Low-cost large-area fabrication method and surface-enhanced infrared nanoantenna sensors and 3D chiral plasmonic nanostructures

Harald Giessen[1], Jun Zhao[1], Bettina Frank[1], Stefano Cataldo[1], and Frank Neubrech[2]

[1] 4th Physics Institute, University of Stuttgart, Pfaffenwaldring 57, 70569 Stuttgart, Germany
email: giessen@physik.uni-stuttgart.de
[2] Kirchhoff Institute for Physics, University of Heidelberg, Im Neuenheimer Feld 227, 69120 Heidelberg, Germany

Abstract

We use low-cost hole-mask colloidal nanolithography to manufacture large-area resonant split-ring metamaterials, and measure their infrared optical properties. This novel substrate is applied for antenna-enhanced SEIRA measurement using ODT and deuterated ODT, which demonstrates easy adjustability of our material to the vibrational modes. We further show fabrication of 3D staircase-type plasmonic nanospirals. The latter ones exhibit as expected a large circular dichroism.

1. Introduction

Infrared spectroscopy is an important analytical tool for chemistry, biology, pharmacy, and medicine. Dipole- and Raman-active modes provide key information about structural and conformational properties of small molecular species as well as larger units, such as proteins or peptides. Unfortunately, the absorption and scattering cross sections of molecules in the infrared are relatively low, which requires large quantities for analysis. One way to overcome this problem is the use of surface enhanced methods, such as surface enhanced Raman spectroscopy (SERS) and surface enhanced infrared absorption (SEIRA) spectroscopy. In these cases, the local electric field is strongly enhanced by plasmonic effects at rough metal surfaces and hence the lower detection limit is reduced.

Recently, resonantly enhanced SERS and SEIRA methods have been introduced. Halas and coworkers introduced a nanoshell-covered large-area substrate that gives simultaneous SERS and SEIRA enhancement.[1] The SEIRA sensitivity was even further increased to the attomolar level by Neubrech et al.[2] using specifically tailored resonant nanoantennas. Cubukcu et al.[3] utilized metamaterial geometries for SEIRA, however on small-area samples fabricated by e-beam lithography. In order to bring these advances into chemistry and chemistry labs and allow for a plethora of applications, large-area low-cost fabrication is required.

2. Experiment

Here we present an elegant solution to this problem, introducing a low-cost simple fabrication method for resonant nanoantenna SEIRA substrates with cm² of defect-free areas which allow for easy adjustment to the desired vibrational frequencies. We manufacture metallic split-ring-resonator (SRR)

ISBN 978-952-67611-2-1

metamaterial nanoantennas using hole-mask colloidal nanolithography[4] followed by tilted angle metal evaporation. We produced several samples with different SRR geometries and hence a set of different resonance frequencies to demonstrate easy adjustability. SEIRA sensing down to the monolayer sensitivity was observed both for normal as well as deuterated ODT, as shown in Figure 1. At the same time, our manufacturing method represents an elegant method to produce large-area and low-cost SRR metamaterials with resonances in the near- and mid-infrared spectral range.

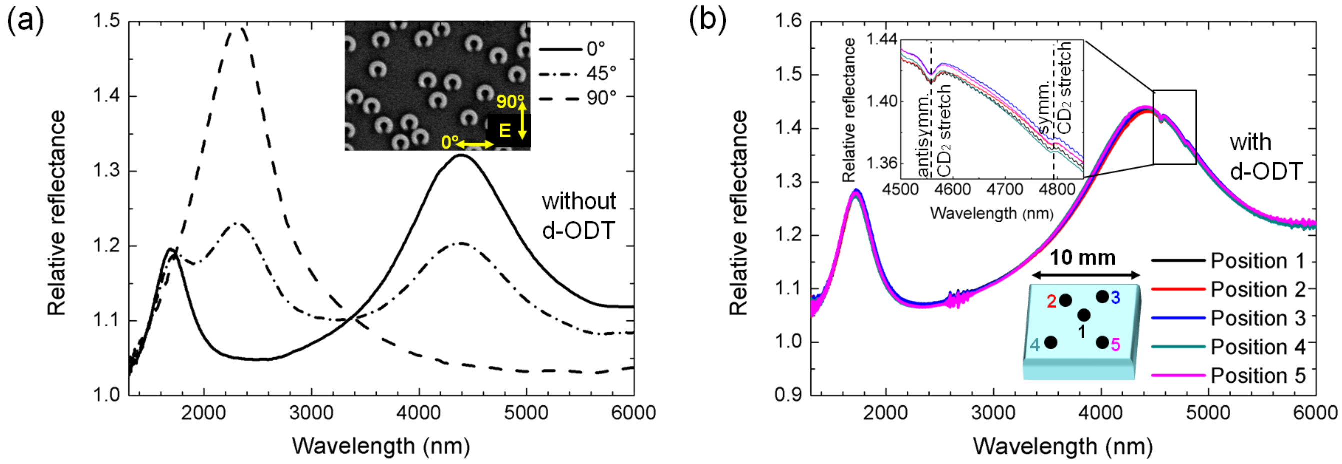

Figure 1: Demonstration of hole-mask colloidal SEIRA substrate using tilted angle evaporation. SRR diameter is 300 nm, gold height is 25 nm. (a) Spectra of SRR structures before deuterated (d-)ODT deposition with linearly polarized light at angles 0°, 45°, and 90° with respect to the gap, which is illustrated in the inset. (b) Spectra of the structures after d-ODT deposition using linearly polarized light parallel to the gap. The different spectra are measured at different positions of the sample, which is illustrated in the cartoon in the lower right corner. The spectra in the upper left corner show the two strongest modes of d-ODT: antisymmetric CD_2 stretch at 4559 nm (2193 cm^{-1}) and symmetric CD_2 stretch at 4793 nm (2086 cm^{-1}).

To further demonstrate the potential of our method, we fabricated by this method [5] three-dimensional nanospirals over a cm² area. First, MgF_2 was evaporated, using both the possibility to decrease the azimuthal evaporation angle while increasing the polar (rotation) angle. The key technique was to slow down the polar rotation during evaporation, so that a spiral ramp was manufactures. Second a 20 nm layer of gold on a 2 nm Cr adhesion layer was evaporated on top of that ramp. The stacking alignment is perfect, as the evaporation uses the same holes as templates. Figure 2a shows an SEM image of the manufactured spirals, and figure 2b shows the measured circular dichroism spectra using a forward-backward measurement technique which accounts for the fact that our structure does not possess C3 or C4 symmetry [see 5, supplemental information]. The figure displays the spectra for left-handed 3D chiral spirals as blue curve and for right handed spirals as red curve. The differences in amplitude arise from the fact that the density of the nanospirals varies somewhat on different samples. The spectral resonances correspond to the first, second, and third plasmonic resonance in a split-ring resonator geometry.

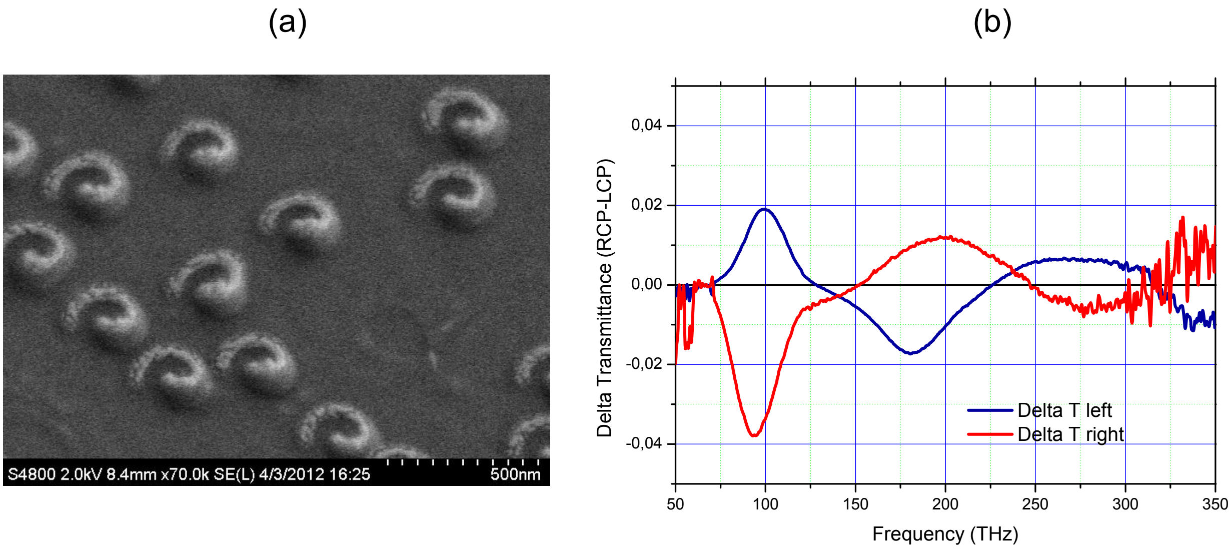

Figure 2: (a) SEM image of 3D plasmonic nanospirals fabricated by colloidal nanopinhole lithography [5]. The structures consist of a MgF_2 spacer layer and 20 nm gold spiral on top. The height difference between start and end is 30 nm. (b) Transmission difference between incident LHC and RHC polarized light, corresponding roughly to the circular dichroism of the sample. The values reach 0.04, which corresponds to a CD of about 1200 mdeg. The blue curve represents left-handed 3D plasmonic spirals, and the red one right-handed spirals.

3. Conclusion

We have demonstrated that colloidal pinhole nanolithography is able to manufacture low-cost, large-area plasmonic nanostructures that are well suited for SEIRA sensing in the infrared as well as for 3D chiral plasmonic nanostructures, which can also be used as broadband spiral nanoantennas.

4. Acknowledgements

We acknowledge support from DFG, BMBF, GIF, AvH, BW Stiftung, and Zeiss Foundation.

References:

1. Kundu, J., Le, F., Nordlander, P., Halas, N. J. “Surface enhanced infrared absorption (SEIRA) spectroscopy on nanoshell aggregate substrates”, *Chem. Phys. Lett.*, Vol. 452, No. 1-3, 115–119, 2008.
2. Neubrech, et al. “Resonant plasmonic and vibrational coupling in a tailored nanoantenna for infrared detection”, *Phys. Rev. Lett.* Vol. 101, 157403-1-4, 2008.
3. Cubukcu, E., Zhang, S., Park, Y. S. Bartal, G. and Zhang, X. “Split ring resonator sensors for infrared detection of single molecular monolayers”, *APL*, Vol. 95, 043113–1-3, 2009.
4. Fredriksson, H. et al. “Hole-mask colloidal lithography”, *Adv. Mater.* Vol. 19, No. 23, 4297-4302, 2007.
5. S. Cataldo, J. Zhao, B. Frank, F. Neubrech, C. Zhang, P. V. Braun, and H. Giessen, „Hole-Mask Colloidal Nanolithography for Large-Area Low-Cost Metamaterials and Antenna-Enhanced SEIRA Substrates“, *ACS Nano 6*, 979 (2012)