Surface Plasmon assisted extraordinary transmission in metallic nanohole arrays and its suitability as a bio-sensor

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Abstract. In this work plasmonic nanostructures in the form of free standing films of sub-wavelength holes are fabricated and characterised using a variety of methods. It is shown how the light transmitted through a nanohole array is altered by the dielectric constant of the medium above the array facilitating the development of new types of plasmonic and photonic devices for future bio-sensing applications.

1. Introduction
There has been considerable interest in the emerging field of nanoplasmonics enhanced extraordinary transmission through sub wavelength nanohole arrays since the phenomena was first reported [1]. Surface plasmon polaritons (SPPs) exist as propagating waves on planar metal films with amplitudes that extend further into the dielectric region compared with the metal region [2]. Thus, the electromagnetic field is confined to the vicinity of the interface between the metal and dielectric. There is an enhancement of the field in this area which results in a high sensitivity of SPPs to the surface conditions enabling a wide variety of application areas that can use this sensitivity [3]. These include: surface adsorbate characterization, determination of surface roughness, in addition to chemical and biological sensors [4]. To excite SPPs on a surface using free-space light, additional momentum additional must be provided. One method to provide this extra momentum is by the patterning of an optical grating structure on the film [5]. The SPP waves interact with periodic structures on the metal surface leading to enhanced or extraordinary transmission [6]. This enhanced transmission leads to much smaller devices areas. In this paper we develop an approach for development of a nano SPP device and discuss its potential applications to a range of different areas including emitters and detectors.

Extraordinary transmission through sub-wavelength periodic nanopore arrays, fabricated in ultrathin metal films, may be attributed to the excitation of surface plasmon polaritons of specific resonant orders. The approximate equation for the SPP Block wave modes ($\lambda_{SPP}$) in a gold film when the incident light is normal to a square array of nanoholes with a periodicity $P$ in a gold film is given by
\[ \lambda_{SPP} = \frac{P}{(i^2 + j^2)^{1/2}} \left( \frac{\epsilon_{Au} \epsilon_d}{\epsilon_{Au} + \epsilon_d} \right)^{1/2} \]

where \(i\) and \(j\) define the order of the Block mode, \(\epsilon_{Au}\) is the permittivity of Au and \(\epsilon_d\) the permittivity of the adjacent dielectric material [7]. This is used to calculate the wavelengths an array of a certain period will have enhanced transmission and whether it is caused by the metal-substrate interface or the metal-dielectric interface as is required. The location of the peaks exhibited in extraordinary transmission spectra are dependant not only on the periodicity of the optical grating but also on the optical characteristics, i.e., the refractive index of the dielectric. Increasing the dielectric constant results in red-shifting of resonant SPP block wave modes. This well known phenomenon has been exploited by many research groups as a transducer signal for sensing devices [8-10].

Nanoplasmonic optical sensors are typically fabricated by focused ion beam milling nanohole arrays into thin gold films. A key limitation with this approach is that the depth of milling is extremely difficult to control. In this way, the underlying transparent substrate can be damaged, significantly decreasing the amount of transmitted light. Recently, the Odom group has demonstrated fabrication of nanohole arrays on gold films deposited on sacrificial chrome layers. Following fabrication, the underlying chrome layer is wet etched to release the nano-patterned gold. A self-assembly approach is then employed to deposit the gold layer on a transparent substrate for subsequent characterization. In this paper we apply this approach for fabrication of gold films bearing nanohole arrays and explore their positional as future nanoplasmonic sensors platforms [11-12].

2. Experimental section

![Schematic showing fabrication process for nanohole array in gold film.](image)

**Figure 1.** Schematic showing fabrication process for nanohole array in gold film.
2.1. Fabrication of nanohole arrays
To fabricate nanohole arrays, a 5 nm Cr film was first deposited on a clean Si substrate by e-beam evaporation, followed by evaporation of 50 nm thick Au layer. The sample was then loaded into the Quanta 3D 200i dual-beam Focused Ion Beam (FIB). Individual 60 µm × 60 µm periodic nanohole arrays were fabricated on the sample by focused ion beam milling; 30 kV beam voltage, 100 pA beam current, 1 pass, a defocus of 14 µm and dwell time of 5.5 ms. Individual nanoholes had a diameter of 110 nm and a pitch of 450 nm were routinely fabricated. The gold film was then freed from the underlying Si substrate by wet etching the chromium layer (Chrome Etchant Lodyne, Grower Chemicals Ltd.) for 10 minutes. The chip was then removed and immersed into deionised water where the Au film floated on the surface due to surface tension of the water meniscus while the Si substrate sank to the bottom. Using this approach the highly fragile gold films were easily freed from the silicon substrate in a contactless manner and prevented any damage occurring to the film. Finally, a glass microscope slide was immersed under the gold nanostructured film and used to lift the film from the water and dried for 24 hours. After transfer, the film adhered strongly to the glass substrate via Van Der Waals interaction, which permitted its optical characterization.

![Figure 2. Schematic diagram of the setup used to characterise the samples.](image)

2.2. Optical characterisation system
The normal transmission spectra of the sample were collected with a combination of an Olympus IX71 inverted microscope and an Acton SP2300i spectrograph. A 100W Halogen white light source was used to illuminate the sample, with the incident angle of light within 10 degrees with respect to the normal of sample. A crude microfluidic cell was constructed by gluing two pieces of 0.15 mm thick cover slip on either side of the adsorbed film (using UV curable glue) on a microscope slide. A third cover slip was bridged over these pieces of cover to form a lid of the cell. Spectra were acquired in air and in a range of saline solutions with refractive index varying from 1.33 to 1.37 by varying the concentration of NaCl in deionised water.
3. Results and Discussion

Figure 3(a) shows an optical image of a 60 µm by 60 µm array of nanopores using a calibrated microscope (Axioskop II, Carl Zeiss Ltd.) equipped with a charge-coupled detector camera (CCD; DEI-750, Optronics). Optical images gave a good first indication of whether the transfer process had damaged the film or not. In a few cases small wrinkles were visible. Figure 3(b) shows a scanning electron microscope image of a portion of the nanohole array on the Si substrate prior to lift-off. Scanning electron microscopy (SEM) images of nanohole arrays were acquired using a field emission SEM (JSM-6700F, JEOL UK Ltd.) operating at beam voltages between 3 and 5 kV. SEM analysis was undertaken for visual characterization of array quality and to determine the pitch and size of the nanoholes. Nanoholes with diameters of 110 nm and a pitch of 450 nm are routinely fabricated. If the Ion beam in the FIB was not perfectly focused the size of the nanoholes would be altered. Similarly the stigmatism of the FIB affects the shape of the hole and consequently the spectrum of transmission light. If the stigmatism is slightly off it results in nanoholes which not circular. Each array was checked after fabrication to ensure the nanoholes were as required.

The topography of the films was characterized using a calibrated atomic force microscope (AFM; Dimension 3100, Veeco Instruments Inc.) in tapping mode with commercial tapping mode probes (MP-11100, Veeco Instruments Inc; typical radius of curvature ~ 10 nm and front/side cone angles of 15°/ 17.5°, respectively). Figure 3 (c) shows a typical AFM image of a portion of an array. The depth of the holes was measured alone with the roughness of the Au surface.

Figure 3(d) show an optical micrograph of light transmitted through a nanohole array patterned in a gold film. The skin depth of gold is ~ 30 nm above which light will not be transmitted through the gold film. It is clear from the image that light is only transmitted through the array as expected.
3.1. Spectroscopic characterisation

Figure 4 shows the transmission spectra measured for a nanohole array in the presence of solution of varying refractive index (n=1.333 – n=1.37). Arrays with a pitch of 450 nm and a nanohole diameter of 110 nm, exhibited a broad characteristic peak of the bulk gold plasmon resonance at 500 nm and spectral peaks characteristic of SPPs at 680 nm and 630 nm, respectively. For a periodicity of 450 nm, one expects a (1,0) Au, NaCl solution SPP peak between 620 nm and 700 nm. However there is a Rayleigh-Wood anomaly at approximately 660 nm which interacts with the peak to form two separate peaks at either side. Rayleigh-Wood anomaly’s occurs when light is diffracted at an angle parallel to the surface of the gold film [13]. It occurs for wavelengths satisfying the following equation

$$\lambda_{RA} = \frac{P}{\left(i^2 + j^2\right)^{1/2}} \sqrt{\varepsilon}$$

where $P$ is the periodicity of the hole structure, $i$ and $j$ the integer pair that corresponds to the particular order of the RA and $\varepsilon$ the permittivity of the substrate. The main peak at 680 nm has the narrowest spectral features but a smaller shift in nm compared to the broader peak at 630 nm or to the trough at 660 nm. When the refractive index of the top surface is changed from that of water (n=1.333) to that of a 21% NaCl solution the peaks shift to longer wavelengths as expected. This is the property of the nanohole array suitable for bio-sensing applications. When a molecule is attached to the film the peak will be at a specific wavelength. Any change to the surface of the Au (be it addition of another molecule or removal of the first) would produce a shift in the SPP peak which would be used to detect said change.

![Figure 4](image_url)

**Figure 4.** Transmission Spectra through Nanohole array in the presence of solution of varying refractive index (n=1.333 – n=1.37). The spectra are offset for clarity. The peaks shift to the right as the refractive index increases showing how the spectral features from the Nanohole arrays can be exploited for highly sensitive refractive sensing.

To determine the optimal size of the array a number of different size arrays were fabricated varying in size from 10 µm by 10 µm, to 100 µm by 100 µm. Spectra were acquired through each of these arrays and the relative peak intensity measured. As is shown in figure 5(a), it was found that the optimal size of an array for our optical setup was about 60 µm x 60 µm as intensity of transmitted light reached a maximum at this size.
The peak shift versus refractive index is plotted in figure 5(b). For a 0.023 RIU (refractive index unit) change there is a 8 nm shift in the peak which shows a sensitivity of 347 nm/RIU which is in line with similar research [14]. Therefore it should be possible to detect when a monolayer is attached to the gold surface. When molecules are attached to the Au surface, RI of superstrate deviates from 1.333, the value for water. The change of RI varies with the type of molecules as well as the thickness of the attached layer. For example, a 7 ~ 15 nm thick molecular layer, with RI of 1.45 will give a roughly equivalent effect of a superstrate with RI of 1.342, if we assume that the light extends 300 nm into the superstrate. Work in now ongoing to apply this approach for the sensitive detection of a variety important of chemical and biological monolayers.

References

1. Ebbesen, T.W., et al., Extraordinary optical transmission through sub-wavelength hole arrays. Nature, 1998. 391(6668): p. 667-669.

2. Raether, H., Surface plasmons. 1988, Springer, Berlin.

3. Zayats, A.V., I.I. Smolyaninov, and A.A. Maradudin, Nano-optics of surface plasmon polaritons. Physics reports, 2005. 408(3-4): p. 131-314.

4. Wong, D., Chemical and Biochemical Sensing with Optical Fibers and Waveguides. Measurement Science and Technology, 1997. 8.

5. Henzie, J., M.H. Lee, and T.W. Odom, Multiscale patterning of plasmonic metamaterials. Nature nanotechnology, 2007. 2(9): p. 549-554.

6. Degiron, A. and T. Ebbesen, The role of localized surface plasmon modes in the enhanced transmission of periodic subwavelength apertures. Journal of Optics A: Pure and Applied Optics, 2005. 7: p. S90.

7. McMahon, J.M., et al., Tailoring the sensing capabilities of nanohole arrays in gold films with Rayleigh anomaly-surface plasmon polaritons. Optics Express, 2007. 15(26): p. 18119-18129.
8. Liang, W., et al., *Highly sensitive fiber Bragg grating refractive index sensors*. Applied Physics Letters, 2005. 86: p. 151122.

9. Polynkin, P., et al., Evanescent field-based optical fiber sensing device for measuring the refractive index of liquids in microfluidic channels. Optics letters, 2005. 30(11): p. 1273-1275.

10. Krioukov, E., et al., *Sensor based on an integrated optical microcavity*. Optics letters, 2002. 27(7): p. 512-514.

11. Gordon, R., et al., *A new generation of sensors based on extraordinary optical transmission*. Accounts of chemical research, 2008. 41(8): p. 1049-1057.

12. Brolo, A.G., et al., Surface plasmon sensor based on the enhanced light transmission through arrays of nanoholes in gold films. Langmuir, 2004. 20(12): p. 4813-4815.

13. Chang, S.H., S. Gray, and G. Schatz, Surface plasmon generation and light transmission by isolated nanoholes and arrays of nanoholes in thin metal films. Optics Express, 2005. 13(8): p. 3150-3165.

14. Henzie, J., et al., *Nanofabrication of Plasmonic Structures*. Annual review of physical chemistry, 2009. 60: p. 147-165.