopy, infrared optics, and data analysis

MSc in Photonics | 2014-2016 | Lund University

• Photonics, optical design, tissue optics, microscopy, and data analysis

BSc in General Physics | 2011-2014 | University of Latvia

• General physics, mathematics, optics, atomic physics and lasers

Work experience

Doctoral assistant | EPFL | 2016 - 2021

• Nanophotonics, numerical simulations, nanofabrication, optical characterization and data analysis

Research assistant | Lund University, Atomic physics Division | 2015-2016

• Optical design, microscopy and experimental realization of selective plane illumination microscopes

Research assistant | Laser Centre of the University of Latvia | 2013-2014

• Fundamental research on manipulation of electron quantum states in atomic systems

Awards and Honors

- MDPI Photonics Travel Award (2021)
- MDPI Nanomaterials Travel Award (2021)
- Invited talk in the V International Conference on Metamaterials and Nanophotonics (2020)
- Finalist of the "My thesis in 180 seconds" pitch presentation contest at EPFL (2020)

- Zeiss/Gloor Swiss Nanotechnology PhD award (2019)
- European Physical Society Travel Grant Student Awards (2019)
- Award for the best poster presentation at the EPFL Bioengineering day (2019)
- Second place in the OSA Innovation School business pitch contest (2019)
- La Forge award in the Innosuisse business concept course (2019)
- Poster presentation award at the 2019 engineering PhD summit on intelligent systems (2019)

List of publications and patents

[1] <u>A. Leitis</u>, A. Hessler, S. Wahl, M. Wuttig, T. Taubner, A. Tittl and H. Altug. All-dielectric programmable Huygens' metasurfaces. *Adv. Funct. Mater*. (2020), 30, 1910259. (frontispiece cover art https://doi.org/10.1002/adfm.202070122)

[2] <u>A. Leitis</u>, A. Tittl, M. Liu, B. H. Lee, M. B. Gu, Y. S. Kivshar and H. Altug. Angle-multiplexed alldielectric metasurfaces for broadband molecular fingerprint retrieval. *Science Advances*, 5.5 (2019): eaaw2871.

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[4] A. Leitis, M.L. Tseng, A. John-Herpin, Y. S.

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[5] <u>A. Leitis</u>, F. Richter and H. Altug. Hyperspectral vibrational imaging and biosensing with all-dielectric metasurfaces. (Manuscript in preparation).

[6] <u>A. Leitis</u>, C. Boutry, F. Richter and H. Altug. Tidal microfluidics for imaging-based labelfree biosensing with high-Q pixelated metasurfaces. (Manuscript in preparation).

[7] M.L. Tseng*, Y. Jahani*, <u>A. Leitis*</u> and H. Altug, Dielectric Metasurfaces enabling advanced optical biosensors. *ACS Photonics*, (2020), *https://doi.org/10.1021/acsphoton-ics.0c01030* (*co-first authorship and accepted cover art).

[8] A.Tittl, A. John-Herpin, <u>A.Leitis</u>, E.R. Arvelo, H. Altug, 2019. Metasurface-based molecular biosensing aided by artificial intelligence. *Angew. Chem. Int. Ed.10.1002/anie.201901443*.

[9] <u>A. Leitis</u>, A. Heßler, S. Wahl, M. Wuttig, T. Taubner, A. Tittl and H. Altug. Programmable Huygens' metasurfaces for active optical phase control. *CLEO/EUROPE-EQEC 2021*, Optical Society of America.



[10] <u>A. Leitis</u> and H. Altug, Functional Mid-Infrared Metasurfaces for Optical Wavefront Manipulation, Sensing and Dynamic Phase Control. *OSA Optical Design and Fabrication congress 2021.*

[11] <u>A.Leitis</u>. Dielectric metasurfaces for biochemical sensing and active wavefront control in the infrared. *METANANO 2020 V International Conference on Metamaterials and Nanophotonics*, 2020, (invited talk).

[12] <u>A. Leitis</u>, A. Tittl, M. Liu, F. Yesilkoy, D.Y. Choi, D.N. Neshev, Y.S. Kivshar and H. Altug, 2019. All-dielectric Metasurfaces for Infrared Absorption Spectroscopy Applications. *CLEO: 2019*, Optical Society of America.

[13] <u>A. Leitis</u>, A. Tittl, M. Liu, F. Yesilkoy, D.Y.



Choi, D.N. Neshev, Y.S. Kivshar and H. Altug. All-dielectric High-Q Metasurfaces for Infrared Absorption Spectroscopy Applications. *CLEO/EUROPE-EQEC 2019*, Optical Society of America.

[14] H. Altug, D. Etezadi, A. Tittl, D. Rodrigo, A. John-Herpin. and <u>A. Leitis</u>, 2018, July. Mid-IR Nanophotonics for Surface-Enhanced Spectroscopy. In *Novel Optical Materials and Applications* (pp. NoTu4J-4). Optical Society of America.

[15] M. Bruvelis, A. Cinins, <u>A. Leitis</u>, D.K. Efimov, N.N. Bezuglov, A.S. Chirtsov, F. Fuso and A. Ekers. Particularities of optical pumping effects in cold and ultra-slow beams of Na and Cs in the case of cyclic transitions. *Optics and Spectroscopy*, *119* (6), pp.1038-1048, (2015).

[16] H. Altug, A.Tittl and <u>A.Leitis</u>. Method and spectrometer apparatus for investigating an infrared absorption of a sample. Patent, *WO2019206430*, (2019).

Peer review contributions

• Reviewer for journals such as *Optica* and *Journal of the Optical Society of America B*

Teaching experience

- Teaching assistant for master level biomicroscopy I course (3 semesters), biomicroscopy II (2 semesters), and plasmonics practical (2 semesters)
- Supervised two master student projects and a bachelor student project on dielectric metasurfaces and infrared spectroscopy

Technical skills

Data analysis and numerical simulations

• Proficient with Matlab and Python programming languages for data visualization, spectral and image analysis, and hyperspectral imaging data analysis. Proficient with the imageJ software for image analysis.

• Proficient with CST and COMSOL multiphysics software for designing metasurfaces for various applications. Knowledge in Zemax and FRED ray-tracing software for designing optical systems

Nanofabrication

• Established multiple process flows for nanofabrication of various metasurfaces. Experienced with numerous nanofabrication tools and processes, such as electron beam, ultraviolet, and deep ultraviolet lithography, thin-film deposition methods (sputtering, evaporation, atomic layer deposition, and chemical vapor deposition), dry and wet etching processes as well as nanostructure and material characterization techniques (scanning electron microscopy, energy dispersive x-ray spectroscopy, optical microscopy, and ellipsometry).

Optical design and spectroscopy

• More than five years of experience in infrared optics, spectroscopy, optical design, and microscopy

Biosensing and surface functionalization

• Five years of experience with optical biosensors and surface functionalization methods

Transferable Skills

• Great critical thinking, organization and problem solving skills. Good communication skills acquired through international academic and industrial collaborations. Comfortable working both in teams and independently as well as in the positions of leadership and mentorship.

Additional Skills

- Rendering of high-resolution images with and their post processing. Two scientific artworks have been selected for the ACS Photonics cover and Advanced Functional Materials frontispiece cover (https://doi.org/10.1002/adfm.202070122).
- Scientific figure processing with Adobe Illustrator and Inkscape software

Extracurricular Activities

- I have represented the Lausanne University Volleyball Club (LUC) at the Swiss National League B (2017-2019).
- I regularly participate in Swiss national beach volleyball tournaments (2020-present).
- I am a three-time bronze medalist in Latvian national championships in the long jump and triple jump events (2010-2014).