Elliptical nanohole array in thin gold film as micrometer sized optical filter set for fluorescent-labelled assays.

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Abstract. In this paper, we study the polarisation properties of light transmitted through an array of elliptical nanoholes patterned in a thin gold film. The light transmitted through the sample strongly depends on the polarization of the excitation light and shows two distinct peaks, separated by 65 nm. These peaks are related to Rayleigh-Woods anomaly on the Au/glass interface. This type of devices has tremendous potential as micrometer size optical filter set for fluorescent-labelled assays.

1. Introduction
Since Ebbesen [1] observed a strong and unexpected enhancement of light transmission through arrays of subwavelength holes, numerous experiments have been performed to characterize and model this abnormal transmission. This effect, known as extraordinary optical transmission, is generally admitted to be due to excitation of surface plasmons on the upper and lower surfaces of the metallic array [2]. A typical transmission spectrum shows one or multiple peak whose wavelength could be simply tailored by changing the periodicity of the array or the dimension of the nanoholes. While arrays of circular nanohole have been thoroughly studied, less work has been done on other shape of nanoholes. Degiron [3] showed that, for an equivalent surface area, transmission through rectangular nanohole is ten times the one of circular nanohole. Also, it was demonstrated that the shape anisotropy of elliptical or rectangular nanohole induced polarisation sensitive transmission spectra in both single nanohole and arrays [4-9]

In this paper, we study the polarisation properties of light transmitted through an array of elliptical nanoholes in a thin gold film. The light transmitted through the sample strongly depends on the polarization of the excitation light and shows two distinct peaks in the far visible. These peaks can be related to Rayleigh-Woods anomaly on the Au/glass interface. This type of samples may find application as miniaturised spectral filters for on chip fluorescent-labelled assays.

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2. Experimental section

2.1. Fabrication of the array of elliptical nanohole in thin gold film

10 nm Cr film was first deposited on the clean Si substrate by e-beam evaporation, followed by 50 nm thick Au layer deposition. The sample was then loaded into the Quanta 3D 200i dual-beam Focused Ion Beam (FIB). Patches of 60 µm × 60 µm periodic nanohole arrays were fabricated on the sample by focused ion beam. The elliptical nanoholes had diameters of 150 nm and 350 nm and were spaced by 450 nm in each direction. The long axis of the nanohole had a 45° angle with respect to the array. The perforated Au layer was transferred to a microscope glass slide using a lift-off procedure. The gold film was freed from the Si substrate by wet etching the Chromium layer in Chrome Etchant Lodyne (Grower Chemicals Ltd.). The chip was lowered into water where the Au film floated on the surface and the Si substrate sank. A glass microscope slide was used to lift the film out of the water and dried for 24 hours.

2.2. Optical characterisation of the sample

Transmission spectra of the nanohole arrays in Au thin film were recorded using a home-built optical system, see Scheme S1. The light from a Xe arc lamp was collimated by a combination of lenses, pinhole and slightly focused onto the sample. The angle of incidence of the beam was chosen to be 90°. The transmitted light (in zeroth-order diffraction) through the sample was collimated by a 50X objective (LMPlanFL, Olympus, n.a. 0.5)) and focused onto a collection fiber bundle connected to a Triax 190 0.19 metre monochromator (1200 lines / mm grating). Visible spectra were recorded at an integration time of 0.1 second using a R928 PMT (Hamamatsu Photonics). Infrared spectra were recorded at an integration time of 0.1 second using a nitrogen cooled germanium detector (EI-L, Edinburgh Instruments). All acquired spectra were divided the one of a glass substrate. Analysis was performed using Jobin-Yvon’s SpectRad software. A CMOS camera (DCC1645C, Thorlabs) was used to assure proper focusing of the nanohole array. Polarised measurements were performed by adding a Glan-Thomson polarizer (NT47-045, Edmund Optics Ltd.) in the incident and/or collection path. Polarisation bias of the optical setup was determined by taking spectra of a blank substrate with light polarized every 15°. No polarization bias was observed.

Scheme S1. Schematic of the optical set-up used for measurements of transmission spectra of nanohole array in thin Au film.
2.3. Finite Difference Time Domain (FDTD) Simulations:

Scheme S2. computational domain used for the FDTD simulation

2.3.1. Computational volume. Finite Difference Time Domain (FDTD) simulations were performed using JFDTD3D (version 2.0) program available under the General Public License (GPL) (www.thecomputationalphysicist.com). The program was based on a 3-D, parallel FDTD implementation using the Message Passing Interface library. The code was run on 8 nodes, each node having 2 Opteron CPUs (2.6GHz, 4GB RAM). The grid spacing in each spatial dimension was 5 nm. The computational grid was chosen to be 450x450x1600 nm³, see Scheme S2. The extra lengths in the z directions allowed the resolution of Wood's anomalies, if present. Periodic boundary conditions (450 nm) in the x and y directions were applied to simulate an infinite square array. Perfectly Matching Layers (PML) boundary conditions were imposed in the z direction in order to avoid reflections from the edges of the computational window. The setup was modelled (see Scheme S2) by a 50 nm Au film with a 650 nm thick glass substrate ($\varepsilon_{\text{Glass}} = 2.31\varepsilon_0$) and a 900 nm air ($\varepsilon_{\text{Air}} = \varepsilon_0$) superstrate. In the plane of the film, the nanohole was centered in the middle of the square ($x_0 = y_0 = 225.10^{-4}$ m) and the equations used to define the ellipse were:

$$\sqrt{2} \cdot \left[ (x_{\text{pos}} - x_0) + (y_{\text{pos}} - y_0) \right]^2 \leq 1 \quad (1),$$

and

$$\sqrt{2} \cdot \left[ (x_{\text{pos}} - x_0) - (y_{\text{pos}} - y_0) \right]^2 \leq 1 \quad (2).$$

2.3.2. Permittivity of Gold. The permittivity of gold was modelled using a Drude plus two-pole Lorentz model:

$$\varepsilon_\omega (\omega) = \varepsilon_\infty + \sum_i \frac{\omega_i^* \Delta \varepsilon_i \omega}{\omega (\omega + i \delta_i) - \omega_i^*} - \frac{\omega_i^*}{\omega^2 + i \gamma_i \omega} \quad (3)$$

With Drude parameters

$$\varepsilon_\infty = 5.40, \gamma_\omega = 0.103 \times 10^{15} \text{ Hz} \quad \text{and} \quad \omega_c = 0.140 \times 10^{17} \text{ Hz}$$
And Lorentz parameters:
\[ \omega_{z_1} = 0.42 \times 10^6 \text{ Hz}, \quad \omega_{z_2} = 0.523 \times 10^6 \text{ Hz}, \quad \Delta \epsilon_{z_1} = 2.542 \times 0.279, \quad \Delta \epsilon_{z_2} = 2.542 \times 0.721, \]
\[ \delta_{z_1} = 0.435 \times 10^6 \text{ Hz and } \delta_{z_2} = 0.661 \times 10^6 \text{ Hz}. \]

2.3.3. Transmission spectrum. In order to simulate the excitation source, a Gaussian damped sinusoidal pulse (having a frequency content of 1 to 6 eV) with a 45° polarisation was launched from the glass side and simulation run (for 200.10^{-15} sec) in the time domain. Total transmission spectra were obtained by Fourier transforming the simulated electric and magnetic fields on a surface above the holes and constructing the surface integral of the outward Poynting vector.

3. Results and Discussion

3.1. Optical imaging of the sample

Figure 1. (a) scanning electron microscope and (b) optical image of the elliptical nanohole array after the transfer. The periodicity of the nanohole structure is 450 nm in each direction. The ellipses are oriented at 45° and have a 350 nm long axis and a 150 nm short axis. The sample is a 50 nm thick Au film. The array is 60x60μm²

Figure 1a shows a scanning electron microscope image of the gold thin film on the Si substrate. High quality array of elliptical nanohole have been successfully made. The inset of figure 1a shows the surface of the film appears smooth and the edges of the nanohole sharp and well defined. Figure 1b shows an optical micrograph (50X objective) of the sample after the transfer onto a microscope slide. Despite being only 50 nm in thickness, the film was strong enough to survive the transfer. However, in some samples, SEM images performed on thin film after the lift off process showed localized wrinkles. After the transfer, the film adhered to the glass substrate via Van Der Waals interaction, which permitted its optical characterization.
3.2. Polarised transmission through the sample

Figure 2. FDTD-simulated (black) and measured (red) zero-order transmission through the elliptical nanohole array on a glass substrate. Excitation polarisation along (a) the short axis and (b) the long axis of the ellipses.

3.2.1. Eigenmodes of the system. Polarised transmission spectra of the sample were acquired using the system and method described in section 2.2. For any polarisation state of the excitation, the spectrum could always be described as a combination of the two spectra shown in figure 2a and 2b. These two spectra thus describe the two eigenmodes of the sample. They correspond to excitation light polarized along the short and the long axis of the nanohole structure.

3.2.2. Comparison with FDTD simulation. FDTD simulations (see section 2.3 for details) were carried out for the two polarizations states. As can be seen in figure 2, there is a very good agreement between the experimental data and the simulated one, in terms of peak position and overall trend. The discrepancy in the relative intensity can be attributed to minor imperfections in the experimental hole structure or the simulated one (errors in the holes dimensions, imperfection in the Drude-Lorentz model).

3.2.3. Rayleigh-Woods anomaly and Surface Plasmon polariton

Both spectra exhibited a broad peak around $\lambda=490$ nm, with a transmission of 20-35% (simulation and experiment, respectively). This corresponds to the intraband transition for gold (direct transmission), and occurs irrespective of the incident polarization [10]. However, the rest of a spectrum differs significantly for the two polarisation states.

When light is polarized along the short axis of the ellipse (figure 2a), two peaks can be observed, a sharp, asymmetric, one at $\lambda=690$ nm and a broad one in the near infrared at $\lambda=980$ nm. In between these two peaks, transmission reaches zero at $\lambda=750$ nm. This dip in the transmission spectrum can be assigned to the (1,1) Rayleigh-Wood anomaly on the glass-gold interface. Rayleigh-Wood anomaly corresponds to light diffracted at an angle parallel to the surface of the gold film. It occurs for wavelengths satisfying equation [11] (4)

$$
\lambda_{\text{EI}} = \frac{P}{(n^2 + n^2_s)} \frac{1}{\sqrt{\varepsilon}}
$$

(4)
where $P$ is the periodicity of the hole structure, $n_x$ and $n_y$ integer numbers indicating the exciting diffraction order and $\varepsilon$ the permittivity of the external dielectric. In the present case of a grating with a periodicity of 450 nm, one expects a (1,1) Rayleigh-Wood anomaly at 735 nm for the glass-Au interface, close to the observed minimum at 750 nm.

When the light is polarised along the long axis of the ellipse, one can observe that above 900 nm, the transmission is very low and this is due to the cut-off wavelength of the nanohole waveguide along this direction. Also noticeable on this spectrum is a shoulder at $\lambda=580$ nm in the intraband transition peak. The shoulder can be assigned to the (1,1) SPP peak on the glass-gold interface (i.e., coupling of light to propagating plasmon mediated by the grating). For normal incidence of light onto a square-symmetry periodic lattice, the transmission maxima occur at the wavelengths satisfying a two-dimensional grating coupling condition for surface Plasmon \[12\] (this equation is intrinsic as $\varepsilon_{ss}$ is dependant on $\lambda$):

$$\lambda_{SPP} = \frac{P}{(n_x^2 + n_y^2)\sqrt{\left(\frac{\varepsilon_{ss} \varepsilon}{\varepsilon_{ss} + \varepsilon}\right)}}^{1/2}$$ \hspace{1cm} (5)

For a periodicity of 450 nm, one expects a (1,1) SPP peak at 572 nm, close to the observed shoulder at 580 nm. Lastly, the most interesting feature in figure 2a is a very sharp, asymmetric peak at $\lambda=720$ nm with an associated minimum at 700 nm. The special shape of this peak suggests a Fano resonance.

### 3.2.4. Fano resonances.

Fano resonances are a general characteristic of systems where two transmission pathways interfere, a resonant and a non-resonant one, or, expressed differently, between a discrete resonance and a continuum. The general equation describing a Fano resonance can be written as \[13\]:

$$I \sim \frac{(q \gamma + \omega - \omega_{b})}{(\omega - \omega_{b})^2 + \gamma^2}$$ \hspace{1cm} (6)

Where $\omega_{b}$ and $\gamma$ are the position and the width of the resonance, respectively, and $q$ the Fano factor, describing the ratio of probability of taking the first path (resonant) over the second path (non resonant). In the present case, the continuum could be represented by scattered light transmitted through the hole, and the resonant process by the (1,1) Rayleigh-Wood anomaly (which is the same as in section 3.2.3, i.e., at 735 nm). Fitting the experimental peak with equation (6) gave a resonance position at 714 nm, a width of 9.5 nm a $q$ factor of 1.4.
3.2.5. Arrays of elliptical nanohole as microscale filter for fluorescent label assay

It can be seen on figure 2a and 2b that in the 650-750 nm range, the maximum transmission for one polarisation corresponds to the minimum transmission for the other transmission. This means that two of these filters in a crossed configuration could be used as micrometer sized optical filter set for on-chip transmission fluorescence assay [14]. For examples, iFluor™ 700 dyes from BIOMOL GmbH have fluorescence excitation and emission maxima close to 690 nm and 710 nm respectively and would be a suitable label for the current sample. Also, equation (4) and (5) show that changing the periodicity of the array allows the tuning of the wavelength at which the zero transmission or maximum transmission occurs. This suggests that changing the periodicity would allow different filter sets to be made and so different labels to be probed. Work is ongoing to explore this effect.

![Diagram](image)

**Figure 3.** Schematics showing how the elliptical nanohole array could be integrated into an on-chip fluorescence assay.

4. Conclusion

Array of elliptical nanohole have been successfully patterned in thin gold film by focused ion beam. The thin film could be lifted off and transferred onto a glass substrate. Transmission of polarized light through the sample showed two eigenmodes for the system. The two modes corresponded to light polarized along the short and the long axis of the ellipses. When the light was polarized along the short axis, a broad peak could be seen at 980 nm, and a sharper one at 690 nm. The latter was assigned to Rayleigh-Wood anomaly at the glass-Au interface. When the light was polarized along the long axis, a sharp, asymmetric peak was observed at 720 nm. This peak was described as a Fano resonance between the Rayleigh-Wood anomaly and direct transmission. In the 650-750 nm range, the maximum transmission in one polarisation corresponds to the minimum transmission in the other one. This means two of these filters in a crossed configuration could be used as miniaturised optical filter set for on-chip fluorescence assay.

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