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

Shkondin, Evgeniy; Repän, Taavi; Panah, Mohammad Esmail Aryae; Lavrinenko, Andrei; Takayama, Osamu

Published in:
ACS Applied Nano Materials

Link to article, DOI:
10.1021/acsanm.7b00381

Publication date:
2018

Document Version
Peer reviewed version

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

Evgeniy Shkondin, Taavi Repän, Mohammad Esmail Aryae Panah, Andrei V. Lavrinenko, and Osamu Takayama

DTU Fotonik – Department of Photonics Engineering, Technical University of Denmark, Ørsteds Plads 343, DK-2800 Kgs. Lyngby, Denmark

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

Midinfrared (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. 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 production to gas sensing. Mid-IR spectroscopy has been applied for the label-free detection of various biochemical specimens, for example, proteins, to study their folding, unfolding, and membrane characteristics. Moreover, mid-IR spectroscopy also holds promise for the clinical and biomedical analysis of human breath and biofluids, such as urine, serum, and blood to diagnose diabetes, cancers, and different viruses. Clinical studies have been conducted for the detection of biomarkers of acute myocardial infarction, such as cardiac troponin T. 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 dielectric and plasmonic waveguide structures. Surface enhanced infrared absorption spectroscopy (SEIRAS) 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 SiO2 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 μm 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 SiO2 layer emulating the presence of an analyte. The SiO2 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 SiO2 film deposited by ALD has a phonon absorption at around 8.07 μm (1239 cm⁻¹), which is away from the typical absorption bands of water molecules and, therefore, offers itself as a good model
analyte.\textsuperscript{36} We demonstrate over 9% increase in absorption of mid-IR light by the SiO\textsubscript{2} layer. To the best of our knowledge, this is the first report on mid-IR absorption spectroscopy based on nanotrench HMM structures.

\section*{EXPERIMENTAL SECTION}

Fabrication of AZO trench HMMs and deposition of 5 nm SiO\textsubscript{2} layer. Two types of samples were fabricated: AZO/Air trench structures and Si trench structures with and without 5 nm of ALD deposited SiO\textsubscript{2} (see Figure 1). The structures are grown on the Si substrate. These two types of trenches are the result of one fabrication flow. The full description of the fabrication procedure including deep UV lithography, deep reactive ion etching (DRIE), and atomic layer deposition (ALD) is reported elsewhere.\textsuperscript{35} Both structures have trenches of 2.7 \mu m height and 200 nm wide with a period of \Lambda = 0.4 \mu m providing effective anisotropy in the long wavelength regime. The extraordinary permittivity is relevant for electric fields orthogonal to this plane.

Extreme anisotropy of the HMMs with the ability to support propagation of waves with high vectorial fields orthogonal to this plane, while the extraordinary permittivity is relevant for fields orthogonal to this plane. For naturally occurring materials the ordinary (\epsilon\textsubscript{o}) and extraordinary (\epsilon\textsubscript{e}) permittivity components are typically positive, resulting in spherical dispersion in the case of equal permittivities (isotropic materials) or elliptical dispersion when slightly different positive components represent uniaxial materials. The different situation happens when one of the permittivity components becomes negative; in this case, the isofrequency contour has the hyperbolic shape supporting propagation of abnormally high-\kappa waves. There are limited cases when such phenomena are encountered in natural materials,\textsuperscript{58} 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\textsuperscript{5} and metallic wires in a dielectric host.\textsuperscript{56,64} The case where \epsilon\textsubscript{o} > 0 and \epsilon\textsubscript{e} < 0 describes a 2-fold hyperboloid and refers to a so-called type-I HMM. It is common for a wire medium and will not be considered here. The opposite scenario, \epsilon\textsubscript{o} < 0 and \epsilon\textsubscript{e} > 0, with one-fold symmetry (type-II HMM) mainly represents multilayer structures. Expressions for the ordinary and extraordinary permittivities can be derived within the effective medium approximation (EMA),\textsuperscript{65} under the condition that the thicknesses of individual layers are deeply subwavelength:

\[ \epsilon_{\text{o}} = f_{\text{m}} \epsilon_{\text{m}} + f_{\text{d}} \epsilon_{\text{d}} \]  

(2)

\[ \epsilon_{\text{e}} = \frac{\epsilon_{\text{m}} \epsilon_{\text{d}}}{f_{\text{d}} \epsilon_{\text{m}} + f_{\text{m}} \epsilon_{\text{d}}} \]  

(3)

where \epsilon\textsubscript{m} and \epsilon\textsubscript{d} are the permittivities of metal and dielectric, and \( f_{\text{m}}, f_{\text{d}} \) are the corresponding fractions of metal and dielectric in the multilayer. The trench structure we fabricated is an example of a multilayer with vertically arranged layers. The period of trenches (\Lambda = 0.4 \mu m) is deeply subwavelength for the mid-IR wavelength range \lambda = 6.25\text{–}10 \mu m (1600\text{–}1000 cm\textsuperscript{-1}) allowing application of the effective media theory and subsequent introduction of the
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 \(\varepsilon_e > 0\))\(^{42}\) 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.\(^{42}\) Wavelengths longer than 3 \(\mu\)m cover most of the absorption bands of interesting/biologically relevant molecules.\(^3\) Moreover, most of the important absorption resonances in the biomedical sensing are ranged between 2.5 and 10 \(\mu\)m (4000 to 1000 cm\(^{-1}\)).\(^6\)

**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,\(^{61}\) 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.\(^{51}\) 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.
AZO trench

AZO trench + 5nm SiO2

Reflection difference

Figure 4. Absorption spectra. Measured free-space reflection of AZO trench HMM structures (a) without and (b) with a 5 nm thick SiO2 layer. (c) Reflection difference for $\phi = 12^\circ - 50^\circ$ 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 reflection 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 reflection of Si trench structures with (dotted pink) and without (dotted black) the 5 nm thick SiO2 layer. (e) Reflection difference. (f) Reflection 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.

Figure 4a,b shows the measured reflectance for the samples with and without 5 nm thick SiO2 analyte layers. There is a reflection dip associated with the phonon absorption of the SiO2 stretching that appears around 8.07 $\mu$m (Figure 4b). In order to highlight the absorption enhancement, Figure 4c presents the reflection difference of both samples, giving the absorption equivalent of SiO2 layers. The reflection difference is the highest at the lowest angle of incidence, $\phi = 12^\circ$, reaching 0.09 (9%). Figure 4a and b shows the reflectance spectra and their difference at $\phi = 12^\circ$. The real and imaginary part of SiO2’s refractive index is shown in Figure 5c for reference. Note that multiple reflection dips below 7.5 $\mu$m are caused by the water absorption. We assume that absorption from the SiO2 film follows the Beer–Lambert law, exhibiting the saturation of absorption as the thickness increases.62 The AZO trench structures exhibit a high reflection difference of approximately 9.4%, which shows qualitatively good agreement with the prediction of Figure 3.

In order to clarify the contribution of enlarged surface area and bulk plasmon modes, we also characterize reflection 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 reflection 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 cm$^{-1}$). The enhancement originates from nanostructurization of large active surfaces with plasmonic trenches, and as shown it can be used for effective molecular
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.

**AUTHOR INFORMATION**

**Corresponding Author**

*E-mail: otak@fotonik.dtu.dk. Phone: +45 4525 6571. Fax: +45 4593 6581.*

**ORCID**

Andrei V. Lavrinenko: 0000-0001-8853-2033
Osamu Takayama: 0000-0003-3525-3262

**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.

**ACKNOWLEDGMENTS**

This work was supported by Villum Fonden "DarkSILD project" (11116) and Direktør Ib Henriksens Fond, Denmark. The authors would like to acknowledge the support from the Danish National Center for Micro- and Nanofabrication (DTU Danchip). O.T. sincerely acknowledges Dr. M. D. Stine Munkholm-Larsen, Resident Medical Officer, The Doctors in Gothersgade, Copenhagen K, Denmark, for fruitful discussion and valuable comments on the detection of antibodies and proteins, and clinical diagnoses.

**REFERENCES**


