Localised modes of sub-wavelength hole arrays in thin metal films

J. Parsons, E. Hendry, B. Auguié, W. L. Barnes, J. R. Sambles
School of Physics, University of Exeter, Stocker Road, Exeter, EX4 4QL, United Kingdom.

ABSTRACT

When perforated metal films are sufficiently thin, in addition to exciting surface plasmon-polariton (SPP) modes by conventional two dimensional grating scattering, there is also the possibility of coupling to the localised modes associated with the holes. Here, experimental transmission spectra are obtained from focused ion beam fabricated hole arrays exhibiting localized modes in the visible frequency region. We employ both analytical and numerical (finite element) modeling to understand the fundamental properties of the localized mode. Finally, the sensitivity of the optical response to changes in refractive index is explored, and its potential for sensing applications is discussed.

Keywords: surface plasmon ; localised surface plasmon ; sub-wavelength hole arrays; optically thin films; Fano analysis

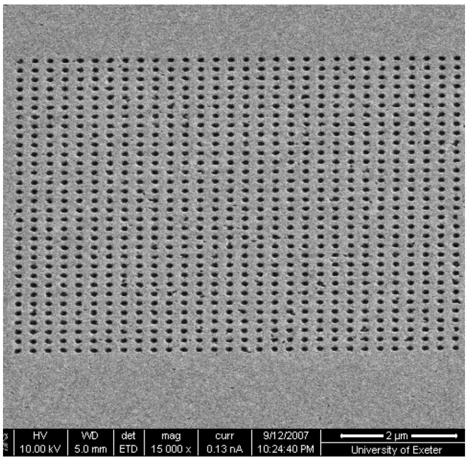
I. INTRODUCTION

Much interest has surrounded recent work which discusses the significantly enhanced transmissive properties of optically thick metal films which have been perforated with two dimensional arrays of sub-wavelength holes [1-5]. This enhancement has largely been attributed to the excitation, and subsequent coupling of surface plasmon modes on either side of the metal film by evanescent diffracted orders, giving rise to transmission maxima at wavelengths related to the periodicity of the array. Typically the periodicity is the same order of magnitude as the incident wavelength, and the enhancement can be suitably observed across all frequencies of the electromagnetic spectrum (visible, IR, THz or GHz domain).

Recent work [6-9] has shown that holes in thin metal films can also exhibit *localised* resonances analogous to the so-called particle plasmon widely investigated in metal nanoparticles [9-12]. First demonstrated in a thin gold film perforated with a random arrangement of nanoholes[13,14], we investigate here the electromagnetic properties of these 'hole plasmon' modes as part of a regular array having sub-wavelength periodicity. We show that the hole plasmon resonance, which can be tuned by varying the periodicity of the array, is characterised by a high field strength within the hole, making it a promising candidate for sensing and non-linear optical applications.

II. EXPERIMENTAL METHOD AND SIMULATION

Gold (Au) films of thickness 20 ± 2 nm were fabricated by thermal evaporation on a glass substrate at a pressure of 1×10^{-6} mbar and deposition rate of 5 Ås^{-1}. A Focused Ion Beam (FIB) was used to mill 8μm square arrays of 90 nm diameter holes from the planar film, with periodicities of 200 nm, 225 nm and 250 nm and hole diameters ranging from 70 nm to 100 nm. Fig. 1 shows a Scanning Electron Microscope (SEM) image of a 8μm square array of 90 nm diameter holes with periodicity 200 nm.



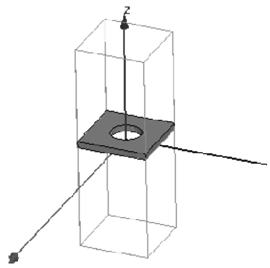


Figure 1 - left: SEM image of a 8μm square array of 90 nm holes fabricated with periodicity 200 nm viewed at 15000x magnification (52° tilt). above: FEM unit cell used for simulating the optical response.

Bright field transmission spectra were obtained by illuminating the sample with collimated light from a tungsten halide source at normal incidence. An objective with magnification 100x was used to focus the light onto a spectrometer. Spectra were obtained in air and using an oil immersion lens with matching fluid of index n = 1.52. The optical response of the arrays were simulated using a Finite Element Method (FEM) [15] with a mesh size of 0.001 nm. A convergence test was used to check the suitability of the mesh and for regions of instability. The substrate is non-dispersive over the frequency range of interest, with optical constants n_r= 1.52 and n_i= 0.00. Permittivity values for gold were taken from data published by Sambles et al. [16] and are well described by a Drude model with permittivity $\varepsilon = 1 - \frac{\omega_p^2}{\omega^2}$ where $\omega_p \approx 8$ eV.

III. RESULTS AND DISCUSSION

a) Hole resonances

Fig. 2 shows a comparison between experimental and simulated transmittance spectra for an array of 90 nm diameter holes with periodicity 200 nm, illuminated at normal incidence in air and using refractive index matching liquid. In the asymmetric configuration of air-sample-glass, minima occur against the Au background at approximately 600 nm, whilst in matching fluid this is red-shifted to approximately 650 nm. It should be noted that in the structures discussed in this paper we do not expect coupling to surface plasmon-polaritons on the gold surfaces [17-21], since the periodicity of the array is significantly smaller than the incident wavelength. In both cases in Fig. 2, however, there is a clear Fano type line resonance shape. Such a shape manifests itself through Fano's 'coupled channel' approach [22,23], which considers the interference between two contributions arising from resonant and non-resonant elements: here, light directly transmitted through the Au film interferes with that which is reradiated following the excitation of localised hole modes. There is a net phase difference between these two contributions. The shape of the Fano resonance is determined by the ratio of the relative intensities of the directly transmitted and reradiated light, which strongly depends on the degree of coupling to the localised mode. Resonance lineshape is therefore highly sensitive to effects such as film thickness and profile of the structure. This has been observed experimentally (not shown).

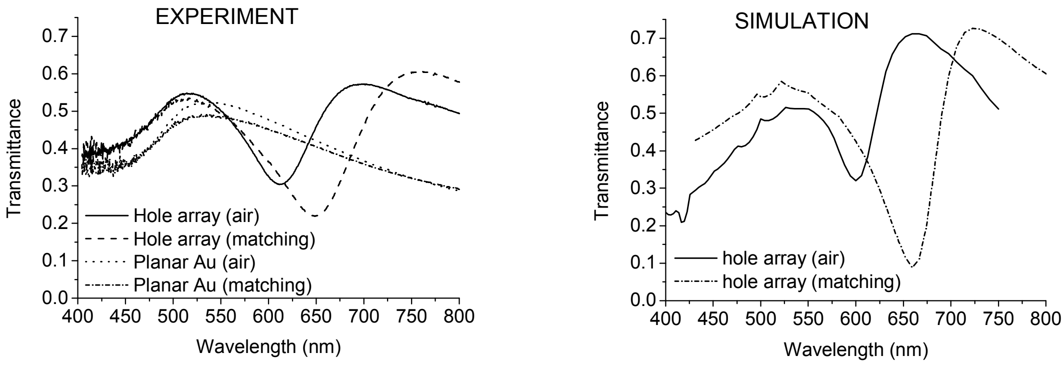


Figure 2: Experimental (left) and simulated (right) transmittance spectra obtained for 8um square arrays of varying periodicity illuminated at normal incidence in air and using refractive index matching liquid.

The optical response associated with a single nanohole has been previously reported [7-9]. In the presence of a hole, thin film plasmons are able to acquire dipole moments due to localized surface charges induced in the rim of the hole, in a manner analogous to metal nanoparticles. A computation has been performed using a finite element method for the hole array structures. The resonant frequency of a structure is determined by the frequency at which maximum absorbance occurs. Fig. 3 shows simulated absorbance spectra for an infinite array of holes. It can be seen that the absorption maximum occurs at approximately 640 nm. In Fig. 3, we also evaluate the scattered electric field magnitude and vector field profiles for the hole array at the resonant frequency, taking a cross section parallel to the substrate. The incident electric field has magnitude 1.0 Vm^{-1}. We note that significant field enhancement occurs inside the hole. The polarisability of an arbitrary shaped inclusion with permittivity ε_p inside a medium ε_m is approximated using a modified Clausius-Mossotti relation [19-20,23]:

$$\alpha = \frac{(\varepsilon_p - \varepsilon_m)}{3[\varepsilon_m + (\varepsilon_p - \varepsilon_m)L]} \quad . \tag{3.1}$$

The shape factor is defined by **L**. For a spherical inclusion **L = 1/3**, while for an infinitely long cylinder **L = 1/2**. Since the holes being considered have near straight edges perpendicular to the metal surface, we consider **L = 1/2** [24-25]. Substituting this into Equation 3.1, and considering a Drude model permittivity for the medium and inclusion allows the resonant frequency for the structure to be approximated.

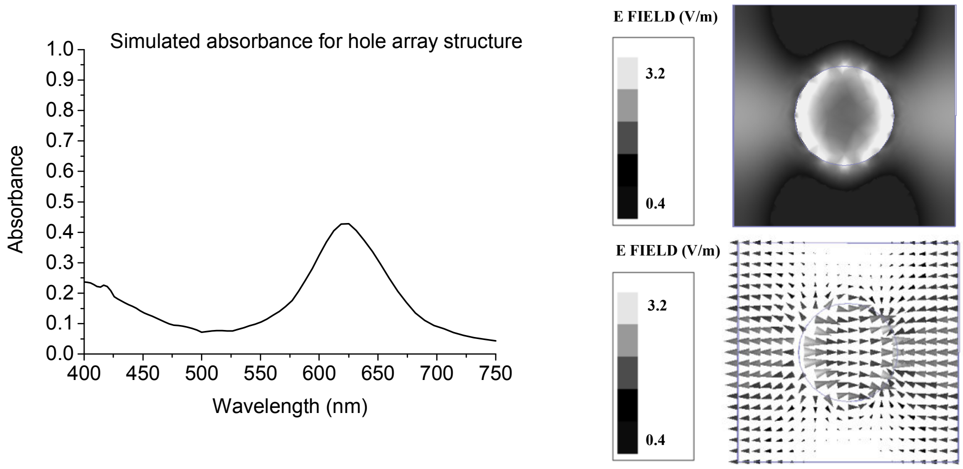


Figure 3 – left : Simulated absorbance spectra are shown for an infinite array of 90 nm diameter holes (200 nm periodicity) in a 20 nm thick Au film. Figure 3 – right: Field profiles at the resonant frequency for the hole array structures corresponding to the complex magnitude of the electric field (top) and the instantaneous electric field vector (bottom).

b) Effects of periodicity, hole size and geometry variation

In this section we investigate the effects of periodicity and hole size/shape on the "hole plasmon" resonance. In Fig. 4, experimental transmittance spectra are compared against simulated data for 90 nm diameter hole arrays with three different periodicities (200 nm, 225 nm, 250 nm). Clearly, the resonant transmission can be tuned by varying the periodicity of the structure. Changing the periodicity modifies the relative coupling strength between the localized resonances, an effect which has been observed for particle arrays [9-11,14].

In the previous section we considered the polarisability of a single hole using the Clausius-Mossotti relation. Here, we consider the effect of hole coupling in our composite structure using a Maxwell-Garnet effective medium approximation [27]. It is straight forward to derive from Eq. 3.1 a relation for an effective dielectric function of our material:

$$\varepsilon_{eff} = \frac{\varepsilon_m\left[(L-1)(s-1)\varepsilon_m+(L+s-Ls)\varepsilon_p\right]}{(1+sL-L)\varepsilon_m+L(1-s)\varepsilon_p} \ . \qquad (3.2)$$

Here, s is the filling factor of the structure, defined as the percentage volume occupied by the inclusions. It is possible to use this expression to evaluate the relationship between the filling factor and the resonant frequency (when the denominator of Eq. 3.2 is zero) for the case of a cylindrical inclusion within metallic surroundings, again assuming **L = 1/2**. This results in the simple relation for the resonant frequency $\omega_o = \omega_p\sqrt{\frac{(1+s)}{2}}$. Clearly, the resonant frequency is expected to increase with increasing fractional occupancy of the hole (i.e. we expect a red shifting in resonant wavelength with increasing periodicity), and is precisely what is observed in Fig. 4. At very small separations, neighbouring resonances are strongly coupled, resulting in an increase in magnitude and spectral broadening of the absorbance. At larger separations (but still less than the diffracting limit), the coupling strength is weaker and the optical response tends towards that of a single hole.

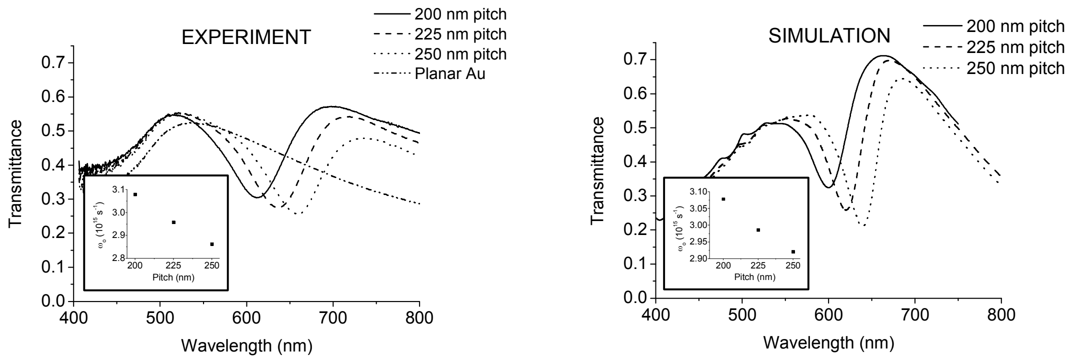


Figure 4: - Comparison between experimental (left) and simulated (right) transmission spectra for 90 nm diameter hole arrays with periodicity 200 nm, 225 nm and 250 nm. (Inset) – Resonant frequency plotted as a function of periodicity.

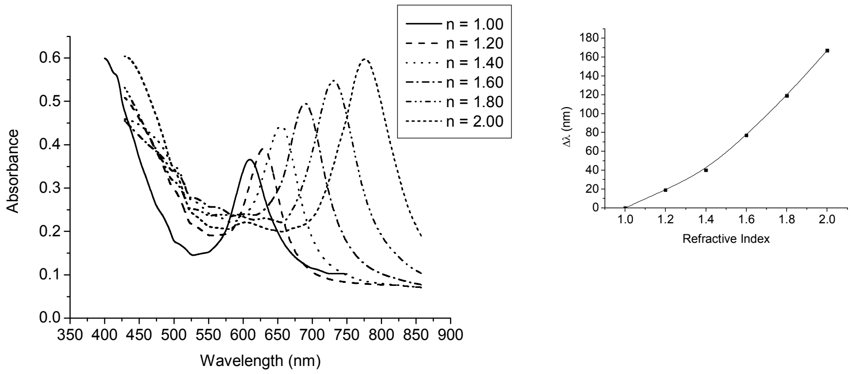
We have also investigated the effect of geometry on the response of the array. Numerical simulations have been performed for structures with similar cross sectional area to that of an array of 90 nm diameter cylindrical holes. First, we considered an array of square holes with side length 80 nm. On resonance, it was found that the strength of the scattered field inside the hole was enhanced along surfaces lying perpendicular to the incident polarisation, with particular enhancement around the vertices of the hole. An array of rectangular holes with dimensions 45 nm x 135 nm (aspect ratio 8:3) was also considered with incident radiation polarised along the short axis of the slit. This showed even greater resonant field enhancement, although the transmittance feature was red shifted out of the visible domain. The high degree of field localisation inside the hole renders these arrays particular sensitive to refractive index changes in the ambient medium, and as such could enable them to be utilised as the mechanism for useful applications.

IV. SENSING AND NON-LINEAR OPTICAL APPLICATIONS

The suitability of utilising a configuration which exhibits a localised resonance for possible sensing and/or non-linear optical applications [28,29] has attracted significant interest. It is well established that localised particle plasmons have several desirable properties, including the strong enhancement and confinement of the electric field in the vicinity of the particle, which is necessary for non-linear optical techniques such as enhanced Raman spectroscopy [30]. There has also been considerable research directed at the development of particle arrays for sensing applications [31-33]. In Fig. 3 it has already been shown that a localised hole plasmon can exhibit very strong field enhancement inside the hole, making it a suitable candidate for such applications. Furthermore, from a practical perspective, it is easier to engineer hole array structures via a single process of focused ion beam milling as opposed to particle structures of similar dimensions which require several stages in an electron beam lithography technique. We briefly show that the high tunability of hole plasmons has excellent potential for sensing applications.

In Fig. 5 we plot simulations showing the absorbance of arrays of 90 nm diameter holes with 200 nm periodicity on a glass substrate with varying ambient medium ranging from refractive index of n = 1.00 to n = 2.00. The ambient medium is permitted to cover the upper surface of the gold film and entirely fill the hole. Increasing the refractive index of the ambient medium shows a red-shift and increase in magnitude of spectral features. For refractive indices of n = 1.80 and n = 2.00, the absorbance is increased by over 50 percent, and transmittance at the Fano minimum tends to zero.

As a bulk change from n = 1.00 to n = 2.00, the system exhibits a bulk sensitivity corresponding to 170 nm per Refractive Index Unit (RIU) change. This is not observed as a linear change, initial variations from n = 1.00 to n = 1.20 yield a shift of only 20 nm, which corresponds to a bulk sensitivity of 100 nm per RIU. A high degree of asymmetry between substrate and ambient medium leads to a greater sensitivity, and this is shown at larger refractive indices. The sensitivity corresponding to a bulk change from n = 1.80 to n = 2.00 is 240 nm per RIU.



<u>Figure 5 (above left)</u>: Simulated absorbance from an array of circular holes 90 nm in diameter with periodicity 200 nm in a Au film of thickness 20 nm. The refractive index of the ambient medium has been varied from n = 1.00 to n = 2.00 in 0.20 increments.
<u>(above right):</u> The shift in resonant wavelength Δλ is plotted as a function of refractive index of the ambient medium.

There appears to be two control parameters when optimising such a hole array structure for refractive index sensing applications. The first consideration is the choice of the initial optical response, centred about a wavelength and refractive index range where sensitivity is most desired. This has been shown in our structures to be affected by factors such as geometry, periodicity, film thickness and the refractive index of the substrate. The second part is determining a configuration which gives maximum bulk refractive index sensitivity about the initial spectral position. This is also determined by the previous factors, but the greatest sensitivity appears to occur when there is a high degree of asymmetry between the refractive index of the substrate and the medium.

The optimisation of the sensing capabilities of hole arrays which exhibit transmittance enhancement have been discussed in other literature [31-33]. It should be noted that the mechanism giving rise to the optical response is coupling to propagating SPPs by diffraction [17], which is somewhat different to the method of coupling to the localised resonances studied here. For diffractive structures, the sensitivity is typically of the order of 150 nm to 200 nm per RIU. Arrays of nanoparticles have been shown to exhibit sensitivities of up to 300 nm per RIU. Our structures show a sensitivity of up to 240 nm per RIU, which is comparable with both approaches. Moreover, there is also the added benefit that these structures exhibit a single feature in the absorbance spectra, which as previously discussed can be highly tuned with respect to the array periodicity.

IV. CONCLUSIONS

Using an array of holes perforated in an optically thin Au film, we have shown that for periodicities much smaller than the incident wavelength, it is possible to couple to localised modes associated with the geometry of the holes. A finite element modelling technique has shown that on resonance the magnitude of the electric field within the holes can be extremely high, which offers possible advantages for sensing or non-linear applications. By varying the bulk refractive index of the ambient medium the sensitivity of the array is determined and is found to be comparable to particle plasmon sensing techniques, with the added benefit that hole arrays of this dimension can be fabricated with greater ease using focused ion beam milling .

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