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Multiplexed Chemoselective Sensors based on Metal Nanohole Arrays

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Introduction

Recently the extraordinary transmission of light through arrays of subwavelength holes in metals [1-3] has been demonstrated as a chemical/biological sensor platform [4-5]. Like the reflection from surface plasmon resonators (SPR) the spectral response of this transmission can be very sensitive to the microscopic surface chemistry in the vicinity of the nanoholes. Noble metals such as gold offer excellent surfaces to perform various binding chemistries making them attractive for chemical sensors.

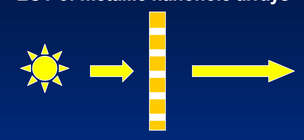
Motivation

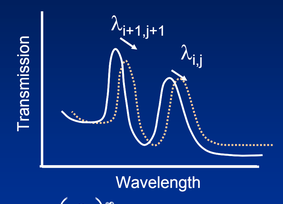
The choices for making sensitive chemical sensors are very limited. Most optical based sensors suffer from very large dimensions. Lately, nanohole-arrays have emerged as a plausible platform with much smaller dimensions. By using the extraordinary transmission of these nanohole-arrays and specially designed molecules to ligate desired analytes it should be possible to design an arrayed detector for high-sensitivity gaseous detection.

Previous Work

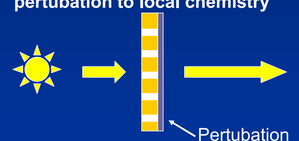
EOT of metallic nanohole arrays

$$\lambda(i,j) = \frac{a}{\sqrt{i^2 + j^2}} \sqrt{\frac{\varepsilon_m \varepsilon_d}{(\varepsilon_m + \varepsilon_d)}}$$





Nanohle array with a pertubation to local chemistry

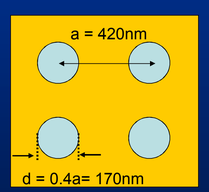


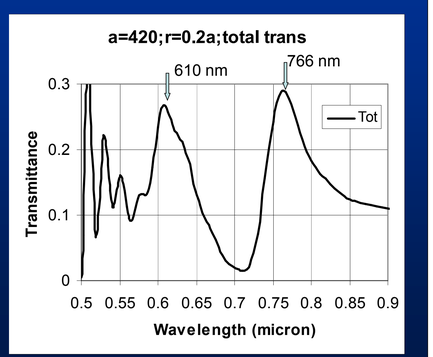
$$n_{eff} = \left(\frac{2}{I_d}\right)\int_0^{\infty} n(z)\exp(-2z/I_d)dz$$

A change of the chemistry in the vicinity of the nanoholes causes a resonant shift. [6]

Modeling

FDTD Simulations were performed using OptiFDTD allowing for the arrays to be dimensioned before any fabrication.

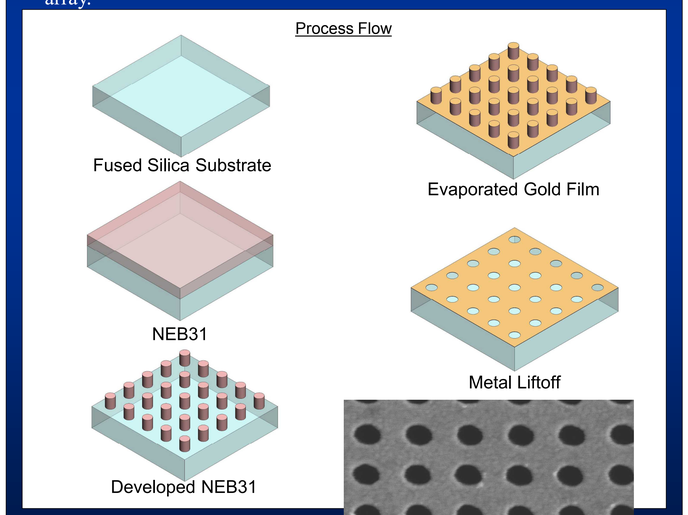


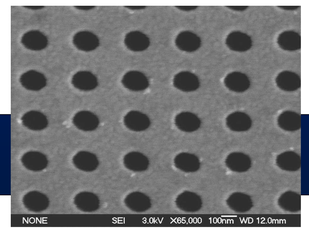


Fabrication

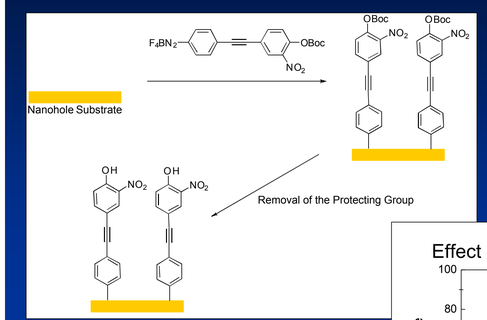
Nanohole arrays were fabricated using negative tone e-beam lithography. E-beam lithography scales to larger areas much better than FIB techniques. The steps for this process are as follows:

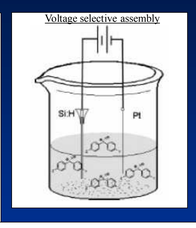
1. A flash layer to prevent charging is applied to the surface of a fused silica substrate.
2. Negative tone resist (NEB31) is spun onto the substrate for the patterning of the nanohole-array.
3. The resist is patterned by an JEOL 9300FS lithography tool and developed leaving behind pillars of resist.
4. 10 Å of Titanium and 100 Å Gold is evaporated onto the surface to form the metallic film.
5. The remaining resist is lifted off with NMP to form the nanohole-array.



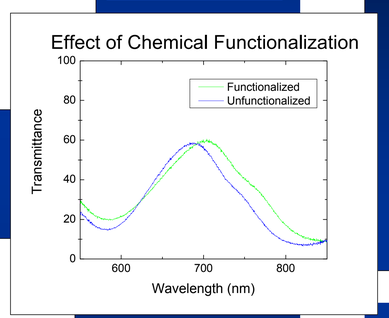


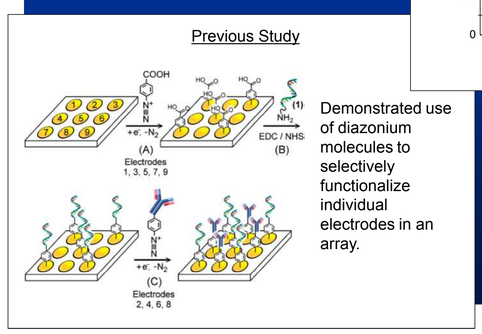
Chemical Functionalization





Deprotection of sensing compound.





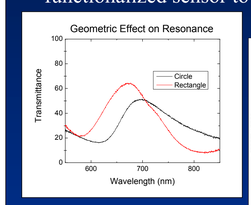
Demonstrated use of diazonium molecules to selectively functionalize individual electrodes in an array.

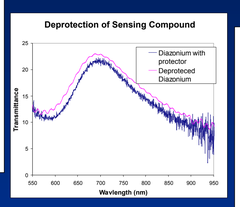
The voltage selective functionalization allows for

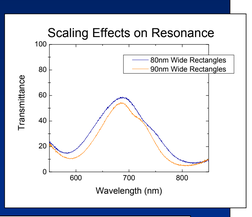
- Very small sensing surfaces
- A variety of chemistries
- Multiplexed Sensing

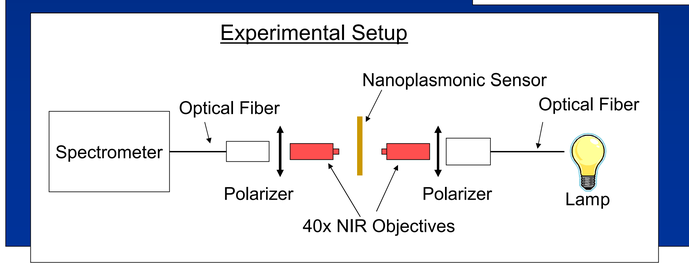
Transmission Characterization

- Nanohole arrays with and without chemical functionalization have been optically characterized.
- Deprotecting the diazonium causes a small blue shift.
- Current work is focused on investigating the sensitivity of the functionalized sensor to the chemical weapon surrogate DMMP.

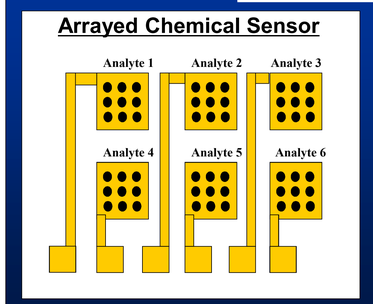




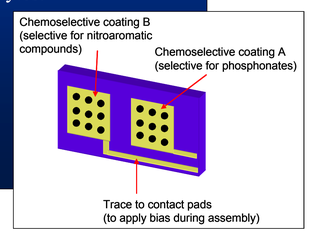




Future Work



Trials are underway to attach two different ligands to one arrayed sensor. This will lead to a sensor capable of distinguishing between different analytes.



Summary

- We have demonstrated a submicron periodic metal nanohole array with a voltage selective chemical functionalization.
- We have further shown device functionalization using another ligand which is capable of sensing the chemical weapon stimulant (DMMP.)
- Experiments are in progress for making multiplexed arrays for detection of multiple compounds in an on chip fashion with ultra-compact geometry.

References

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