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Chemoselective Metal Nanohole Arrays for Compact Multiplexed Chemical Sensors

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Abstract: Chemoselective functionalization of nanohole arrays can enable ultracompact on-chip multiplexed chemical detection with integrated detection capability. We describe a sensor paradigm based on directed assembly technique to reductively assemble diazonium molecules (e.g. 4-nitrodiazonium tetrafluoroborate) on to a subwavlength nanohole array fomed in Au film. The compounds have selective binding to various molecules of interest. A spectral shift of ~ 70nm was observed when a chemical functionalization was carried out.

OCIS codes: (000.0000) General; (000.0000)

1. Introduction

Demonstration of extraordinary transmission of light through arrays of subwavelength holes in metals [1-3] in the recent years has opened up the possibility of using such structures as chem./bio sensor platforms [4-5]. This transmission can be exquisitely 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. We propose an approach for a compact sensor geometry with potential for multiplexed chemical detection and ambient visible light operation using a combination of approach based on 1) electron-beam lithography which enables the patterning of an array of ~50-150nm periodic features of controllable shape and dimensionality and 2) voltage sensitive directed assembly technique that we have developed at Sandia to reductively assemble diazonium molecules designed to interact with specific classes of compounds. In this paper we present prelimary results showing e-beam based fabrication of nanohole arrays in Au film with < 500nm periodicity followed by the corresponding effect on transmission characterisitics upon voltage sensitive chemical functionalization with a model compound 4-nitrodiazonium tetrafluoroborate.

2. Electron-beam lithography based fabrication of metal nanohole arrays

Subwavelength apertures and periodic hole arrays have been frequently fabricated using a single step approach of direct focused ion-beam milling of metallic films[6,7]. Other approaches have used photolithography followed by etching of the metal [8]. We have fabricated our nanohole arrays by two different techniques one based on metal etching and the other based on evaporation and liftoff. In the first approach we deposited a ~ 100nm Au film on a SiO_2 substrate (e.g. cover glass slip) coated with 1nm of Ti adhesion layer. This was followed by a spin of ~ 250nm thick polymethylmethacrylate (PMMA) e-beam resist. Sets of 100μm X 100μm square regions each with different periodicities 'a' of 275nm and 420nm with circular holes (nominal design radius 0.15 -0.2 x a) and triangular holes (sides ~0.5 x a) was patterned by e-beam lithography on a JEOL 9300FS system. The patterned resist was developed away followed by ion milling of the Au film using the resist as the etch mask. While this approach was successful in etching the metal under the exposed regions it had two undesirable aspects 1) flaring of the metal at the edges due to redeposition 2) shape distortion due to mask damage during the aggressive metal etching process (Figure1a).

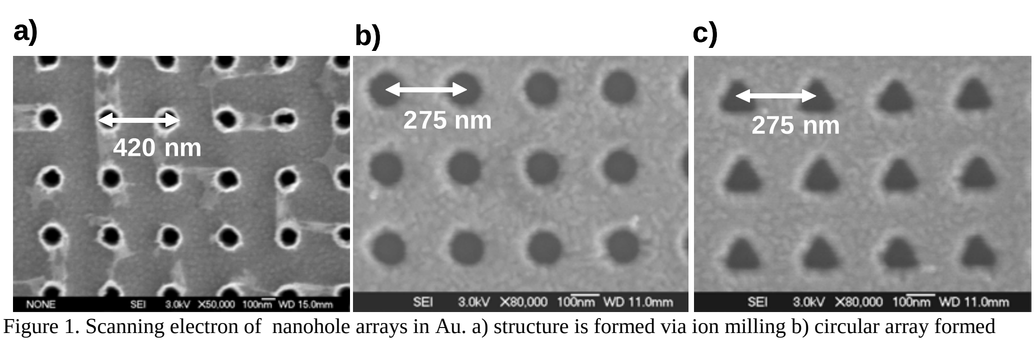

Figure 1. Scanning electron of nanohole arrays in Au. a) structure is formed via ion milling b) circular array formed using lift-off process c) triangular array formed via lift-off process.

An alternate approach is to use a negative tone resist (e.g. NEB31). In this case, a layer of the resist is spun on to the substrate followed by e-beam exposure of the pattern. After development the exposed regions are left behind while the remaining area is clear of resist. A ~ 100nm thick layer of Au is evaporated and the substrate is soaked in N-methylpyridine (NMP) at 85^{o}C to lift off the metal in the patterned region. This approach yielded patterned structure with cleaner and sharper edges maintaining the designed shape. Figure 1b shows a square array of circular holes with a period of 275nm and figure 1c square array of triangular holes. Triangular hole arrays have recently been demonstrated to have higher transmission throughput than circular hole arrays due to larger perimeter effect[9].

3. **Chemical functionalization of nanohole array**

In order to impart chemoselectivity to our nanohole arrays we use a directed assembly technique [10] to reductively assemble diazonium molecules designed to interact with specific classes of compounds. The coating is applied by negatively biasing the array in the presence of a desired diazonium. The diazonium salt will be reduced expelling nitrogen and will form a covalent metal-carbon bond on the biased array. Assembling the sensor in this way provides a scalable technique to build larger arrays if needed in addition to reduced interaction of the compound with common interferants like diesel fuel. Test assembly experiments were performed using the model compound 4-nitrodiazonium tetrafluoroborate (figure 3).

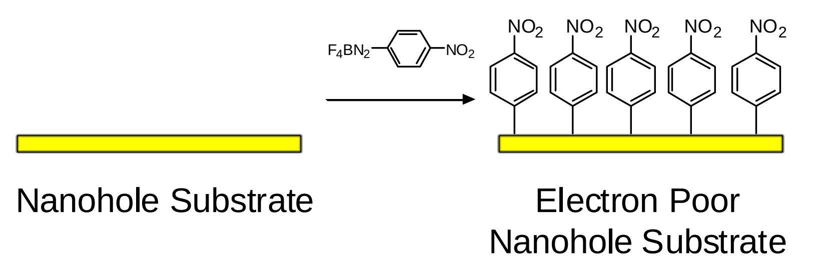

Figure 3: Assembly of a model diazonium compound onto a metal nanohole substrate.

4. Optical characterization

Optical transmission measurement was performed by selectively illuminating of the nanhole array patch at a time. This was accomplished by collimating the light from a fiber coupled lamp and focusing it on to the sample using an imaging objective (figure 4a) producing a small spot size (~ 50 µm).

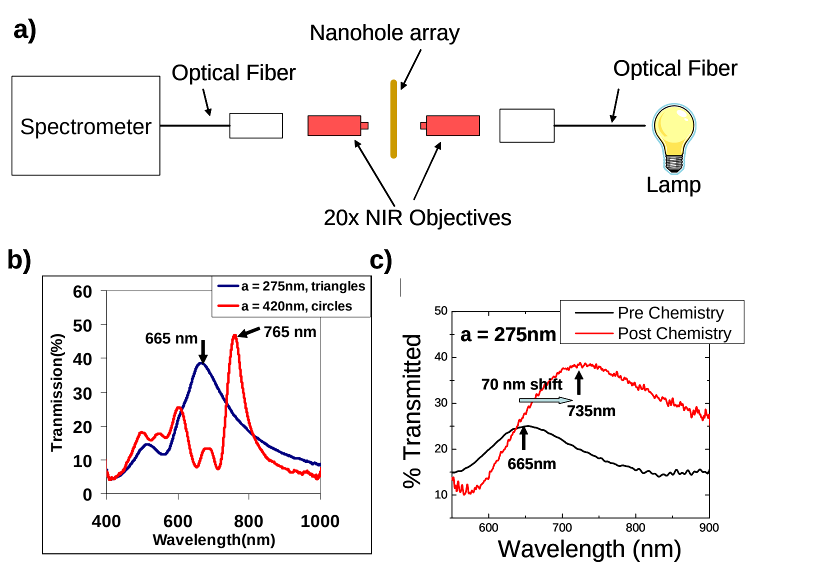

Figure 4: Optical characterization of the metal nanohole array. a) Schematic of the optical transmission setup. b) Optical transmission response from un-functionalized Au nanohole array of 100nm thickness. c) Change in the optical transmission response before and after chemical functionlization with 4-nitrodiazonium tetrafluoroborate showing a spectral red shift of 70nm.

On the output side an imaging objective collected the transmitted light which was then focused onto an optical fiber that leads to a spectrometer where the light is spread spectrally and the information is digitized. Accurate alignment is facilitated by the use of beam splitters on either side of the objective pair to cameras allowing real time imaging of both surfaces of the sample. Transmission of the input light without the nanohole array ws measured and used as reference to determine the relative transmission of the plasmonic structures. First we measured the optical transmission through an un-functionalized nanohole array device. A sharp transmission resonance near 760 nm wavelength is seen for a=420nm lattice period (figure 4b) The resonance for the device with a=275nm with triangular holes appears at ~665 nm.

The next studied the effect of functionalization of the nanohole array with model sensing compound , 4-nitrodiazonium tetrafluoroborate.. We measured the spectral shift of the transmission spectrum of the a=275 nm period device with circular hole as it was in the center of our measurement range, before and after chemical functionalization. A clear 70nm redshift of the resonance as well as 15% enhancement in the transmission (figure 4c) was observed upon chemical functionalization indicating that such a system can be potentially used for sensing small quantities of molecules.

5. Summary

We have demonstrated the fabrication of a metal nanohole array with submicron periodicity and voltage selective chemical funtionalization with chemical detection compound 4-nitrodiazonium tetrafluoroborate). The transmission spectra through the nanohole structures show a typical enhancement of ~ 1.5X. The chemical functionalization results in a clear spectral shift of the transmission peak ~ 70nm indicating the potential for use high sensitivity detection. Further experiments will be carried out in the future for making multiplexed arrays for detection of multiple compounds in an on chip fashion with utra-compact geometry.

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6. References

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