Mid-Infrared SEIRA Sensors Employing Liquid-Metal-Based Nanophotonic Structures

Xianglong Miao[1], Ting Shan Luk[2], Peter Qiang Liu[1,*]
[1]*Department of Electrical Engineering, University at Buffalo, The State University of New York, Buffalo, NY 14260, USA*
[2]*Center for Integrated Nanotechnologies, Sandia National Laboratories, Albuquerque, NM 87123, USA*
**E-mail address: pqliu@buffalo.edu*

Abstract: We demonstrate mid-infrared SEIRA sensors employing an unconventional liquid-metal-based nanophotonic structure, which allows for convenient delivery of thin film analytes into the sensing hot spots. State-of-the-art SEIRA sensing performance was demonstrated for sensing monolayer 1-octadecanethiol.

1. Introduction

Surface-enhanced infrared absorption (SEIRA) spectroscopy is a powerful technique to achieve highly sensitive detection and sensing of trace amount of analytes. Resonant nanophotonic structures which can confine light in subwavelength volumes are usually employed in SEIRA sensors to significantly enhance the interactions between light and analytes. In general, the SEIRA signal is proportional to the enhancement factor of electric field intensity as well as the spatial overlap between the analytes and the significantly enhanced field. One effective way to achieve extreme confinement and enhancement of light is employing nanophotonic structures which have nanometric hot spots, such as nano-gaps [1]. However, delivering analytes into such nanometric hot spots can be very challenging and inefficient, and therefore the overall SEIRA sensing performance may not benefit from the frequently used strategy of reducing the size of the hot spots to improve field confinement/enhancement. To address this conflict between field confinement/enhancement and analyte delivery, we demonstrate an unconventional SEIRA sensor based on nano-patch antennas that employ liquid metal as the ground plane. Our liquid-metal-based SEIRA sensor structures not only provide exceedingly high field confinement/enhancement in the nanometric gaps of the nano-patch antennas, but also allow for convenient and efficient delivery of analytes into these nanometric gaps (i.e., hot spots). Our sensors demonstrated state-of-the-art SEIRA sensing performance for sensing self-assembled monolayer (SAM) 1-octadecanethiol (ODT) in the spectral region around 3000 cm^{-1}, and also achieved excellent sensing performance for sensing spin-coated PMMA nanometric films in the spectral region around 1500 cm^{-1}.

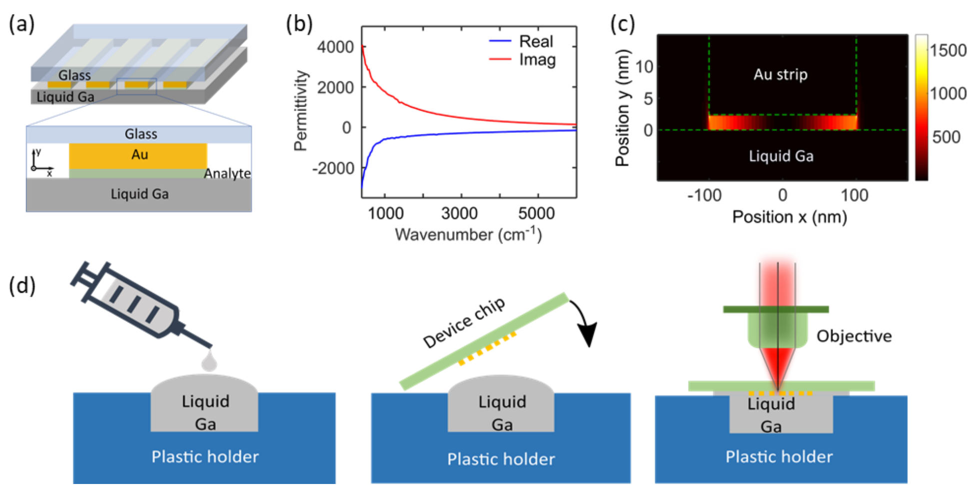

Figure 1. (a) Schematic of the liquid-metal-based nano-patch antenna structure. (b) Relative permittivity of liquid gallium extracted from spectroscopic ellipsometry characterization. (c) Simulated electric field intensity distribution of a liquid-gallium-based nano-patch antenna structure at its resonance frequency. (d) Schematics of the procedure for forming complete liquid-gallium-based nano-patch antenna sensors.

2. Device design and fabrication

A schematic of our sensor structure is illustrated in Fig. 1a, which is essentially an array of nano-patch antennas [2]. Each nano-patch antenna structure consists of an elongated gold nano-patch separated from the liquid-metal (i.e., liquid-gallium) ground plane by an ultra-thin film of analytes (with nanometric thickness). We choose liquid gallium as the ground plane metal, mainly because gallium is a non-toxic metal with suitable optical properties (see Fig. 1b) and a low melting point (~30 °C). As shown in the simulated near-field intensity distribution Fig. 1c, the electric field intensity is indeed highly confined and enhanced in the nanometric gap of the nano-patch antenna and has nearly ideal spatial overlap with the analyte thin film. Both of these advantageous characteristics are expected to produce large enhancement of the SEIRA signals associated with the analytes.

Thanks to the fluidic nature of liquid gallium, the complete sensor structure can be formed by first coating the target analyte thin film on the gold nano-patches (i.e., the sensor chip surface), and then simply placing the sensor chip on liquid gallium to complete the nano-patch antenna structures, as illustrated in Fig. 1d. Such a sensor preparation procedure is not only simple and suitable for point-of-care applications, but also makes the delivery of analytes highly efficient, as the analyte is delivered before the complete nanometric cavities (hot spots) are formed.

As a proof-of-concept demonstration, we fabricated such sensor structures targeting SEIRA sensing in different mid-infrared spectral regions. Elongated gold nano-patches of various widths (70 nm thick) were patterned on glass substrates (for the spectral region above 2000 cm^{-1}) or CaF_2 substrates (for even wider spectral region, i.e., above 900 cm^{-1}) using electron-beam lithography. We used SAM ODT (~2.4 nm thickness) and spin-coated nanometric PMMA films as model analytes to demonstrate the functionality and performance of these SEIRA sensors.

3. Results

Figure 2a shows the experimental reflection spectra of a set of SEIRA sensors with SAM ODT adsorbed on the surface of the gold nano-patches. The broadband reflection dips are the resonances of the set of nano-patch antennas with the specified widths. The relatively narrow spectral features around 2900 cm^{-1} are associated with the four molecular vibrational modes of ODT [3] in this spectral region. The net reflection changes induced by the SAM ODT (i.e., the SEIRA signals) were extracted from the reflection spectra in Fig. 2a by performing a baseline subtraction, and the corresponding results are shown in Fig. 2b. The sensors with 380 nm or 400 nm wide gold nano-patches have resonant frequencies matching the ODT molecular absorption lines well, and the extracted SEIRA signals are close to 10%, which represent the state-of-the-art SEIRA performance for sensing SAM ODT in the literature. Figure 2c shows the experimental reflection spectra of a set of SEIRA sensors with ~30 nm PMMA spin-coated on the surface of the gold nano-patches, which also exhibit excellent sensing performance for sensing the PMMA molecular vibrational modes in the spectral region from 1200 cm^{-1} to 1700 cm^{-1}.

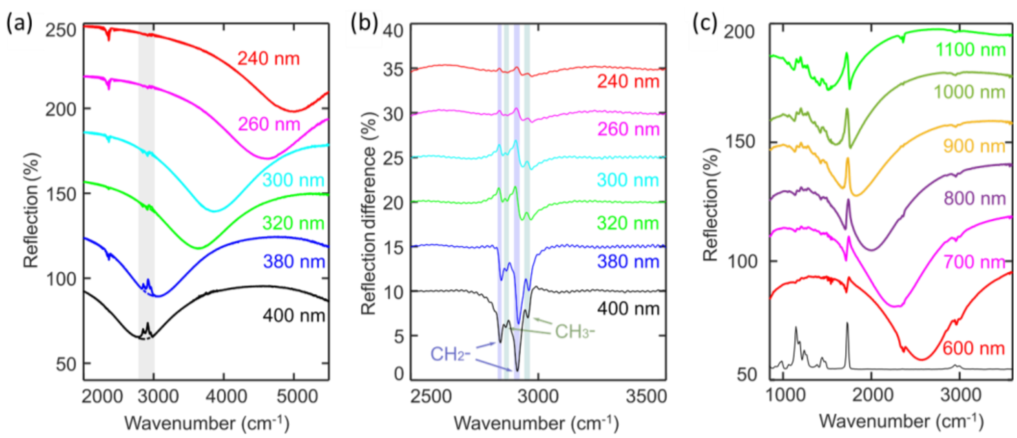

Figure 2. (a) Measured reflection spectra of a set of SEIRA sensors with SAM ODT as the target analyte. The sensors have different gold nano-patch widths. Dashed lines represent the baseline fitting. (b). Extracted net SEIRA signals associated with the SAM ODT from the spectra in (a). (c) Measured reflection spectra of a set of SEIRA sensors with a spin-coated PMMA thin film (~30 nm thick) as the target analyte.

4. Conclusion

In summary, we experimentally demonstrated high-performance SEIRA sensors based on nano-patch antennas which employ liquid gallium as the ground plane. Our sensor structures allowed for convenient and efficient delivery of thin film analytes into nanometric hot spots with exceedingly high field enhancement, and demonstrated state-of-the-art SEIRA sensing performance for sensing SAM ODT in the spectral region around 3000 cm^{-1}, and also achieved excellent performance for sensing nanometric PMMA films in the spectral region around 1500 cm^{-1}.

This works is supported in part by NSF (ECCS-1847203, ECCS-1919798), and the Center for Integrated Nanotechnologies, an Office of Science User Facility operated for the U.S. Department of Energy Office of Science.

References

[1] L. Dong et al., "Nanogapped Au antennas for ultrasensitive surface-enhanced infrared absorption spectroscopy," Nano Lett. **17**, 5768 (2017).
[2] G. M. Akselrod et al., "Probing the mechanisms of large Purcell enhancement in plasmonic nanoantennas," Nat. Photon., **8**, 835-840 (2014).
[3] X. Chen et al., "Plasmonic vertically coupled complementary antennas for dual-mode infrared molecule sensing," ACS Nano **11**, 8034 (2017).