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High Aspect Ratio Plasmonic Nanotrench Structures with Large Active Surface Area for Label-Free Mid-Infrared Molecular Absorption Sensing

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ABSTRACT: Mid-infrared spectroscopy offers unique sensing schemes to detect target molecules thanks to the absorption of infrared light at specific wavelengths unique to chemical compositions. Due to the mismatch of the mid-infrared light wavelength on the order of micron and nanometer size molecules, the interaction between them is typically weak, resulting in small signatures of absorption. Plasmonics can play an important role, enhancing photon–matter interactions by localization of light in small volumes or areas. Thus, it enables the increase of light absorption by molecules providing higher sensitivity. Here, we demonstrate the enhancement of infrared absorption in plasmonic trench structures that function as hyperbolic metamaterials. The metamaterial is composed of plasmonic trenches made of aluminum-doped zinc oxide. We use a 5 nm thick silica layer as a model analyte conformally coated around the plasmonic trenches, which absorbs light with wavelengths around 8 μm. The enhanced absorption is achieved by the interaction of bulk plasmon modes propagating in the trenches with the analyte silica layer on the pronounced extended surface area of the trench structure. Such plasmonic nanotrench structures may serve as a highly sensitive bio- and chemo-sensing platform for mid-infrared absorption spectroscopy.

KEYWORDS: mid-infrared absorption spectroscopy, metamaterials, plasmonic materials, transparent conductive oxide, hyperbolic metamaterials, label-free detection, surface-enhanced infrared spectroscopy, SEIRAS

INTRODUCTION

Mid-infrared (IR) light with wavelengths between 2.5 and 20 μm (4,000–500 cm⁻¹) is typically utilized for molecular detection with the technique generally termed as mid-IR spectroscopy.¹⁻³ Mid-IR absorption spectroscopy is a powerful tool to identify chemical species due to their particular absorption bands specific for each molecular bond irrespective of the presence of macrophase as gas, liquid, or solid. It offers a wide variety of applications from industrial process monitoring for pharmaceutical production⁴ to gas sensing.⁵ Mid-IR spectroscopy has been applied for the label-free detection of various biochemical specimens, for example, proteins,⁶⁻¹⁰ to study their folding, unfolding, and membrane characteristics. Moreover, mid-IR spectroscopy also holds promise for the clinical and biomedical analysis of human breath¹¹ and biofluids,¹² such as urine, serum, and blood to diagnose diabetes,¹³ cancers,¹⁴ and different viruses.¹⁵ Clinical studies have been conducted for the detection of biomarkers of acute myocardial infarction, such as cardiac troponin T.¹⁶ However, due to the huge spacial difference of the wavelength (several microns) and target molecules (typically on the order of several nanometers), in this particular case 3 orders of magnitude, interactions are weak, and therefore, it is challenging to detect very trace amounts of molecules. In order to address this issue, there have been considerable efforts to improve the absorption by localizing mid-IR light in dielectric²⁻⁷⁻¹⁰ and plasmonic waveguide structures.¹¹ Moreover, surface enhanced infrared absorption spectroscopy (SEIRAS)²² has been extensively developed in the last several years with the help of plasmonic nanostructures used to confine mid-IR light at the nanoscale.
and improve photon–matter interactions. Certain progress is reported with sensing schemes exhibiting sensitivity toward individual molecules. The schemes typically involve in-plane and vertical pillar plasmonic nanoantennas. 

In these studies, vertical pillars of indium tin oxide (ITO) with protein as an analyte and porous Au coated by 3 nm thick SiO$_2$ as an analyte exhibit absorption of several percent, in which pillars act as a plasmonic monopole antenna that supports plasmonic modes. Furthermore, a graphene metasurface with voltage tuning was demonstrated. 

Thanks to the advent of commercially available quantum cascade lasers (QCLs) that are tunable and able to cover a broad wavelength range in the mid-IR, on-chip chemo-biosensors based on principles of vibrational spectroscopy may become feasible. 

AZO exhibits the plasmonic response (that is a negative real part of the permittivity) in the near- and mid-IR wavelength regions between 1.8 and 3.5 $\mu$m depending on doping and fabrication schemes. 

Its permittivity can be widely tuned by doping from near-IR to mid-IR. AZO can be deposited by the atomic layer deposition (ALD) technique, allowing a conformal and uniform coating of deep trenches. For demonstration of the potential of the trench HMMs for sensing, we coat the trench structure with a 5 nm thick SiO$_2$ layer emulating the presence of an analyte. The SiO$_2$ layer represents a monolayer of proteins, because as was shown in numerous studies of proteins, they typically have thicknesses from 2 to 8 nm. 

An amorphous SiO$_2$ film deposited by ALD has a phonon absorption at around 8.07 $\mu$m (1239 cm$^{-1}$), which is away from the typical absorption bands of water molecules and, therefore, offers itself as a good model
analyzer. Dynamic LIBS were used to perform spatially resolved analysis and to assess the on-chip uniformity of the layers. These results were found to be consistent with the recent bonding of the Si wafer to the LNO single crystal. Furthermore, the bonded wafer was characterized by Raman spectroscopy and X-ray photoelectron spectroscopy (XPS) to confirm the formation of the SiC layer. The XPS measurements indicated the presence of Si, C, and O signals, which is consistent with the proposed bonding mechanism. Finally, the bonding interface was analyzed by atomic force microscopy (AFM), which revealed a smooth surface with distinct features that are characteristic of the SiC layer.

The results from these measurements provide strong evidence for the successful bonding of the Si wafer to the LNO single crystal, which is a crucial step towards the integration of silicon-based devices with oxide electronics. The uniformity and quality of the bonded interface are critical for the performance of these devices, and the findings from this study highlight the potential of this approach for future applications in silicon photonics and quantum computing.

EXPERIMENTAL SECTION

Fabrication of AZO trench HMMs and deposition of 5 nm SiO₂ layer. Two types of samples were fabricated: AZO/Air trench structures and Si trench structures with and without 5 nm of ALD deposited SiO₂ (see Figure 1). The structures were grown on the Si substrate. These two types of trenches are the result of one fabrication process. The full description of the fabrication procedure including deep UV lithography, deep reactive ion etching (DRIE), and atomic layer deposition (ALD) is reported elsewhere. Both structures have trenches of 2.7 μm height and 200 nm wide with a period of Λ = 0.4 μm providing effective anisotropy in the long wavelength regime. The extraordinary permittivity is relevant for electric fields in the plane of the individual trenches, while the extraordinary permittivity is relevant for fields orthogonal to this plane.

Extreme anisotropy of the HMMs with the ability to support propagation of waves with high vectorial components leads to a wide variety of potential applications such as broadband enhancement in the mid-IR wavelength range. The detailed description of the fabrication of the HMMs is presented in Figure 2a, as well as the permittivity of the 100 nm AZO film in Figure 2b. The ordinary permittivity is relevant for electric fields in the plane of the individual trenches, while the extraordinary permittivity is relevant for fields orthogonal to this plane.

For naturally occurring materials the ordinary (ε₁) and extraordinary (εₐ) permittivity components are typically positive, resulting in spherical dispersion in the case of equal permittivity components. The different situations happen when one of the permittivity components becomes negative; in this case, the isofrequency contour has the hyperbolic shape supporting propagation of anomalously high-k waves. There are limited cases in which such phenomena are encountered in natural materials, but they all suffer from high losses and narrow bandwidths. Therefore, such structures need to be artificially designed. Two types of geometries are proposed and realized: metal-dielectric multilayers and metallic wires in a dielectric host. The case where ε₁ > 0 and εₐ < 0 describes a 2-fold hyperboloid and refers to a so-called type-II HMM. It is common for a wire medium and will not be considered here. The opposite scenario, ε₁ < 0 and εₐ > 0, with one-fold symmetry (type-I HMM) mainly represents multilayer structures. Expressions for the ordinary and extraordinary permittivities can be derived within the effective medium approximation (EMA), under the condition that the thicknesses of individual layers are much smaller than the wavelength. The expressions for the ordinary (εₒ) and extraordinary (εₐ) permittivity components are given by:

\[
εₒ = f_m ε_m + f_d ε_d
\]

\[
εₐ = \frac{ε_m ε_d}{f_d ε_m + f_m ε_d}
\]

where f_m and f_d are the fractions of metal and dielectric, and ε_m, ε_d are the permittivities of metal and dielectric, respectively.
effective parameters. Our AZO/Air trench structure has a zero crossing wavelength for $\varepsilon_o$ around 2.7 $\mu$m and becomes Type II HMMs ($\varepsilon_o < 0$ and $\varepsilon_e > 0$) within an extremely wide band; see Figure 2b. Theoretically our AZO trench HMM supports bulk plasmon modes at 3 $\mu$m and above in a wide wavelength range. Wavelengths longer than 3 $\mu$m cover most of the absorption bands of interesting/biologically relevant molecules. Moreover, most of the important absorption resonances in the biomedical sensing are ranged between 2.5 and 10 $\mu$m (4000 to 1000 cm$^{-1}$).

**Numerical simulation.** The differences in reflection of two samples, field profiles, and absorption in Figure 3 were calculated by the Comsol Multiphysics software package. The permittivities of AZO, Si, and SiO$_2$ were taken from refs 41, 42, and 45, respectively. The simulations were conducted for both TE- and TM-polarized light with the angle of incidence 12° counted from the optical axis as shown in the inset of Figure 2b. Figures 3a and 3b show the simulated reflection difference between the samples with and without the 5 nm SiO$_2$ layer with reduced and realistic losses of AZO, respectively. The absorption of the real structure drops to approximately 0.1 (10%) from the reduced loss case of 0.15 (15%). This suggests that a material with lower absorption, such as a doped semiconductor, can improve the absorption. From Figure 3, the optimum height of the trenches is 2.5 to 2.7 $\mu$m in both cases. Therefore, we choose the trench height to be 2.7 $\mu$m, providing almost optimum absorption around 8 $\mu$m in wavelength. In a different sensing situation, where targeted analytes exhibit absorption for different wavelengths, the structural parameters, especially the height of the trenches, should be optimized to operate effectively at certain wavelengths. Figure 3e shows the electric field profile in a trench. We can see the presence of a strong field between the AZO trenches, indicating the feature of a bulk plasmon that propagates in the bulk of the structure. Figure 3f shows enhanced absorption in trenches, stemming from the interaction between the bulk plasmons and analyte. According to Figure 3e, there are hot spots at the four edges of the trenches, and corresponding absorption at these places is high (Figure 3f). However, from the color bar in Figure 3e, the hot spots have the field enhancement factor of 2−3, which are not so significant, and they occupy relatively small volumes of the entire trenches. Therefore, most of absorption originates from the middle of the trenches as shown in Figure 3f. This also suggests that the analyte should be preferably located between the trenches rather than on the top or bottom close to the hot spots for enhanced absorption. In general this structure would be very suitable for “gas” sensing when analyte molecules are equally located inside the trenches rather than located on the top or bottom of the trenches. There are mainly two mechanisms of absorption enhancement: (1) Extended surface area of the trench structures—ca. 14.5 times more surface area in the trench structure relative to a flat surface with the same footprint. (2) The HMM structures support bulk plasmon modes in the trenches which bounce between the top and bottom interfaces of the trenches, interacting with the analyte and resulting in higher absorption in comparison with the surface waves case.

In contrast with the TM-polarized incident light, the TE-polarized light sees the structure as a metal since the electric field is oscillating along the trenches (x-axis in the inset of Figure 2b), experiencing $\varepsilon_o < 0$. Hence, incident light is reflected from the structure and does not propagate inside the trenches, resulting in weak interaction with the SiO$_2$ analyte layer.
Figure 4a,b shows the measured reflectance for the samples with and without 5 nm thick SiO₂ analyte layers. There is a reflectance dip associated with the phonon absorption of the SiO₂ stretching that appears around $\lambda = 8.07 \, \mu m$ (Figure 4b). In order to highlight the absorption enhancement, Figure 4c presents the reflectance difference of both samples, giving the absorption equivalent of SiO₂ layers. The reflectance difference is the highest at the lowest angle of incidence, $\phi = 12^\circ$, reaching 0.09 (9%). Figure 5a and b shows the reflectance spectra and their difference at $\phi = 12^\circ$ with TM-polarized incidence light. The absorption associated with the SiO₂ layer is indicated by an arrow.

Figure 5. Absorption enhancement. (a) Measured free-space reflectance of AZO trench structures with (dotted pink) and without (dotted black) the 5 nm thick SiO₂ layer. (b) Reflection difference. (c) Real ($n$) and imaginary part ($k$) of the refractive index of SiO₂ from ref 45. (d) Measured reflectance of Si trench structures with (dotted pink) and without (dotted black) the 5 nm thick SiO₂ layer. (e) Reflection difference. (f) Reflectance from the 100 nm AZO film on the Si substrate with and without the 5 nm SiO₂ film, as well as from the Si substrate with and without the 5 nm SiO₂ film. Note that Si trenches and substrates have a few nanometers of a native oxide layer. The angle of incidence is $\phi = 12^\circ$ with TM-polarized incidence light for all reflection measurements. Colored shade represents an error bar.

In order to clarify the contribution of enlarged surface area and bulk plasmon modes, we also characterize reflectance from a Si trench structure, a 100 nm AZO film on the flat Si substrate, and the flat Si substrate with and without conducted 5 nm SiO₂ layers. The 5 nm SiO₂ films on the flat AZO and Si surface do not give detectable absorption around $\lambda = 8 \, \mu m$ [Figure 5f]. Figure 5d and 5e show the measured reflectance and its difference of the Si trench structures, resulting in 5.7% difference. Since the Si trenches are dielectric, they do not support any bulk plasmon mode. We deduce that this absorption is caused by the enlarged surface area of the trench structure. Therefore, the rest of 9.4 – 5.7% = 3.7% is the contribution of the bulk plasmon modes, resulting in more than 50% enhancement of absorption over the surface effect.

**CONCLUSIONS**

In conclusion, we demonstrate the enhancement of absorption by a 5 nm thick SiO₂ layer in the mid-IR wavelength range of 6.25 – 10 $\mu m$ ($1600 – 1000 \, \text{cm}^{-1}$). The enhancement originates from nanostructurization of large active surfaces with plasmonic trenches, and as shown it can be used for effective molecular absorption enhancement.
sensing. The structures are composed of multiple high-aspect ratio (1.6–7) subwavelength AZO trenches on a Si substrate, providing 14.5 times more surface area for residing of analyte molecules than the flat surface. The fabrication process for the trench structures is fully compatible with the large-scale CMOS technology. Moreover, the doping level of AZO can be changed to adjust its plasmonic properties for desired wavelengths, leading to the optimum sensitivity of molecules on demand. The AZO trench HMM exhibits broadband performance in the range of wavelengths important for molecular sensing. We report about over 9% absorption increase. This enhancement is enabled by a combination of the extended surface area and the bulk plasmon modes supported by the trench structure. Our demonstration shows that such structures can be effectively designed to detect traces of a target analyte and molecular sensing in mid-IR spectroscopy.

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Author Contributions
E.S. fabricated the samples. T.R. conducted modeling of the structure. O.T. conceived the idea, designed and performed the experiments, and supervised the work. M.E.A.P. and A.V.L. contributed to the discussions of results and manuscript writing. All authors have given approval to the final version of the manuscript.

Notes
The authors declare no competing financial interest.

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