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Intersubband Polaritonic Metasurfaces for Flat Nonlinear Optics

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Intersubband Polaritonic Metasurfaces for Flat Nonlinear Optics

by

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Dedication

For my family and friends, whose shoulders I've leaned on.

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I've found that the most rewarding parts of any scientific work are the innumerable collaborations, conversations, and arguments that often occur behind the scenes. For this reason, I'm very thankful for the opportunity to place the spotlight on the wonderful people that have supported me, before delving into what has kept me pre-occupied these last 6 years.

First and foremost, I cannot express how much I've appreciated and treasured the opportunity to work with my advisor, Professor Mikhail A. Belkin. I must admit that I had little understanding of what an advisor-graduate student relationship would be when beginning my PhD, but whatever expectations I had have paled in comparison to the level of advice, knowledge, and support I've received. I often think about the person I was when I first walked through those doors to MRC and can't help but reflect on how much of my attitude and focus have changed over the years as a result of his mentorship (for the better I'd say!). I've picked up so many lessons along the way, but the ones that will stick to me relate to his perpetual enthusiasm and passion for new ideas or science, his insistence on simplifying complex topics to clear physical arguments, and the great level of self-confidence that I feel whenever I embark on something new.

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Abstract

Intersubband Polaritonic Metasurfaces for Flat Nonlinear Optics

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Much attention has been drawn in recent years towards the creation of two-dimensional equivalents of traditionally three-dimensional optical elements. The reduction in dimensionality offers advantages such as a smaller spatial footprint, reduced manufacturing and operating complexity, and access to more exotic optical functionalities than can be achieved in a traditional bulk optics approach. *Metasurface*-based flat optical components, comprised of arrays of subwavelength-spaced scatterers, have emerged as a promising candidate for the realization of this vision, but have been largely constrained to the domain of linear interactions of light with matter. Nonlinear effects are intrinsically weak in bulk materials, and even more so across subwavelength volumes, meaning realization of practical and efficient nonlinear optical metasurfaces has generally been out of reach.

In this thesis, a series of metasurface designs are proposed and experimentally verified to exhibit record setting nonlinearities across deeply subwavelength volumes. The metasurfaces are comprised of metallic nanoantennas patterned onto multiple-quantum well structures possessing tailored intersubband electronic resonances. We term

the ensemble structure an *Intersubband Polaritonic Metasurface* (IPM), owing to the nature of the coupling of the electromagnetic antenna mode with the electronic intersubband transition. Suitable design of the antenna geometry allows one to access and enhance the giant intrinsic nonlinearity of intersubband transitions, which are subject to polarization-selection rules that typically inhibit their operation configuration. Further, due to their subwavelength thickness, IPMs are not constrained to the typical phase-matching considerations of bulk nonlinear optics.

In the first part of this study, we investigate IPMs for efficient second-harmonic generation. A novel architecture consisting of etched nanoantenna volumes is proposed and experimentally demonstrated to exhibit a record setting second-order nonlinearity in the mid-infrared spectral range. Using this design, we experimentally demonstrate a means to control the phase of the generated nonlinear signal via the Pancharatnam-Berry geometric phase approach. We then present and demonstrate a simplified fabrication procedure for the creation of efficient IPMs, forgoing the rather cumbersome wafer-bonding and substrate removal process inherent to earlier designs. Finally, we propose and verify a metasurface design exhibiting an ultrafast third-order nonlinearity.

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Chapter 1: Introduction

1.1 OVERVIEW

The field of optical metamaterials has shown exciting advances in recent years, with many demonstrated applications based on their linear interaction with light, including super-resolution imaging [1], cloaking [2–4], and wavefront control [5,6]. Concurrently, ultrathin (sub-wavelength thickness) nonlinear metasurfaces have been put forward to achieve frequency mixing with relaxed phase-matching conditions [7–10], to implement nonlinear photonic crystal structures [11], and to enable the control of the output wavefront by continuously tailoring the phase of the local nonlinear response [12,13]. For all practical purposes, however, the level of nonlinear responses enabled by traditional materials, such as metals and dielectric crystals, is too weak, and nonlinear metasurfaces with orders of magnitude larger nonlinear susceptibilities are necessary to realistically enable such a new paradigm in nonlinear optics. Ideally, the successful development of flat nonlinear optical elements would be based on efficient frequency mixing in sub-wavelength films with relaxed phase-matching conditions and local in-plane phase and amplitude control of the nonlinear response.

Separately, it has been known since the late 1980s that n-doped coupled Multiple Quantum-Wells (MQWs) may be designed to have second-order nonlinear susceptibilities ($\chi^{(2)}$) up to 4-5 orders of magnitude larger and third-order nonlinear susceptibilities ($\chi^{(3)}$) up to 6-7 orders of magnitude larger than that in traditional bulk nonlinear materials[14,15]. These properties were harnessed for a variety of nonlinear optical applications, including second harmonic generation[16–18], optical rectification[19], sum- and difference-frequency generation (SFG and DFG)[20,21], Raman amplification[22], optical phase conjugation[23], two-phonon absorption[24], and other four-wave mixing processes[25]. The basic design approach is based on

tailoring the composition and widths of wells and barriers in MQW structures to engineer electron subbands so as to maximize the quantum mechanical expressions for $\chi_{zz}^{(2)}$ or $\chi_{zzz}^{(3)}$ for a particular nonlinear process by tailoring transition dipole moments and energy levels positions[16].

However, optical transitions between electron subbands in MQWs are intrinsically polarized along the surface normal (z-axis) to MQW layers. Consequently, this means that the giant nonlinear response is only present for input E-fields polarized normal to the MQW layers, and that maximum nonlinear response is achieved for TM-polarized light propagating parallel to the MQW layers, vanishing under normal incidence. Outcoupling of the z-polarized nonlinear radiation usually presents similar challenges; typical free-space experiments utilize exotic geometries to couple pump field(s) into MQW layers and to out-couple the nonlinear frequency output to free space. Here, the input field(s) and the nonlinear output are in/out-coupled through a prism or a 45-degree polished semiconductor substrate. Further, the MQW layer thickness is limited to below $\sim 10\mu\text{m}$ by practical limitations of the epitaxial growth techniques and is typically too thin for efficient frequency conversion. Additionally, because both input and output beams must be TM-polarized, birefringence phase-matching techniques used in traditional nonlinear crystals cannot be implemented for MQW nonlinear elements. As a result, applications of intersubband optical nonlinearities for free-space optical systems have until recently been limited and far from practical use.

To address these drawbacks, our group has in recent years explored a different approach to harness the high nonlinearities of intersubband transitions. By patterning metallic nano-resonators on top of the quantum-engineered MQW heterostructures, one can circumvent the intersubband selection rules by converting the intrinsic giant nonlinear susceptibility of the MQW, $\chi_{zz}^{(2)}$, into any in-plane element $\chi_{ijk}^{(2)}$ (i,j,k = x or y)[26]. The metallic nanoresonators resonantly couple impinging pump fields at the fundamental frequencies and produce a strong

component of electric field normal to the surface in the MQW layer. This electric field then produces the second-order (or higher) nonlinear polarization at the nonlinearly generated frequency, which is efficiently out-coupled to free space by the same nano-resonators. The coupling between the optical modes of the nano-resonators and the electronic transitions within highly-doped MQWs give rise to so-called intersubband polaritons, and we refer to the composite metasurface geometries as Intersubband Polaritonic Metasurfaces (IPMs). This platform has proven to be readily scalable and flexible across a range of mid-infrared (mid-IR) wavelengths, with design guidelines as simple as tailoring multi-quantum-well transition energies and nonlinearities via appropriate choices of barrier- and well-widths to tuning the antenna resonance of the patterned metallic nano-resonators, which at mid-IR wavelengths also generally reduces to a simple geometric scaling problem. Since their inception, IPMs have been demonstrated to achieve strong second-harmonic[8,26–28], difference-frequency[29,30], and third-harmonic generation[31], and additionally, their polaritonic nature has unveiled applications beyond nonlinear frequency generation, such as voltage-controlled tunable filtering[7,32], and all-optical control.

1.2 DISSERTATION OUTLINE

A brief overview of the physics behind intersubband nonlinearities and flat nonlinear optics is presented in Chapter 2. In the course of the present dissertation work, our group has improved upon the initial demonstration of optical nonlinearities in IPMs by demonstrating second-harmonic-generation (SHG) efficiencies of close to 0.08% under kW/cm² of pumping intensities for a pump wavelength of 9.9 μm , and this effort is outlined in Chapter 3 [8,33]. Our results were largely achieved both by a more careful engineering of the nonlinearities in the MQW, and a redesign of the nano-resonator itself, where we discovered that etching into the MQW material surrounding the metallic resonators induced higher field localization and a larger

nonlinear response compared with the initial demonstration of unetched structures. Our MQW was designed to support giant nonlinear SHG at $1/\lambda \approx 1015 \text{ cm}^{-1}$ ($\lambda \approx 9.85 \text{ }\mu\text{m}$ or 125 meV photon energy), with an intrinsic nonlinear response $\chi_{MQW,zz}^{(2)}$ as high as $2.8 \times 10^5 \text{ pm/V}$ [8,13]. The overall nonlinear response of the metasurface is given as a product of both the electromagnetic field overlap between fundamental frequency (FF) and second-harmonic (SH) modes within the resonator, and the intrinsic nonlinear response of the MQW, where careful design of the resonator geometry affects the overlap and allowed us to exceed the intrinsic susceptibility value, demonstrating an effective nonlinear susceptibility, $\chi_{yxx}^{(2)}$, of $1.2 \times 10^6 \text{ pm/V}$.

In Chapter 4, we show that by employing the concept of geometric phase to SHG IPMs, we were able to demonstrate the ability to continuously control the phase over the nonlinearly generated beam, and were successfully able to steer our SH beam[13,34,35]. To attain continuous phase control with our nonlinear metasurface modality, we employ the Pancharatnam-Berry method, where we control the phase at the individual resonator level by rotating each resonator in the metasurface plane. This approach requires us to operate in a circular polarization (CP) basis, where, for example, assuming a right-circular polarized (RCP) incident beam, a varying resonator rotational angle φ along the x direction introduces a phase factor $\exp[-3i\varphi(x)]$ and $\exp[-i\varphi(x)]$ for RCP and LCP components of the outgoing SH beam, respectively. Importantly, the magnitude of the SH response remains relatively constant across the array of resonators, preserving the giant level of nonlinear response. For this effect, we settled on a split-ring resonator design for our resonators which offers a small spatial footprint and a square unit-cell that allows arbitrary rotation. When the resonators are spatially arranged with a rotational step between adjacent resonators of $\Delta\varphi$, the nonlinear response of the resulting metasurface provides a linear phase gradient along the rotational direction. From basic reflectarray theory, any normally incident FF RCP(LCP) beam will then generate two outgoing SH beams, one RCP (LCP) at an angle

determined by $\theta_{R(R)} = \arcsin[(3\Delta\varphi/360^\circ)\lambda_{2\omega}/d]$, and another LCP (RCP) at an angle determined by $\theta_{L(R)} = \arcsin[(\Delta\varphi/360^\circ)\lambda_{2\omega}/d]$, where $\lambda_{2\omega}$ is the SH wavelength, and d is the width of one unit cell. Finally, we were able to successfully demonstrate nonlinear beam steering of the generated second harmonic wave by fabricating and testing the far field emission of several arrays of split ring resonators with varying rotational steps $\Delta\varphi$.

We believe the combination of high nonlinear efficiency and the ability to control the phase of the generated light from these metasurfaces can potentially unveil a new paradigm towards achieving true flat, nonlinear optical elements, where efficient nonlinearities can be achieved in ultrathin platforms, free of phase-matching considerations.

Fabrication of these first several generations of IPMs consisted of first performing a transfer of the epitaxially-grown MQW layer onto an Au-coated substrate before patterning and etching the resonator geometries, in order to create a metal-backplane in a metal-dielectric-metal cavity for optimal high field enhancement. Such a design choice presents a few problems, as it introduces additional fabrication complexity, and in some materials systems (such as III-nitrides), selective substrate removal and subsequent epitaxial transfer is simply not feasible [28]. 2.8×10^5 pm/V 2.8×10^5 pm/V transmission 2.8×10^5 pm/V mode geometry. One goal for the IPM platform is to remain largely material agnostic, meaning any heterostructure forming well-defined conduction band barriers and wells to support electronic states could be used as a nonlinear material. Therefore, in Chapter 5, we show that rather than employing what we term a “full-metal backplane” (FBP) (where the metal backplane spans the area beneath the resonator), we developed and investigated the performance of an “incomplete-metal backplane” (IBP) design, where the resonators are first etched and patterned into the non-epitaxially-transferred MQW layer, before a single metal layer is deposited on top of and adjacent to the etched volumes. While, as we expected, our investigation revealed that the IBP metasurface generally did not

perform as well as the FBP design, the added degree of flexibility in agnosticism towards material-system, as well as the ability to operate in transmission mode, offers additional support for the viability of the IPM modality [33].

Finally, so far much of the work surrounding IPMs has involved optimization of the efficiency and phase response of the second order nonlinear optical response. Third order nonlinearities enable additional functionalities including four-wave mixing processes, third-harmonic generation, optical phase conjugation, all-optical control, and others. In Chapter 6, we present an IPM design exhibiting a record-high $\chi^{(3)}$ nonlinearity, where the effect is achieved by exploiting the intensity-dependent saturation of the MQW loss. Strong optical pumping of IPMs has a significant effect over the distribution of carriers within the MQWs, and as we found in prior studies of our $\chi^{(2)}$ metasurfaces [36], results in a saturation of the nonlinearity and a deviation from the expected second-harmonic output power. However, we show that this optically saturable response can be harnessed for other applications where it can result in more desirable phenomena, such as saturable absorption and optical power limiting. Specifically, saturable absorption forms the basis for a set of technologies used for passive mode-locking and all-optical control. Furthermore, the opposite of this phenomenon, optical power limiting, where transmission or reflection of an optical element is reduced with incident intensity, is desirable in scenarios where one would want to limit the power of an incident source from damaging sensitive elements. In this work, we show that by optical pumping of the IPM, we are able to control the degree of coupling between the antenna and electronic resonances, transitioning from a strong-coupled state in the low intensity case, when the two spectrally overlap, to a weakly-coupled state in the limit of high intensity pumping. When pumped at the intersubband/bare-cavity resonance, the IPM operates as an optical limiter, exhibiting a strong reduction in reflectivity, and when pumped away from resonance, it can operate as a saturable absorber. The dynamics of

intersubband nonlinearities occur via ultrafast Longitudinal-Optical (LO) phonon scattering with ps and sub-ps time constants, meaning our IPMs operate on a similar timescale. Experimentally, we observe a 60% reduction in reflectivity in an optical limiting configuration across a pumping range of a few 100 kW/cm², and from the results of a degenerate ps-scale pump-probe experiment, we demonstrate modulation of this response on the scale of a few ps. Fitting the intensity-dependent response of our IPM allows us to extract a record value of $\chi^{(3)}$ for the mid-infrared spectral range of approximately $6 \times 10^{-13} \text{ m}^2/\text{V}^2$.

Chapter 2: Theoretical Background

2.1 FLAT NONLINEAR OPTICS

In conventional (i.e. linear) optics, the induced linear polarization of a material's response to incident light depends on the acting E-field, and can be described as

$$\tilde{P}(t) = \varepsilon_0 \chi^{(1)} \tilde{E}(t). \quad (2.1)$$

where $\chi^{(1)}$ is referred to as the linear optical susceptibility. The premise of the field of nonlinear optics comes into light as we generalize and expand the polarization $\tilde{P}(t)$ as a power series of the field strength $\tilde{E}(t)$ as

$$\begin{aligned} \tilde{P}(t) &= \varepsilon_0 [\chi^{(1)} \tilde{E}(t) + \chi^{(2)} \tilde{E}^2(t) + \chi^{(3)} \tilde{E}^3(t) + \dots] \\ &\equiv \tilde{P}^{(1)}(t) + \tilde{P}^{(2)}(t) + \tilde{P}^{(3)}(t) + \dots \end{aligned} \quad (2.2)$$

The quantities $\chi^{(2)}$ and $\chi^{(3)}$ are referred to as the second- and third-order nonlinear optical susceptibilities and $\tilde{P}^{(1)}(t)$ and $\tilde{P}^{(2)}(t)$ as the second- and third-order nonlinear polarizations. Here the vector-nature of the fields is ignored for simplicity, but taking them in to account reveals $\chi^{(1)}$ to be a second-rank tensor, $\chi^{(2)}$ to be a third-rank, and so on [37].

At low incident light intensities, the scattered field is linearly proportional to the applied, and Equation 2.1 is enough to describe the material response, encapsulating linear optical effects such as refraction and reflection. However, if the impinging field is sufficiently large, the electronic orbits of the material get distorted, and the optical response of the material becomes intensity-dependent. In this regime, the higher order polarization terms in Equation 2.2 become non-negligible, and the material response becomes nonlinear. Whereas in linear optics, the polarization $\tilde{P}^{(1)}(t)$ oscillates at the frequency of the acting field, ω , the nonlinear polarizations $\tilde{P}^{(2)}(t)$ and $\tilde{P}^{(3)}(t)$ and so on contribute terms oscillating at various frequencies. Under strong monochromatic illumination, these terms may include ω (optical Kerr effect), 2ω (second-harmonic

generation), 3ω (third-harmonic generation), as well as constant terms resulting in the intensity-dependent refractive index and stemming from optical rectification. Similarly, an impinging field with two frequencies ω_1 and ω_2 leads to nonlinear terms that oscillate at frequencies $\omega_1 \pm \omega_2$, referred to as sum- and difference-frequency generation, respectively, as well as others.

2.1.1 Symmetry considerations

Unlike linear optical effects, even order nonlinear phenomena are subject to symmetry constraints that arise once we consider the vector form of the second-order nonlinear polarization density

$$\vec{P}^{(2)} = \varepsilon_0 \chi^{(2)} (\vec{E})^2 \quad (2.3)$$

If the material under consideration is centrosymmetric (i.e. spatial inversion does not change its structure), and an acting field $-\vec{E}$ is applied, the polarization density now becomes

$$-\vec{P}^{(2)} = \varepsilon_0 \chi^{(2)} (-\vec{E})^2. \quad (2.4)$$

Comparing Equations 2.3 and 2.4, we immediately see that in order for both to be satisfied, $-\vec{P}^{(2)} = \vec{P}^{(2)}$, implying that $\chi^{(2)} = 0$. This result is of fundamental importance to the field of nonlinear optics, as it forbids even order nonlinear responses from particular types of material structures. The same symmetry argument can be made for two-dimensional (i.e. flat) metasurfaces, and imposes design criteria on the geometry and operation of successful meta-atoms [37–39].

2.1.2 Nonlinear optical metasurfaces

Equation 2.2 suggests that in order to generate an appreciable nonlinear response, the appropriate nonlinear polarization density must be comparable in magnitude to the

linear term. Typical values of $\chi^{(1)}$ are on the order of 1, and in the case of second order effects, the typical value of $\chi^{(2)}$ for a bulk nonlinear crystal is 10^{-10} m/V [37]. In order for the nonlinear response to be comparable to the linear, the product of $\chi^{(2)}$ with the applied field has to be about 1, which can practically occur only under extremely high intensities of PWs/cm². Such intensities are well above material damage thresholds and unfortunately quite difficult to achieve without complex fs laser systems. As a result, the nonlinear term is typically much smaller than the linear, and so to generate appreciable nonlinearity, one needs to use long crystal lengths where light can propagate over multiple wavelengths and the polarizable dipoles of the medium can add up coherently.

This issue of coherence is further encapsulated by a *phase-matching* condition that must be satisfied for all nonlinear processes. Essentially, the k-vectors of the incident light must equal that of the nonlinearly generated light. In the example of a second order nonlinear process, this requires

$$\vec{k}_1 + \vec{k}_2 = \vec{k}_{NL}, \quad (2.5)$$

where $\vec{k}_1$ and $\vec{k}_2$ are the wavevectors of the incident pump light, and $\vec{k}_{NL}$ is that for the generated nonlinear signal. In bulk crystals, owing to chromatic dispersion, this phase-matching condition is non-trivial to achieve and is not automatically fulfilled for the pump and nonlinear signals. As a consequence, one must use techniques such as exploiting crystal birefringence, rotation, quasi-phase matching via introducing additional wavevector from gratings, and others [37,38]. In general, phase matching is a nontrivial condition to achieve and largely limits the broadband operation of nonlinear processes.

On the other hand, if one manages to achieve a strong nonlinear response within a structure of subwavelength thickness, such as a metasurface, phase-matching along the normal direction is irrelevant as the structure is optically thin, and is satisfied automatically along the direction parallel to the surface, as it essentially means the angle

of incidence is equivalent to that of reflection. Figure 2.1 depicts the advantages conferred from implementing nonlinear processes in sub-wavelength thick structures.

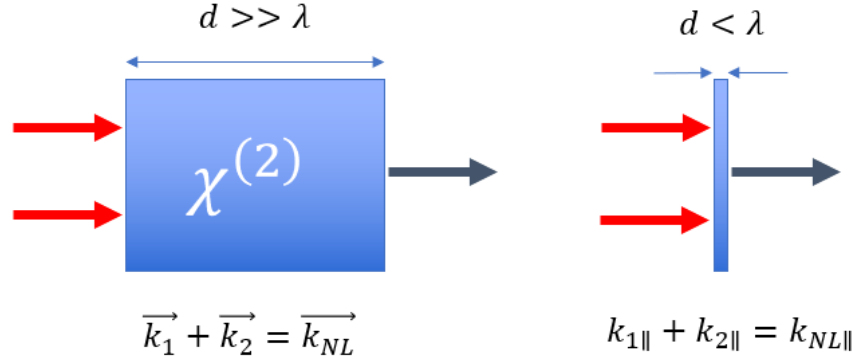


Figure 2.1: Phase matching in a bulk (l) and flat (r) approach to nonlinear optics. Employing a nonlinear medium of sub-wavelength thickness allows one to ignore phase-matching conditions that typically hamper the efficiency of nonlinear processes in bulk materials.

Recent years have found much research focus on modalities to generate nonlinear response within subwavelength thickness structures. These approaches can largely be broken down into three categories: (1) Plasmonic metasurfaces exploiting the strong light-matter interaction from localized surface plasmons at metal-dielectric interfaces, (2) High-index all-dielectric metasurfaces based on Mie-type resonances, and (3) Intersubband Polaritonic Metasurfaces based on the coupling of electromagnetic modes of metallic or dielectric nanoresonators to intersubband transitions supported within semiconductor multi-quantum wells.

The strong field enhancements offered by plasmonic structures comprised of metal nanoantennas patterned on dielectric substrates have unveiled a host of successful demonstrations of nonlinear optical effects and strong light-matter interactions [40–42]. The surface of virtually any material can support a nonlinear response, due to the lack of symmetry of electron potentials at the metal-dielectric interface [43,44]. In contrast to

bulk nonlinear media, nonlinear metasurfaces exploiting surface plasmons at optical and mid-infrared frequencies are tightly bound to this interface and enable strong functionalities in polarization and phase control [12]. Certain considerations must be taken however, as even-order nonlinear effects are subject to modal symmetry constraints similar to bulk nonlinear crystals. Geometries such as L- [45], G-shaped [46,47] and split-ring resonators [48,49] have been employed in literature to some degree of success. However the limiting factors in achieving high nonlinear power conversion efficiencies, defined as $\eta_{SHG} = P_{SHG}/P_{FF}$ for the case of second-harmonic generation is the relatively low nonlinear susceptibilities, $\chi^{(2)}$, of 10^{-11} m/V [50], and high losses associated with metals, leading to very low optical damage thresholds [39].

One way to mitigate the issue of low nonlinear conversion efficiencies from plasmonic metasurfaces due to high dissipative losses and low damage thresholds is to bypass the use of metals all together, and instead employ an all-dielectric platform. Here, high-index materials are generally patterned into cylindrical resonators that can support both electric and magnetic resonances. In contrast to plasmonic metasurfaces, the modes here are confined within the volume of the resonator rather than the surface. While this tends to reduce the high field enhancements offered by plasmonic approaches, dielectric resonator modes carry larger modal volumes that can compensate the low field enhancement with more nonlinear material. Si and Ge have been considered excellent material platforms for third-order nonlinearities, given their large refractive index ($n_{Si} \approx 3.7$ and $n_{Ge} \approx 4.46 - 5.81$), and relatively high third order nonlinearities ($\chi_{Si}^{(3)} \approx 2.8 \times 10^{-18} \text{ m}^2/\text{V}^2$ and $\chi_{Ge}^{(3)} \approx 5.65 \times 10^{-19} \text{ m}^2/\text{V}^2$) [51,52]. Here, symmetry breaking is again an issue at the material level, as to enable even-order nonlinear effects, one needs to employ materials such as III-V semiconductors that do not possess inversion symmetry. Semiconductors such as GaAs and AlGaAs possess both high refractive

indices and large nonlinearities, with $\chi^{(2)} \approx 200 \times 10^{-12} \text{ m/V}$ [53], larger than typical nonlinearities found in conventional nonlinear media such as LiNbO_3 . Despite the relatively high damage thresholds (and thus, the ability to optically pump indiscriminately) demonstrated conversion efficiencies have been still quite low for practical applications, reaching $\approx 2 \times 10^{-5}$ at pump intensities of 3.4 GW/cm^2 [53].

In this dissertation work, we instead turn our attention to a platform that enables record-breaking nonlinearities and conversion efficiencies at low intensities. The structures under consideration here consist of metallic nanoresonators tied to nonlinearities stemming from intersubband transitions within semiconductor multi-quantum wells. Such structures are referred to as Intersubband Polaritonic Metasurfaces (IPMs), stemming from the polaritonic nature of the coupling of electromagnetic modes to electronic resonances [26]. Intersubband transitions have been known to support the largest nonlinearities in condensed matter systems in the mid-infrared spectral range, possessing $\chi^{(2)} \approx 10^{-6} \text{ m/V}$, several orders of magnitude larger than pure dielectric materials and nonlinearities from plasmonic nanostructures. Consequently, conversion efficiencies of 10^{-6} have been demonstrated at relatively low pump intensities of only 15 kW/cm^2 [13]. However, as the nonlinearities stem from electron populations residing in engineered potentials, optical saturation tends to rather quickly hamper conversion efficiencies under strong optical pumping, with a characteristic saturation intensity of the bare MQW being 1 MW/cm^2 , a value further reduced due to the field enhancements offered by IPMs [36]. Table 1 summarizes the overall properties of the various demonstrated nonlinear optical metasurface platforms discussed in the preceding sections, and indicates that no particular design supports practical levels of nonlinear efficiencies over a large input range. However, it has been theorized that optimized material growths and resonator design (in addition to potentially foregoing the use of

metals all together) can lead to IPMs with percent-level conversion efficiencies at accessible intensities [8,36].

Nonlinear medium	Max η_{SHG}	$\chi_{eff}^{(2)}$, m/V	Phase control	Advantages	Disadvantages
Plasmonic metasurfaces	10^{-9}	$\sim 10^{-11}$	Yes	Strong field enhancement	Low optical damage threshold
Dielectric metasurfaces	10^{-6}	$\sim 10^{-12}$	Yes	High optical damage threshold	Moderate field enhancement
IPMs	10^{-4}	10^{-6}	Yes	High efficiency for low input intensities	Low saturation intensity

Table 1.1: Comparative table of state-of-the-art nonlinear metasurface media, adapted from Reference [39].

2.2 INTERSUBBAND TRANSITIONS IN N-DOPED SEMICONDUCTORS

Intersubband transitions in n-doped multi-quantum-well semiconductor heterostructures are electronic transitions that occur between confined electronic states within a semiconductor conduction band, collectively referred to as electronic subbands. The phenomena arise from the quantum confinement of electrons within ultra-thin layers of semiconductor and are formed when consecutive layers of semiconducting materials with dissimilar band gaps are brought together. They were first experimentally realized in the 1960s following the development of advanced epitaxial growth techniques such as Molecular Beam Epitaxy (MBE) by Arthur and Cho [54] and Metallo-Organic Chemical Vapor Deposition (MOCVD) by Manasevit [55].

Depending on the relative band offsets of the two semiconductor materials, electrons can be confined in one dimension in the conduction band, with the formation of

discretized energy levels along the growth direction. By alternating material layers with high and low conduction band offsets, the conduction band profile mimics a series of quantum wells. The position of these energy levels can be modified readily by simply changing the thicknesses of the constituent barriers and wells. Optical transitions can take place between these electronic subbands, enabling the possibility to engineer energy level transitions spanning the infrared and terahertz spectral ranges. By judiciously choosing lattice matched or strain compensated materials, arbitrarily thick structures can be grown. Intersubband transitions are unique in the space of optoelectronics, owing to their quantum-engineered emission and absorption wavelengths, atomic-like joint density of states, and ultrafast (ps and sub-ps) carrier dynamics [56]. In the decades following the introduction of practical growth mechanisms, inventions such as the Quantum-Well Infrared Photodetector (QWIP) and Quantum Cascade Lasers (QCL) revolutionized the fields of infrared and terahertz optoelectronics, enabling an unprecedented degree of flexibility in communication and sensing applications [57,58].

2.2.1 Dielectric function of intersubband transitions

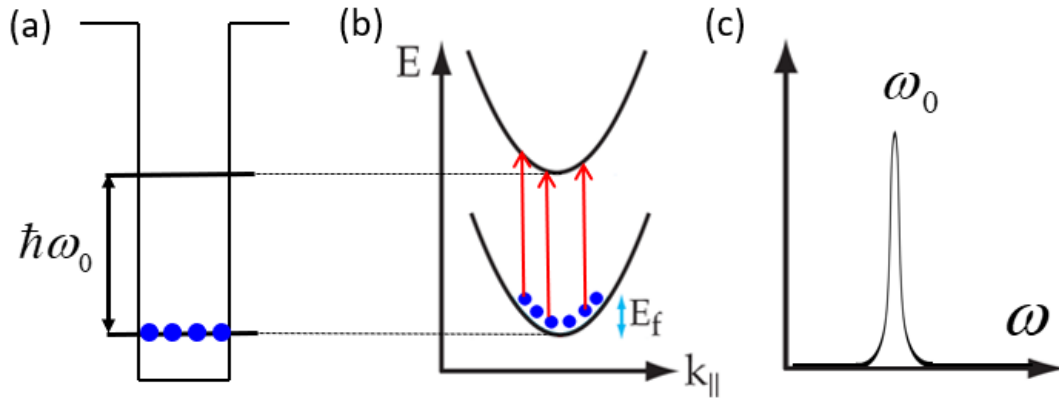


Figure 2.2: **a**, Conduction band profile of a single MQW period, depicting an intersubband transition spaced by energy $\hbar\omega$. **b**, Energy-momentum dispersion of an intersubband transition demonstrating verticality in k -space. **c**, Example spectrum of intersubband absorption line.

Figure 2.2a illustrates the conduction band profile of a single period of a semiconductor heterostructure quantum well, supporting two electronic subbands spaced by an energy $\hbar\omega$. From a solution to the 1D-Schrödinger equation (following effective-mass theory), the total energy eigenvalue of the bound electron in a given quantum well is

$$E_n(k_{\parallel}) = E_n + \frac{\hbar^2 k_{\parallel}^2}{2m^*}, \quad (2.1)$$

Corresponding to the sum of the eigenenergies, E_n , and the kinetic energy associated with electron movement in the in-plane direction. Here $k_{\parallel}$ is the in-plane electron wavevector, m^* is the effective electron mass in the well. Figure 2.2b depict the in-plane energy dispersion wavevector as parabolic, which is only true if the effective mass does not depend on energy and one neglects the subband nonparabolicity. Using this assumption, the energy separation between consecutive subbands is constant and independent of $k_{\parallel}$. Thus, the joint density of states of intersubband transitions is very sharp, and the confined electrons experience a very atom-like strong absorption line, depicted in Figure 2.2c [56].

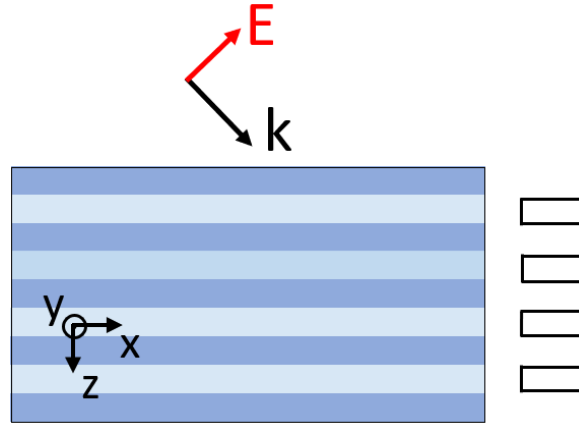


Figure 2.3: (l) Graphic depiction of MQW heterostructure consisting of alternating layers of semiconducting materials and (r) representation of conduction band diagram illustrating the series of potential wells

Electromagnetic treatment of the MQW layers can be treated via an effective medium approximation, since the individual quantum well thicknesses are two orders of magnitude smaller than the wavelength of light. Here, the permittivity $\varepsilon(\omega)$ is anisotropic and can be decomposed into in-plane, $\varepsilon_{\parallel}$, and out-of-plane (growth direction), $\varepsilon_{\perp}$, components, corresponding to As the real and imaginary parts of the dielectric function are correlated via the Kramers-Kronig relations, this sharp absorption line allows for a large change in permittivity along the growth direction, given as

$$\varepsilon_{\perp} = \varepsilon_{\infty} - \frac{\varepsilon_{\infty} f_{12} \omega_p^2}{\omega^2 - \omega_{21}^2 + 2i\omega\gamma}, \quad (2.2)$$

where ε_{∞} is the permittivity at the high frequency limit, γ is the half-width-half-max (HWHM) of the intersubband absorption line, and ω_p is the plasma frequency given as

$$\omega_p = \sqrt{\frac{N_e e^2}{\varepsilon_{\infty} \varepsilon_0 m^*}}, \text{ where } N_e \text{ is the three-dimensional bulk carrier density. Here, } f_{12} \text{ is the}$$

dimensionless oscillator strength between energy states 1 and 2, used to compare transition strengths in different physical systems, and is given by

$$f_{12} = \frac{2m^* \omega_{21}}{\hbar} |\langle 1 | z | 2 \rangle|^2 = \frac{2m^* \omega_{21}}{\hbar} z_{12}^2, \quad (2.3)$$

where z_{12} is known as the transition dipole element. The in-plane permittivity, $\varepsilon_{\parallel}$, experiences no effects due to quantum confinement and thus can be modeled as a Drude plasma, with τ_D as the relaxation time for in-plane transport:

$$\varepsilon_{\parallel} = \varepsilon_{\infty} - \frac{\varepsilon_{\infty} \omega_p^2}{\omega^2 + i\omega/\tau_D}. \quad (2.4)$$

When $\omega \approx \omega_{21}$, an approximation of the denominator of Equation 2.2 $\omega^2 - \omega_{21}^2 = (\omega_{21} + \omega)(\omega_{21} - \omega) \approx 2\omega(\omega_{21} - \omega)$ can be applied, and the expression for $\varepsilon_{\perp}$ can be rewritten as

$$\varepsilon_{\perp} = \varepsilon_{\infty} - \frac{N_e (ez_{12})^2}{\varepsilon_0 \hbar ((\omega_{21} - \omega) - i\gamma_{21})}. \quad (2.5)$$

Importantly, the prior analysis assumes the electron population resides in the ground state, which is an approximation valid at room temperature for all of the structures presented in this dissertation, unless the acting optical field produces significant optical saturation. Generalizing the results for any arbitrary transition from state i to state j allows us to rewrite $\varepsilon_{\perp}$ and $\varepsilon_{\parallel}$ as the sum of the undoped dielectric constant of the MQW (i.e. $N_e = 0$), $\varepsilon_{core}(\omega)$, and the simplified oscillator/Drude terms:

$$\varepsilon_{\perp} \approx \varepsilon_{core}(\omega) + \frac{N_e (ez_{12})^2}{\varepsilon_0 \hbar ((\omega_{ji} - \omega) - i\gamma_{ji})}. \quad (2.6)$$

and

$$\varepsilon_{\parallel} \approx \varepsilon_{core}(\omega) + i \frac{N_e e^2 \tau}{\omega(1 - i\omega\tau_D)}. \quad (2.7)$$

2.2.2 Intersubband Nonlinearities

Intersubband transitions in MQWs have been theorized and experimentally realized to exhibit the largest nonlinearity across the mid-infrared spectral range for a condensed matter system. The ability to engineer electronic subbands by tailoring transition dipole moments and energy level positions allows one an unprecedented degree of control over various elements of nonlinear susceptibility tensors. As optical transitions between electron subbands in MQWs are intrinsically polarized along the surface normal to the MQW layers, the giant nonlinear response only exists for input E-fields parallel to this growth axis, i.e. the z -direction, meaning the only giant elements of the second- and third-order nonlinear susceptibility tensor are $\chi_{zzz}^{(2)}$ and $\chi_{zzzz}^{(2)}$.

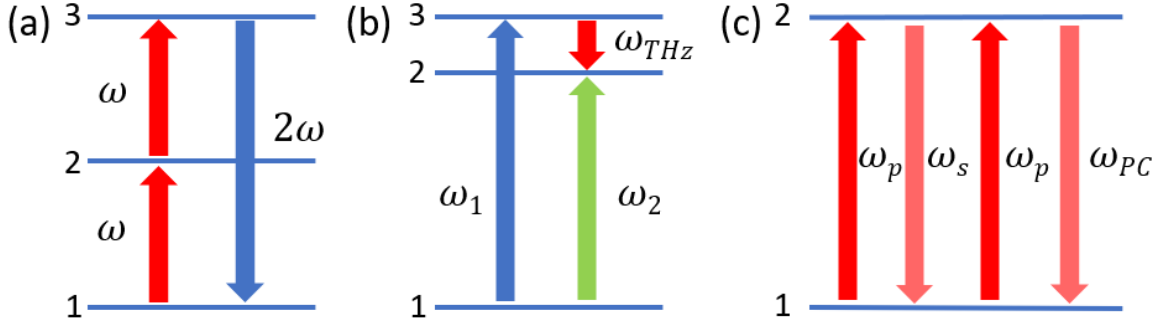


Figure 2.4: Optical transitions and associated nonlinear processes in a MQW structure for **a**, second-harmonic generation, **b**, difference-frequency generation, and **c**, optical phase conjugation. For phase conjugation, the subscript p refers to the pump, s refers to signal wave, and PC is the generated phase-conjugated output.

In a resonant three-level system, the full quantum mechanical expressions for the second- and third- order nonlinear susceptibility are simplified for frequencies close to the intersubband resonances. Here the resonant term is dominant, and for second-harmonic generation, depicted in Figure 2.4a, we obtain [16,37]

$$\chi_{zz}^{(2)}(\omega \rightarrow 2\omega) \approx N_e \frac{e^3}{\hbar^2 \epsilon_0} \frac{z_{12} z_{23} z_{31}}{(\omega_{31} - 2\omega - i\gamma_{31})(\omega_{21} - \omega - i\gamma_{21})} \quad (2.8)$$

where ω is the pump frequency, e is the electron charge, N_e is the average bulk doping density, $\hbar\omega_{ij}$, $\hbar\gamma_{ij}$, and ez_{ij} are the transition energy, linewidth, and dipole moments, respectively, between states i and j .

For THz difference-frequency generation, depicted in Figure 2.4b, we obtain [21]

$$\chi_{zz}^{(2)}(\omega_1 - \omega_2 \rightarrow \omega_{THz}) \approx N_e \frac{e^3}{\hbar^2 \epsilon_0} \frac{z_{12} z_{23} z_{31}}{(\omega_{23} - \omega_{THz} - i\gamma_{32})} \left(\frac{1}{(\omega_{31} - \omega_1 - i\gamma_{31})} + \frac{1}{(\omega_{21} - \omega_2 - i\gamma_{21})} \right) \quad (2.9)$$

And for optical phase conjugation in a resonant two-level system, depicted in Figure 2.4c, we obtain [25]

$$\chi_{zzzz}^{(3)}(\omega + \omega - \omega \rightarrow \omega) \approx N_e \frac{e^4}{4\hbar^3 \epsilon_0} \frac{z_{12}^4}{(-i\gamma_{22})(\omega - \omega_{21} - i\gamma_{21})} \left(\frac{1}{(-\omega - \omega_{12} + i\gamma_{21})} + \frac{1}{(\omega - \omega_{12} + i\gamma_{21})} \right) \quad (2.10)$$

The derivations of the preceding formulas all neglect bulk crystal nonlinearities, as they are negligible compared to the giant intersubband nonlinearities under consideration here.

Strong optical pumping acts to reduce the overall nonlinearity, as the bulk carrier concentration N_e changes as electrons residing in lower subbands are promoted. The saturation intensity I_s for a two-level system is given as [59]

$$I_s = \frac{cn\epsilon_0\hbar^2}{e^2 z_{12}^2 \tau g(\nu)} \quad (2.11)$$

where n is the refractive index of the MQW, τ is the lifetime of the upper state, and $g(\nu)$ is the normalized Lorentzian lineshape function, which can be written as

$$g(\nu) = 2\hbar \frac{\gamma_{12}}{(\hbar\nu - E_{12})^2 + \gamma_{12}^2}. \quad (2.12)$$

At the resonance peak, $g(\nu) = 2\hbar/\gamma_{12}$. For typical intersubband transitions, with $\gamma_{12} \approx 15\text{meV}$, $z_{12} \approx 2\text{nm}$, and $\tau \approx 1\text{ps}$, Equation 2 yields $I_s \approx 1\text{MW}/\text{cm}^2$.

Chapter 3: Intersubband Polaritonic Metasurfaces for Efficient Second Harmonic Generation¹

In recent years, intersubband polaritonic metasurfaces based on coupling electromagnetic modes in plasmonic nanoresonators with quantum-engineered intersubband nonlinearities in multi-quantum-well (MQW) semiconductor heterostructures have been shown to exhibit very strong nonlinear responses. This approach allows one to harness and enhance the intrinsically large nonlinear susceptibility of MQW structures, $\chi_{MQW,zzz}^{(2)}$, which is polarized in the direction normal to the surface. to engineer ultrathin metasurfaces with giant effective nonlinear susceptibility tensor components in the metasurface plane $\chi_{ijk}^{(2)}$ ($i, j=x$ or y), free of any phase-matching constraints associated with traditional nonlinear materials. In this chapter, we explore deeply-subwavelength ($\sim\lambda/20$) MQW-based metasurfaces with record-high second order nonlinear susceptibility of 10^6 pm/V at $\lambda\approx 10$ μm and experimentally achieved conversion efficiencies up to 0.075% using pumping intensities of only ~ 15 kW/cm², well below materials damage threshold even for continuous-wave operation.

3.1 INTRODUCTION

Ultrathin (sub-wavelength thickness) nonlinear metasurfaces have been put forward to achieve super-resolution imaging [60], implement nonlinear photonic crystal structures [61], enable optical switching and memories at the nanoscale [62], produce frequency mixing with relaxed phase-matching constraints [26], and allow control of the

¹ The results from this chapter are published in: J. Lee, N. Nookala, J. S. Gomez-Diaz, M. Tymchenko, F. Demmerle, G. Boehm, M. Amann, A. Alù, and M. A. Belkin, "Ultrathin second-harmonic metasurfaces with record-high nonlinear optical response," *Adv. Opt. Mater.* **4**, 664–70 (2016). Nishant Nookala conducted sample fabrication, experimental characterization, data analysis, and contributed to drafting the manuscript.

output wavefront by continuously tailoring the phase of the local nonlinear response [12,13,27,34,63,64]. However, for all practical purposes, the level of nonlinear responses enabled by traditional materials, such as metals and dielectric crystals [37,38], and metasurfaces based on metallic nanoresonators [12,61,65,66] is far too weak to enable a new paradigm [26,34] in nonlinear optics, based on which properly designed ultrathin metasurfaces provide efficient frequency conversion without the conventional phasematching constraints of bulk nonlinear crystals, and have the ability to manipulate the wavefront of the nonlinear signal output with subwavelength resolution, enabling advanced functionalities such as beam-steering or focusing [12,13,27,34,61,63,64]. Here we experimentally demonstrate nonlinear metasurfaces for mid-infrared second-harmonic generation (SHG) with a second-order nonlinear susceptibility of 1.2×10^6 pm/V, which is to the best of our knowledge the largest value of second-order nonlinear response in the infrared/visible spectral range reported for a condensed matter system and 3-5 orders of magnitude higher than that of traditional nonlinear materials and nonlinear metasurfaces based on plasmonic nanoresonators. The giant nonlinear response of our structures enables efficient frequency mixing in optical films of sub-wavelength thickness using pump intensities well below materials damage threshold.

It can be shown that the power conversion efficiency η for second harmonic generation (SHG) in a phased-matched nonlinear medium of thickness d is given by

$$\eta \equiv \frac{I_{2\omega}}{I_{\omega}} = \frac{\pi^2}{n_{\omega} n_{2\omega}} \left(\frac{d}{\lambda_{2\omega}} \right)^2 \left| \chi_{\text{eff}}^{(2)} E_{\omega} \right|^2 \approx \left(\frac{d}{\lambda_{2\omega}} \right)^2 \left| \chi_{\text{eff}}^{(2)} E_{\omega} \right|^2, \quad (3.1)$$

where ω , n_{ω} , I_{ω} (2ω , $n_{2\omega}$, $I_{2\omega}$) are the fundamental (second-harmonic) frequency, refractive index, and intensity, respectively, $\chi_{\text{eff}}^{(2)}$ is the effective nonlinear susceptibility for a particular input-output polarization combination, E_{ω} is the pump electric field, $\lambda_{2\omega}$ is the second harmonic (SH) wavelength, and we have used the undepleted pump

approximation [37,38]. To arrive at this expression, we start with a classical expression for a phase-matched second harmonic generation (SHG) in a nonlinear medium of thickness d in the plane-wave approximation:

$$I_{2\omega} = \frac{(2\omega)^2}{8\epsilon_0 n_\omega n_\omega n_{2\omega} c^3} |\chi_{eff}^{(2)}|^2 d^2 I_\omega^2, \quad (3.2)$$

where I_ω ($I_{2\omega}$) and n_ω ($n_{2\omega}$) are the intensity of the beam and the refractive index of the nonlinear material, respectively, at frequency ω (2ω), $\chi_{eff}^{(2)}$ is the complex value of the effective nonlinear susceptibility of the material for a particular input-output beams polarization, c is the speed of light in vacuum, and d is the materials thickness. The intensity of the pump electromagnetic wave can be expressed through the electric field amplitude as

$$I_\omega = 2n_\omega \epsilon_0 c |E_\omega|^2, \quad (3.3)$$

where we follow the formalism of Refs. in which the real E-field in the electromagnetic wave is given as $\vec{E}(t) = \vec{E}_\omega e^{j\omega t} + c.c.$ Combining Equations (3.2) and (3.3) we obtain the expression for SHG conversion efficiency presented as Equation (3.1).

Equation (3.1) shows that, in order to provide high nonlinear conversion efficiency in films of sub-wavelength thickness, we need to have $|\chi_{eff}^{(2)} E_\omega| \sim 1$ or, in other words, the nonlinear polarization $\vec{P}^{(2)} = \epsilon_0 \tilde{\chi}^{(2)} \vec{E}_\omega \vec{E}_\omega$ must become comparable to the linear one $\vec{P} = \epsilon_0 \tilde{\chi}^{(1)} \vec{E}_\omega$, where $\tilde{\chi}^{(1)} \sim 1$ is the linear susceptibility. Similar conclusions may be drawn for other three-wave mixing processes (sum- or difference-frequency generation), and for higher-order nonlinear processes.

Traditional nonlinear materials [37,38] and nonlinear metasurfaces based on plasmonic nanoresonators previously demonstrated in the infrared/visible frequencies [12,61,65,66] have second-order nonlinear elements in the range 1-1000 pm/V. Pump intensities ranging from 0.1 TW/cm² to over 100 PW/cm² and optical fields comparable

to atomic fields are needed to achieve the condition $|\chi_{\text{eff}}^{(2)} E_{\omega}| \sim 1$ [37,38]. Such intensities are only possible with high-power ultrafast lasers, and are typically well above the materials damage threshold. In particular, SHG power conversion efficiencies below 10^{-10} were reported for ultra-thin nonlinear metasurfaces pumped with femtosecond pulses with intensities as high as 0.1 GW/cm² in Refs [12,61,65,66].

We have recently reported a different approach to realize nonlinear metasurfaces based on coupling of electromagnetic modes in metallic nanoresonators with quantum-engineered intersubband nonlinearities in multi-quantum-well (MQW) semiconductor heterostructures [26]. This approach allows one to convert the giant nonlinear susceptibility of MQW heterostructures ($\chi_{MQW,zzz}^{(2)}$), which is intrinsically polarized in the z-direction normal to the surface, into any in-plane element $\chi_{ijk}^{(2)}$ (i,j = x or y) of the nonlinear susceptibility tensor of the metasurface. The metallic nanoresonators resonantly couple to the impinging pump field at the fundamental frequency and produce a strong component of the electric field normal to the surface [15,16,67–73] at the fundamental frequency in the MQW layer. This electric field produces second-order nonlinear polarization at the SH frequency in the MQW layer. The oscillating nonlinear polarization couples to the nanoresonators resonant mode at SH frequency, and the SH radiation is efficiently outcoupled to the free space by the nanoresonators. We note that nonlinear metasurfaces operating in transmission and based on nanoresonators with different geometries have also been reported recently [27]. We have speculated [26] that the nanoresonators may be used to produce in-plane elements of the metasurface nonlinear susceptibility tensor that exceed the values of intrinsic MQW nonlinearity $\chi_{MQW,zzz}^{(2)}$. However, this was very hard to achieve in practice with metal nanoresonators and the largest nonlinear coefficient of the metasurface measured experimentally in Ref.

[26] was only 5×10^4 pm/V, below the intrinsic nonlinearity of the MQW structure employed in that work.

In this work, we experimentally demonstrate a MQW-based nonlinear metasurface that utilizes metal-semiconductor nanocavities. Unlike metal nanoresonators used previously, metal-semiconductor nanocavities not only convert z-polarized MQW nonlinear susceptibility into transverse plane but provide further enhancement to the MQW nonlinear response. Combined with innovations in the MQW design, this approach allowed us to produce a metasurface with record value of second-order nonlinear optical response of 1.2×10^6 pm/V, more than 20 times that reported in Reference [26]. Such metasurfaces fulfill the condition $|\chi_{eff}^{(2)} E_\omega| \sim 1$ for pump intensities well below 1 MW/cm^2 and can realistically provide over 2.5% SHG power conversion efficiency for only a few tens of kW/cm^2 of optical pumping intensity and $\lambda/25$ nonlinear layer thickness. Experimentally, we demonstrate nearly 0.1% SHG power conversion efficiency with 400-nm-thick metasurfaces pumped with $\lambda \approx 10 \text{ }\mu\text{m}$ radiation with 15 kW/cm^2 pump intensity.

3.2 METASURFACE HETEROSTRUCTURE DESIGN

3.2.1 Heterostructure design

Figure 3.1a shows the band diagram of a coupled quantum well structure, repeated multiple times to produce a 400-nm-thick MQW layer used in our work. The thickness d of the MQW layer in our case is chosen so as to maximize the product $|\chi_{eff}^{(2)}|d$ in Equation (3.1). The values of energies ($\hbar\omega_{ij}$) and transition dipole moments (ez_{ij}) for transitions between the first three electron subbands ($i,j=1..3$) are shown in the figure. The structure is designed to support giant resonant nonlinear SHG at the optimal pump wavenumber $1/\lambda \approx 1000 \text{ cm}^{-1}$ ($\lambda \approx 10 \text{ }\mu\text{m}$ or 124 meV photon energy). Figure 3.1b

plots the absolute value of the nonlinear susceptibility tensor element $\chi_{MQW,zzz}^{(2)}$ as a function of pump frequency calculated for a bare MQW structure assuming low pump intensity. The nonlinear response peaks at approximately 2.8×10^5 pm/V, 3-4 orders of magnitude larger than the largest $\chi^{(2)}$ coefficient of natural optical materials [37,38].

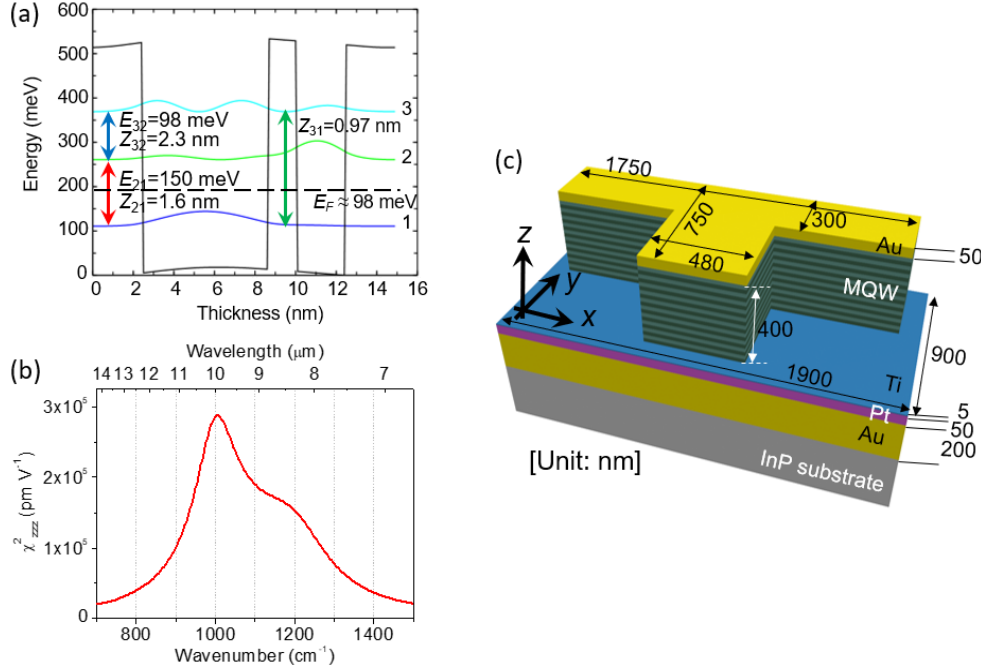


Figure 3.1: Nonlinear metasurface structure. **a**, Conduction band diagram of one period of an $\text{In}_{0.53}\text{Ga}_{0.47}\text{As}/\text{Al}_{0.48}\text{In}_{0.52}\text{As}$ coupled quantum well structure designed for giant nonlinear response for SHG. **b**, Intersubband nonlinear susceptibility of the structure in (a) as a function of pump frequency for SHG. **c**, A schematic of 1900 nm by 900 nm metasurface unit-cell. Dimensions are given in nm.

Unlike doubly-resonant MQW designs ($\hbar\omega_{21} = \hbar\omega_{32} = \hbar\omega_{31}/2$) used in MQW-based metasurfaces previously [26,27], the transition energy between states 1 and 2 in the MQW design used in this work is purposely detuned by approximately 25 meV from the optimal pump photon energy of $\hbar\omega \approx 124$ meV to reduce optical losses in the nanoresonator cavity and avoid saturation of nonlinear optical response by pump light. Saturation in MQWs occurs when the input intensity is so large that the intersubband

absorption empties the quantum-well ground state, reducing the nonlinear response of the MQW system [18,36,72,74]. A theoretical analysis presented by us in Ref. [26,36] indicated that saturation of MQW nonlinearity by pump intensity imposes fundamental limits to the conversion efficiency in MQW-based nonlinear metasurfaces and MQW structures with 1-2 transition detuned from the pump frequency and 1-3 transition coinciding with the second harmonic frequency provide optimal performance.

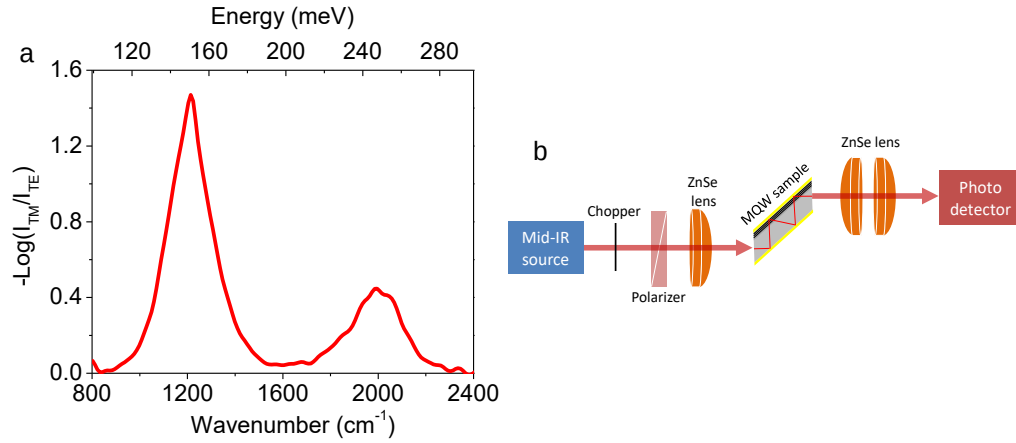


Figure 3.2: **a**, Intersubband absorption spectrum after background correction. **b**, Intersubband absorption measurement setup. Unpolarized mid-IR light from FTIR passes through a linear polarizer and is focused onto one facet of MQW sample. Mid-IR light passed in multipass geometry of MQW sample is then detected from a photodetector.

3.2.2 Experimental multi-quantum well intersubband absorption

Figure 3.2a shows the experimentally-measured intersubband absorption spectrum after background correction. The measurement setup is shown in Figure 3.2b. Our measurement procedure is similar to that described in Ref. [26]. Assuming unpolarized mid-infrared (mid-IR) light illumination from the Fourier Transform Infrared Spectrometer (FTIR) thermal source, the intersubband absorption coefficient α_w is given as:

$$\alpha_w = -\frac{1}{L_{\text{int}}} \ln(10) \text{Log}_{10} \left(\frac{I_{TM}}{I_{TE}} \right), \quad (2.4)$$

where L_{int} is the interaction length defined as

$$L_{\text{int}} = \frac{n_p L_{QW} N}{\cos(\theta)}, \quad (2.5)$$

where θ is the angle of incidence with respect to the normal to the plane of the layers (45° in our case), L_{QW} is the thickness of each coupled quantum well section ($L_{QW}=15 \text{ nm}$ in our case), N is the total number of sections in the multi-quantum well (MQW) sample ($N=26$ in our case), and n_p is the number of passes through the MQW layer. Given our sample geometry (4.9 mm in length and 0.36 mm in thickness), we estimate $n_p=6$.

From the data in Figure 3.2a, we obtain transition $\hbar\omega_{21} \approx 150 \text{ meV}$ and $\hbar\omega_{31} \approx 248 \text{ meV}$ in good agreement with calculated values of 150 meV and 253 meV, respectively. The measured transition linewidths are $2\hbar\gamma_{12} \approx 24.8 \text{ meV}$, $2\hbar\gamma_{13} \approx 29.2 \text{ meV}$ and the peak absorption $\alpha_w=1.01 \times 10^4 \text{ cm}^{-1}$ and $3.09 \times 10^3 \text{ cm}^{-1}$ for 1-2 transition and 1-3 transition, respectively. Given close agreement between calculated and measured transition energies and typically high accuracy of bandstructure calculations, we assume the transition dipole moments for intersubband transitions between states 1,2, and 3 in our structure are the same as simulated in Figure 3.1a. The peak values of intersubband absorption for 1-2 and 1-3 transitions then allow us to estimate the actual doping level N_e in our structure, which may be different from the nominal doping used during growth. To that end, we express α_w through the dielectric constant for out-of-plane ($\varepsilon_\perp$) E-field polarization as

$$\alpha_w = \frac{4\pi}{\lambda} \text{Im}(\sqrt{\varepsilon_\perp}), \quad (2.6)$$

where

$$\varepsilon_{\perp}(\omega) \approx \varepsilon_{core}(\omega) + \frac{N_e (ez_{12})^2}{\varepsilon_0 \hbar ((\omega_{21} - \omega) - i\gamma_{21})} + \frac{N_e (ez_{31})^2}{\varepsilon_0 \hbar ((\omega_{31} - \omega) - i\gamma_{31})}, \quad (2.7)$$

and ε_{core} is the dielectric constant of the undoped heterostructures, ω is the pump frequency, e is the electron charge, N_e is the average bulk doping density, $\hbar\omega_{ij}$, $\hbar\gamma_{ij}$ and ez_{ij} are the energy, linewidth and dipole moment, respectively, for the transition between states i and j .

Plugging the experimental values of $\hbar\omega_{ij}$ and $\hbar\gamma_{ij}$, and calculated transition dipole moments z_{ij} into the expressions above and assuming $N_e = 1.13 \times 10^{18} \text{ cm}^{-3}$ we obtain $\alpha_W \approx 1.01 \times 10^4 \text{ cm}^{-1}$ for 2-1 resonance and $\alpha_W \approx 3.09 \times 10^3 \text{ cm}^{-1}$ for 3-1 resonance, in close agreement with measurements. The value of $N_e = 1.13 \times 10^{18} \text{ cm}^{-3}$ we is used for $\chi^{(2)}$ calculations. We note that this experimentally-deduced value of N_e is a factor of 1.3 smaller than the nominal doping density.

The value of $\chi_{MQW,zzz}^{(2)}$ shown in Figure 3.1b was computed considering only the first three electron subbands as shown in Figure 3.1a using the equation [16,37,38]:

$$\begin{aligned} \chi_{MQW,zzz}^{(2)}(\omega \rightarrow 2\omega) = N_e \frac{e^3}{\varepsilon_0 \hbar} & \left\{ \frac{z_{12} z_{23} z_{31}}{(\omega_{21} - 2\omega - i\gamma_{21})(\omega_{31} - \omega - i\gamma_{31})} \right. \\ & + \frac{z_{12} z_{23} z_{31}}{(\omega_{32} - 2\omega - i\gamma_{32})(\omega_{21} + \omega + i\gamma_{21})} + \frac{z_{12} z_{23} z_{31}}{(\omega_{23} + 2\omega + i\gamma_{23})(\omega_{31} - \omega - i\gamma_{31})} \\ & + \frac{z_{12} z_{23} z_{31}}{(\omega_{31} + 2\omega + i\gamma_{31})(\omega_{21} + \omega + i\gamma_{21})} + \frac{z_{12} z_{23} z_{31}}{(\omega_{31} - 2\omega - i\gamma_{31})(\omega_{21} - \omega - i\gamma_{21})} \\ & + \frac{z_{12} z_{23} z_{31}}{(\omega_{23} - 2\omega - i\gamma_{23})(\omega_{31} + \omega + i\gamma_{31})} + \frac{z_{12} z_{23} z_{31}}{(\omega_{32} + 2\omega + i\gamma_{32})(\omega_{21} - \omega - i\gamma_{21})} \\ & \left. + \frac{z_{12} z_{23} z_{31}}{(\omega_{21} + 2\omega + i\gamma_{21})(\omega_{31} + \omega + i\gamma_{31})} + \frac{z_{31}^2 (z_{11} - z_{33})}{(\omega_{31} - \omega - i\gamma_{31})(\omega_{31} - 2\omega - i\gamma_{31})} \right\}, \quad (2.8) \end{aligned}$$

where ω is the pump frequency, e is the electron charge, N_e is the average bulk doping density of the MQW structure, z_{ij} , $\hbar\omega_{ij}$, and $\hbar\gamma_{ij}$ are the matrix element of electron z -

position, transition energy, and transition linewidth, respectively, between states i and j . For calculations, we have assumed all electron population to reside in state 1 and used the computed values of z_{21} , z_{31} , and z_{32} as shown in Figure 3.1a and $(z_{11}-z_{33})=-1.86$ nm.

The MQW dielectric constant for the in-plane E-field polarization ($\varepsilon_{\parallel}$) is calculated as

$$\varepsilon_{\parallel}(\omega) \approx \varepsilon_{core}(\omega) + i \frac{N_e e^2 \tau_D}{\varepsilon_0 \omega m^* (1 - i \omega \tau_D)}, \quad (2.9)$$

where $\tau_D \approx 10^{-13}$ s is a Drude relaxation time and we assumed free electron motion in the plane of semiconductor layers. The calculated dielectric constants of the MQW for the out-of-plane ($\varepsilon_{\perp}$) and in-plane ($\varepsilon_{\parallel}$) E-field polarization are used for computation of antenna resonances and E-field distribution in the MQW layer. A commercial Maxwell's equation solver based on the finite-integration method (CST studio) was used for computations.

3.3 METASURFACE RESONATOR DESIGN

The MQW layer is transferred onto a metal ground plane by wafer bonding/substrate removal procedure. A pattern of metal-semiconductor nanocavities is then defined in the MQW layer as shown in Figure 3.1c. Details of the processing are given in the Experimental section. The nanocavity configuration enables efficient coupling of x-polarized impinging field beam at fundamental frequency and y-polarized outgoing wave at SH frequency to z-polarized MQW intersubband transitions as discussed in the following.

Figure 3.2a shows the normalized E_z field component induced in the MQW layer for x-polarized fundamental and y-polarized SH light at normal incidence, which represents the optimal SHG polarization combination for our metasurface design. The

computed fields are normalized to the input (transverse) field amplitude, and simulations show up to 16 times local field enhancement in the MQW layer. Figure 3b confirms that the proposed antenna structure possesses strong resonances at both frequencies of interest.

The overall nonlinear response of the proposed metasurface can be obtained by computing its nonlinear susceptibility tensor $\chi_{ijk}^{(2)}$ using the expression [26]

$$\chi_{ijk}^{(2)} = \chi_{MQW,zzz}^{(2)} \left[\frac{\int_{UC} \xi_i^{2\omega}(x, y, z) \xi_j^{\omega}(x, y, z) \xi_k^{\omega}(x, y, z) dV}{V} \right], \quad (2.10)$$

where $\xi_i^{\omega}(\xi_i^{2\omega})$ is the local enhancement of the induced z -polarized E-field in the MQW structure normalized to the i-polarized incident wave ω (2ω), and the expression in square brackets is the nonlinear overlap integral between fundamental and second harmonic modes of the nanoantenna [26] with the integration going over the entire unit-cell (UC) volume. Equation (3.2) shows that maximizing value of the overlap integral is the key parameter in the nonlinear metasurface design.

In contrast to the resonators used previously [26,27], which were made by metal patterning on top of a continuous MQW layer, the resonators used in this work are open metal-semiconductor nanocavities as shown in Figure 3.1c. This solution significantly contributes to enhance the modal overlap integral, due to the large contrast between the permittivity of the MQW substrate and the air gaps, by i) improving the uniformity of the induced field distribution in the MQW regions at both fundamental and second harmonic frequencies, ii) concentrating most of the electric field within the nanocavity, and iii) enhancing the maximum local electric field. We chose nanocavities with a T-shaped geometry that allows the independent control of the fundamental (long arm along the x-axis) and second harmonic (dipole created between the short and long arm) resonances, as illustrated in Figure 3.3a. The adequate combination of all these factors allows a modal

overlap integral above 4.25, around 8 times larger than the one obtained in Ref. [26] and nearly 30 times larger than that obtained for the structures reported in Ref. [27]. Interestingly, this enhancement is realized by removing nonlinear material from the structure, to force the modal fields to be more localized within the volume directly underneath the resonator, maximizing the overlap at the two frequencies.

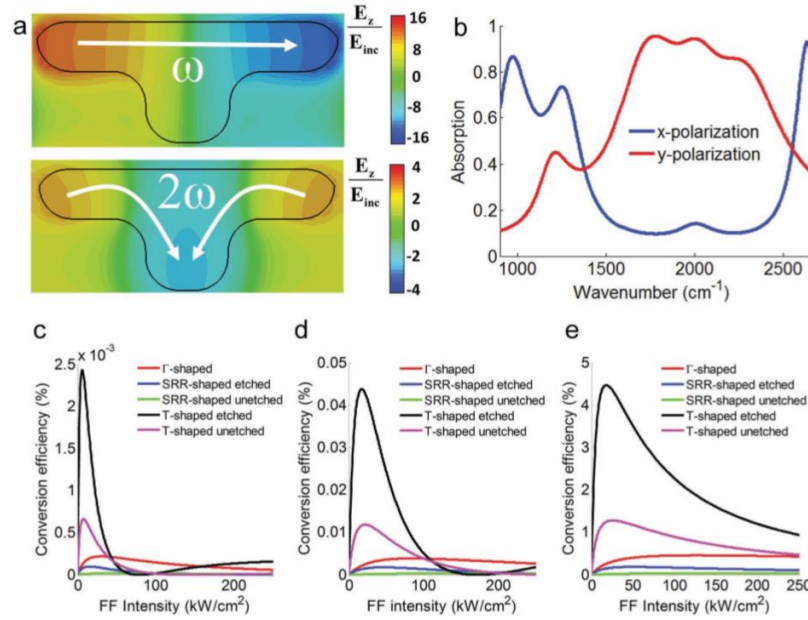


Figure 3.3: Numerical simulations of plasmonic nonlinear metasurfaces. **a**, Top view of the normalized E_z field distribution on the T-shaped resonator at the pump and second harmonic frequencies. **b**, Absorption spectrum of the proposed metasurface for different polarization of the incident light. **c–e**, Metasurface conversion efficiency for several types of resonators and MQW configurations versus pump intensity. The geometries considered are the Γ -shaped structure described in Ref. [26], the T-shaped resonator proposed here, with and without etching, the etched SRR operating in reflection described in Ref. [34] and the unetched SRR operating in transmission of Ref. [27]. The multiquantum-well configurations are described in Ref. [26] for panel **c** and in Figure 3.1 for panel **d**. Panel **e** considers a similar MQW structure as panel **d** but assumes intersubband transition linewidths of 10 meV FWHM for all transitions.

We note that because electron dynamics of intersubband transitions is determined by extremely fast (≈ 0.3 -3 ps) longitudinal optical phonon scattering, surface defects introduce virtually no change in electron scattering times. As a result, unlike interband (electron-hole) transitions, intersubband transitions are virtually unaffected by surface defects as one etches through the MQW heterostructure. This property has allowed for the fabrication of a variety of deep-etched multiquantum-well devices with sacrificing device performance. Quantum confinement due to etching is also not expected to influence intersubband transition energies, unless the transverse dimensions of the etched structures are comparable to the quantum well size (≈ 2 -3 nm). The smallest feature size of our nanoresonator is ≈ 300 nm, and such a dimension introduces a less than 1 meV shift of the electron subband energies due to the quantum confinement. Thus, the nanoresonator width fluctuation is expected to produce intersubband transition energy shifts of much less than 1 meV.

In order to further highlight the significant improvements on the MQW and nanoresonator designs achieved here, in Figures 3.3c-e we show the theoretically predicted SHG conversion efficiency as a function of pump intensity. Our simulations fully incorporate local saturation of intersubband nonlinearity following the approach described in Ref. [36]. We investigate the Γ -shaped nanostructures presented in Ref. [26] and the split-ring resonators (SRR) described in Ref. [27] and in Refs. [13,34], and we compare them to the T-shaped geometry proposed here. In order to illustrate how etching the nanoresonator enhances the response of the nonlinear metasurfaces, we consider SRR and T-shaped geometries with and without etching the MQW layer. The results are computed considering different multi-quantum well configurations: the semiconductor heterostructure described in Ref. [26] (Figure 3.3c), the MQW detailed above (Figure 3.3d) with experimentally-measured transition linewidths of approximately 25-30 meV

full-width-half-maximum (FWHM), and similar MQW structures (see Figure 3.3e) with linewidth reduced to 10 meV FWHM. We note that transition linewidths of 10 meV FWHM were reported previously in heavily-doped semiconductor heterostructures at room temperature, and even narrower linewidths were reported from heavily-doped MQW structures at cryogenic temperatures [75,76]. Our numerical simulations show that, with the current nanoresonator and MQW designs, the conversion efficiency can reach values above 2.5 %, assuming that transition linewidths of 10 meV FWHM can be achieved in our MQW structures. Further improvements are expected with more advanced nanoresonator and MQW designs.

3.4 METASURFACE MODELING

The nonlinear susceptibility tensor of the proposed plasmonic nonlinear metasurface can be described neglecting saturation effects using the overlap integral formalism outlined in the previous section as Refs. [26,36]

$$\chi_{ijk}^{(2)} = \frac{\chi_{zzz}^{(2)}}{V} \int_{UC} \frac{E_{z(i)}^{2\omega}(\mathbf{r})}{E_{inc(i)}^{2\omega}} \frac{E_{z(j)}^{\omega}(\mathbf{r})}{E_{inc(j)}^{\omega}} \frac{E_{z(k)}^{\omega}(\mathbf{r})}{E_{inc(k)}^{\omega}} dV \equiv \chi_{zzz}^{(2)} \frac{\int_{UC} \xi_i^{2\omega}(\mathbf{r}) \xi_j^{\omega}(\mathbf{r}) \xi_k^{\omega}(\mathbf{r}) dV}{V} \equiv \chi_{zzz}^{(2)} I_{ijk}^{overlap}, \quad (2.11)$$

where $I_{ijk}^{overlap}$ (with $i, j, k = \{x, y\}$) denotes the modal overlap integral that provides the enhancement of the intrinsic $\chi_{zzz}^{(2)}$ of MQW, $E_{z(i)}^{\omega}$ ($E_{z(i)}^{2\omega}$) is the z-component of the electric field induced in the MQW at frequency ω (2ω) by an i -polarized impinging field $E_{inc(i)}^{\omega}$ ($E_{inc(i)}^{2\omega}$), and ξ_i^{ω} ($\xi_i^{2\omega}$) are the local enhancement factors, defined as the ratio of the induced z-polarized E-field in the MQW to the E-field amplitude of i -polarized incident wave ω (2ω). These factors are used in Equation (3.10).

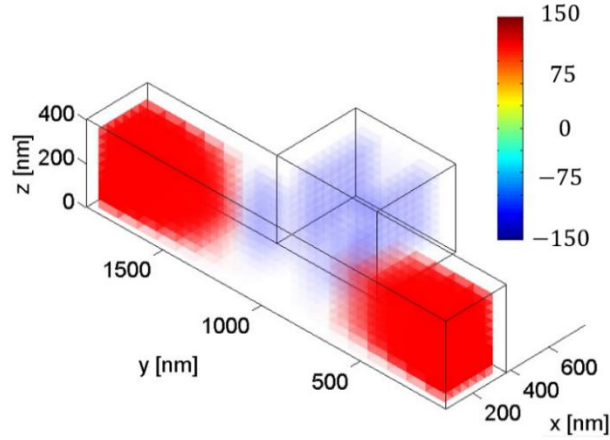


Figure 3.4: Mode overlap (real part) within the MQW of the unit-cell described in Figure 3.1c.

The position-dependent field distribution within the MQW is computed using the full-wave software CST at the frequencies of interest. Figure 3.4 shows an example of the field enhancement distribution across the unit-cell described in Figure 3.1c, where we plot the real part of the product $\xi_i^{2\omega}(\mathbf{r})\xi_j^\omega(\mathbf{r})\xi_k^\omega(\mathbf{r})$ as a function of position in the MQW.

Saturation effects are taken into account by considering the dependence of the intrinsic MQW non-linear susceptibility $\chi_{zzz}^{(2)}$ with the input intensity, which might be large enough to empty the MQW ground state thus reducing the overall efficiency of the non-linear process [36,72,74]. In this case, the metasurface effective non-linear susceptibility is

$$\chi_{ijk}^{(2)}(I^\omega) = \frac{1}{V} \int_{UC} \chi_{zzz}^{(2)}(I_z^\omega(\mathbf{r})) \frac{E_{z(i)}^{2\omega}(\mathbf{r})}{E_{inc(i)}^{2\omega}} \frac{E_{z(j)}^\omega(\mathbf{r})}{E_{inc(j)}^\omega} \frac{E_{z(k)}^\omega(\mathbf{r})}{E_{inc(k)}^\omega} \partial V, \quad (2.12)$$

where $\chi_{zzz}^{(2)}(I_z^\omega)$ becomes now position-dependent due to the different intensities that might be induced across the MQW. The intensity-dependence intrinsic MQW non-linear susceptibility is given by [72]

$$\chi_{zzz}^{(2)}(I_z^\omega) \approx S^{SHG}(I_z^\omega) N_e \frac{q_e^3 z_{12} z_{13} z_{23}}{\epsilon_0 (E - E_{12} - i\hbar\gamma_{12})(2E - E_{13} - i\hbar\gamma_{13})}, \quad (2.13)$$

where $S^{SHG}(I_z^\omega)$ denotes the saturation of the second-harmonic process. In case of low intensities induced in the MQW, the ground state is well-populated and $S^{SHG}(I_z^\omega) \approx 1$, thus simplifying the above expression to usual one in the absence of saturation [26,36]. Considering a three-level system [36,72] and taking into account that our proposed metasurface is electrically very thin, the saturation coefficient can analytically be computed as [36]

$$S^{SHG}(I_z^\omega) \approx \frac{2I_z^\omega \left[I_{S_{12}}^\omega (1 + \tau_{12}/\tau_{13}) - I_{S_{23}}^\omega (1 + \tau_{23}/\tau_{13}) \right] + 4I_{S_{12}}^\omega I_{S_{23}}^\omega (1 + \tau_{23}/\tau_{13})}{3(I_z^\omega)^2 + 2I_z^\omega \left[I_{S_{12}}^\omega (1 + \tau_{12}/\tau_{13}) + 2I_{S_{23}}^\omega (1 + \tau_{23}/\tau_{13}) \right] + 4I_{S_{12}}^\omega I_{S_{23}}^\omega (1 + \tau_{23}/\tau_{13})}, \quad (2.14)$$

where $I_{S_{ij}}^\omega$ denotes the saturation intensity between subbands i and j at frequency ω , and is given by

$$I_{S_{ij}}^\omega = \frac{N_e \hbar \omega}{2\alpha_{ij}^{(0)}(\omega) \tau_{ij}}, \quad (2.15)$$

where τ_{ij} is the relaxation time between subbands i and j , and $\alpha_{ij}^{(0)}(\omega)$ is the absorption coefficient.

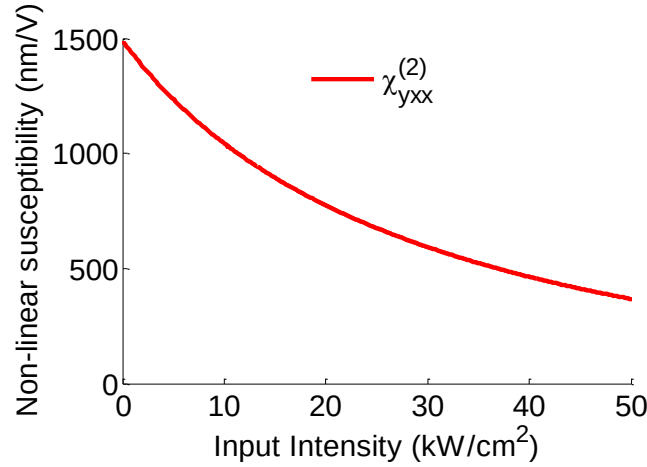


Figure 3.5: Intensity-dependent nonlinear susceptibility of the full metasurface

Figure 3.5 shows the intensity-dependent nonlinear susceptibility of the metasurface. As expected, for low input intensities, this susceptibility is around 4.25 larger than the intrinsic MQW $\chi_{zzz}^{(2)}$, due to the large field enhancement and good modal overlapping provided by our plasmonic structure. In addition, the metasurface nonlinear susceptibility presents a strong dependence with the input intensity, i.e. saturates as input intensity increases. We note that the nanoresonators used in our metasurfaces provide an extremely large field enhancement in some areas, thus producing significant saturation of MQW nonlinearity. This effect is taken into account in our computations as discussed in Ref. [36].

3.5 SHG EXPERIMENTAL RESULTS

3.5.1 Metasurface fabrication

Experimentally, we fabricated a 400 μm by 400 μm metasurface using the unit cell design shown in Figure 3.1c. The $\text{In}_{0.53}\text{Ga}_{0.47}\text{As}/\text{Al}_{0.48}\text{In}_{0.52}\text{As}$ coupled-quantum well structure for nonlinear response shown in Figure 3.1b was designed using a self-consistent Poisson-Schrodinger solver. The layer sequence (in nanometers) is

2.5/6.2/1.4/2.4/2.5 where AlInAs barriers are shown in bold, and the first 1.5 nm of the first 2.5-nm-barrier and the last 1.5 nm of the last 2.5-nm-barrier are n-doped to $6 \times 10^{18} \text{ cm}^{-3}$. A 390 nm-thick MQW layer composed of 26 repetitions of the structure in Figure 3.1a was grown by molecular beam epitaxy on a semi-insulating InP substrate. The growth started with a 300-nm-thick etch-stop layer of $\text{In}_{0.53}\text{Ga}_{0.47}\text{As}$, followed by a 100-nm-thick etch-stop layer of InP, and followed by the MQW layer. A 10-nm-thick layer of titanium, a 50-nm-thick layer of platinum, and a 200-nm-thick layer of gold were sequentially evaporated on top of the MQW layer. The wafer was then thermocompressively bonded epi-side down to a semi-insulating InP wafer coated with same metal layers. The substrate was removed via selective chemical wet-etching, followed by the removal of the etch-stop layers via selective wet-etching to expose the MQW layer. A 5-nm-thick layer of titanium and 50-nm-thick layer of gold were evaporated on top the exposed MQW layer, followed by plasma-enhanced chemical vapor deposition of a 250-nm-thick silicon nitride (SiN) hard-mask layer. Nanoresonators were then patterned on the silicon nitride layer via electron beam lithography and the patterns were etched through the silicon nitride layer and the MQW layer via inductively coupled plasma reactive ion plasma etching, followed by selective removal of the silicon nitride mask layer.

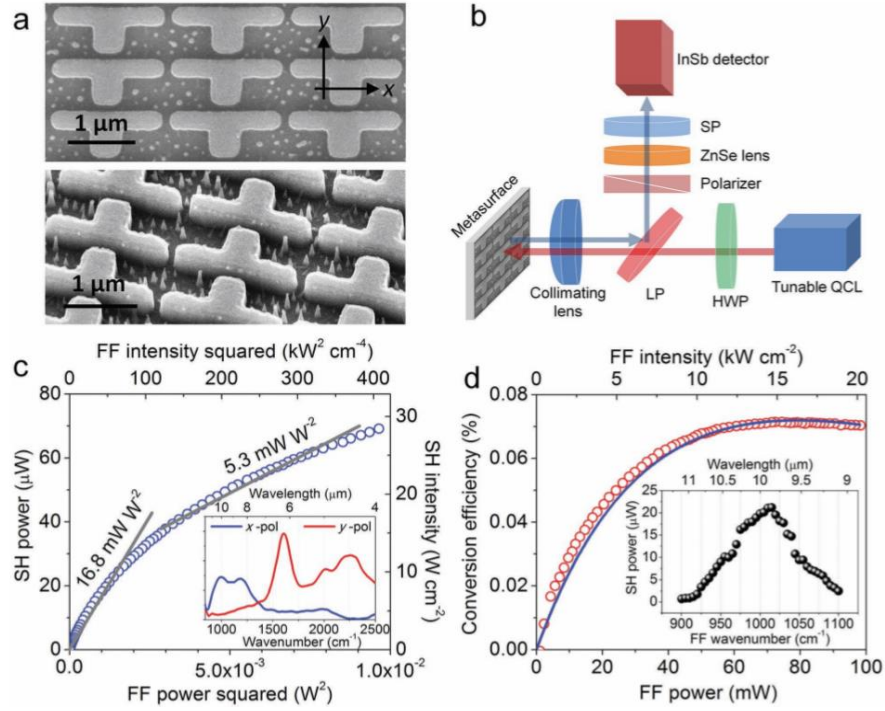


Figure 3.6: Experimental measurements of the nonlinear response from a metasurface. **a**, Scanning electron microscope images of the fabricated metasurface. Top panel represents the top view and the bottom panel is a view at 30° from the surface normal. **b**, Optical setup for metasurface characterization. **c**, SH peak power (left axis) or peak intensity (right axis) as a function of fundamental peak power squared (bottom axis) or peak intensity squared (top axis) at pump wavenumber of 1015 cm⁻¹ ($\lambda_{\omega} \approx 9.9$ μm) for yxx polarization combination. Inset: reflection-absorption spectra of metasurface for x- and y-polarized light. **d**, Experimentally measured (red circles) and theoretically calculated (blue solid line) SHG power conversion efficiency as a function of fundamental peak power (bottom axis) or peak intensity (top axis) at wavenumber of 1015 cm⁻¹ for yxx polarization combination. Inset: SH peak power as a function of pump wavenumber for yxx polarization combination. Pump peak power was fixed at 35 mW for the measurements.

3.5.2 Experimental characterization

Figure 3.6a shows the scanning electron microscope image of the processed structure. The nonlinear response was tested using the experimental setup shown in Figure 3.6b. The linear reflection absorption spectra measured for normally-incident x-

and y- polarized light are shown in the inset of Figure 3.6c. Strong absorption at fundamental and SH frequency is observed for x- and y-polarized inputs, respectively, in good agreement with theory.

Characterization of the second harmonic (SH) response from the fabricated metasurfaces with T-shape nanoresonator array was carried out in a setup shown in Figure 3.6b. We used a pulsed, broadly-tunable quantum cascade laser (QCL) (Daylight Solutions, Inc.; tuning range 900-1190 cm^{-1} and peak power output of 350 mW) tuned to 1015 cm^{-1} as the input pump source. The laser was modulated at 250 kHz, with 400 ns long pulses (duty cycle 10%). Linearly polarized light from the QCL passes through an achromatic half-wave-plate (HWP) for polarization control, a longpass filter (LP, transmission cutoff 1170 cm^{-1}) angled at 45 degrees which we have used as a beam splitter to direct the input beam onto the metasurface and to remove SH light coming from the laser, and a collimating lens (NA=0.5, $f = 5$ mm, beam spot diameter of 35 μm) to the sample. SH output is collected by the same lens and is directed by the LP towards the calibrated InSb photo-detector through a polarizer, a ZnSe lens, and a short pass filter (SP) that is used to block fundamental frequency (FF). SH power output was corrected for the transmission of the collimating lens (95%), the polarizer (75%), the ZnSe lens (97%), and the short-pass filter (91.7%) in the setup. We have assumed the LP to reflect 100% of SH light intensity. Fundamental power was measured with a calibrated thermopile detector at the sample position.

Figure 3.6c shows SHG peak power as a function of the squared fundamental peak power and peak intensity for yxx polarization combination, where the first letter refers to the polarization of the generated SH beam and the other two refer to the polarization states of the pump beams. Other polarization combinations provide much smaller SHG response, since our nanoresonators only provide strong coupling of

incident/outgoing waves to the MQW for x-polarized light at fundamental frequency and y-polarized light at SH frequency (see inset of Figure 3.3c). From Equation (3.1) one expects to observe a linear dependence of SH power on the square of the pump power in Figure 3.3c. However, the slope of the curve in Figure 3.3c changes from 16.8 mW/W² for low input powers to 5.3 mW/W² for higher pump power due to intensity saturation[26,36].

The experimentally measured SHG power conversion efficiency, defined in Equation (3.1), as a function of pump intensity, is shown in Figure 3.6d together with our theoretical predictions, assuming $\chi_{MQW,zzz}^{(2)} \approx 3.5 \times 10^5$ pm/V, 25% higher than that computed directly in Figure 3.1b. We note that this discrepancy could be due to the actual values of transition dipole moments differing slightly from those computed theoretically, or because of the transition linewidth for the 2 to 3 transition is different than assumed. Excellent agreement between experiment and theory is observed. In our numerical simulations, we have kept the theoretical modal overlapping integral and electromagnetic response of the plasmonic nanocavities, and then we have modified the intrinsic MQW nonlinearity to fit the experimental results. This allows to indirectly deduce an intrinsic MQW intersubband susceptibility of $\chi_{MQW,zzz}^{(2)} \approx 3.5 \times 10^5$ pm/V for low pump intensities, which is in good agreement with the theoretical results of Figure 3.1b given the uncertainties in fabrication and measurement processes.

The value of $\chi_{yxx}^{(2)}$ can be obtained using the data in Figure 3.6c and Equation (3.1). We obtain $\chi_{yxx}^{(2)} \approx 1.2 \times 10^6$ pm/V (0.7×10^6 pm/V) for low (high) pump intensity in Figure 3.6c. These numbers represent the largest values of second-order nonlinear susceptibility ever recorded to our knowledge in the infrared-visible range in a condensed matter system. In comparison, the nonlinear response of the best traditional nonlinear materials in infrared/visible range is in the range 1-1000 pm/V [37,38]. Such giant values

of optical nonlinearity allows us to achieve 0.075% conversion efficiency from 400 nm-thick MQW layer using pump intensity in the range 10-15 kW/cm², as shown in Figure 3.6d.

We note that a 700-nm-thick nonlinear metasurface with SHG slope efficiency of 0.45 mW/W² for low-intensity pumping of $\lambda \approx 10 \mu\text{m}$ has been reported in Ref. [27]. Using the listed pump focal spot diameter of 100 μm , we deduce the largest nonlinear element of this metasurface to be $\approx 0.3 \times 10^6$ pm/V or more than 3 times smaller than the metasurface presented in this work. The metasurface in Ref. [27] was designed using unetched split-ring resonators and operated in transmission mode. According to our calculations, this metasurface design is expected to provide lower conversion efficiency compared to the one presented in this work, assuming an identical MQW nonlinearity. We can explain the results reported in Ref. [27] by assuming that the value of the intersubband nonlinearity of the MQW heterostructure is more than one order of magnitude larger than the one used in this work. We then expect that the nanoresonators presented in this work combine with the MQW materials used in [27] may be able to produce metasurfaces with $\chi_{yxx}^{(2)} > 10^7$ pm/V, and SHG conversion efficiencies well over 1%.

The values of conversion efficiencies achieved in our structures are already sufficient for practical applications, such as optical gating or second-order autocorrelation characterization of mid-infrared pulses. In particular, our metasurfaces may be used for pulse characterization of mid-infrared quantum cascade lasers, instead of cryogenically-cooled two-photon photodetectors [77]. Due to the sub-wavelength thickness, phase matching in the direction normal to the surface of our metasurfaces is no longer important and phase matching is always automatically satisfied for wave vector components parallel to the slab for any input frequencies and incidence angles. This relaxation of the

phase matching requirements significantly simplifies the realization of many nonlinear optical experiments. Improvements in metasurface design and MQW material quality is expected to lead to even higher conversion efficiencies as discussed in Figure 3.2, which will facilitate the practical development of a flat nonlinear optics paradigm.

3.6 CONCLUSIONS

We note that the metasurfaces reported in this work can be tailored for operation anywhere in the entire mid- and far-infrared spectral range ($\lambda = 3\text{-}30\text{ }\mu\text{m}$ and $30\text{-}300\text{ }\mu\text{m}$, respectively). They may be used for a wide range of applications, such as to perform optical gating (e.g. for spectroscopic applications and light detection and ranging), to extend the spectral range of mid-infrared and THz laser sources (e.g., by frequency doubling or via sum-frequency or difference-frequency generation), to provide nonlinear medium for autocorrelation short-pulse characterization, as well as up-conversion (via sum-frequency generation) from one spectral range to another for detection and imaging.

In summary, we have demonstrated metasurfaces based on metal-MQW semiconductor nanocavities with record-large second-order nonlinear susceptibility of $1.2 \times 10^6\text{ pm/V}$. Our work demonstrates the feasibility of achieving efficient frequency mixing in optical films of sub-wavelength thickness using pumping intensity well below materials damage threshold even for continuous-wave excitation. These results open a new paradigm in nonlinear optics, based on which efficient frequency conversion may be achieved in deeply subwavelength metasurfaces with greatly relaxed phase-matching conditions and with the possibility of controlling the output wavefront at the individual nanoresonator level with deeply subwavelength resolution [13,34].

Chapter 4: Gradient Nonlinear Intersubband Polaritonic Metasurfaces²

Gradient metasurfaces have recently been demonstrated to provide control of the phase of scattered fields over subwavelength scales, enabling a broad range of linear optical components in a flat, ultrathin, integrable platform. Additionally, the development of *nonlinear metasurfaces* has disrupted conventional nonlinear optical device design by relaxing phase matching constraints, reducing size and dimensionality, and providing record values of localized nonlinear response. However, extending the ‘flat optics’ paradigm to the nonlinear case faces important challenges, since we are required to simultaneously achieve efficient frequency conversion and sub-diffractive phase control. Here, we experimentally demonstrate continuous phase control of the giant nonlinear second harmonic optical response from metasurfaces tied to intersubband transitions in semiconductor multi-quantum wells, establishing an exciting path towards realizing the vision of flat nonlinear optics.

4.1 INTRODUCTION

Gradient metasurfaces, i.e., ultrathin optical components with engineered transverse impedance gradients along the surface, have recently been demonstrated to provide control of the phase of the scattered fields over subwavelength scales, enabling a broad range of “flat” linear optical components in ultrathin, integrable platform [78–82]. More recently, optical metamaterials with tailored nonlinear response have provided new degrees of freedom in metamaterial design, with potential applications such as super-resolution imaging [60], frequency conversion with greatly relaxed phase-matching

² The results from this chapter are published in: N. Nookala, J. Lee, M. Tymchenko, J. Sebastian Gomez-Diaz, F. Demmerle, G. Boehm, K. Lai, G. Shvets, M.-C. Amann, A. Alù, and M. A. Belkin, "Ultrathin gradient nonlinear metasurface with a giant nonlinear response," *Optica* 3(3), 283–88 (2016). Nishant Nookala conducted sample fabrication, experimental characterization, data analysis, and contributed to drafting the manuscript.

conditions [83], and in all-optical switching and memories at the nanoscale [62]. It is highly desirable to extend the concept of “flat optics” [82] to the nonlinear case, leading to ultrathin nonlinear optical metasurfaces with embedded features able to full control the wavefront of the nonlinear output. This new paradigm faces important challenges, since it is required to simultaneously achieve *high conversion efficiency* and *sub-diffractive phase control* over ultrathin, deeply subwavelength, and largely uncoupled structures.

To achieve efficient frequency conversion in a nonlinear metasurface of sub-wavelength thickness, the product of the second-order nonlinear response $\chi^{(2)}$ and the pump electric field intensity E_{pump} must be $|\chi^{(2)}E_{\text{pump}}| \approx 1$. In traditional nonlinear crystals this condition is achieved when the pump field intensity is comparable with atomic fields (see, e.g., [9] p.3), which inevitably leads to materials damage. Thus, any practical flat nonlinear optical system must have nonlinear response much higher than that of traditional materials to enable $|\chi^{(2)}E_{\text{pump}}| \approx 1$ condition for pump intensities below materials damage threshold. Nonlinear metasurfaces based on plasmonic nanoresonators demonstrated previously in the infrared/visible frequencies [11,12,66,84] have second-order nonlinear elements $\chi^{(2)} \sim 1\text{-}100$ pm/V. Pump intensities ranging from 10 TW/cm² to over 100 PW/cm² are needed to achieve $|\chi^{(2)}E_{\text{pump}}| \approx 1$. Such intensities are only possible with high-power ultrafast lasers and are well above the metal damage threshold. As a result, second harmonic generation (SHG) power conversion efficiencies below 10^{-10} were achieved in these structures using femtosecond pulses with intensities ~ 0.1 GW/cm² [11,12,66,84]

Ultrathin metasurfaces based on coupling electromagnetic modes in plasmonic nanoresonators with quantum-engineered intersubband nonlinearities in multi-quantum-well (MQW) semiconductor heterostructures have been shown to exhibit very strong nonlinear responses [8,26,27]. This approach allows one to harness and enhance the

intrinsically large nonlinear susceptibility of MQW structures, $\chi_{MQW,zzz}^{(2)}$, which is polarized in the direction normal to the surface [16], to engineer ultrathin metasurfaces with giant effective nonlinear susceptibility tensor components in the metasurface plane $\chi_{ijk}^{(2)}(i, j=x \text{ or } y)$. We have recently reported deeply-subwavelength ($\sim\lambda/20$) MQW-based metasurfaces with record-high second order nonlinear susceptibility of 10^6 pm/V at $\lambda\approx 10$ μm and experimentally achieved conversion efficiencies up to 0.075% using pumping intensities of only ~ 15 kW/cm² [8,26,27], well below materials damage threshold even for continuous-wave operation. Based on a similar concept, conversion efficiencies up to 0.14% for pulse-operation and relatively high-power incident beams have been reported in parallel in Ref. [27]. These nonlinear metasurfaces may provide the foundation for the proposed flat nonlinear optics paradigm if we find an efficient way to enable continuous control of the phase of the giant nonlinear response at the individual nanoresonator level.

Towards this goal, we have recently theoretically described a generalization of the Pancharatnam-Berry (PB) phase approach to nonlinear optics [34], which enables controlling the phase of the nonlinear optical response at the individual nanoresonator level by engineering its rotation in the metasurface plane. We note that, in contrast to the formalism presented in [12], our theoretical approach does not impose any restriction on the nanoresonator shape, and it is applicable to any configuration, including non-symmetrical nanoresonators used in MQW-based metasurfaces able to maximize the nonlinear optical response. Very recently, several approaches have also been introduced to control the phase of the NL wavefront, including binary modulation of the resonators [27,64], adiabatic rotation of symmetric nanostructures [12], and modification of the aspect ratio of gold nanocavities [63]. These techniques have then been applied to demonstrate functionalities such as beam steering and focusing of the nonlinear generated beam. Even though these approaches enable full manipulation of the NL phase of the

generated beam, they do not necessarily enable a strong nonlinear response, and consequently lead to metasurfaces with small conversion efficiencies that cannot be employed in practice. Here we report the first experimental demonstration of a MQW-based PB nonlinear gradient metasurface. We *simultaneously* achieve giant second-order nonlinear optical response of over 3×10^5 pm/V and full 360° phase control of the nonlinear optical response at the individual nanoresonator level.

We operate in a circular polarization (CP) basis, transforming the metasurface susceptibility tensor elements from $\chi_{ijk}^{(2)}$ (where i, j , and k can be x or y of a Cartesian coordinate system with z -axis normal to the metasurface) into $\chi_{\alpha\beta\gamma}^{(2)}$, where α, β , and γ are R or L , corresponding to right circular polarization (RCP) or left circular polarization (LCP), respectively, of the input (the last two indices) or the output (the first index) beams normal to the surface. It can then be shown (see Supplementary Information and [34]) that, in this circular-polarization basis, the local phase of the generated SH signal in each cell is linearly proportional to the orientation angle φ of its plasmonic resonator. More specifically, assuming RCP pump beam, a varying rotation angle $\varphi(x)$ of the nanoresonator along the x direction of the metasurface results in a phase factor $\exp[-3i\varphi(x)]$ and $\exp[-i\varphi(x)]$ for the RCP and LCP components of the second harmonic output, respectively. Importantly, the magnitude of the SH response remains nearly constant for all nanoresonator rotation angles, as long as the nanoresonator geometry is not changed [9].

These features are ideal for the purpose of locally controlling the phase of the giant nonlinear response in MQW-based metasurfaces. Different from conventional PB approaches based on linear phenomena [85,86] – whose overall efficiency is largely dependent on the resonator design – here we can easily split the design of nonlinear gradient metasurfaces into two distinct steps. First, we focus on the design of optimal

MQWs and nanoresonators to provide the largest possible localized nonlinear response. Then, we rotate the optimized nanoresonator design in different unit cells to imprint the desired transverse phase pattern on the metasurface plane.

4.2 METASURFACE DESIGN

4.2.1 Heterostructure design

The semiconductor MQW heterostructure design employed in this work, and its associated second-order nonlinear optical susceptibility $\chi_{MQW,zzz}^{(2)}$, are shown in Figure 3.1a and Figure 3.1b, respectively. The heterostructure is designed to support giant nonlinear SHG at $1/\lambda \approx 1015 \text{ cm}^{-1}$ ($\lambda \approx 9.85 \text{ }\mu\text{m}$ or 125 meV photon energy) with a nonlinear response as high as $\sim 2.8 \times 10^5 \text{ pm/V}$, 3-4 orders of magnitude higher than the largest $\chi^{(2)}$ coefficient of natural optical materials[37,87]. Unlike doubly-resonant MQW designs (with $\omega_{12}=\omega_{23}$) used in MQW-based metasurfaces previously [26,27], the transition energy between states 1 and 2 in the MQW design used in this work is purposely detuned by approximately 25 meV from the pump photon energy to reduce optical losses in the nanoresonator cavity and avoid saturation of nonlinear optical responses by pump light. Saturation in MQWs occurs when the input intensity is so large that the intersubband absorption empties the quantum-well ground state, limiting the maximum achievable overall nonlinear response of the MQW system [26]. Analysis presented in [8,36] indicated that saturation of MQW nonlinearity is reduced and overall SHG efficiency may be improved by detuning transition energy between states 1 and 2 away from the pump frequency. Overall, the MQW structure employed here supports nearly 7 times higher saturation intensity, and 6 times higher $\chi_{MQW,zzz}^{(2)}$, than the MQW structure reported in [26], the latter being achieved by increasing MQW doping. The structure is identical to

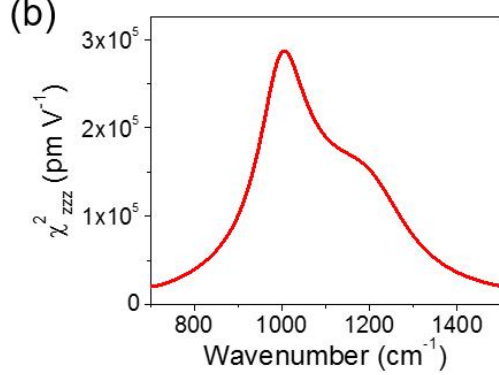


Figure 4.1: Nonlinear metasurface structure. **a**, Conduction band diagram of one period of an $\text{In}_{0.53}\text{Ga}_{0.47}\text{As}/\text{Al}_{0.48}\text{In}_{0.52}\text{As}$ quantum well structure designed for giant nonlinear SHG response. Shown are the square of electron subband wavefunctions and intersubband transition energies and dipole moments. The layer sequence in nm is **2.5/6.2/1.4/2.4/2.5** where $\text{Al}_{0.48}\text{In}_{0.52}\text{As}$ barriers are shown in bold, and the first 1.5 nm of the first 2.5-nm-barrier and the last 1.5 nm of the last 2.5-nm-barrier are n-doped to $6 \times 10^{18} \text{ cm}^{-3}$. **b**, Second-order nonlinear susceptibility for SHG in MQW structure in **a** as function of pump frequency. **c**, 1800 nm by 1800 nm unit cell of the metasurface with key dimensions given in nm.

4.2.2 Metasurface unit cell design

For the design of the metasurface unit cell, we focused on the split-ring resonator (SRR) depicted in Figure 4.1c, which offers a small spatial footprint in all dimensions

and a square unit-cell that allows arbitrary rotation. Details of the fabrication procedure of such structures are given further below. In contrast to the resonators used in previously-published MQW-based metasurfaces [26,34], which were made of metal patterning on top of a continuous MQW layer, the resonators used in this work are open metal-semiconductor nanocavities with MQW layer outside of the nanoantenna pattern etched away. Due to the large contrast between the permittivity of the MQW substrate and the air gap, this approach leads to significant enhancement of the field intensities at fundamental and second harmonic frequencies in the MQW layer, and reduction of the cross-talk between adjacent nanoresonators, as confirmed by numerical simulations. The resonator dimensions and unit cell have been optimized to provide strong absorption for x -polarized beams at the fundamental frequency and for y -polarized beams at the second harmonic frequency for a cell with $\varphi=0$, i. e. without any rotation. This enables efficient coupling of x -polarized light at fundamental frequency to z -polarized intersubband transitions in the MQW and provides efficient outcoupling of z -polarized nonlinear polarization in the MQW layer to the y -polarized beam at the second harmonic frequency [26]. The computed normalized z -polarized electric field distribution in the MQW structure 100 nm below the top metal surface in the nanoresonators is shown in Figure 3.2a for the case of excitation with x -polarized fundamental light at $1/\lambda \approx 1015 \text{ cm}^{-1}$ (left panel) and y -polarized second-harmonic light at $1/\lambda \approx 2030 \text{ cm}^{-1}$ (right panel). These wavenumbers correspond to the maximum of MQW nonlinear response as shown in Figure 3.1b. The computed fields are normalized to the input (transverse) field amplitude and simulations show up to 3 times local field enhancement in the MQW layer. Figure 3.2a confirms that the proposed structure possesses strong resonances at both frequencies of interest. The overall nonlinear response of the metasurface can be obtained by computing its nonlinear susceptibility tensor using the expression [26]

$$\chi_{ijk}^{(2)} = \chi_{MQW,zzz}^{(2)} \left[\frac{\int_{UC} \xi_i^{2\omega}(x, y, z) \xi_j^{\omega}(x, y, z) \xi_k^{\omega}(x, y, z) dV}{V} \right], \quad (4.1)$$

where ξ_i^{ω} ($\xi_i^{2\omega}$) is the local enhancement of the induced z-polarized E-field in the MQW structure normalized to the i -polarized incident wave at ω (2ω), and the expression in square brackets is the nonlinear overlap integral between fundamental and second harmonic modes of the nanoantenna with the integration going over the entire unit-cell (UC) volume. Our numerical calculations produce $\chi_{yxx}^{(2)} = 2.4 \times 10^5$ pm/V and $\chi_{xyy}^{(2)} = \chi_{yyx}^{(2)} = 0.4 \times 10^5$ pm/V with other components of the $\chi^{(2)}$ tensor of the metasurface in the Cartesian coordinate system being much lower. In the CP basis, the second-order nonlinear susceptibility tensor elements are $\chi_{RRR}^{(2)} = \chi_{LLL}^{(2)} = 1.1 \times 10^5$ pm/V and $\chi_{LRR}^{(2)} = \chi_{RLL}^{(2)} = 0.6 \times 10^5$ pm/V.

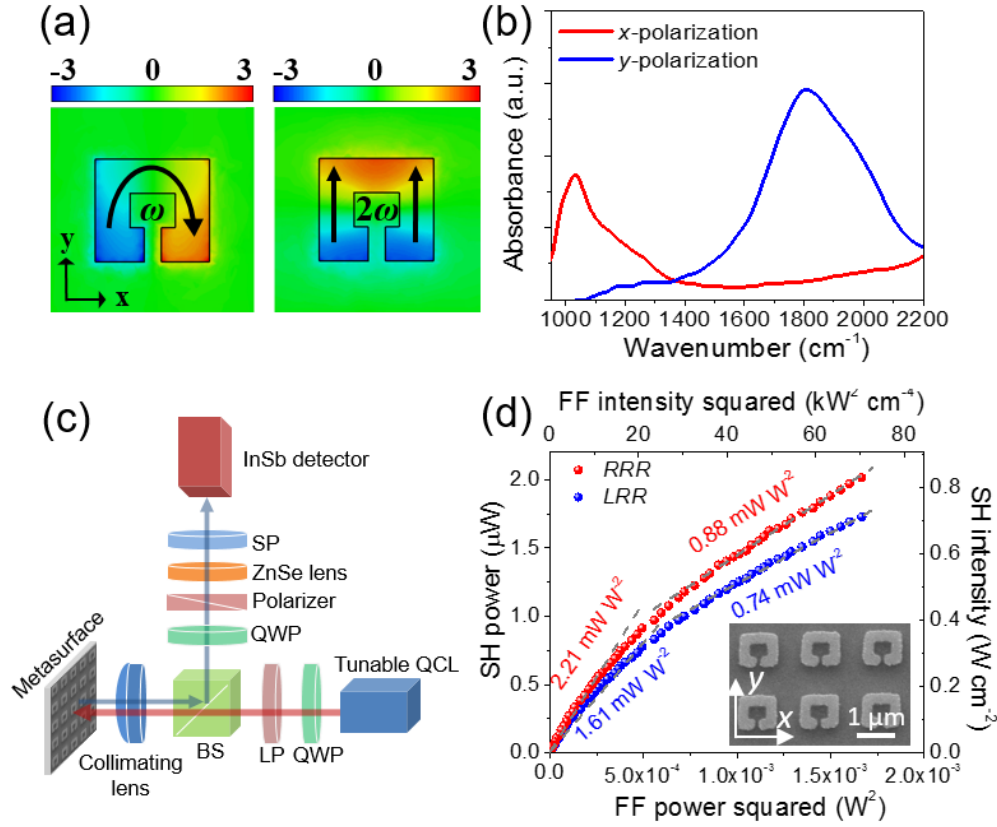


Figure 4.2: Second-harmonic response of the SRR structure. **a**, Simulated normalized E_z field distribution in MQW layer of proposed SRR structures. The SRRs are doubly resonant at the fundamental frequency (FF) and second harmonic (SH); responding to x-polarized light at the FF, and y-polarized at the SH. **b**, Experimental absorption spectrum of fabricated SRR structures, demonstrating resonance at FF and SH as described. **c**, Optical set up for second harmonic power characterization. Linearly-polarized light from a tunable QCL at wavenumber 1015 cm^{-1} passes through a quarter-wave plate (QWP) and is converted to RCP light, followed by long-pass filter (LP) to block SH from the laser, and is focused onto an array of un-rotated SRRs by a numerical aperture 0.5 collimating lens. The generated second harmonic reflects off the beam-splitter and is converted to linearly polarized light after passing through another QWP. RCP and LCP SH light is discriminated by the linear polarizer, and the resulting beam is focused onto a liquid-nitrogen cooled InSb detector after passing through a short pass filter (SP) to block out FF reflection from the pump. **d**, SH peak power (left axis) or peak intensity (right axis) as a function of FF peak power squared (bottom axis) or peak intensity squared (top axis). Inset: SEM of fabricated SRR structure.

4.3 EXPERIMENTAL CHARACTERIZATION

4.3.1 Metasurface Fabrication

To perform the initial characterization of our metasurface design, we fabricated a 300 μm by 300 μm metasurface made of the unit cells shown in Figure 4.1c with the same orientation of SRRs in all cells. A 390 nm-thick MQW layer composed of 26 repetitions of the MQW structure depicted in Figure 3.1a was grown via molecular beam epitaxy on a semi-insulating InP substrate. The growth started with a 300-nm-thick etch-stop layer of $\text{In}_{0.53}\text{Ga}_{0.47}\text{As}$, followed by a 100-nm-thick etch-stop layer of InP, and finished with the MQW layer. A 10-nm-thick layer of titanium, 50-nm-thick layer of platinum, and a 200-nm-thick layer of gold were sequentially evaporated on top of the MQW layer. The wafer was then thermo-compressively bonded epi-side down to another semi-insulating InP wafer coated with the same metal layers. The epi-side substrate of the resulting sandwiched wafer was then removed by mechanical polishing and selective chemical wet-etching, followed by the removal of the etch-stop layers via selective wet-etching to expose the MQW layer. A 5-nm-thick layer of titanium and a 50-nm-thick layer of gold were evaporated on top of the exposed MQW layer, followed by plasma enhanced chemical vapor deposition of a 250-nm-thick silicon nitride hard-mask layer. The nanoresonators with dimensions depicted in Figure 3.1c were then patterned on the silicon nitride layer via electron beam lithography and the patterns were etched through the silicon nitride and MQW layers via inductively coupled plasma reactive ion plasma etching, and finally finished by removal of the silicon nitride mask layer.

4.3.2 Linear and nonlinear optical characterization

The resulting metasurface exhibited linear absorption characteristics as shown in Figure 3.2b, with a strong resonances at $1/\lambda \approx 1050 \text{ cm}^{-1}$ for x-polarized excitation and

$1/\lambda \approx 1850 \text{ cm}^{-1}$ y-polarized SH resonance. The experimentally-measured resonance positions were close to the target values of $1/\lambda \approx 1015 \text{ cm}^{-1}$ and $1/\lambda \approx 2030 \text{ cm}^{-1}$, corresponding to the target fundamental and SHG frequencies. For the characterization we used the setup shown in Figure 3.2c, where we employed a pulsed broadly-tunable quantum cascade laser (QCL) tuned to 1015 cm^{-1} as the input pump source. The laser was modulated at 250 kHz, with 400 ns pulses (duty cycle 10%). Linearly polarized light from the QCL passes through a quarter-wave-plate (QWP) to convert into circular polarization, a long-pass filter to filter out SH signal from the QCL, a non-polarizing achromatic 50/50 beam splitter (BS) angled at 45 degrees, and a collimating lens with a focal spot diameter of $35 \text{ }\mu\text{m}$ to the sample. The SHG beam from the metasurface traces the incident FF beam path backwards to the beam splitter and is reflected towards the InSb detector, passing through a quarter-wave-plate (QWP) designed for the second harmonic frequency and a linear polarizer to filter out LCP or RCP components of SH beam. The beam is then focused by a ZnSe lens onto a calibrated InSb detector. A short-pass filter (SP) in front of the InSb detector filters out any FF component in the reflected beam. Fundamental power was measured at the sample position and the SHG power output was corrected for the beam splitter reflectivity (53.5%) and the transmission of the collimating lens (95%), the quarter-waveplate (95%), the polarizer (75%), the ZnSe lens (97%), and the short-pass filter (91.7%) in the setup.

The SHG peak power (left axis) as a function of the pump peak power squared (bottom axis) and the pump peak intensity squared (top axis) for the SRR metasurface with no rotation is plotted in Figure 3.2d for RRR and LRR polarization combinations, from which effective nonlinear susceptibilities of $|\chi_{RRR}^{(2)\text{eff}}| = 4.2 \times 10^5 \text{ pm/V}$ ($3.1 \times 10^5 \text{ pm/V}$) and $|\chi_{LRR}^{(2)\text{eff}}| = 3.6 \times 10^5 \text{ pm/V}$ ($2.9 \times 10^5 \text{ pm/V}$) for low (high) pump intensity are obtained, with the dependence on intensity due to intensity saturation in the MQW [26,36]. The

values of the nonlinear susceptibility elements are nearly 10 times higher than that reported in [26] and approximately three orders of magnitude higher than that of traditional nonlinear crystals [37,87] and nonlinear metasurfaces based on plasmonic resonators used in the infrared/visible spectrum exhibit values in the range of 1-300 pm/V [12,37,61,84]. Further, these values exceed the intrinsic $\chi_{MQW,zzz}^{(2)}$ of the MQW layer, demonstrating the role that the FF and SH modal overlap play in the design of optimal nanoresonators.

4.4 GRADIENT NONLINEAR METASURFACE CHARACTERIZATION

4.4.1 Analytical model of spatial phase modulation

The SH response of the proposed nonlinear metasurface can be described using the effective local nonlinear susceptibility tensor $\chi_{eff,ijk}^{(2)}$, and neglecting saturation effects, as [26]

$$\begin{aligned}\chi_{ijk}^{(2)} &= \frac{\chi_{MQW,zzz}^{(2)}}{V} \int_{UC} \frac{E_{z(i)}^{2\omega}(\mathbf{r})}{E_{inc(i)}^{2\omega}} \frac{E_{z(j)}^{\omega}(\mathbf{r})}{E_{inc(j)}^{\omega}} \frac{E_{z(k)}^{\omega}(\mathbf{r})}{E_{inc(k)}^{\omega}} dV \\ &= \chi_{MQW,zzz}^{(2)} \frac{\int_{UC} \xi_i^{2\omega}(\mathbf{r}) \xi_j^{\omega}(\mathbf{r}) \xi_k^{\omega}(\mathbf{r}) dV}{V} \\ &\equiv \chi_{MQW,zzz}^{(2)} I_{ijk}^{overlap},\end{aligned}\tag{4.2}$$

where $I_{ijk}^{overlap}$ (with $i, j, k = \{x, y\}$) denotes the modal overlap integral that provides the enhancement of the intrinsic $\chi_{MQW,zzz}^{(2)}$ of MQW, $E_{z(i)}^{\omega}$ ($E_{z(i)}^{2\omega}$) is the z-component of the electric field induced in the MQW at frequency ω (2ω) by an i -polarized impinging field $E_{inc(i)}^{\omega}$ ($E_{inc(i)}^{2\omega}$), and ξ_i^{ω} ($\xi_i^{2\omega}$) are the local enhancement factors, defined as the ratio of the induced z-polarized E-field in the MQW to the E-field amplitude of i -polarized incident wave ω (2ω). This expression relates the average nonlinear polarization density in the metasurface to the impinging pump wave. Note that the overlap integral in Equation 4.2

between the field distribution at fundamental and second harmonic frequency automatically accounts for the presence of any type of symmetry in unit cells. If the metasurface consists of identical unit cells, then under normal illumination by a plane wave the radiated field will be also a plane wave propagating normally away from the metasurface.

Let us consider now the scenario in which neighboring cells are weakly coupled, so that the effective local nonlinear susceptibility tensor $\chi_{ijk}^{(2)}$ in each of them is nearly independent from its neighbors. If the cells contain polarization-sensitive elements, like plasmonic resonators responding to particular field polarizations, then the nonlinear response will depend on their orientation. If we rotate all the elements in the metasurface by an angle φ around the z -axis (see Figure 3.3), the new effective nonlinear susceptibility of the metasurface $\chi_{ijk}^{(2)}(\varphi)$ will be equal to

$$\chi_{ijk}^{(2)}(\varphi) = \sum_{i'j'k'} R_{ii'}(\varphi) \chi_{i'j'k'}^{(2)} R_{jj'}(-\varphi) R_{kk'}(-\varphi), \quad (4.3)$$

where $\chi_{i'j'k'}^{(2)} \equiv \chi_{i'j'k'}^{(2)}(\varphi=0)$ is the susceptibility tensor of a non-rotated cell, and $R_{ij}(\varphi)$ is a standard rotation matrix

$$R_{ij}(\varphi) = \begin{pmatrix} \cos \varphi & -\sin \varphi \\ \sin \varphi & \cos \varphi \end{pmatrix}. \quad (4.4)$$

We note that such metasurface with all rotated elements is still radiating normally. From Equations 4.3 and 4.4 it is seen that in the $\{x, y\}$ basis the dependence of tensor components on the elements' orientation φ is rather complicated. Let us rewrite Equations 4.3 and 4.4 in a circular polarization (CP) basis $\{R, L\}$ associated with right-hand and left-hand circularly polarized waves (RCP and LCP, respectively). For the rotation matrix we have

$$\begin{aligned}
R_{\alpha\beta}^{\pm} &= \sum_{ij} [\Lambda^{\pm}]_{\alpha i} R_{ij} [(\Lambda^{\pm})^{-1}]_{j\beta} \\
&= \begin{pmatrix} \exp(\mp i\varphi) & 0 \\ 0 & \exp(\pm i\varphi) \end{pmatrix}.
\end{aligned} \tag{4.5}$$

where $\alpha, \beta = \{R, L\}$, and $\Lambda^{\pm}$ is a transformation matrix for CP waves propagating in $\pm z$ direction,

$$\Lambda_{\alpha i}^{\pm} = \frac{1}{\sqrt{2}} \begin{bmatrix} 1 & \mp i \\ 1 & \pm i \end{bmatrix}. \tag{4.6}$$

For the susceptibility tensor we have

$$\chi_{\alpha\beta\gamma}^{(2)}(\varphi) = \sum_{\alpha' \beta' \gamma'} R_{\alpha\alpha'}^+(\varphi) \chi_{\alpha'\beta'\gamma'}^{(2)} R_{\beta'\beta}^-(\varphi) R_{\gamma'\gamma}^-(\varphi). \tag{4.7}$$

with $\alpha, \beta, \gamma = \{R, L\}$, and

$$\begin{aligned}
\chi_{\alpha'\beta'\gamma'}^{(2)} &\equiv \chi_{\alpha\beta\gamma}^{(2)}(\varphi = 0) \\
&= \sum_{ijk} [\Lambda^+]_{\alpha i} \chi_{ijk}^{(2)} [(\Lambda^-)^{-1}]_{j\beta} [(\Lambda^-)^{-1}]_{k\gamma}.
\end{aligned} \tag{4.8}$$

In Equations 4.7 and 4.8 we take into account that the pump and second harmonic waves propagate along $-z$ and $+z$ directions, respectively. Substituting Equation 4.5 into 4.7 and using the fact that $R_{\alpha\beta}^{\pm}$ is diagonal, we obtain

$$\chi_{\alpha\beta\gamma}^{(2)}(\varphi) = R_{\alpha\alpha}^+(\varphi) \chi_{\alpha\beta\gamma}^{(2)} R_{\beta\beta}^-(\varphi) R_{\gamma\gamma}^-(\varphi) \tag{4.9}$$

In particular, it is easy to show that

$$\begin{aligned}
\chi_{RRR}^{(2)}(\varphi) &= \chi_{RRR}^{(2)} \exp(-i3\varphi), \\
\chi_{LRR}^{(2)}(\varphi) &= \chi_{LRR}^{(2)} \exp(-i\varphi), \\
\chi_{RLL}^{(2)}(\varphi) &= \chi_{RLL}^{(2)} \exp(+i\varphi), \\
\chi_{LLL}^{(2)}(\varphi) &= \chi_{LLL}^{(2)} \exp(+3i\varphi),
\end{aligned} \tag{4.10}$$

which are the expressions employed in the following section. From Equation 4.10 it is evident that under CP normal illumination of the metasurface with all elements rotated by an angle φ , the RCP and LCP components of the second harmonic signal will acquire different phase shift. We want to emphasize that Equations 4.10 were derived for SHG in

the “reflection” regime. Similar expressions can be easily obtained for a SHG metasurface operating in transmission. With the use of Equation 4.10, we can now design a metasurface able to tailor the SH RCP or LCP wave phase profile at will. If the unit cells are subwavelength and their orientations change adiabatically from element to element as $\varphi(x, y)$, the spatial variation of the local effective nonlinear susceptibility tensor will be

$$\begin{aligned}\chi_{RRR}^{(2)}(x, y) &= \chi_{RRR}^{(2)} \exp[-i3\varphi(x, y)], \\ \chi_{LRR}^{(2)}(x, y) &= \chi_{LRR}^{(2)} \exp[-i\varphi(x, y)], \\ \chi_{RLL}^{(2)}(x, y) &= \chi_{RLL}^{(2)} \exp[+i\varphi(x, y)], \\ \chi_{LLL}^{(2)}(x, y) &= \chi_{LLL}^{(2)} \exp[+3i\varphi(x, y)].\end{aligned}\tag{4.11}$$

When the resonators are spatially arranged as shown in Figure 4.3, with an angular rotation step of $\Delta\varphi$ between resonators of adjacent unit cells along one direction, the metasurface provides a nonlinear response with a linear phase gradient along the same direction. Then, from basic reflectarray theory [34,78–82] it is easy to show that a normally incident RCP beam generates two SH beams: one RCP polarized towards the direction $\theta_{R(R)} = \arcsin[(3\Delta\varphi/360^\circ)\lambda_{2\omega}/d]$ and another one LCP polarized towards $\theta_{L(R)} = \arcsin[(\Delta\varphi/360^\circ)\lambda_{2\omega}/d]$, where $\lambda_{2\omega}$ is the SH wavelength, and d is the width of one unit cell.

4.4.2 Experimental demonstration of SH beam-steering

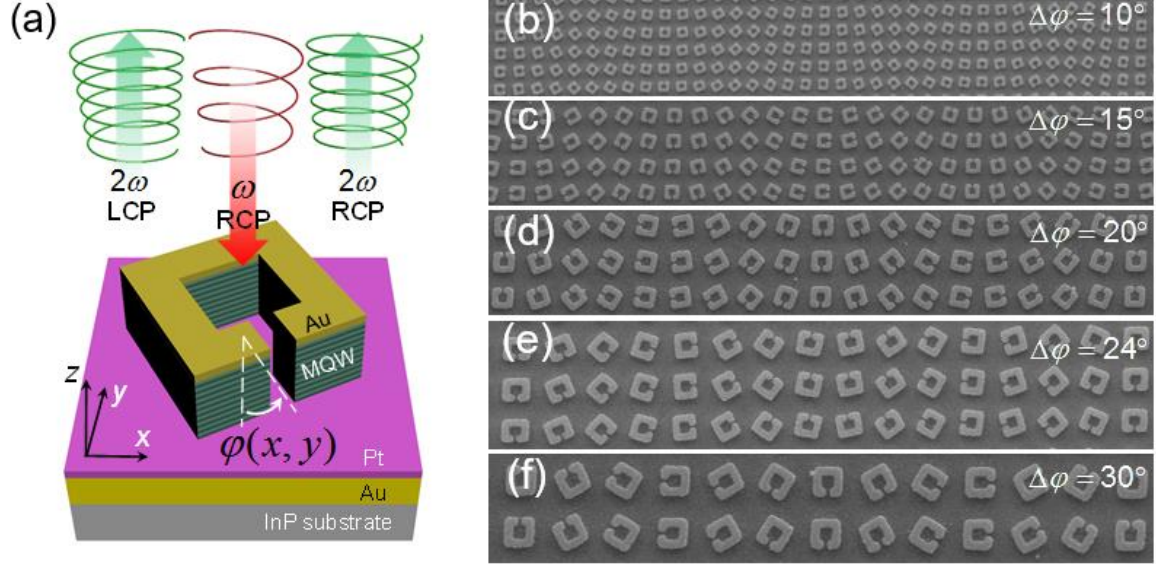


Figure 4.3: Phase gradient nonlinear metasurface. (a) Schematic of metasurface unit cell, with cartoon depiction of RCP incident FF light converting to RCP and LCP SH beams. (b)-(f) SEMs of fabricated gradient SRR arrays, with differing angular rotational step. 5 samples with angular steps $\Delta\phi$ of 10, 15, 20, 24, and 30 degrees were fabricated and tested.

To demonstrate SH beam steering, we fabricated metasurfaces with $\Delta\phi$ of 10, 15, 20, 24, and 30 degrees following the same procedure outlined for the non-rotated sample. Scanning electron microscope images of the fabricated linear phase-gradient nonlinear metasurfaces are shown in Figure 4b-f. Following the previous formulation, under RCP incidence, we expect to observe RCP (LCP) SH output at 13.3, 20.2, 27.4, 33.5, and 43.7 (4.4, 6.6, 8.8, 10.6, and 13.3) degrees for $\Delta\phi$ of 10, 15, 20, 24, and 30 degrees, respectively.

For the far-field measurements, we used a continuous-wave CO₂ laser operating at 9.83 μm to illuminate our PB metasurface samples. The beam was directed through a quarter-wave plate (QWP) to convert to RCP light, chopped at 400 Hz (duty cycle of 50%), and focused onto our sample by a ZnSe lens ($f = 6$ inch, beam spot diameter of 100

μm). The average power at the sample position was measured with a thermopile detector to be approximately 500 mW. Additionally, the QWP was measured to have a retardation of 0.25λ at a wavelength of $8\ \mu\text{m}$, and approximately 0.21λ at the operating wavelength $9.83\ \mu\text{m}$. We observed that this imperfect retardation introduces both RCP and LCP components into the incident pump, distorting the CP light into elliptical polarization, and further caused spurious SH signals to be generated at both positive and negative angles with respect to normal. Therefore, to achieve proper, single-direction beam steering, we had to verify our FF pump was purely RCP. We accomplished this by noting that the optical path length for either s and p polarizations incident on the QWP changes with the introduction of tilt along the fast or slow axis of the QWP, thereby affecting the overall retardation offered by the element. By tilting the QWP by approximately 5 degrees along the fast axis, we were able to significantly reduce the ellipticity of the incident FF pump, from 1.5 to 1.1, where the ellipticity is defined as the ratio of power along the major to minor axes of the elliptical beam (for purely RCP or LCP light, the ellipticity is 1).

Slightly different optical setups were used to measure far-field of SHG output for angles greater and smaller than ~ 15 degrees, due to constraints imposed by the size of our optical components and the numerical aperture of our focusing lens. For angles greater than 15 degrees, the setup depicted in Figure 4.4a was used. Generated SH light from the metasurface passes through a shortpass filter (SP) to remove any reflected FF light, and RCP/LCP light is then discriminated via a combination of a QWP and linear polarizer, and is finally incident on a liquid-nitrogen cooled InSb detector. For angles smaller than 15 degrees (setup depicted in Figure 4.4b we employed a beam splitter angled at 45 degrees in front of the chopper, to reflect the collimated SHG signal onto the same polarization control optics and InSb detector as in the large angle setup. Angular resolution in this configuration was achieved by noting that SHG away from the surface

normal to the sample produces a lateral shift of the SH beam at the detector position. The shift is given as $f \tan \theta$, where f is the focal length of the lens (6 inch) and θ is the angle of SHG generation with respect to normal. Thus, by scanning the detector in the direction transverse to the beam path, one can resolve the far-field profile of SHG emission for small angles. The measured results, shown in Figure 4.4c for *RRR* polarization combination and Figure 4.4d for *LRR*, are in excellent agreement with our predictions, fully confirming the accurate phase control of the generated SH beam with subwavelength resolution. Small peaks appearing in our measurements are explained by the fact that the QWP that we use in the experiment, in fact, does not provide perfect circular polarization at 1015 cm^{-1} . As a result, for example, the incident “RCP wave” is not purely right-circularly polarized, meaning there is also a LCP pump component, for which the same metasurface steers the SH radiation in other directions. The same effect applies to the analyzer system in the detection setup; that is, when the analyzer is set to transmit only right-circularly polarized SHG light, there is a small LCP SHG component that can reach the detector.

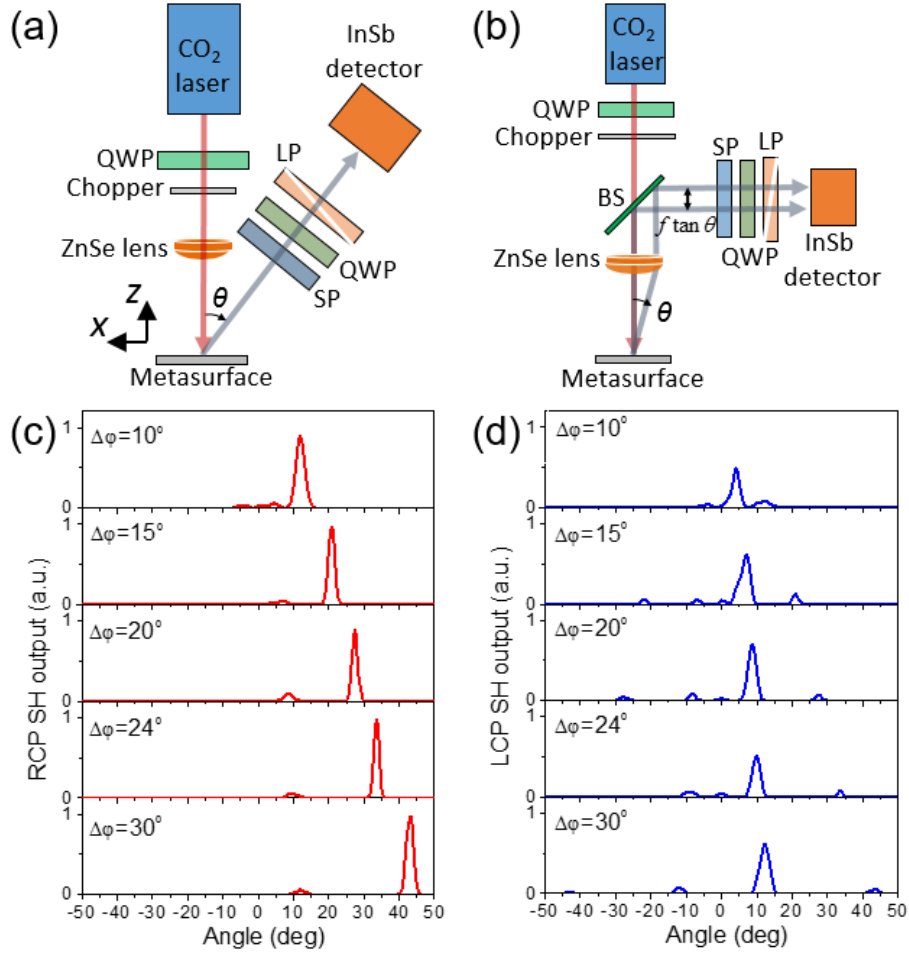


Figure 4.4: Phase-gradient nonlinear metasurface characterization. (a) Optical setup for large angle nonlinear beam steering measurement. Linearly polarized light from a continuous-wave CO₂ laser at 1015 cm⁻¹ passes through a quarter-wave-plate (QWP) to convert to RCP light, followed by a mechanical chopper, and then a ZnSe lens with 6-inch focal length to focus on the sample. The SH beam is generated towards an angle θ , and passes through a short pass filter (SP) to remove FF light and through a QWP/linear polarizer (LP) to select the LCP or RCP components. The signal is finally detected by an InSb photodetector with approximately 900 $\mu\text{m} \times 900 \mu\text{m}$ sensor size positioned 30 cm away from the sample. (b) Optical setup for small angle NL beam steering measurement. The setup is largely the same as (a), save for the inclusion of a beamsplitter to reflect collimated SH light to the polarization control optics and InSb detector. Angular resolution is determined via detection in the plane transverse to beam direction. (c) Far field profiles of RCP SH output from phase-gradient metasurfaces with $\Delta\phi$ of 10, 15, 20, 24, and 30 degrees. (d) Same as (c), but for LCP SH output.

4.5 CONCLUSIONS

In summary, we have experimentally demonstrated the generalization of the gradient linear metasurface paradigm introduced in [82] to the nonlinear domain, theoretically envisioned in [34], by merging optical metasurfaces with giant nonlinear optical response and the generalized Pancharatnam-Berry phase approach. Our results indicate that we can achieve full control over the phase of the giant nonlinear signal at the individual nanoresonator level. This allows one to attain continuous SHG beam steering, as well as arbitrary patterning of the SHG output wavefront with subwavelength resolution. Future improvements of this approach, both at the MQW and resonator design levels, will lead to highly-efficient nonlinear metasurfaces[8,36] able to manipulate the generated wavefront at will, unveiling a practical and exciting approach to flat nonlinear optics.

Chapter 5: Intersubband Polaritonic Metasurfaces with an Incomplete-metal Backplane³

In this chapter, we report the design and operation of a nonlinear intersubband polaritonic metasurface for mid-infrared second harmonic generation. The metasurface is made of metallic nanoresonators filled with a multiple-quantum-well semiconductor heterostructure. Unlike the designs reported in prior chapters that employ full metal backplanes below the etched metal-semiconductor nanoresonators, the metasurface reported here employs an incomplete backplane that is complementary to the pattern of the top metallization of the etched semiconductor heterostructure nanoresonators. The new approach produces high electric field localization and enhancement in the nanoresonators, while requiring simplified fabrication and allowing for operation in both transmission and reflection regimes.

5.1 INTRODUCTION

Recent interest in enhancing optical nonlinearities has unveiled a host of promising engineered designs beyond conventionally-used bulk crystals, including novel waveguiding schemes [51,88], micro-cavity-based approaches [89], and metallic nano-antenna arrays [90]. In particular, metasurface-based flat optical components have been put forward to achieve a variety of exotic linear and nonlinear effects, potentially replacing bulky three-dimensional analogues with more compact and versatile two-dimensional equivalents with sub-wavelength thickness [8,13,26,82,91]. The field of nonlinear optics, can benefit greatly from the introduction of sub-wavelength thickness nonlinear metasurfaces to provide efficient nonlinear frequency mixing without the

³ The results from this chapter are published in: N. Nookala, J. Xu, O. Wolf, S. March, R. Sarma, S. Bank, J. Klem, I. Brener, and M. A. Belkin, "Mid-infrared second-harmonic generation in ultra-thin plasmonic metasurfaces without a full-metal backplane," *Appl. Phys. B* (2018). Nishant Nookala conducted sample fabrication, experimental characterization, data analysis, and contributed to drafting the manuscript.

phase-matching constraints of bulk nonlinear crystals [37] and with the ability to control the phase front of the output beam [12,13,27,61].

To achieve efficient frequency mixing in films of sub-wavelength thickness using pumping intensities below the materials' damage thresholds, metasurfaces need to have nonlinear susceptibility several orders of magnitude larger than that of natural nonlinear crystals [8]. Nonlinear intersubband polaritonic metasurfaces [8,26,27] currently provide the largest second-order nonlinear response of all metasurfaces demonstrated so far. They consist of plasmonic nanoresonators filled with multiple-quantum well (MQW) semiconductor heterostructures designed to possess giant nonlinear response associated with intersubband transitions, as shown in an example in Figure 5.1. Nonlinear intersubband polaritonic metasurfaces can be designed for operation anywhere in the mid-infrared (mid-IR) spectral range (3-30 μm wavelength) [8,27,28] as well as at near-infrared wavelengths [28] and can achieve continuous phase control over the nonlinearly generated beams [13,27,34], presenting an effective case for the platform to pioneer a path towards the realization of efficient, flat nonlinear optical elements.

Recently, we reported a nonlinear polaritonic metasurface that exhibits what we believe to be the largest value for second-order nonlinear susceptibility for second harmonic generation (SHG) in the mid-IR spectral range of 1.2×10^6 pm/V [8], which is 3-6 orders of magnitude larger than that of traditional nonlinear optical crystals [37,87] as well as nonlinear metasurfaces reported earlier [12,61,66,84]. We experimentally demonstrated SHG power conversion efficiency of 0.075% with this metasurface, which was only $\lambda/25$ in thickness, at a pump wavelength of 10 μm [8].

These metasurfaces were based on an array of metal-MQW-metal nanoresonators, shown in Figure 5.1a. The metallic resonators are designed to resonantly couple the x-polarized fundamental-frequency (FF) wave from free-space and produce a strong z-

polarized electric field component normal to the surface at the metal-MQW nanocavity as shown in Figure 5.2. Z-polarized electric field at the pump frequency couples to the intersubband transitions in the MQW and produces a z-polarized nonlinear polarization oscillating at the second-harmonic (SH) frequency. The polarization couples to the second-harmonic nanocavity resonance shown in Figure 5.2 and radiates y-polarized radiation to free space. This approach allows for the efficient coupling of the optical fields of the incoming and outgoing waves normal to the metasurface with z-polarized intersubband transitions in the MQW heterostructure and further enhances the already large nonlinear susceptibility of the MQW [8,26].

A metal backplane underneath the MQW resonators was the key element of the metasurface design in Ref. [4] that allowed us to produce high and uniform field enhancement in the MQW layers that resulted in the record metasurface performance. The MQW layer was transferred onto a layer of metal using wafer bonding and subsequent selective substrate removal [8,26,36]. However, this approach has several drawbacks. First, it results in a considerable fabrication complexity. Secondly, it cannot be applied to all materials systems; in particular, it would be extremely challenging to apply this fabrication method to create nonlinear metasurfaces based on GaN/AlGaIn heterostructures [28] grown on sapphire substrates. The GaN/AlGaIn materials system offers very high conduction band offsets and may enable the extension of the operation range of the nonlinear intersubband polaritonic metasurfaces to the near-infrared regime ($\lambda \approx 0.7\text{-}3\text{ }\mu\text{m}$) [28,92,93]. Finally, the metal ground plane prevents operation of the nonlinear polaritonic metasurfaces in transmission mode, which is preferable for many experimental implementations. We note that nonlinear polaritonic metasurfaces made of nanoresonators without ground planes were also reported previously [27]; however, the

lack of the ground plane leads to smaller FF and SH field enhancements, which result in a weaker nonlinear metasurface response as discussed further below.

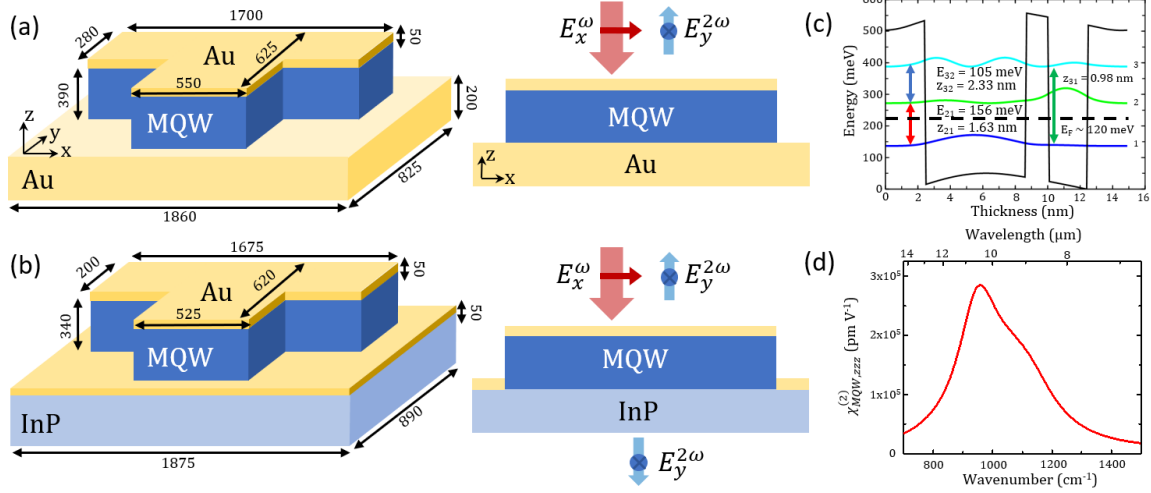


Figure 5.1: **a**, Graphic perspective (l) and side (r) views of one unit cell of a second harmonic generating metasurface with a full-metal backplane; dimensions given in nm. **b**, Same as **a**, but showing the unit cell of our proposed “incomplete-metal backplane” nonlinear metasurface. **c**, Conduction band diagram of one period of an In_{0.53}Ga_{0.47}As/Al_{0.48}In_{0.52}As coupled quantum well structure designed for giant second harmonic nonlinear response. Shown are the electron energy levels and the square of electron states wavefunctions, measured energy transitions, and calculated transition dipole moments, z_{ij} , between states i and j . Also shown is the room-temperature Fermi energy (E_F). Details of the structure are given in the main text. **d**, Calculated intersubband second-order nonlinear susceptibility for the structure in **c** as a function of pump frequency.

Here we report a SHG metasurface fabricated using an “incomplete-metal-backplane” process that is readily amenable to GaN/AlGaN heterostructures, and can operate both in transmission and reflection modes. Graphic perspectives and side-views of the full-metal-backplane [8] and the incomplete-metal-backplane structures are presented in Figure 5.1a and 5.1b, respectively. The fabrication procedure of the incomplete-metal backplane design is vastly simplified when compared to the full-metal

backplane design, with the epitaxially grown MQW wafer being first patterned and etched via electron beam lithography and a reactive-ion etch process (using a SiNx dielectric hard mask), before a gold layer is unidirectionally evaporated on the tops of the individual resonators as well as in the gaps in between adjacent unit cells. This approach preserves the index-guided mode confinement (and thus, field enhancement) offered by etched resonator volumes, while the metal deposited adjacent to the base of the resonators presents an effective approximation to a full-metal backplane, resulting in a uniform field distribution and high field enhancement in the nanoresonator.

5.2 METASURFACE DESIGN

To evaluate the efficiency of this novel incomplete-metal backplane approach, we designed, fabricated, and tested two metasurface samples following the outlined full- and incomplete-metal-backplane strategies, using the same MQW heterostructure for both methods. The bandstructure of a single period of the MQW heterostructure showing relevant electron subbands is presented in Figure 5.1c. It was designed to provide strong SH response at a pump wavelength of 10 μm (roughly 124 meV photon energy), and is similar to one reported in our prior work [8]. Unlike a doubly-resonant design (where $E_{12} = E_{23} = E_{13} / 2$), the 1-2 transition is purposefully detuned by approximately 25 meV from the FF energy to avoid the excessive optical losses at pump frequency and to delay the onset of intensity saturation of the nonlinear optical response [8,36]. The 1-3 transition stays in resonance with the SH frequency to maintain large nonlinear optical response. The resulting design consists of 26 periods of an $\text{In}_{0.53}\text{Ga}_{0.47}\text{As}/\text{Al}_{0.52}\text{In}_{0.48}\text{As}$ structure with the layer sequence (in nm, and $\text{Al}_{0.52}\text{In}_{0.48}\text{As}$ barriers in bold) **2.5/6.2/1.4/2.4/2.5**, and was grown via a Molecular Beam Epitaxy (MBE) process. The first 1.5 nm of the first 2.5 nm barrier and the last 1.5 nm of the last 2.5 nm barrier are n-

doped to $7.3 \times 10^{18} \text{ cm}^{-3}$, where we increased the dopant concentration by roughly 20% compared with the structure in our previous work [8], as $\chi_{MQW,zz}^{(2)}$ is expected to scale with the average bulk doping density [37,94]. The MBE growth was carried out on a double-side polished semi-insulating InP wafer, starting with a 300 nm $\text{In}_{0.53}\text{Ga}_{0.47}\text{As}$ and 100 nm thick InP etch stop layers (included for the full-metal-backplane process), followed by the 390 nm MQW region.

The intersubband absorption spectrum of the produced MQW heterostructure was obtained in a single pass total-internal-reflection geometry, where the epi-side of the MQW wafer is sandwiched against a Ge prism, and light from a Fourier Transform Infrared (FTIR) source is directed through the prism at an angle beyond the critical angle at the Ge-MQW interface (approximately 60 degrees from normal). We can attribute any reflectance dips in the spectrum of the signal for p-polarized incident light compared with s-polarized light to intersubband absorption within the MQW layer, noting again that the selection rules for the intersubband absorption only permit light with polarization components parallel to the growth direction to be absorbed. Following this method, we obtain $E_{12} = 140 \text{ meV}$ and $E_{13} = 235 \text{ meV}$, with full-width at half maximum (FWHM) transition linewidths of 28 and 36 meV, respectively. We note a slight peak shift in the transition energies of the present structure from the identical MQW structure (20% lower doped) reported previously [8], which we attribute mostly to deviations in growth calibration at their respective times of fabrication. Considering the transition energies, dipole moments, linewidths, and carrier concentration allows us to estimate the nonlinearity, $\chi_{MQW,zz}^{(2)}$, of the MQW, which we plot in Figure 5.1d, and peaks at a pump wavelength of $10.45 \text{ }\mu\text{m}$, with $\chi_{MQW,zz}^{(2)} \approx 2.85 \times 10^5 \text{ pm} \cdot \text{V}^{-1}$.

It can be shown [26] that the relationship between the extrinsic susceptibility of the coupled polaritonic metasurface system and the intrinsic susceptibility of the MQWs

alone can be encapsulated in the following equation for SHG, derived via Lorentz Reciprocity:

$$\chi_{ijk}^{(2)} = \chi_{MQW,zzz}^{(2)} \frac{\int_{UC} \xi_i^{2\omega}(x, y, z) \xi_j^{\omega}(x, y, z) \xi_k^{\omega}(x, y, z) dV}{V}, \quad (5.1)$$

where the second order susceptibility tensor element $\chi_{ijk}^{(2)}(i, j, k = x, y, \text{ or } z)$ of the metasurface is related to the intrinsic susceptibility of the MQW, $\chi_{MQW,zzz}^{(2)}$, by a volume-averaged overlap integral of the product of the local enhancement of the induced z-polarized E-field in the MQW. Here, $\xi_j^{\omega}(\xi_i^{2\omega})$ is the local enhancement of the induced z-polarized E-field in the MQW structure normalized to the $j(i)$ -polarized incident wave $\omega(2\omega)$, and the integration occurs over the entire unit-cell of volume V . Importantly, by virtue of this electromagnetic overlap integral, the metasurface unit cell can be designed to exhibit an effective susceptibility that significantly exceeds that of the MQW alone. This overlap integral also encapsulates the symmetry and geometric considerations inherent to a nanoresonator design suited for an efficient second order nonlinear optical process. We found that etching the resonators by removing MQW volume surrounding the metal antenna serves to further confine and localize the plasmonic modes due to the index contrast of the MQW and surrounding free-space, resulting in an increased polarization response due to the stronger field enhancement, and larger nonlinear conversion efficiencies. This approach can also be exploited for individual control and decoupling of the local phase of neighboring nano-resonators, enabling continuous phase control of the nonlinearly generated beam at the individual nano-resonator level [13,34].

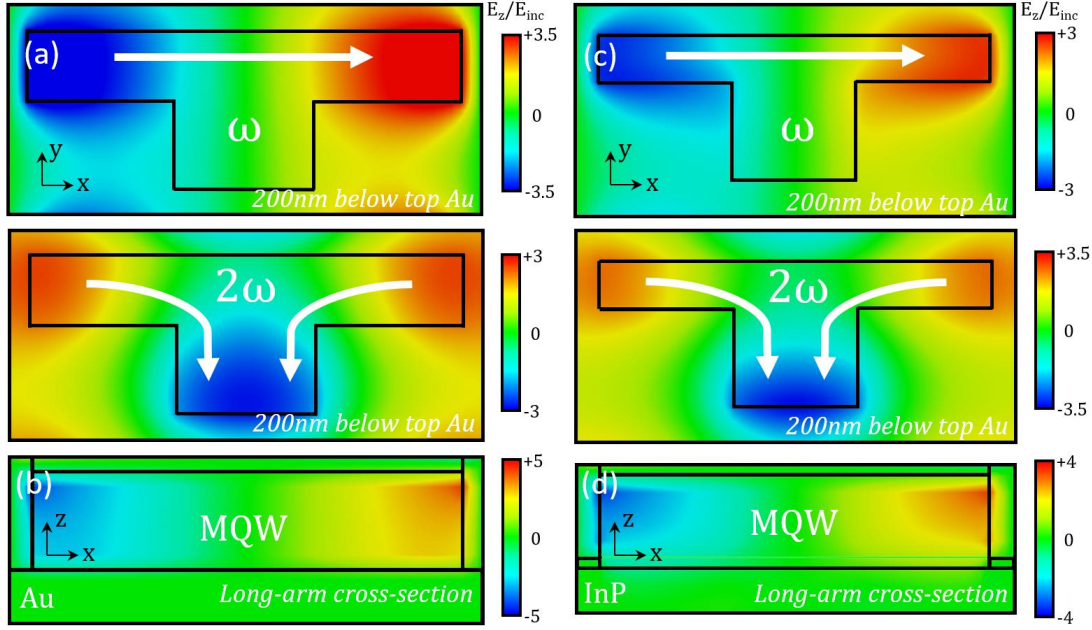


Figure 5.2: Numerical simulations of the plasmonic nonlinear metasurfaces under study. **a**, Top-down view (200 nm below the top gold) of the E_z field distribution (normalized to the field amplitude E_{inc} on the normally-incident excitation plane wave) in the etched-T full-metal-backplane geometry for pump and second harmonic frequencies. **b**, Side-view of the normalized E_z field distribution along a middle cross-section of the x-aligned arm of the T-structure. **c-e** Same as **a-b** but for the incomplete-metal backplane geometry discussed in this work.

The resonator geometries for both full-metal and incomplete-metal backplane processes were optimized using a commercially available frequency-domain Maxwell's equations solver, with the goal of maximizing the calculated overlap integral for a given unit cell geometry. Figures 5.2a and 5.2c plot the z-polarized electric field contributions on an x-y plane 200 nm beneath the top gold layer at fundamental and second harmonic wavelengths of 10.45 and 5.23 μm for the full and incomplete-metal backplane structures with dimensions given in Figures 5.1a and 5.1b. The etched T geometry supports independently-tuned cross-polarized resonances along the x-direction in the long arm at the FF, and y-direction in the short arm at the SH frequency, correlating to a strong

effective $\chi_{yxx}^{(2)}$ response. Figures 5.2b and 5.2d show the electric field enhancement in the x-z plane at a cross-section along the x-directed long arm at the FF for full- and incomplete-backplane structures. Importantly, the field enhancement factors and spatial E_z distribution are comparable in magnitude for both designs. This is especially intriguing in the case of the incomplete-backplane design as there is no metal underneath the QW, and the metal deposited to the sides of the etched MQW volumes seems to serve as an adequate substitute for a complete metal backplane. From our simulations, we calculate the volume averaged overlap integrals from Equation 4.1 to be 3.4 and 1.1 for the full-metal and incomplete-metal backplane designs, respectively, correlating to $\chi_{yxx}^{(2)} \approx 9.7 \times 10^5 \text{ pm} \cdot \text{V}^{-1}$ and $3.1 \times 10^5 \text{ pm} \cdot \text{V}^{-1}$. All the other nonlinear susceptibilities are computed to be at least an order of magnitude smaller than these two components for the two metasurfaces, respectively.

As we mentioned previously, nanoresonators without a metal ground plane results in relatively low field enhancements [27] that lead to small values of the overlap integral. We have verified this point by computing the overlap integrals for the optimized T-shaped nanoresonators fabricated on top of InP substrate without using any metal backplane (complete or incomplete). The obtained values are 0.16 and 0.1 for the etched and non-etched T-shaped resonators with top metallization only, respectively. These values are much smaller than that obtained for the structures with the metal backplanes.

Fabrication of the full-metal backplane structure was carried out as described previously, starting with a 100-nm thick gold deposition for the creation of the backplane, thermo-compressive wafer bonding to a separate InP substrate with an equivalent-thickness gold layer, and MQW substrate removal via mechanical polishing and selective wet etching. 50 nm of Au was then deposited by an electron-beam evaporation process to form the layer on top of the resonators, following which approximately 200 nm of a SiN_x

hard mask was grown by a plasma-enhanced chemical vapor deposition process. The SiN_x was then patterned by electron-beam lithography and a reactive-ion etch process into a 300 μm -by-300 μm array of resonators with dimensions given in Figure 5.1a. Finally, the metal-QW stack underneath the SiN_x was etched to form the individual QW resonator cavities by an inductively-coupled reactive-ion-etch (ICP-RIE) process, and the SiN_x was selectively removed in a wet etch step. In contrast, fabrication of the incomplete-metal backplane structure is much less complicated, with schematic depictions of each step given in Figures 5.3a-c alongside scanning electron microscope images of the sample at each step. Approximately 200 nm of SiN_x was first deposited and patterned on a bare QW wafer, followed by electron-beam lithography and definition of the resonator geometry in SiN_x (dimensions given in Figure 5.1b). An ICP-RIE process was then used to define the QW nano-cavities using SiN_x as a dielectric hard mask. Finally, the SiN_x was selectively removed, and the incomplete-metal backplane and top-gold were simultaneously created by a single 50-nm thick evaporation of Au at normal incidence. The spectral and reflectance response of the nano-resonator antennas was determined from a reflectance measurement in a FTIR microscope system for incident x- and y- polarized light and given in Figure 5.3d, where we note strong absorption resonances at the FF and SH frequencies of 955 and 1910 cm^{-1} , in agreement with our numerical simulations.

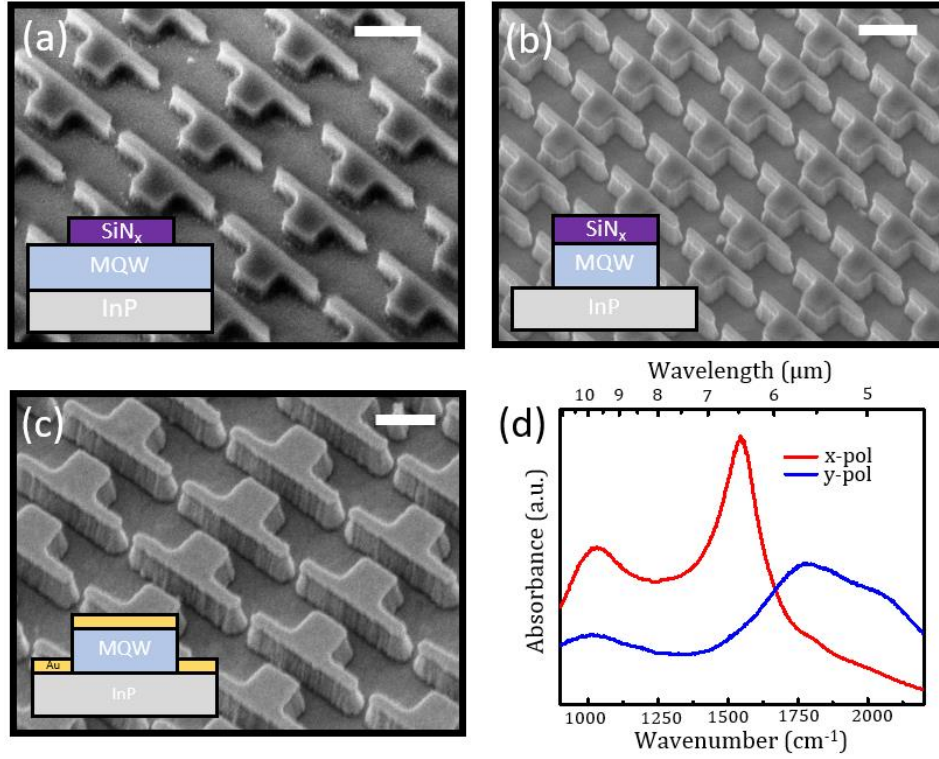


Figure 5.3: **a-c**, Perspective scanning electron microscope images (rotated in-plane by 45 degrees and tilted 30 degrees from normal) of the intermediate steps in fabrication of an incomplete-metal-backplane SHG metasurface. The inset graphic depicts a side-view of the material stack present in each step. **a**, Image of the SiNx dielectric hard mask used to etch the MQWs following an electron-beam lithography step. **b**, Image of the MQW nanoresonators capped with SiNx following an inductively-coupled-plasma etch. **c**, Image of the fabricated metasurface following removal of the SiNx hard mask and gold evaporation formation of the incomplete-metal backplane and plasmonic-cap. **d**, Linear absorption spectra for x- and y-polarized light (red and blue curves, respectively) of the fabricated incomplete-backplane metasurface.

5.3 EXPERIMENTAL CHARACTERIZATION

Neglecting the pump depletion due to frequency conversion, the SHG intensity $I_{2\omega}$ is given as [37]

$$I_{2\omega} = \frac{(2\omega)^2}{8\epsilon_0 c^3} |\chi_{yxx}^{(2)}|^2 I_{\omega}^2 d^2, \quad (5.2)$$

where $d \approx 400$ nm is the thickness of the nonlinear MQW region, 2ω is the SH frequency, I_ω is the FF field intensity, and we assumed the FF beam to be polarized along x-direction and the SH beam to be polarized along y-direction (cf. Figure 5.1 or Figure 5.2). In our analysis below we also assume a Gaussian beam intensity distribution in the FF and SH waves, with the FF beam given as

$$I_\omega(x, y) = I_\omega^0 \times \text{Exp}\left(-2 \frac{(x^2 + y^2)}{w_0^2}\right), \quad (5.3)$$

and the SH beam described as

$$I_{2\omega}(x, y) = I_{2\omega}^0 \times \text{Exp}\left(-4 \frac{(x^2 + y^2)}{w_0^2}\right). \quad (5.4)$$

We experimentally characterized the nonlinear response of both metasurfaces in a reflection configuration using the experimental set-up described in Figure 5.4a. Normally incident light from a wavelength-tunable quantum-cascade laser (QCL, Daylight Solutions, Inc.) operating in pulsed mode (250 kHz repetition rate with 400 ns pulse width) is tuned to the MQW nonlinearity peak at $10.45 \mu\text{m}$ and focused onto the metasurface by a collimating lens (NA=0.5, with focal spot diameter $2w_0 = 35 \mu\text{m}$ measured by the knife-edge technique) after passing through a half-wavelength-plate for polarization control and a long-wavelength-pass filter with transmission cutoff below the FF light operating as a beam-splitter. The reflected SH light is discriminated from the pump by a ZnSe wire-grid linear polarizer to pass the y-polarized SH light and block the x-polarized FF and a short-wavelength-pass filter with a wavelength cut-off below the FF light. The SH light is focused onto a calibrated, liquid-nitrogen cooled InSb detector, and the reflected SH power is recorded as a function of input intensity, after being corrected for the power loss over the optical path. The lack of a full metal backplane beneath the

resonators in the incomplete-metal design also allows for illumination and measurement in a transmission configuration, depicted in Figure 5.4b. Here, the set-up is largely similar to the reflection configuration, but instead of employing a single collimating lens for focusing of the FF light and collection of the SH, we use two identical ZnSe objectives ($NA = 0.25$, with focal spot diameter $2w_0 = 40\mu\text{m}$) for focusing of the FF light onto the sample and collection of the generated SH.

These results for the full- and incomplete-metal backplane samples are given in Figures 5.4c and 5.4d, for reflection and transmission modes, respectively. The reflection data in Figure 5.4c was corrected for the optical transmission of our setup, and the data for SHG power in transmission mode in Figure 5.4d was corrected for both the optics transmission (97.5% for the ZnSe objective, 85% for the short-wavelength pass filter, and 90% for the ZnSe lens) and the Fresnel reflection (26%) of the generated SH signal at the InP-air interface in the incomplete-metal backplane sample. The reflection loss at the InP-air interface can, in principle, be reduced to nearly zero by introduction of an anti-reflection coating for SH light.

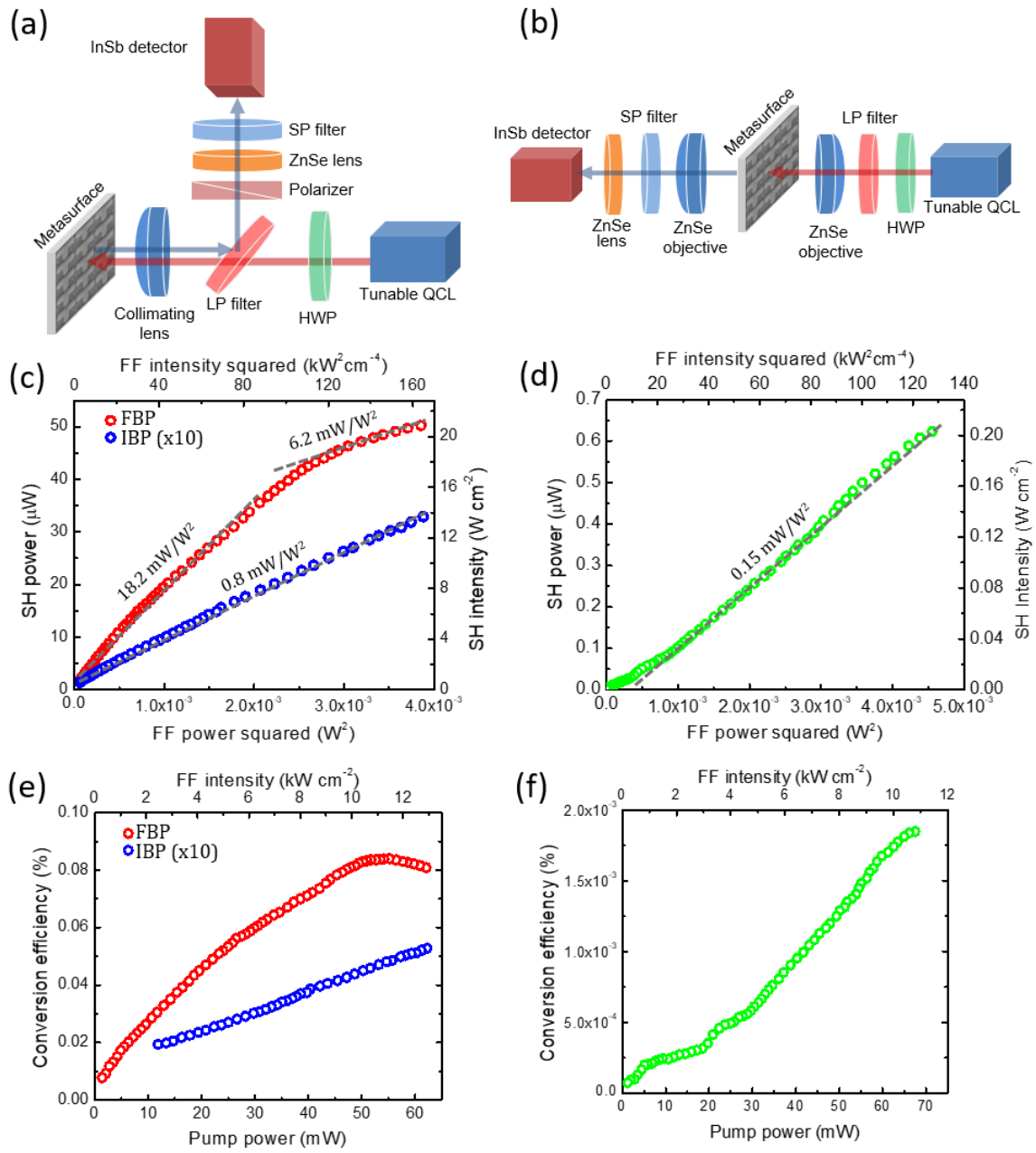


Figure 5.4: Continued on next page.

Figure 5.4: Experimental optical set-ups and characterization results of the full- and incomplete-metal backplane SHG metasurfaces. **a**, Optical set-up for characterization of the metasurfaces in a reflection configuration. Linearly polarized light from a tunable quantum cascade laser (QCL) passes through an achromatic half-wave plate (HWP), a long-wavelength pass dichroic beam-splitter (LP), and collimating lens to the sample. The reflected SHG light is redirected towards an InSb detector via a ZnSe wire-grid linear polarizer (LP) and short-wavelength pass filter (SP). **b**, Optical set-up for the metasurface SH characterization in a transmission configuration. Here, the light from the QCL is directed to a metasurface through a HWP, a LP filter, and a ZnSe objective. An identical objective is placed on the backside of the sample to collect the transmitted SHG light and direct it to the InSb detector through a SP filter. **c**, SH power (left axis) and intensity (right axis) as a function of the FF pump power squared (bottom axis) and intensity squared (top axis) for reflection measurements of the full-metal backplane (FBP, red circles) and incomplete-metal backplane (IBP, blue circles) metasurfaces. The measurements are performed at the pump wavelength of 10.45 μm and yxx polarization combination. The data for the IBP is multiplied by a factor of 10 so that the same power and intensity scale bar can be used for both IBP and FBP data. **d**, SH power (left axis) and intensity (right axis) as a function of the pump power squared (bottom axis) and intensity squared (top axis) for transmission measurements of the IBP metasurface. **e**, SHG conversion efficiency as a function of FF pump power (bottom axis) and intensity (top axis) for the FBP (red circles) and IBP (blue circles) obtained from the data shown in panel **c**, with the IBP data again scaled by a factor of 10. **f**, Conversion efficiency a function of FF power (bottom axis) and intensity (top axis) for the IBP in transmission mode from the data in panel **d**.

In Figure 5.4e, we plot the conversion efficiency for the peak intensities of the FF and SH Gaussian beams defined as $\eta = \frac{P_{2\omega}^0}{P_{\omega}^0} = \frac{I_{2\omega}^0}{2I_{\omega}^0}$ (cf. Equations (5.2), (5.3), and (5.4))

for the full- and incomplete-metal backplane samples operating in reflection mode. From Figure 5.4e, we note that we achieve approximately 0.083% SH conversion efficiency at a pump intensity of only 10 kW/cm^2 for the full-metal backplane sample and 0.01% for the incomplete-metal backplane. Figure 5.4f depicts the measured conversion efficiencies in transmission mode, where we observe a conversion efficiency of 1.8e-3% for the

incomplete-metal back-plane sample at an intensity of 11 kW/cm². From the quadratic dependence of the SHG intensity on the pump intensity in Equation 4.2, we expect a linear increase in η with the pump intensity. However, due to optical saturation of the 1-2 intersubband transition for high incident powers, the conversion efficiency experiences saturation as shown in Figure 5.4e. The effect is particularly strong in the case of the complete-metal-backplane due to strong field enhancement in the nanoresonators. From these conversion efficiency values, we can deduce the metasurface nonlinearity using Eq. (2). We obtain $\chi_{yxx}^{(2)}$, of $1.54 \times 10^6 \text{ pmV}^{-1}$ for low intensity excitation of the full-backplane sample and $3.27 \times 10^5 \text{ pmV}^{-1}$ for the incomplete-backplane sample in reflection geometry. Both are within reasonable agreement with our theoretically predicted values, and orders of magnitude larger than values achievable in traditionally-used nonlinear crystals [37,87]. At higher pumping intensities $\sim 10 \text{ kW/cm}^2$ the value $\chi_{yxx}^{(2)}$ becomes $9.37 \times 10^5 \text{ pmV}^{-1}$ for the full-backplane sample, while we do not observe any significant onset of intensity saturation in the incomplete-backplane sample, which is due to the lower field enhancement in the nanoresonator for the latter case.

The results indicate that the incomplete-metal-backplane intersubband polaritonic metasurface design can offer a viable alternative to the full-metal-backplane design, particularly for higher pumping intensities. The incomplete-backplane metasurface also possesses an effective nonlinear response in the transmission geometry, with $\chi_{yxx}^{(2)} \sim 4.21 \times 10^4 \text{ pmV}^{-1}$. We also note that the value of $\chi_{yxx}^{(2)}$ for the full-backplane sample corresponds to a roughly 10% improvement over our previous record [8], and represents the new record for second-order nonlinearity in the IR-visible range for a condensed matter system. The observed improvement over our previous work could be due to several factors, including employment of a slightly different, better optimized resonator design and a higher-quality fabrication. Finally, we stress that further improvements to

resonator and MQW design and fabrication could potentially lead to further significant advancements over our presented results [8,36].

5.4 CONCLUSIONS

In summary, we have presented the design, fabrication, and experimental operation of a SHG metasurface based on coupling electromagnetic modes in plasmonic nanoresonators to intersubband transitions in the MQW heterostructures using a nanoresonator design that does not require the formation of a metal backplane. The metasurface design is suitable for operation in transmission mode and it can be implemented with III-nitride MQWs where processes for selective substrate removal are challenging to implement. Our results show a roughly four times reduction in the overall nonlinearity of the incomplete-backplane design compared to the full-backplane design at pumping intensities $\sim 10 \text{ kW/cm}^2$.

Chapter 6: Ultra-fast Optical Switching and Power Limiting in Intersubband Polaritonic Metasurfaces

Highly-nonlinear optical materials with fast electronic third-order nonlinear optical response are crucial for operation of all-optical photonic devices, such as all-optical switches for signal processing and computation, optical power limiters, and saturable absorbers. The nonlinear electronic response in traditional optical materials is weak and very high light intensities are required to induce significant changes in their optical properties. Here we show that optical control of the polaritonic coupling strength in sub-wavelength metal-capped nanocavities coupled to intersubband transitions in multi-quantum-well (MQW) semiconductor heterostructures can provide giant third-order nonlinear response of the order of $3 \times 10^{-13} \text{ m}^2/\text{V}^2$ with picosecond response time. We utilize this effect to construct intersubband polaritonic metasurfaces and demonstrate their operation as highly-nonlinear saturable absorbers, optical power limiters, and elements for all-optical-modulation and control with approximately 2 ps characteristic response time. Our approach can enable a plethora of compact, low-power, nonlinear optical devices with spectral and time response tailored by design.

6.1 INTRODUCTION

Highly nonlinear metasurfaces are desirable for a wide range of applications, including wave mixing without phase-matching constraints, control of the phase output, all-optical switching and beam steering, optical limiting and phase conjugation. To this end, a number of approaches have been pursued to achieve large $\chi^{(2)}$ and $\chi^{(3)}$ in metasurfaces: intrinsic metal or dielectric nonlinearities, coupling to epsilon-near-zero materials[95], coupling to J-aggregates[96,97] or other dyes[98], and more. It has recently been shown that intersubband polaritonic metasurfaces, based on coupling

between plasmonic resonators and intersubband transitions in multi-quantum wells (MQWs), can produce an effective $\chi^{(2)}$ far exceeding those from other approaches[26,99]. The large advantage of this approach stems from simultaneous quantum engineering of the electronic states in the MQW heterostructure, which by itself enables one of the largest known nonlinear responses in bulk materials[16], with electromagnetic engineering of the resonant field profiles, enabling highly confined, strong electric fields with ideal overlap with the MQW transition dipole moment. This approach has enabled metasurfaces with tailored nonlinear response, across a wide range of frequencies, from near- to far-infrared, a frequency range where naturally occurring nonlinearities are generally weak.

Here, we demonstrate a mid-infrared metasurface exhibiting giant $\chi^{(3)}$ combined with ultrafast responses, ideal for optical limiting operations. Rather than resonantly enhancing the intrinsic nonlinearity, as in the aforementioned $\chi^{(2)}$ metasurfaces, we instead rely on depletion of the ground state of the MQW, depicted in Figures 6.1a and 6.1b. While much of the work into developing nonlinear IPMs has unveiled a strong case for efficient three-wave mixing in ultra-thin nonlinear materials, one drawback of these structures is that the strong level of field localization in the deeply subwavelength nano-resonator volumes leads to rapid saturation of the ISB nonlinear response. However, the optically saturable response of IPMs can be harnessed for other applications where such an effect is desirable. Specifically, saturable absorption forms the basis for a set of technologies used for passive mode-locking of laser pulses and all-optical control. Furthermore, the opposite to this phenomenon, optical power limiting, where transmission or reflection reduce with incident intensity, is desirable in scenarios where one would want to limit the power of incident optical source from damaging sensitive elements. Thus, developing a platform for the cumulative control over intensity-

dependent optical properties in the mid-IR, with key parameters such as operating wavelength, saturation intensity, response time, etc., tailorable by design is an attractive goal.

Depletion reduces the intersubband dipole moment, which in turn reduces the coupling rate between the plasmonic resonance and the intersubband transition:

$$\Omega^2 \propto \Omega_R^2 (n_g - n_e) \quad (6.1)$$

where n_g and n_e are the ground and excited state occupancies in the MQW (assuming that it can be described by a two level system), and Ω_R is the vacuum Rabi frequency

$$\Omega_R = \int \mathbf{E}_v(\mathbf{r}) \cdot \mathbf{d} dV \quad (6.2)$$

Here $\mathbf{E}_v$ is the vacuum cavity field (the resonant electric field in the ground state) and $\mathbf{d}$ is the dipole moment density of the MQW transition.

Nonlinear tunability of the coupling coefficient enables dramatic control over the overall system response. As the coupling rate vanishes, the dynamics of the polaritonic system are strongly affected: in the unsaturated case coherent energy transfer occurs between the antenna resonance and the intersubband transition, while in the saturated case only the antenna resonator is excited. In the frequency domain this implies a transition from two peaks in the unsaturated regime, due to mode splitting, to a single peak in the spectrum when the ground state is saturated, depicted in Figures 6.1c and 6.1d. The nonlinear transition from strong to weak coupling has been observed before in semiconductor microcavities [100,101], and, more recently, in plasmonic arrays coupled to molecules [96–98]. Here, we show that the synergy between the quantum-engineered extremely large MQW dipole moment and the plasmonic metasurface dramatically enhances the nonlinear response, demonstrating record $\chi^{(3)}$ at low input powers and ultrafast switching between the two states. This functionality enables ultralow power

optical limiters, which strongly reflect at low intensity but limit the amount of reflection at high intensity, or reverse saturable absorbers for mode-locking [102].

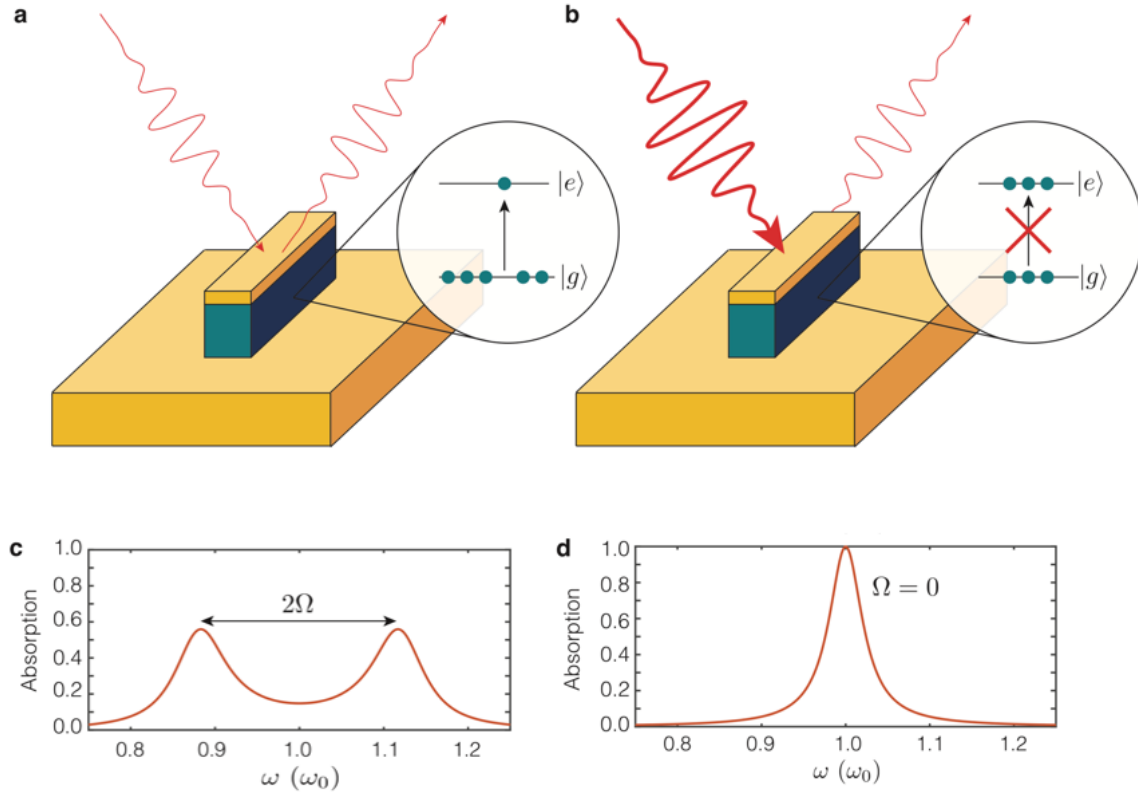


Figure 6.1: Ultrafast, highly nonlinear metasurface limiting. **a**, At low intensities, the metallic patch antenna is strongly coupled to an intersubband transition in the MQW (shown in green). As a result, polariton splitting is observed at the central frequency and the incident radiation is reflected. **b**, At high intensities, the intersubband transition is saturated, and the plasmonic resonance can no longer strongly couple to it. The incident pulse is now largely absorbed, leading to an optical limiting response. **c**, The low intensity spectrum shows clear signature of mode splitting due to strong coupling, while **d**, at high intensity only the plasmonic resonance is observed in the spectrum.

6.2 OPTICAL LIMITER DESIGN

An ideal reflective optical limiter would reflect highly at low intensity optical pumping and absorb strongly at the limit of high intensity pumping. Within the context of IPMs formed of a MQW layer sandwiched by metallic nanoantennas and a metal

backplane, it is helpful to approach this design problem by viewing it through the lens of achieving critical coupling in the limit of full saturation of the intersubband transition. In this limit, the metasurface response is ideally dominated by the antenna mode, free of the influence of the MQW transition.

6.2.1 MQW design

The design process is broken down into two parts, as in prior iterations of our nonlinear IPMs. First, we focus on the design of a MQW suitable for strong optical saturation at a designer frequency of interest, and then we settle on a geometry for the resonator that serves to in- and out- couple light. For the MQW, we settled on the coupled quantum well depicted in Figure 6.2a and consisting of $\text{In}_{0.53}\text{Ga}_{0.47}\text{As}$ wells and $\text{In}_{0.48}\text{Al}_{0.52}\text{As}$ barriers. The layer structure of the designed and grown structure in nanometers is as follows, with barriers indicated in bold: **2.5/6.9/1.5/2/2.5**. The outer 1.5 nm of the barriers is Si-doped to $8.3 \times 10^{18} \text{ cm}^{-3}$, correlating to a Fermi level 40 meV below the second confined energy level. Experimentally, intersubband absorption was characterized by a multi-pass waveguide experiment (described in more detail in Chapter 3), with sample dimensions given in Figure 6.2b. Finally, we include the results of this experiment in Figure 6.2c, where we note strong observation of 1-2 and 1-3 transitions, at 165 meV (1330 cm^{-1}) and 226.3 meV (1825 cm^{-1}). The ideal implementation of a saturable absorbing IPM would employ a MQW structure with only 1-2 transition, however given that the 2-3 transition is detuned significantly from 1-2, we do not expect the third state to significantly influence the IPM operation. Taking into account the HWHM linewidth γ_{21} of 22.7 meV, transition dipole moment z_{12} of 1.76 nm, and state 2 lifetime τ_2 of 1.6 ps, we estimate the characteristic saturation intensity of the bare MQW to be [72,74,103]:

$$I_{sat} = \frac{cn_{MQW}\epsilon_0\hbar\gamma_{21}}{2e^2z_{12}^2\tau_2} = 1.4 \text{ MW/cm}^2 \quad (6.3)$$

6.2.2 IPM resonator design

For the design of the resonator, we settled on a simple metal-capped etched dipole, where electric field polarized along the dipole axis is resonantly coupled to the MQW. Unlike our past iterations of $\chi^{(2)}$ IPMs, there are no symmetry constraints placed on the geometry of the antenna. Here, the length of the dipole shifts the bare antenna resonance, and the unit cell size affects the radiative loss of the structure. Our main design goal is to settle on a combination of these parameters that will allow us to achieve critical-coupling in the limit of high intensity optical pumping, meaning every photon incident on the IPM is lost non-radiatively. Here, it is imperative that as the MQW becomes lossless through optical bleaching, the structure is impedance-matched to free-space [104].

The elements of the metasurface are composed of an InGaAs/AlInAs MQW strip sandwiched between a gold substrate and a thin gold strip, as shown schematically in Figure 6.3a. The gold structure forms a plasmonic patch antenna, engineered so that at resonance almost all the stored electric field in the MQW is aligned along the transition dipole moment, maximizing the coupling rate [26,99]. Combined with the resonant enhancement *and* the dramatic plasmonic field confinement, this results in a triple reduction of the saturation intensity compared to planar MQW systems.

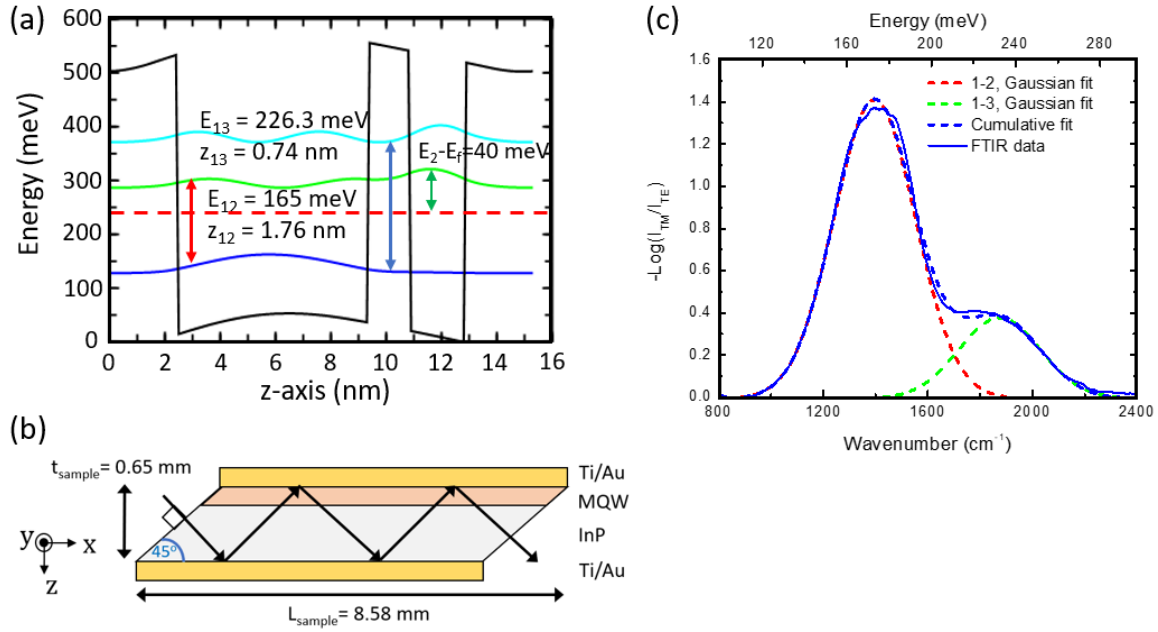


Figure 6.2: Multi-Quantum Well (MQW) design employed for $\chi^{(3)}$ metasurfaces. **a**, Conduction energy band diagram of a single period of the **In_{0.52}Al_{0.48}As/In_{0.53}Ga_{0.47}As** structure employed in this work. Shown are the measured energy level transitions between states i and j , E_{ij} , and associated transition dipole moments, z_{ij} . The red dashed line indicates the Fermi level. **b**, Multi-pass waveguide geometry for experimental intersubband absorption measurements. The epitaxially-grown MQW wafer is cleaved and facets are polished at 45-degree angles into the dimensions shown, with metal layers deposited on top and bottom-side. Light from a FTIR spectrometer illuminates one facet and transmits through the MQW geometry for both TM and TE polarizations, with the intersubband absorption discriminated by background correcting the TE transmission. **c**, Measured intersubband absorption spectra (solid) and Gaussian fits (dashed) depicting 1-2 and 1-3 MQW transitions.

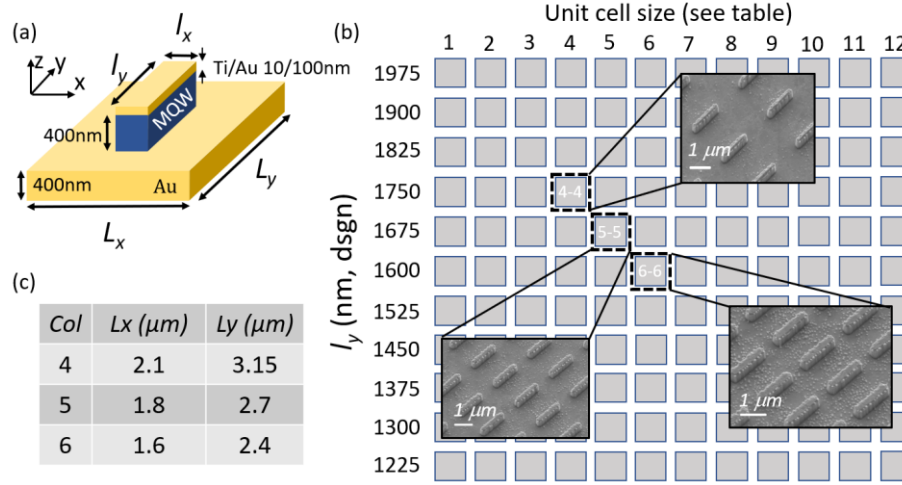


Figure 6.3: Fabricated $\chi^{(3)}$ IPM. **a**, Graphic depiction of a single unit cell of the etched dipole resonator, with fixed dimensions labeled. **b**, IPM sample layout. To account for deviations from theory in nonradiative losses due to metals and radiative losses due to resonator design, we fabricated a large parameter space of IPM arrays with varying dipole length (corresponding to each row, and controlling bare antenna resonance) and unit cell size (corresponding to each column, and controlling radiative losses). Highlighted are three particular unit cell and dipole designs that exhibited the strongest degree of polaritonic coupling in FTIR reflectance studies, and are investigated further for strong $\chi^{(3)}$ response, with unit cell dimensions given in **c**.

Fabrication of the IPMs is carried out as described in prior chapters. The MQW is first metallized thermo-compressively bonded to a foreign InP substrate to form the backplane. The original substrate is then removed via mechanical polishing and wet chemical etching. Resonators are then defined via top-metal and hard-mask deposition, followed by electron-beam lithography and dry etching. Due to the uncertainty of material parameters (in particular, Au loss), and experimental radiative loss of the dipole array, we fabricated a large range etched dipole IPMs with varying lengths and unit cell sizes. A schematic of the unit cell is shown in Figure 6.3a, and the fabricated sample is shown in Figure 6.3b, where each row corresponds to a differing dipole length, and each

column corresponds to a different unit cell size. Three particular patterns are highlighted with SEMs of the fabricated dipoles shown in the inset, and unit cell sizes given in 6.3c.

6.3 IPM EXPERIMENTAL RESULTS

To observe strong-coupling in the IPM spectra, we performed FTIR spectroscopy of the fabricated IPMs, and present the results in Figures 6.4b-d. Each set of plots corresponds to a particular unit cell size, with each curve representing spectra from an IPM array with a different dipole length. As expected, as the dipole length is tuned through the fixed intersubband transition, we observe strong polaritonic splitting due to the overlapping resonances. Away from the transition, we observe the emergence of a bare cavity resonance representing the antenna mode uninfluenced by the MQW. We expect the greatest reflectivity contrast to be observed for the pattern exhibiting the greatest degree of polaritonic splitting. Here, this corresponds to pattern 4-4, with spectrum highlighted in dark purple in Figure 6.4c.

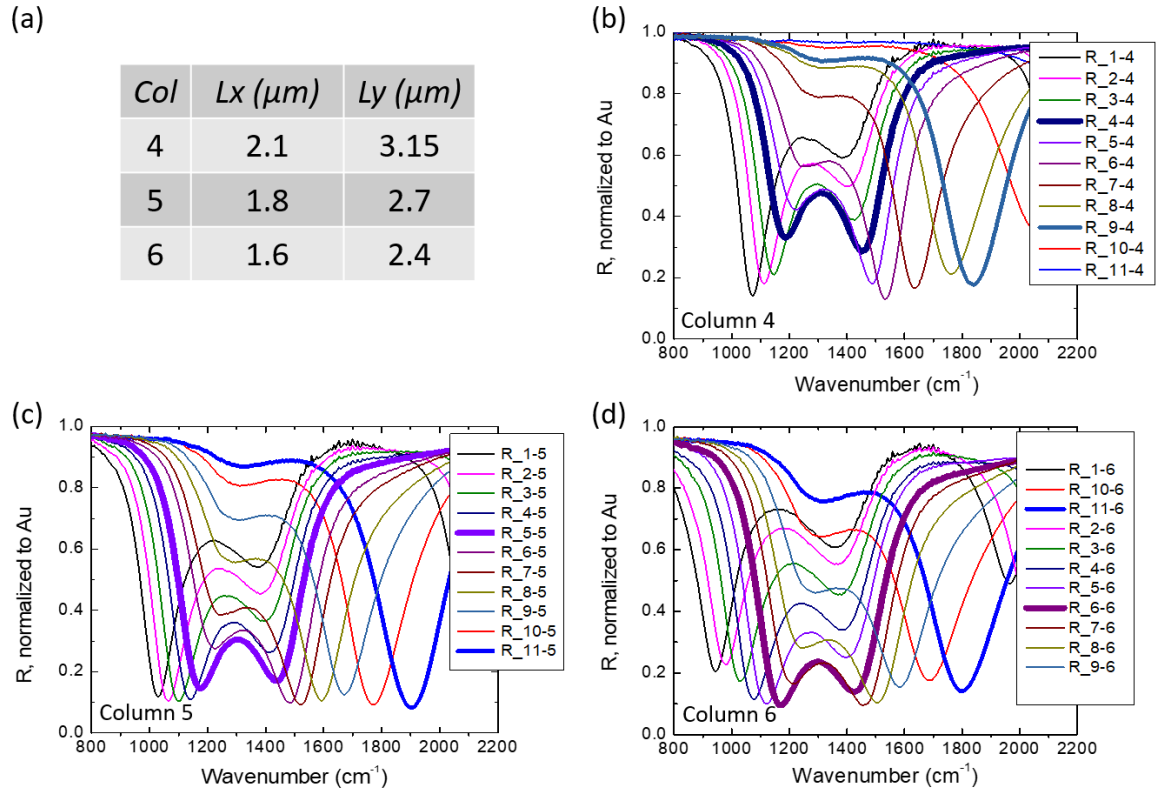


Figure 6.4: FTIR reflectance studies of fabricated $\chi^{(3)}$ IPMs for fixed unit cell sizes but varying dipole length. **a**, Unit cell size dimensions for the three columns of IPMs exhibiting greatest degree of polaritonic coupling. **b-d**, FTIR reflectivity spectra, normalized to a Au-coated Si reference wafer, for fabricated columns of IPMs with unit cell dimensions given in **a**. Each curve corresponds to a separate array of resonators with differing dipole length. The spectral trends show that the effect of polaritonic mode splitting is strongly modified as the cavity resonance is tuned through the intersubband resonance.

6.3.1 Nonlinear response

We now turn to the nonlinear response. We use a tunable ps laser (~ 0.5 THz bandwidth) to measure the reflectivity as a function of incident intensity at different frequencies and intensities. A schematic of our experimental setup is given in Figure 6.5a, where we simultaneously measure a fraction of the incident and reflected beams

using two separate detectors to account for any variations in laser power, and normalize results from our IPMs to a Au mirror reference (which should not produce an intensity-dependent optical response). In Figure 6.6a we show the pulsed reflectivity spectra at low peak intensity (70 kW/cm^2) and higher peak intensity (700 kW/cm^2). At low peak intensity, we still observe the characteristic mode splitting, while at higher peak intensity the mode splitting has vanished, and instead we observe a single dip. This implies that the coupling coefficient has saturated sufficiently for the patch antenna to be weakly coupled to the MQW transition.

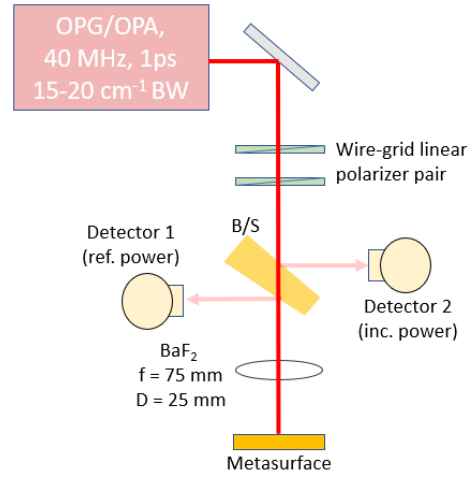


Figure 6.5: Experimental set-up for optical limiting. The mid-IR output of a ps-OPG/OPA system is focused onto the metasurface under study through a mid-IR transmissive BaF₂ lens. The incident and reflected power are measured simultaneously by two Mercury-Cadmium-Telluride (MCT) photodetectors placed on either side of a wedge beam-splitter (B/S) to account for fluctuations in input pump power. We control the intensity of the pump source by using a wire-grid linear polarizer pair, where the first polarizer is rotated to attenuate the polarized output of the OPG/OPA throughout the intensity-dependent measurements, and the second polarizer is rotated and held constant to ensure light is polarized along the IPM dipole axis.

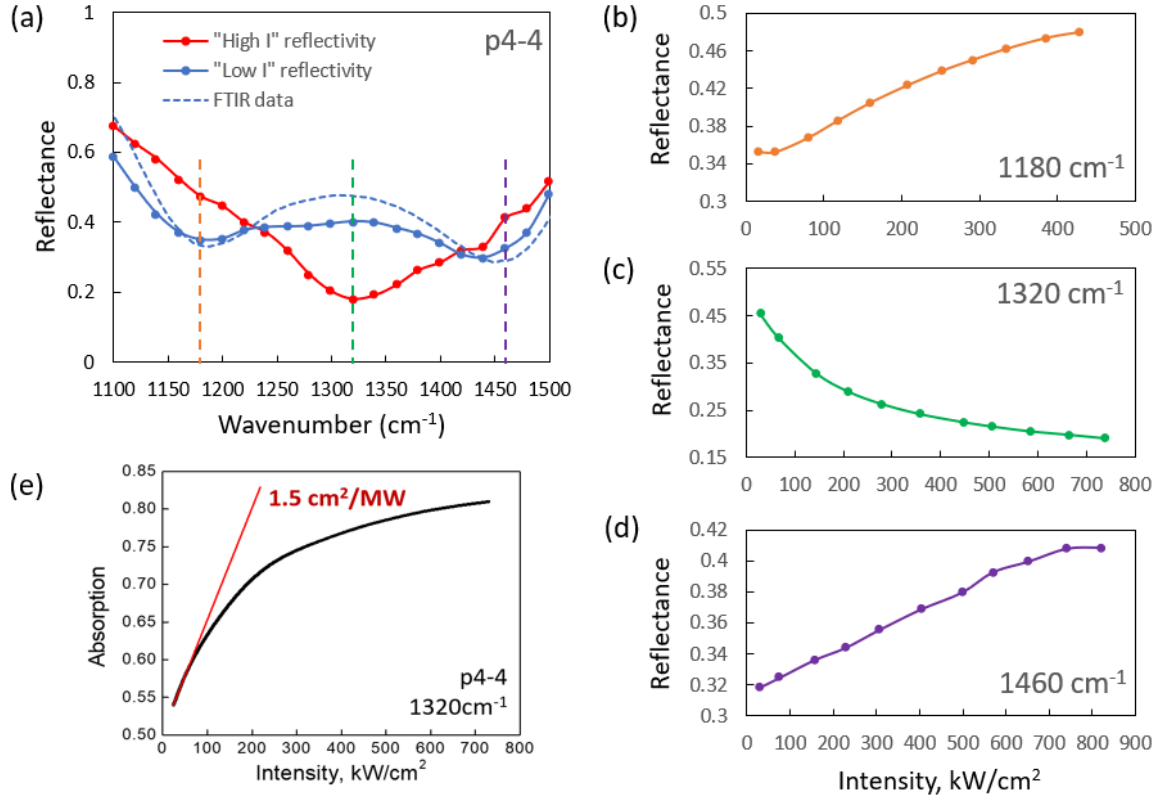


Figure 6.6: Experimental $\chi^{(3)}$ optical limiting and saturable absorption results. **a**, Intensity-dependent “spectra” retrieved for low and high intensity optical pumping from the OPG/OPA system. The dashed line corresponds to low-intensity FTIR data for the IPM under test. Blue data points were taken at an intensity of approximately 70 kW/cm², and red were taken at 700 kW/cm². Experimentally we see a transition from a strong coupling regime, exhibiting clear polaritonic splitting, to a single cavity resonance emerging as the MQW is optically saturated. **b-d**, Intensity-dependent reflectivity results taken at three different pump wavenumbers, with colors corresponding to dashed lines in **a**. **b** and **d** correspond to saturable absorption, where reflectivity increases with incident intensity (i.e. absorption decreases), and **c** corresponds to optical limiting operation, with reflectivity decreasing with intensity. **e**, Same as **c** but replotted as absorption instead of reflectance, with a nonlinear curve fit applied to interpolate the data. The red line indicates the slope dI/I of the data at low intensities, from which we can derive a value of $\chi^{(3)}$.

To observe the nonlinearity more clearly, we show the evolution of the reflectivity as a function of the pulse peak intensity for three separate pump frequencies,

of 1180, 1320, and 1460 cm^{-1} in Figures 6.6b-d. A dramatic change in the reflectivity is visible at low peak intensities, while at higher intensities the response is clearly saturating. For pump wavenumber at the intersubband resonance of 1320 cm^{-1} , the IPM acts as an optical power limiter, and when pumping at either of the two polariton branches (1180 and 1460 cm^{-1}) the IPM acts as a saturable absorber, demonstrating the great degree of flexibility in saturable response. In fact, from the slope at low intensities we can estimate the nonlinear absorption coefficient. In order to fully capture this intensity dependent absorption, we can invoke the two-photon absorption coefficient, β as follows [37]:

$$\frac{dI}{dz} = -\alpha \times I - \beta \times I^2, \quad (6.4)$$

where α is the linear absorption coefficient, I the applied intensity, and dI/dz the change in intensity per unit length. Rearranging the equation yields

$$dI = -\alpha \times dz \times I - \beta \times dz \times I^2, \quad (6.5)$$

where if we divide through by I , and replace dz with the thickness of the IPM, d , we get

$$\frac{dI}{I} = -\alpha \cdot d - \beta I \cdot d. \quad (6.6)$$

β is in effect the slope of the absorption vs intensity curve, which we can create by noting that as there is no transmitted signal in our IPMs due to the presence of a metallic ground plane, $A=1-R$. We replot the data from 6.6c in 6.6e and take the slope at low intensities of this curve to be $\beta = 1.5 \times 10^7 \text{ cm/GW}$. Finally, through the relation [37]

$$\beta = \frac{3\Im(\chi^{(3)})\omega}{2\epsilon_0 c^2 n^2}. \quad (6.7)$$

we arrive at $\Im(\chi^{(3)}) = 3 \times 10^{-13} \text{ m}^2 / \text{V}^2$. These values are, as far as we are aware, the highest reported at infrared or optical frequencies. Importantly, the sign and magnitude of β depend on the frequency: from Figures 6.6b and d it is apparent that β must be positive at both of the low intensity peaks, where absorption decreases with increasing intensity. By further engineering the hybrid system, the spectral dependence of β may be tuned precisely. For example, for a weakly coupled system that is overdamped at low intensity β will be positive over the entire spectrum, while β may be negative over the entire spectrum in a system that is critically coupled at low intensity.

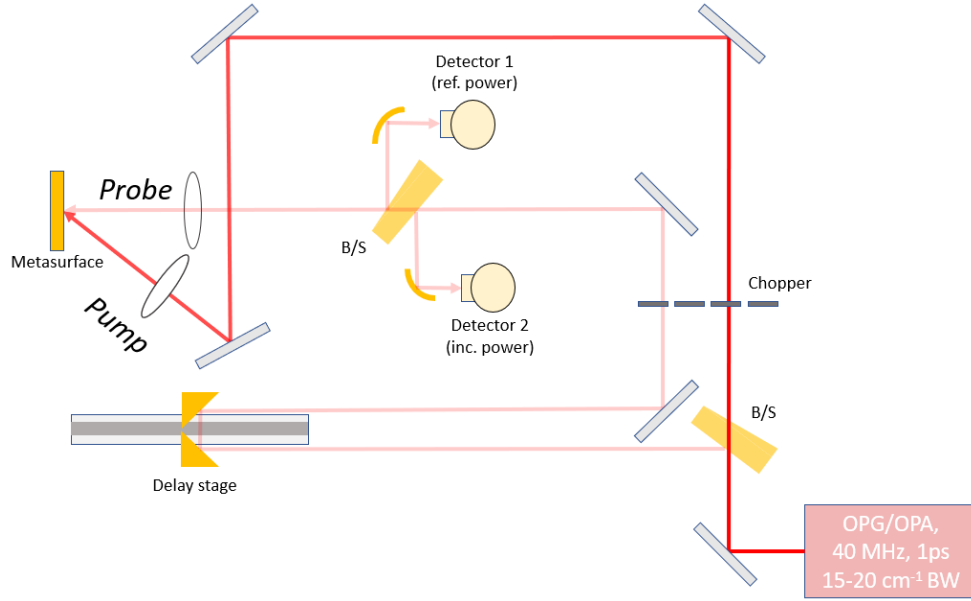


Figure 6.7: Optical set-up for degenerate pump-probe experiment. The mid-IR output of a ps-OPG/OPA system is split into strong pump (bold) and weak probe beampaths. The pump beam is focused onto the IPM under test at an angle, spatially discriminating it from the probe. Here, the probe is instead directed towards a retroreflector mounted on a delay stage, and then focused at normal incidence onto the IPM. The incident and reflected powers of the probe path are simultaneously monitored by way of two mercury cadmium-telluride (MCT) photodetectors placed on either side of a beam-splitter (B/S) in front of the sample, and time-dependent reflectivity is retrieved by monitoring the reflectivity recovered from the pump beam as a function of the pump-probe delay.

6.3.2 Pump-probe measurement

Despite the extremely large $\chi^{(3)}$, the response of the metasurface is ultrafast. We studied the temporal dynamics of the nonlinear metasurface with degenerate pump-probe reflection measurements, with the experimental setup depicted in Figure 6.7. Figures 6.8a and 6.8b depict the results from this measurement, away from the intersubband resonance at the lower polariton branch (1180 cm^{-1}) and at the intersubband resonance (1320 cm^{-1}), respectively. As expected, at 1320 cm^{-1} pumping, we observe a dip in the reflection as the coupled system transitions from strongly coupled to weakly coupled. The rise time of the system in this measurement is constrained by the pulse length, which is about a ps, indicating that the system has nonlinearity onset dynamics significantly below a ps. The recovery time of the system is limited by the relaxation time of the excited state, $T_1 \approx 2 \text{ ps}$. From Figure 6.7 we find that the overall response time is about 4 ps, enabling ultrafast all-optical low power manipulation of optical signals.

In table 6.1, we compare the value of $\chi^{(3)}$ and response time to those from other nonlinear mechanisms. In context, the IPMs presented in this work present order of magnitude larger nonlinearity, while maintaining an ultrafast response time. Of note, in 2018 Robert Boyd's group introduced a metasurface formed via an epsilon-near-zero material demonstrating a slightly faster response, but the $\chi^{(3)}$ demonstrated of $10^{-15} \text{ m}^2/\text{V}^2$ is also a little over an order of magnitude lower than what we've presented here [95].

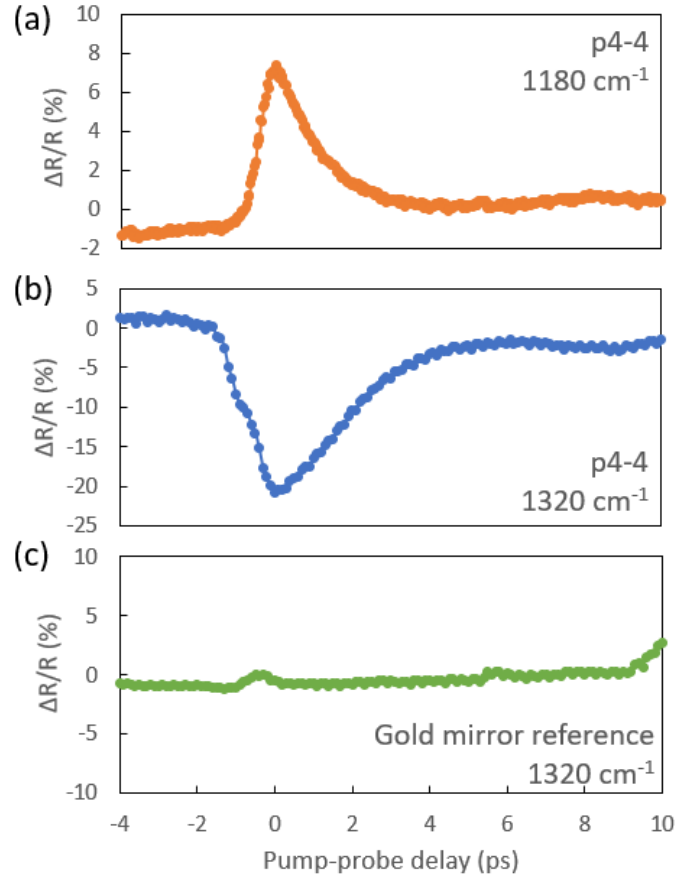


Figure 6.8: Degenerate pump-probe results of the ultrafast nonlinear metasurface under study, depicting strong optical control at ps-timescales. The IPM is illuminated with a ps-source, with experimental setup shown in Figure 6.7, and operates in two regimes: **a**, saturable absorption and **b**, optical limiting. **c**, Pump-probe results of a bare-gold mirror, showing no reflectivity modulation due to the pump modulation.

6.4 CONCLUSIONS

In summary, in this chapter we have reported optical control of the coupling constant between a MQW intersubband transition and a plasmonic resonator in the mid infrared, demonstrating ultrafast switching between strong and weak coupling. As far as we are aware, the presented structure has the largest ultrafast nonlinear absorption coefficient reported in the mid infrared, enabling dramatic spectral changes at low input

powers. Potential applications of such a metamaterial would be an optical limiter, switches, or reverse saturable mirrors for mode-locking. From the perspective of $\chi^{(3)}$, we evaluate the response of our metasurface to be $\Im(\chi^{(3)}) = 3 \times 10^{-13} \text{ m}^2 / \text{V}^2$, which we believe to be a record for a condensed matter system in the mid-infrared spectral range. We expect that further improvements to the optical limiting and saturable absorber performance can be found through more optimized MQW and resonator geometries. We emphasize that all of the important parameters such as operating wavelength, optical saturation intensity, and response time can all be optimized and tailorable by design by judicious MQW and resonator engineering. In particular, the saturation intensity, a key parameter derived directly from the structure of the MQW, can be further reduced significantly by employment of MQWs with narrower linewidths through improved growth quality, and longer upper state lifetimes by way of, for example, engineering diagonal electronic transitions [105].

Mechanism	$\chi^{(3)} (\text{m}^2 / \text{V}^2)$	Response time (s)
Electronic polarization	10^{-22}	10^{-15}
Molecular orientation	10^{-20}	10^{-12}
Electrostriction	10^{-20}	10^{-9}
Saturated atomic absorption	10^{-16}	10^{-8}
Thermal effects	10^{-12}	10^{-3}
ENZ NLO [95]	10^{-15}	$\sim 0.5 \times 10^{-12}$
IPMs [this work]	6×10^{-13}	2×10^{-12}

Table 6.1: Comparison of $\chi_{eff}^{(3)}$ nonlinearities and response time from various nonlinear mechanisms, modeled after Reference [37], and including IPMs presented in this work. Our results indicate order-of-magnitude improvements over other nonlinear media, while simultaneously exhibiting ps response time.

Chapter 7: Conclusions

Through the course of this thesis, we have presented a novel architecture for creating flat nonlinear optical elements. These elements, termed Intersubband Polaritonic Metasurfaces (IPMs), are comprised of electromagnetic nanoantennas coupled to intersubband electronic transitions within semiconductor Multiple-Quantum-Wells (MQW) and possess the highest effective nonlinearity of any condensed matter system in the mid-infrared spectral range, enabling significant nonlinear optical response at low pump intensities. IPMs are inherently deeply sub-wavelength in thickness, freeing them from the traditional constraints of bulk nonlinear crystals, and are readily tailorable for any particular nonlinear optical process or operating frequency.

Our initial experiments consisted of enhancement of second harmonic generation (SHG) over the exiting state-of-the-art IPM results. We achieved a 0.075% SHG conversion efficiency in a $\lambda/20$ -thick metasurface. Our design was improved over prior results by careful engineering of the nanoantenna and MQWs. We found that the field enhancement offered by the resonators was actually improved by etching into the MQW material and provided higher nonlinear response when compared to unetched structures. Further, we doped the MQW more heavily than had been done before, and designed our structure to delay the onset of intensity saturation of the nonlinear response.

We believe that IPMs can unveil a paradigm shift in our approach to nonlinear optics, and to adequately do so, it is necessary to have control over the phase response of the nonlinear signal. By invoking concepts of Pancharatnam-Berry geometric phase, we present a means to have continuous control over the phase of the SHG signal created from our IPMs. We use this method to experimentally demonstrate beam-steering of the SH signal and pave a way for creating arbitrary phase fronts of generated nonlinear signals.

Our existing process flow for fabrication of IPMs consists of a rather cumbersome substrate removal and transfer process to create a metal backplane that spans the area of the metasurface, which is often not as amenable to novel materials systems such as GaN that are important for near-infrared optics. In order to provide an architecture for nonlinear optics that is materials agnostic, we investigated the SHG response of a fabrication procedure that does not require such a complex procedure. Our results indicated that while the nonlinear response was reduced compared to the original approach, we were successful in observing significant nonlinearity in IPMs fabricated in this manner.

Lastly, in prior works and demonstrations of IPMs we had focused primarily on the second order nonlinear response. Third-order nonlinearities unveil a host of important and useful processes, ranging from optical phase-conjugation to all-optical control. We found that by exploiting the saturation of the optical response of the MQWs under high optical pumping intensities, we were able to control the coupling rate between the nanoresonator and MQW and observe significant changes in the absorption and reflectivity characteristics of our IPMs. These changes yielded experimentally observable optical power-limiting and saturable absorbing response with record third-order nonlinearities and further, importantly, through performing degenerate pump-probe measurements, we were able to confirm that this nonlinearity has a picosecond-response time, enabling ultrafast control over their nonlinear response.

Bibliography

1. J. B. Pendry, "Negative refraction makes a perfect lens," *Phys. Rev. Lett.* **85**(18), 3966–3969 (2000).
2. J. B. Pendry, D. Schurig, and D. R. Smith, "Controlling electromagnetic fields,," *Science* **312**(5781), 1780–82 (2006).
3. W. Cai, U. Chettiar, A. Kildishev, and V. Shalaev, "Optical cloaking with metamaterials," *Nat. Photonics* **1**, 224–27 (2007).
4. P. Y. Chen, J. Soric, and A. Alù, "Invisibility and cloaking based on scattering cancellation," *Adv. Mater.* **24**(44), 281–304 (2012).
5. X. Ni, N. K. Emani, A. V Kildishev, A. Boltasseva, V. M. Shalaev, V. G. Veselago, J. B. Pendry, Z. Liu, H. Lee, Y. Xiong, C. Sun, X. Zhang, J. B. Pendry, D. Schurig, D. R. Smith, and N. Yu, "Broadband light bending with plasmonic nanoantennas,," *Science* **335**(6067), 427 (2012).
6. N. Yu, P. Genevet, M. A. Kats, F. Aieta, J.-P. Tetienne, F. Capasso, and Z. Gaburro, "Light propagation with phase discontinuities: generalized laws of reflection and refraction," *Science* **334**(6054), 333–337 (2011).
7. J. Lee, S. Jung, P. Chen, F. Lu, F. Demmerle, G. Boehm, M. Amann, A. Alù, and M. A. Belkin, "Ultrafast Electrically Tunable Polaritonic Metasurfaces," *Adv. Opt. Mater.* **2**, 1057–63 (2014).
8. J. Lee, N. Nookala, J. S. Gomez-Diaz, M. Tymchenko, F. Demmerle, G. Boehm, M. Amann, A. Alù, and M. A. Belkin, "Ultrathin second-harmonic metasurfaces with record-high nonlinear optical response," *Adv. Opt. Mater.* **4**, 664–70 (2016).
9. M. W. Klein, C. Enkrich, M. Wegener, and S. Linden, "Second-harmonic generation from magnetic metamaterials," *Science* **313**(5786), 502–04 (2006).
10. J. D. Caldwell, A. V Kretinin, Y. Chen, V. Giannini, M. M. Fogler, Y. Francescato, C. T. Ellis, J. G. Tischler, C. R. Woods, A. J. Giles, M. Hong, K. Watanabe, T. Taniguchi, S. A. Maier, and K. S. Novoselov, "Sub-diffractive volume-confined polaritons in the natural hyperbolic material hexagonal boron nitride," *Nat. Commun.* **5**(5221), 1–9 (2014).
11. N. Segal, S. Keren-Zur, N. Hendler, and T. Ellenbogen, "Controlling light with metamaterial-based nonlinear photonic crystals," *Nat. Photonics* **9**(3), 180–184 (2015).
12. G. Li, S. Chen, N. Pholchai, B. Reineke, P. W. H. Wong, E. Y. B. Pun, K. W. Cheah, T. Zentgraf, and S. Zhang, "Continuous control of the nonlinearity phase for harmonic generations," *Nat. Mater.* **14**(6), 607–612 (2015).
13. N. Nookala, J. Lee, M. Tymchenko, J. Sebastian Gomez-Diaz, F. Demmerle, G. Boehm, K. Lai, G. Shvets, M.-C. Amann, A. Alù, and M. A. Belkin, "Ultrathin gradient nonlinear metasurface with a giant nonlinear response," *Optica* **3**(3), 283–88 (2016).
14. E. Rosencher, P. Bois, J. Nagle, and S. Delattre, "Second harmonic generation by intersub-band transitions in compositionally asymmetrical MQWs," *Electron. Lett.*

- 25(16), 1063 (1989).
15. F. Capasso, C. Sirtori, and A. Y. Cho, "Coupled Quantum Well Semiconductors with Giant Electric Field Tunable Nonlinear Optical Properties in the Infrared," *IEEE J. Quantum Electron.* **30**(5), 1313–1326 (1994).
 16. E. Rosencher, A. Fiore, B. Vinter, V. Berger, P. Bois, and J. Nagle, "Quantum Engineering of Optical Nonlinearities," *Science* **271**(5246), 168–173 (1996).
 17. C. Sirtori, F. Capasso, D. L. Sivco, S. N. G. Chu, and A. Y. Cho, "Observation of large second order susceptibility via intersubband transitions at $\lambda \sim 10 \mu\text{m}$ in asymmetric coupled AlInAs/GaInAs quantum wells," *Appl. Phys. Lett.* **59**, 2303 (1991).
 18. K. L. Vodopyanov, K. O'Neill, G. B. Serapiglia, C. C. Phillips, M. Hopkinson, I. Vurgaftman, and J. R. Meyer, "Phase-matched second harmonic generation in asymmetric double quantum wells," *Appl. Phys. Lett.* **72**, 2654 (1998).
 19. E. Rosencher, P. Bois, B. Vinter, J. Nagle, and D. Kaplan, "Giant nonlinear optical rectification at 8-12 μm in asymmetric coupled quantum wells," *Appl. Phys. Lett.* **56**, 1822 (1990).
 20. C. Sirtori, F. Capasso, J. Faist, L. N. Pfeiffer, and K. W. West, "Far-infrared generation by doubly resonant difference frequency mixing in a coupled quantum well two-dimensional electron gas system," *Appl. Phys. Lett.* **65**(445), (1994).
 21. E. Dupont, Z. R. Wasilewski, and H. C. Liu, "Terahertz emission in asymmetric quantum wells by frequency mixing of midinfrared waves," *IEEE J. Quantum Electron.* **42**(11), 1157-74 (2006).
 22. H. C. Liu, I. W. Cheung, A. J. SpringThorpe, C. Dharma-Wardana, Z. R. Wasilewski, D. J. Lockwood, and G. C. Aers, "Intersubband Raman laser," *Appl. Phys. Lett.* **78**, 3580 (2001).
 23. I. Gravié, M. Segev, and A. Yariv, "Observation of phase conjugation at 10.6 μm via intersubband third-order nonlinearities in a GaAs/AlGaAs multi-quantum-well structure," *Appl. Phys. Lett.* **60**(22), 2717 (1992).
 24. E. Dupont, P. Corkum, H. C. Liu, P. H. Wilson, M. Buchanan, and Z. R. Wasilewski, "Two-photon intersubband transitions in quantum well infrared photoconductors," *Appl. Phys. Lett.* (1994).
 25. D. Walrod, S. Y. Auyang, P. A. Wolff, and M. Sugimoto, "Observation of third order optical nonlinearity due to intersubband transitions in AlGaAs/GaAs superlattices," *Appl. Phys. Lett.* **59**(23), 2932 (1991).
 26. J. Lee, M. Tymchenko, C. Argyropoulos, P.-Y. Chen, F. Lu, F. Demmerle, G. Boehm, M.-C. Amann, A. Alù, and M. A. Belkin, "Giant nonlinear response from plasmonic metasurfaces coupled to intersubband transitions.," *Nature* **511**(7507), 65–69 (2014).
 27. O. Wolf, S. Campione, A. Benz, A. P. Ravikumar, S. Liu, T. S. Luk, E. A. Kadlec, E. A. Shaner, J. F. Klem, M. B. Sinclair, and I. Brener, "Phased-array sources based on nonlinear metamaterial nanocavities," *Nat. Commun.* **6**, 7667 (2015).
 28. O. Wolf, A. A. Allerman, X. Ma, J. R. Wendt, A. Y. Song, E. A. Shaner, and I. Brener, "Enhanced optical nonlinearities in the near-infrared using III-nitride

- heterostructures coupled to metamaterials," *Appl. Phys. Lett.* **107**, 151108 (2015).
29. Y. Liu, J. Lee, S. March, N. Nookala, D. Palaferri, J. F. Klem, S. R. Bank, I. Brener, and M. A. Belkin, "Difference-Frequency Generation in Polaritonic Intersubband Nonlinear Metasurfaces," *Adv. Opt. Mater.*, 1800681 (2018).
30. M. Tymchenko, J. S. Gomez-Diaz, J. Lee, M. A. Belkin, and A. Alu, "Highly-efficient THz generation using nonlinear plasmonic metasurfaces," *J. Opt.* **19**(10), 104001 (2017).
31. J. Yu, S. Park, I. Hwang, D. Kim, J.-Y. Jung, and J. Lee, "Third-Harmonic Generation from Plasmonic Metasurfaces Coupled to Intersubband Transitions," *Adv. Opt. Mater.*, 1801510 (2019).
32. R. Sarma, S. Campione, M. Goldflam, J. Shank, J. Noh, L. T. Le, M. D. Lange, P. D. Ye, J. Wendt, I. Ruiz, S. W. Howell, M. Sinclair, M. C. Wanke, and I. Brener, "A metasurface optical modulator using voltage-controlled population of quantum well states," *Appl. Phys. Lett.* **113**(20), 1101-5 (2018).
33. N. Nookala, J. Xu, O. Wolf, S. March, R. Sarma, S. Bank, J. Klem, I. Brener, and M. A. Belkin, "Mid-infrared second-harmonic generation in ultra-thin plasmonic metasurfaces without a full-metal backplane," *Appl. Phys. B* (2018).
34. M. Tymchenko, J. S. Gomez-Diaz, J. Lee, N. Nookala, M. A. Belkin, and A. Alù, "Gradient Nonlinear Pancharatnam-Berry Metasurfaces," *Phys. Rev. Lett.* **115**(20), 207403 (2015).
35. M. Tymchenko, J. Lee, N. Nookala, M. A. Belkin, and A. Alù, "Advanced control of nonlinear beams with Pancharatnam-Berry metasurfaces," *Phys. Rev. B* **94**, 214303 (2016).
36. J. S. Gomez-Diaz, M. Tymchenko, J. Lee, M. A. Belkin, and A. Alù, "Nonlinear Processes in Multi-Quantum-Well Plasmonic Metasurfaces: Electromagnetic Response, Saturation Effects, Limits and Potentials," *Phys. Rev. B* **92**, 125429 (2015).
37. R. W. Boyd, *Nonlinear Optics* (Academic Press, 2008).
38. Y. R. Shen, *Principles of Nonlinear Optics* (Wiley-Interscience, 2002).
39. A. Krasnok, M. Tymchenko, and A. Alù, "Nonlinear metasurfaces: a paradigm shift in nonlinear optics," *Mater. Today* **21**(1), 8-21 (2018).
40. A. F. Koenderink, A. Alù, and A. Polman, "Nanophotonics: Shrinking light-based technology," *Science* **348**(6234), 516-21 (2015).
41. J. A. Schuller, E. S. Barnard, W. Cai, Y. C. Jun, J. S. White, and M. L. Brongersma, "Plasmonics for extreme light concentration and manipulation," *Nat. Mater.* **9**, 193-204 (2010).
42. E. Ozbay, "Plasmonics: Merging photonics and electronics at nanoscale dimensions," *Science* **311**, 189-93 (2006).
43. R. Reinisch and M. Nevière, "Electromagnetic theory of diffraction in nonlinear optics and surface-enhanced nonlinear optical effects," *Phys. Rev. B* **28**(4), 1870-85 (1983).
44. M. B. Raschke and Y. R. Shen, "Nonlinear optical spectroscopy of solid interfaces," *Curr. Opin. Solid State Mater. Sci.* **8**(5), 343-52 (2004).

45. R. Czaplicki, M. Zdanowicz, K. Koskinen, J. Laukkanen, M. Kuittinen, and M. Kauranen, "Dipole limit in second-harmonic generation from arrays of gold nanoparticles," *Opt. Express* **19**(27), 157528 (2011).
46. E. A. Mamonov, I. A. Kolmychek, S. Vandendriessche, M. Hojeij, Y. Ekinici, V. K. Valev, T. Verbiest, and T. V. Murzina, "Anisotropy versus circular dichroism in second harmonic generation from fourfold symmetric arrays of G-shaped nanostructures," *Phys. Rev. B* **89**, 121113 (2014).
47. V. K. Valev, A. V. Silhanek, N. Verellen, W. Gillijns, P. Van Dorpe, O. A. Aksamitov, G. A. E. Vandenbosch, V. V. Moshchalkov, and T. Verbiest, "Asymmetric optical second-harmonic generation from chiral G-shaped gold nanostructures," *Phys. Rev. Lett.* **104**, 127401 (2010).
48. M. W. Klein, M. Wegener, N.-A. Feth, and S. Linden, "Experiments on second- and third-harmonic generation from magnetic metamaterial," *Opt. Express* **15**(8), 5238-47 (2007).
49. B. Wang, J. Zhou, T. Koschny, and C. M. Soukoulis, "Nonlinear properties of split-ring resonators," *Opt. Express* **16**(20), 101130 (2008).
50. S. D. Gennaro, M. Rahmani, V. Giannini, H. Aouani, T. P. H. Sidiropoulos, M. Navarro-Cía, S. A. Maier, and R. F. Oulton, "The Interplay of Symmetry and Scattering Phase in Second Harmonic Generation from Gold Nanoantennas," *Nano Lett.* **16**, 5278-85 (2016).
51. B. Corcoran, C. Monat, C. Grillet, D. J. Moss, B. J. Eggleton, T. P. White, L. O'Faolain, and T. F. Krauss, "Green light emission in silicon through slow-light enhanced third-harmonic generation in photonic-crystal waveguides," *Nat. Photonics* **3**(4), 206–210 (2009).
52. Y. Yang, W. Wang, A. Boulesbaa, I. I. Kravchenko, D. P. Briggs, A. Poretzky, D. Geohegan, and J. Valentine, "Nonlinear Fano-Resonant Dielectric Metasurfaces," *Nano Lett.* **15**, 7388-93 (2015).
53. S. Liu, M. B. Sinclair, S. Saravi, G. A. Keeler, Y. Yang, J. Reno, G. M. Peake, F. Setzpfandt, I. Staude, T. Pertsch, and I. Brener, "Resonantly Enhanced Second-Harmonic Generation Using III-V Semiconductor All-Dielectric Metasurfaces," *Nano Lett.* **16**, 5426-32 (2016).
54. W. P. Mccray, "MBE deserves a place in the history books," *Nat. Nanotechnol.* **2**, 259-61 (2007).
55. H. M. Manasevit, "Single-crystal gallium arsenide on insulating substrates," *Appl. Phys. Lett.* **12**, 156-59 (1968).
56. H. C. Liu and F. Capasso, *Intersubband Transitions in Quantum Wells: Physics and Device Applications* (Academic Press, 2000).
57. Y. Yao, A. J. Hoffman, and C. F. Gmachl, "Mid-infrared quantum cascade lasers," *Nat. Photonics* **6**, 432-39 (2012).
58. B. F. Levine, K. K. Choi, C. G. Bethea, J. Walker, and R. J. Malik, "New 10 μm infrared detector using intersubband absorption in resonant tunneling GaAlAs superlattices," *Appl. Phys. Lett.* **50**(16), 1092-94 (1987).
59. K. L. Vodopyanov, V. Chazapis, C. C. Phillips, B. Sung, and J. S. Harris Jr.,

- "Intersubband absorption saturation study of narrow III–V multiple quantum wells in the $\lambda = 2.8\text{--}9\ \mu\text{m}$ spectral range," *Semi. Sci. Technol.* **12**, 708-14 (1997).
60. J. B. Pendry, "Time Reversal and Negative Refraction," *Science* **322**(5898), 71–73 (2008).
 61. N. Segal, S. Keren-Zur, N. Hendler, and T. Ellenbogen, "Controlling light with metamaterial-based nonlinear photonic crystals," *Nat. Photonics* **9**(3), 180–184 (2015).
 62. C. Argyropoulos, P. Y. Chen, F. Monticone, G. D'Aguanno, and A. Alù, "Nonlinear plasmonic cloaks to realize giant all-optical scattering switching," *Phys. Rev. Lett.* **108**(26), 263905 (2012).
 63. S. Keren-Zur, O. Avayu, L. Michaeli, and T. Ellenbogen, "Nonlinear Beam Shaping with Plasmonic Metasurfaces," *ACS Photonics* **3**, 117-23 (2015).
 64. E. Almeida, G. Shalem, and Y. Prior, "Nonlinear Phase Control and Anomalous Phase Matching in Plasmonic Metasurfaces," *Nat. Commun.* **7**, 10367 (2015).
 65. F. B. Niesler, N. Feth, S. Linden, J. Niegemann, J. Gieseler, K. Busch, and M. Wegener, "Second-harmonic generation from split-ring resonators on a GaAs substrate," *Opt. Lett.* **34**(13), 1997-99 (2009).
 66. W. Fan, S. Zhang, K. J. Malloy, S. R. J. Brueck, N. C. Panoiu, and R. M. Osgood, "Second harmonic generation from patterned GaAs inside a subwavelength metallic hole array.," *Opt. Express* **14**(21), 9570–5 (2006).
 67. E. Rosencher, P. Bois, J. Nagle, and S. Delaitre, "Second harmonic generation by intersub-band transitions in compositionally asymmetrical MQWS," *Electron. Lett.* **25**(16), 1063-65 (1989).
 68. D. A. B. Miller, D. S. Chemla, T. C. Damen, A. C. Gossard, W. Wiegmann, T. H. Wood, and C. A. Burrus, "Electric field dependence of optical absorption near the band gap of quantum-well structures," *Phys. Rev. B* **32**(2), 1043-60 (1985).
 69. K. Vijayraghavan, Y. Jiang, M. Jang, A. Jiang, K. Choutagunta, A. Vizbaras, F. Demmerle, G. Boehm, M. C. Amann, and M. A. Belkin, "Broadly tunable terahertz generation in mid-infrared quantum cascade lasers," *Nat. Commun.* **4**, 2021 (2013).
 70. M. Jang, R. W. Adams, J. X. Chen, W. O. Charles, C. Gmachl, L. W. Cheng, F. S. Choa, and M. A. Belkin, "Room-temperature operation of $3.6\ \mu\text{m}$ $\text{In}_{0.53}\text{Ga}_{0.47}\text{As}/\text{Al}_{0.48}\text{In}_{0.52}\text{As}$ quantum cascade laser sources based on intracavity second harmonic generation," *Appl. Phys. Lett.* **97**, 141103 (2010).
 71. M. A. Belkin, F. Capasso, A. Belyanin, D. L. Sivco, A. Y. Cho, D. C. Oakley, C. J. Vineis, and G. W. Turner, "Terahertz quantum-cascade-laser source based on intracavity difference-frequency generation," *Nat. Photonics* **1**, 288-92 (2007).
 72. I. Vurgaftman, J. R. Meyer, and L. R. Ram-Mohan, "Optimized second-harmonic generation in asymmetric double quantum wells," *IEEE J. Quantum Electron.* **32**(8), 1334–1346 (1996).
 73. J. R. Meyer, C. A. Hoffman, F. J. Bartoli, E. R. Youngdale, and L. R. Ram-Mohan, "Momentum-Space Reservoir for Enhancement of Intersubband Second-Harmonic Generation," *IEEE J. Quantum Electron.* **31**(4), 706-14 (1995).

74. K. L. Vodopyanov, V. Chazapis, C. C. Phillips, B. Sung, and J. S. Harris, "Intersubband absorption saturation study of narrow III - V multiple quantum wells in the spectral range," *Semicond. Sci. Technol.* **12**(6), 708–714 (1997).
75. H. Asai and Y. Kawamura, "Intersubband absorption in highly strained InGaAs/InAlAs multiquantum wells," *Appl. Phys. Lett.* **56**, 746-48 (1990).
76. P. Von Allmen, M. Berz, G. Petrocelli, F. K. Reinhart, and G. Harbeke, "Inter-subband absorption in GaAs/AlGaAs quantum wells between 4.2 K and room temperature," *Semicond. Sci. Technol.* **3**, 1211-16 (1988).
77. C. Y. Wang, L. Kuznetsova, V. M. Gkortsas, L. Diehl, F. X. Kärtner, M. A. Belkin, A. Belyanin, X. Li, D. Ham, H. Schneider, P. Grant, C. Y. Song, S. Haffouz, Z. R. Wasilewski, H. C. Liu, and F. Capasso, "Mode-locked pulses from mid-infrared Quantum Cascade Lasers," *Opt. Express* **17**(15), 12929-43 (2009).
78. N. Yu, P. Genevet, M. A. Kats, F. Aieta, J.-P. Tetienne, F. Capasso, and Z. Gaburro, "Light propagation with phase discontinuities: generalized laws of reflection and refraction," *Science* **334**(6054), 333–337 (2011).
79. X. Ni, N. K. Emani, A. V. Kildishev, A. Boltasseva, and V. M. Shalaev, "Broadband Light Bending with Plasmonic Nanoantennas," *Science* **335**(6067), 427 (2012).
80. F. Monticone, N. M. Estakhri, and A. Alù, "Full control of nanoscale optical transmission with a composite metascreen," *Phys. Rev. Lett.* **110**, 203903 (2013).
81. C. Pfeiffer and A. Grbic, "Metamaterial Huygens' surfaces: Tailoring wave fronts with reflectionless sheets," *Phys. Rev. Lett.* **110**(19), 197401 (2013).
82. N. Yu and F. Capasso, "Flat optics with designer metasurfaces," *Nat. Mater.* **13**(2), 139–150 (2014).
83. A. Rose and D. R. Smith, "Overcoming phase mismatch in nonlinear metamaterials," *Opt. Mater. Express* **1**(7), 1232-43 (2011).
84. F. B. P. Niesler, N. Feth, S. Linden, J. Niegemann, J. Gieseler, K. Busch, and M. Wegener, "Second-harmonic generation from split-ring resonators on a GaAs substrate," *Opt. Lett.* **34**(13), 1997–1999 (2009).
85. M. V. Berry, "The Adiabatic Phase and Pancharatnam's Phase for Polarized Light," *J. Mod. Opt.* **34**(11), 1401–1407 (1987).
86. Z. Bomzon, G. Biener, V. Kleiner, and E. Hasman, "Space-variant Pancharatnam-Berry phase optical elements with computer-generated subwavelength gratings," *Opt. Lett.* **27**(13), 1141–1143 (2002).
87. Y. R. Shen, *The Principles of Nonlinear Optics* (Wiley-Interscience, 2002).
88. C. Wang, Z. Li, M. H. Kim, X. Xiong, X. F. Ren, G. C. Guo, N. Yu, and M. Lončar, "Metasurface-assisted phase-matching-free second harmonic generation in lithium niobate waveguides," *Nat. Commun.* **8**, 2098 (2017).
89. P. S. Kuo, J. Bravo-Abad, and G. S. Solomon, "Second-harmonic generation using quasi-phases matching in a GaAs whispering-gallery-mode microcavity," *Nat. Commun.* **5**, 3109 (2014).
90. M. Celebrano, X. Wu, M. Baselli, S. Großmann, P. Biagioni, A. Locatelli, C. De Angelis, G. Cerullo, R. Osellame, B. Hecht, L. Duò, F. Ciccacci, and M. Finazzi,

- "Mode matching in multiresonant plasmonic nanoantennas for enhanced second harmonic generation," *Nat. Nanotechnol.* **10**(5), 412–417 (2015).
91. A. V. Kildishev, A. Boltasseva, and V. M. Shalaev, "Planar Photonics with Metasurfaces," *Science* **339**(6125), 1232009 (2013).
 92. I. Vurgaftman and J. R. Meyer, "Band parameters for nitrogen-containing semiconductors," *J. Appl. Phys.* **94**, 3675 (2003).
 93. M. Beeler, E. Trichas, and E. Monroy, "III-nitride semiconductors for intersubband optoelectronics: a review," *Semicond. Sci. Technol.* **28**(7), 074022 (2013).
 94. E. Rosencher, A. Fiore, B. Vinter, V. Berger, P. Bois, and J. Nagle, "Quantum Engineering of Optical Nonlinearities," *Science* **271**(5246), 168–73 (1996).
 95. M. Z. Alam, S. A. Schulz, J. Upham, I. De Leon, and R. W. Boyd, "Large optical nonlinearity of nanoantennas coupled to an epsilon-near-zero material," *Nat. Photonics* **12**(2), 79–83 (2018).
 96. P. Vasa, R. Pomraenke, G. Cirmi, E. De Re, W. Wang, S. Schwieger, D. Leipold, E. Runge, G. Cerullo, and C. Lienau, "Ultrafast Manipulation of Strong Coupling in Metal–Molecular Aggregate Hybrid Nanostructures," *ACS Nano* **4**(12), 7559–7565 (2010).
 97. P. Vasa, W. Wang, R. Pomraenke, M. Lammers, M. Maiuri, C. Manzoni, G. Cerullo, and C. Lienau, "Real-time observation of ultrafast Rabi oscillations between excitons and plasmons in metal nanostructures with J-aggregates," *Nat. Photonics* **7**(2), 128–132 (2013).
 98. S. R. K. Rodriguez, J. Feist, M. A. Verschuuren, F. J. Garcia Vidal, and J. Gómez Rivas, "Thermalization and Cooling of Plasmon-Exciton Polaritons: Towards Quantum Condensation," *Phys. Rev. Lett.* **111**(16), 166802 (2013).
 99. J. Lee, N. Nookala, J. S. Gomez-Diaz, M. Tymchenko, F. Demmerle, G. Boehm, M. Amann, A. Alù, and M. A. Belkin, "Ultrathin Second-Harmonic Metasurfaces with Record-High Nonlinear Optical Response," *Adv. Opt. Mater.* **4**(5), 664–670 (2016).
 100. G. Khitrova and H. M. Gibbs, "Nonlinear optics of normal-mode-coupling semiconductor microcavities," *Rev. Mod. Phys.* **71**(5), 1591–1639 (1999).
 101. R. Butté, G. Delalleau, A. I. Tartakovskii, M. S. Skolnick, V. N. Astratov, J. J. Baumberg, G. Malpuech, A. Di Carlo, A. V. Kavokin, and J. S. Roberts, "Transition from strong to weak coupling and the onset of lasing in semiconductor microcavities," *Phys. Rev. B* **65**(20), 205310 (2002).
 102. U. Keller, K. J. Weingarten, F. X. Kärtner, D. Kopf, B. Braun, I. D. Jung, R. Fluck, C. Hönninger, N. Matuschek, and J. Aus Der Au, "Semiconductor saturable absorber mirrors (SESAM's) for femtosecond to nanosecond pulse generation in solid-state lasers," *IEEE J. Sel. Top. Quantum Electron.* **2**(3), 435–451 (1996).
 103. F. H. Julien, J. M. Lourtioz, N. Herschkorn, D. Delacourt, J. P. Pocholle, M. Papuchon, R. Planel, and G. Le, "Optical saturation of intersubband absorption in GaAs-Al_xGa_{1-x}As quantum wells," *Appl. Phys. Lett.* **53**, 116–118 (1988).
 104. C. Feuillet-Palma, Y. Todorov, A. Vasanelli, and C. Sirtori, "Strong near field

- enhancement in THz nano-antenna arrays," *Sci. Rep.* **3**, 1361 (2013).
105. P. Reininger, B. Schwarz, H. Detz, D. Macfarland, T. Zederbauer, A. Maxwell, W. Schrenk, O. Baumgartner, H. Kosina, G. Strasser, P. Reininger, B. Schwarz, H. Detz, D. Macfarland, T. Zederbauer, A. M. Andrews, W. Schrenk, O. Baumgartner, H. Kosina, and G. Strasser, "Diagonal-transition quantum cascade detector," *Appl. Phys. Lett.* **105**, 091108 (2014).