Large Area Periodic Nanogap Arrays for Raman and Fluorescence Enhancement: Modeling and Performance

T. Siegfried¹, Y. Ekinci¹², H. Solak³, O.J.F. Martin⁴, H. Sigg¹
¹Paul Scherrer Institut, 5232 Villigen PSI, Switzerland
²Laboratory of Metal Physics and Technology, ETH Zurich, 8093 Zurich, Switzerland
³Eulitha AG, 5232 Villigen PSI, Switzerland
⁴Nanophotonics and Metrology Laboratory, Swiss Federal Institute of Technology Lausanne, 1015 Lausanne, Switzerland

thomas.siegfried@psi.ch

Abstract: We will discuss the use of dense periodic nanogap arrays for plasmonic sensing applications. A high-throughput fabrication process will be presented, that yields nanogap arrays with periodicities above 150 nm, and with accurately controlled gap widths of ±1.5 nm over mm² large areas.

OCIS codes: (240.6695) Surface-enhanced Raman scattering; (220.4241) Nanostructure fabrication

1. Introduction

Few-nanometer gap sizes between noble metals, like gold and silver can produce highly localized plasmons with tremendously focused electromagnetic energies[1]. These, in return, are the origin for high sensitivity spectroscopy such as surface enhanced Raman scattering (SERS) with a detection threshold as low as a single molecule.

2. Methods

Extreme ultraviolet interference lithography[2] (EUV-IL) was used to provide 1D line arrays or 2D dot arrays on substrates made of float glass or silicon with hydrogen silsesquioxane (HSQ) photo resist. Angular evaporation between 30-60° from the surface normal was then utilized to evaporate metal, typically Au and Ag, directly onto the patterned photoresist (Fig. 1 and 2). The process window could be adjusted to yield nanogap dimensions and metal layer thicknesses from sub-10 nm[3] to above 70 nm and from 20 nm to above 150 nm, respectively. The layer thickness and the width of the pattern could be controlled down to sub-10 nm gap sizes over extremely large areas (mm²).

3. Results

The optical response of these samples was first characterized for varying metal layer thicknesses. By changing the width of the nanogaps, the peak of the plasmon resonance could be tuned between 550 and 850 nm. The enhancement of both Raman and Fluorescence was found to scale with the resonance magnitude and position leading to strongest values when the plasmon resonance is in between the excitation and detection frequency. Average enhancement factors were determined to exceed 1×10⁶ in the case of SERS on a self assembled thiol monolayer and >50 for the fluorophore Dylight 649. Originating from the dense periodic array and the well controlled pattern geometry, the enhancement was found to be highly reproducibly over the whole sensor area with exceptionally low standard deviations below 3 %. Polarization dependent SERS studies (Fig. 3b) reveal the deterministic character of the substrate. The angular deposition process was modeled by a statistical approach yielding realistic cross section geometries for subsequent near-field enhancement simulations. A 3D Finite Element...
Method with a periodic surface integral approach[4] was used for simulations. The obtained reflection spectra were found to be in good agreement with the experiments. The experimental work was further supported by near-field intensity simulations, which provide a better understanding of the SERS enhancement.

![Graphs showing SERS and fluorescence intensity](image)

**Fig. 3:** (a) SERS intensity for varying nanogap size and a gold layer thickness of 100 nm. (b) SERS intensity as a function of the sample rotation for linearly polarized excitation. Values correspond to the 1007 cm\(^{-1}\) peak of a self-assembled benzenethiol monolayer.

**Fig. 4:** Fluorescence and SERS enhancement for a 30 nm thick nanogap array with varying nanogap size. A self-assembled benzenethiol monolayer is used for SERS and a Dylight 649 layer is used for fluorescence experiments.

### 4. Conclusions

Nanogap arrays were fabricated reproducibly over mm\(^2\) large areas using a 2-step process, which enables the realization of a wide range of gap sizes down to sub-10 nm. Plasmon resonances can be tuned over a broad range of the visible spectra throughout the specimen. Key features of these pattern are its uniform average SERS and Fluorescence enhancements of 1x10\(^6\) and 55, respectively, as well as its extremely high area to area reproducibility of 3 %.

### References


