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ARTICLE

Getting real: Influence of structural disorder on the performance of plasmonic hole array sensors fabricated by an bottom-up approach

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Hole arrays in gold films possessing different degrees of order were fabricated by a combination of colloidal lithography and chemical gold deposition. Here, hydrogel spheres were used for the formation of non-close packed microsphere arrays which act as masks for subsequent gold film deposition. The assembly of the soft spheres into arrays possessing different degrees of order was controlled by addition of alcohol and application of mechanical shear. The resulting hydrogel mask is translated into a hole array by functionalization of the glass surface with 3-aminopropyltriethoxysilane, deposition of gold nanoparticles and subsequent gold film growth by electroless deposition. The degree of order of the resulting nanostructures was thoroughly determined by analyzing SEM images and correlated to variations in their transmissive optical properties. In general the degree of order has a tremendous effect on the position of the transmission maxima of the hole arrays. This is not surprising as deviations from the ideal hexagonal packing will lead to an increase of the lattice constant of the array which determines the transmission peak positions. Hence the transmission spectra can be employed for a spectral quality control of the order of the fabricated hole arrays in gold films. However, the sensing performance of the plasmonic hole arrays is only partly influenced by the degree of order. The impact of the degree of order of the hole array on its sensitivity is hereby determined by the spectral feature used for sensing.

Introduction

Since Ebbesen and co-workers observed extraordinary optical transmission (EOT) of light through sub-wavelength hole arrays in metallic films in 1998¹ great progress has been made both in theoretical understanding of EOT and its use in several applications such as surface plasmon resonance based sensors, photonic devices, and surface enhanced spectroscopy (reviewed in ²⁻⁴). There is an ongoing discussion on the physical origin of EOT, but it is generally accepted that surface plasmon polaritons (SPPs) play a key role in this process.^{5, 6} SPPs are waves of oscillating surface charge density propagating at the metal/dielectric interface and are highly sensitive to changes in the refractive index at the metal surface. Consequently, SPPs have successfully been utilized in optical sensors for the sensitive detection of biomolecular interactions.^{7, 8}

Before the discovery of EOT SPP based sensors were most often composed of thin metal films deposited on a prism.⁹ The latter provided the necessary momentum for the excitation of the SPPs which cannot be directly excited by light. In the case of periodic hole arrays in metal films light is diffracted by the grating and thereby its momentum is matched to the SPPs. Hence, SPP resonance occurs at certain wavelengths which are closely related to the geometrical arrangement of the holes in the metal layer resulting in extraordinary transmission of light at these wavelengths. By tailoring the periodicity,^{10, 11} the shape¹¹⁻¹³ and the size of the holes¹⁴ the optical properties of the hole arrays can be easily optimized for the desired application. The possibility to rational design the transmission of these plasmonic sensors and the simplicity of the optical set-up required for their use as sensors has boosted research on these structures.

However, at the beginning studies were mainly focused on controlling the optical properties of periodic sub-wavelength hole arrays and therefore sophisticated methods such as focused ion beam milling^{1, 15, 16} or electron beam lithography¹⁷ were used for their fabrication in order to provide maximal freedom

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in the appearance of the nanostructure.^{18, 19} These techniques are expensive, and provide only small nanostructured areas at low throughput hampering their application to the fabrication of sensors. Alternative approaches have been developed in order to improve the manufacturing process of EOT based sensors. These include soft nanoimprint lithography²⁰, interference lithography²¹ and colloidal lithography.^{22, 23} The latter technique is highly suitable for the cheap and fast fabrication of hole arrays on large areas. Here, monodisperse polymer spheres are self-assembled into hexagonally close-packed monolayers on a substrate. After adjusting the size of the polymer spheres by reactive ion etching the colloidal mask is used for the deposition of a gold film by sputter coating.²⁴ Nanohole arrays prepared by colloidal lithography are not defect free and are characterized by the appearance of grain boundaries, point defects and a lower degree of order in comparison to structures fabricated by more sophisticated methods.

The influence of the degree of order of hole arrays in metallic films on their optical properties have already been investigated theoretically and experimentally. First studies on quasiperiodic hole arrays showed that long-range order is not required for the observation of extraordinary transmission through hole arrays – as long as short-range order is maintained.^{25, 26} This astonishing result was confirmed by Przybilla et al. who analyzed the impact of a gradual increase of disorder in hole arrays on their transmission properties. In general, the transmission peak was characterized by a reduced intensity and a considerable broadening if the disorder in the hole array increased. These optical trends were successfully correlated to the structure factors of the corresponding hole arrays.^{27, 28}

In order to thoroughly control the arrangement of the holes in the investigated random arrays they were produced by focused ion beam milling. This approach was very reasonable for gaining knowledge about the influence of disorder in hole arrays on their optical properties but did not necessarily provide insights on the optical properties and sensor performance of hole arrays fabricated by a combination of colloidal lithography and subsequent gold film deposition. Here, the reproducibility of the formation of highly ordered colloidal masks by self-assembly on large areas and a spectral quality control of the resulting hole array would be highly interesting.

In the present work periodic hole arrays in gold films possessing different degrees of order were fabricated by a modified bottom-up approach developed in our group.^{29, 30} Briefly, hydrogel microspheres were wet-chemically synthesized and deposited onto glass substrates by spin-coating. The degree of order of the formed non-close packed hydrogel microspheres were controlled by the adjustment of the hydrogel microspheres solubility in the dispersion media in combination with the application of mechanical shear. The quasi-hexagonally ordered non-close packed hydrogel spheres acted as a mask for the subsequent gold film deposition using solely chemical methods. The resulting hole arrays in gold films were thoroughly analyzed concerning their degree of order, their transmission properties as well as their sensing performance.

Experimental section

Materials

N-isopropylacrylamide (NIPAM) and 3-aminopropyltriethoxysilane (APTES) were obtained from Acros Organics. $\text{HAuCl}_4 \times 3 \text{H}_2\text{O}$, H_4NOCl , sodium citrate and triethylamine were purchased from Sigma Aldrich. Ethanol, N,N'-methylene bisacrylamide (BIS), HCl, H_2SO_4 and glass cover slips (2 x 2 cm) were received from Carl Roth. HNO_3 and H_2O_2 were supplied from Merck. Potassiumperoxodisulfate (KPS) was obtained from Fluka. Methanol was purchased from BASF. Water was deionized to a resistance of at least 18.2 M Ω (Ultra pure water system (TKA, Germany)). NIPAM was recrystallized from hexane prior to use. All other chemicals were used as received without any further purification.

Fabrication of hole arrays:

Hole arrays in gold films were fabricated using a strategy which has previously been developed in our group.²⁹

PolyNIPAM microspheres

Hydrogel microspheres were synthesized via surfactant-free emulsion polymerization.³¹ Briefly, a three-neck round bottomed flask was filled with 124 mL deionized water. After addition of 2.7 g NIPAM and 0.1 g BIS the solution was stirred under inert atmosphere and heated to 70 °C. 0.04 g KPS dissolved in 4 mL deionized water was injected in order to start the radical polymerization reaction which was carried out for 4 h at 70 °C. The resulting hydrogel microspheres were purified by repeated centrifugation, decantation and redispersion in deionized water (five times). Finally the microgel dispersion was filtered (Acrodisc 25 mm syringe filters with Versapor membranes, pore diameter: 1.2 μm).

PolyNIPAM microsphere arrays

Highly ordered polyNIPAM microsphere arrays were fabricated according to our previously published method.³⁰ Here, glass cover slips were used as substrates which were cleaned by immersion in a 3:1 mixture of H_2SO_4 (95-98%) and H_2O_2 (30%) for 1.5 h. After extensive rinsing with deionized water the glass cover slips were stored in deionized water for 1 - 24 h and dried in a stream of N_2 prior to spin-coating. 40 μL of deionized H_2O and 15 μL of ethanol were placed on a cleaned glass cover slip and mixed. 2.5 μL of polyNIPAM microsphere dispersion were added. A pressure-modulated gas stream was directed to the sample surface. By varying the pressure we were able to generate polyNIPAM crystals of different degrees of order. The process of colloidal crystal formation was visually followed by illumination of the substrate with white light. The appearance of brilliant spectral colours by diffraction of light was an indication for the degree of order in the formed 2D microsphere array. Finally the substrate was dried by spin-coating using a Laurell WS-400A-6NPP Lite spin coater. The substrates were spun for 6 min at 500 rpm followed by 1 min at 6000 rpm using an acceleration of 100 rpm/s. Another type of

disorder was obtained when after annealing with moderate pressure a pipette tip was pierced into the colloidal monolayer at the liquid/air interface. This procedure breaks the crystalline domains. Hence, such structures consisted of separated but well ordered micro domains. The worst order was achieved by air drying the polyNIPAM dispersion on top of a glass cover slip using neither spin coating nor mechanical annealing.

Gold deposition

Glass cover slips decorated with polyNIPAM spheres were functionalized by vapor phase deposition of APTES. The samples and a small dish containing 30 μl of APTES were placed inside a standard desiccator which was evacuated until a pressure of 0.3 mbar was reached. The samples were kept under these conditions for 30 min. Finally the samples were baked at 80 $^{\circ}\text{C}$ for 1 h.

Gold nanoparticles wet-chemically synthesized according to Turkevich et al.³² were deposited onto the functionalized glass surface by placing 80 μl of the colloidal gold solution onto the substrate. The samples were incubated at 40 $^{\circ}\text{C}$ for 30 min and subsequently washed with deionized water ($\sim 18.2 \text{ M}\Omega \text{ cm}$).

Before the growth of a closed gold film using electroless deposition the polyNIPAM microspheres mask was removed by ultrasonication in a $\text{H}_2\text{O}:\text{CH}_3\text{OH}$ (1:20, v/v) mixture for 30 min. Afterwards the samples were placed in 5 ml petri dishes filled with 3 mL of an aqueous solution containing 0.4 mM hydroxylamine hydrochloride and 0.5 % (w/v) $\text{HAuCl}_4 \cdot 3\text{H}_2\text{O}$. The reaction was carried out at RT for 1 h under agitation on a rotating table in order to allow for homogenous growth of a gold film. The resulting hole arrays were rinsed with deionized water ($\sim 18.2 \text{ M}\Omega \text{ cm}$) and dried in a stream of N_2 .

Transmission spectra:

Optical data at normal incidence were collected using a Cary 5000 UV-VIS-NIR Spectrometer (Varian, USA).

Imaging & analysis:

SEM imaging was carried out using a Zeiss Ultra 55 "Gemini" scanning electron microscope. The lattice constant and the open area fraction of the substrates were determined using the protocols embedded in the ImageJ 1.37v software. A self written script was used for the determination of radial distribution functions.

Results and discussion

Figure 1 shows SEM images of hole arrays in gold films possessing different degrees of order. Hole arrays were fabricated by using a previously developed method which is based on a combination of colloidal lithography and chemical gold film deposition.²⁹ Briefly, hydrogel microspheres are self-assembled into 2D non-close packed arrays on glass substrates which are subsequently silanized with an aminosilane in order to bind gold nanoparticles. The gold nanoparticles act as seeds upon electroless deposition of a gold film. Before the gold film growth the colloidal mask was removed by ultrasonication.

Formation of highly ordered arrays of hydrogel spheres on large areas was achieved by exploiting the remarkable properties of hydrogel microgels. Here, hydrogel microspheres were assembled at the liquid/air interface by addition of ethanol to the dispersion and application of mechanical force.³⁰ The domain size of the colloidal crystal was increased by directing a gas stream to the sample surface (figure 1 a) & b). As the assembly of the colloids is highly dependent on the pressure and the concentration of polyNIPAM spheres in the used dispersion, slight variations in the amount of point defects can occur (see b). In figure 1 c) and d) SEM images of hole arrays with decreasing colloidal crystal domain size are displayed. Here, a higher gas pressure and consequently stronger mechanical forces were employed. Figure 1 e) shows a SEM image of a hole array consisting of highly ordered micro domains. This structure was obtained by first preparing a highly ordered hydrogel microsphere array at the water/air interface using a moderate gas pressure which was subsequently destroyed with a pipette tip. A disordered 2D array of hydrogel spheres obtained by air drying is displayed in figure 1 f). Note that the local particle density can increase considerably using this approach ('density stripes'). The colour of the frames around the SEM images corresponds to the colour code which is used in all following figures for the differently ordered hole arrays. An illustration of the employed fabrication procedures can be found in the supporting information (scheme S1).

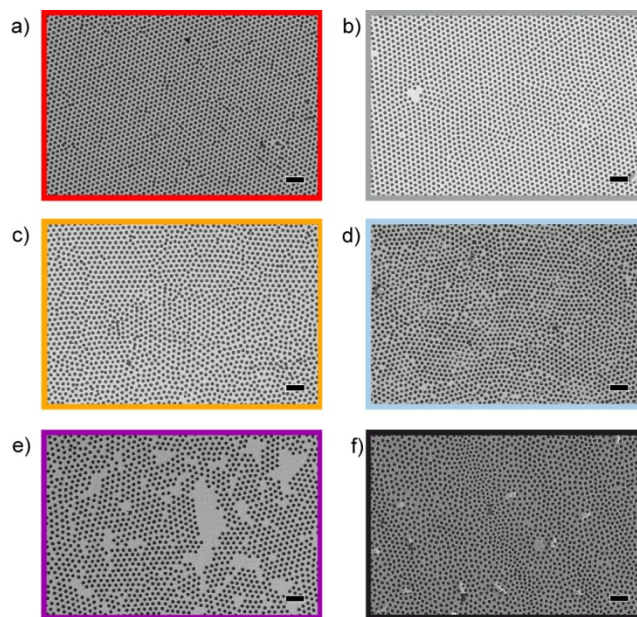


Fig. 1 SEM images of hole arrays in gold films fabricated by a combination of colloidal lithography, silanization, gold nanoparticle deposition, and electroless gold deposition. Different orders were achieved by changing the assembly parameters of the colloidal hydrogel mask (details see text). The scale bar is 4 μm .

In order to quantify the degree of order in the two dimensional arrays SEM pictures of the hole arrays were taken and thoroughly analyzed. Here, 10% of the sample surface which was later illuminated in the transmission measurement was

considered. In other words roughly 180000 holes out of 1 million were processed to guarantee a good statistics for the interpretation of our results. The particle positions were located using the particle analysis function of ImageJ. Based on this data we calculated the radial distribution function $g(r)$ as follows:³³

$$g(r) = N(r) / (2\pi r \Delta r \rho),$$

where $N(r)$ is the number of particles in an annular disc of radii r and $r + \Delta r$ drawn with a particle at the centre, ρ the number of particles per cm^2 . $g(r)$ was averaged over about 35000 particles (the size of the used rectangular SEM image was 0.24 mm x 0.16 mm). The function is shown in figure 2 for two samples with different degrees of order (images a) and f) in figure 1). Reduced order results in an increased peak width and a lower peak height. Higher order peaks become less resolved as the particle positions become less correlated for lower order.

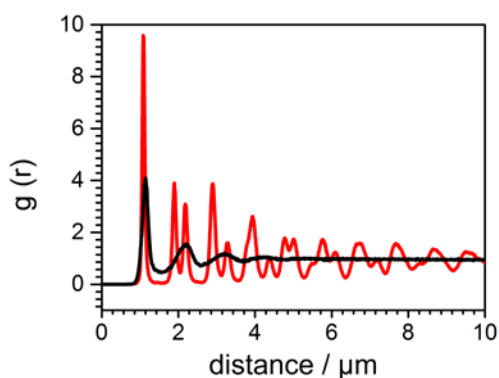


Fig. 2 Radial distribution functions of a highly ordered array (red line, corresponding to structure a) in fig.1) and a highly disordered array (black line, corresponding to structure f) in fig.1).

To determine the lattice constant of the fabricated arrays and to assess their degree of order quantitatively a fast Fourier transform (FFT) was applied to the radial distribution functions. The first peak of the FFT was least square fitted to a Gaussian. The results of the fit gave two important parameters for our analysis. The position of the Gaussian corresponds to the

average lattice constant L_{av} of the hole array, while its full width at half maximum (referred to as standard deviation σ) is a quantitative measure for the spread of these lattice constants and therefore for the degree of order of the investigated hole arrays.³⁴ Note that this means that a high value of σ corresponds to a low degree of order.

Figure 3 a) shows the hole density ρ as a function of the average lattice constant L_{av} of the corresponding hole array. A linear relationship between the hole density ρ and the lattice constant L_{av} is observed. The average lattice constant L_{av} increases with decreasing hole density ρ . In addition the high reproducibility of the fabrication process of highly ordered hole arrays is reflected in their small lattice constant distribution (hole arrays with lattice constants of $1.13 \pm 0.01 \mu\text{m}$). This result is based on the employment of soft hydrogel spheres for the colloidal lithography step which possess self-healing properties and can dissipate defect energy over long range distances through the lattice.³⁵ However, on closer examination of the SEM images the linear relationship between the hole density and the corresponding lattice constant is surprising. Especially the fact that a highly ordered hole array (displayed in grey) and a disordered hole array (displayed in black) possess the same hole density and lattice constant is unexpected. In addition, a mediocre degree of disorder (displayed in bright blue) can show the same hole density and lattice constant as the highly reproducible ordered hole structures. The first assumption would be that the hole diameter of the respective hole arrays would show correlated tendencies. In this case the 'soft' Nature of the employed colloidal particles would allow for the maintenance of the particle density and lattice constant. However, the hole diameter in the fabricated hole arrays shows no dependence on the degree of order of the investigated hole array (figure S1) indicating the important influence of other parameters such as the concentration of the hydrogel spheres and electrostatic interactions. An evidence for the differences in the hole arrays can be noticed in figure 3 b) in which a graph of the lattice constant as a function of its degree of order is displayed. Here, in general the degree of order linearly decreases with increasing lattice constant but two hole arrays are off-beat (bright blue and black points). The corresponding hole arrays are characterized by a low degree of order.

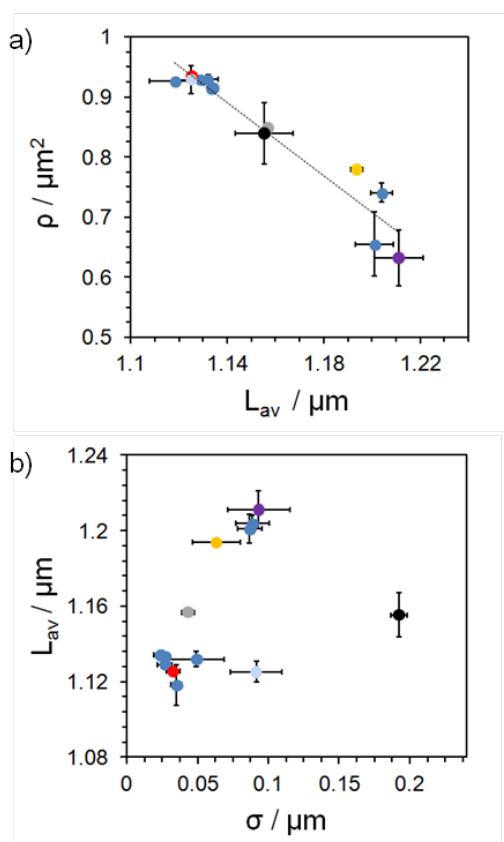


Fig. 3 Characterization of the fabricated periodic hole arrays in gold films. a) Hole density versus average lattice constant. b) Average lattice constant versus degree of order of the hole array.

After analyzing thoroughly the lattice parameters of the fabricated hole arrays in gold films their transmission spectra were collected at normal incidence (figure 4). All spectra showed at least two transmission maxima whose positions are related to the lattice constant of the array (L), the Bragg resonance order (i, j) and the dielectric constants of the surrounding medium and the metal (ϵ_d and ϵ_m) and can be calculated using the following equation:

$$\lambda_{max} = \frac{L}{\sqrt{\frac{4}{3}(i^2 + j^2 + ij)}} \sqrt{\frac{\epsilon_d \epsilon_m}{\epsilon_d + \epsilon_m}}$$

The highest peak in all spectra can be assigned to the (1,0) Au/glass resonance by applying this equation. The second transmission maxima at lower wavelengths correspond to the (1,0) air-glass resonance. Moreover, a very sharp additional peak next to the (1,0) Au/glass mode occurs for hole arrays with a very high degree of order (red spectrum) which vanishes if the degree of order of the hole arrays decreases. According to Kuang et al.³⁶ and Tikhodeev et al.³⁷ this additional peak has its origin in a cavity resonant mode which is a so-called super mode of the periodic array, i.e. its existence depends partly on

the periodic arrangement of circular holes. This theory explains the observation that the mode is lost when the disorder of the array increases.

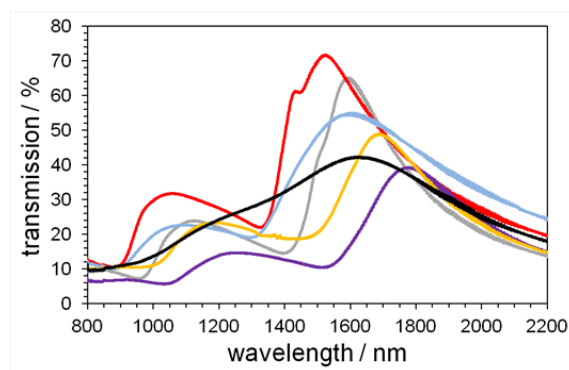


Fig. 4 Transmission spectra of fabricated hole arrays obtained at normal incidence. Highly ordered arrays (red & grey lines) showed the highest transmission. A decrease in the degree of order led to lower transmission and a shift of the resonance peaks to larger wavelengths (light blue, yellow, magenta, black lines).

A closer inspection of the transmission spectra reveals that two hole arrays showed different optical properties in comparison to the others. The transmission peaks in the spectra of the disordered hole arrays labelled in black and blue were unusual broad and the position of their (1,0) gold/glass resonance seems to be not affected by the low degree of order. A plot of the position of the (1,0) gold/glass resonance on the wavelength scale versus the lattice constant of the hole array in a gold film supports this observation (figure S2). Whereas the lattice constant of hole arrays with a higher degree of order correlate linearly with the transmission maximum position the less ordered structures (blue and black) transmission peaks are shifted to shorter wavelengths. This result is more clearly demonstrated in figure 5 a) which displays the position of the (1,0) gold/glass resonance as a function of the degree of order of the investigated hole array. Again, the two hole arrays labelled in bright blue and black do not follow the trend of the other nanostructures. Transmission maxima of all highly ordered structures are located at a wavelength of 1521 ± 6 nm documenting the high reproducibility of our fabrication process once more. Transmission spectra of these highly ordered structures can be found in the supporting information (figure S3).

The influence of the degree of order of the hole arrays on the transmission efficiency is shown in figure 5 b). Astonishingly the transmission efficiency of the hole arrays is not clearly determined by their degree of order. Hence, the transmission properties of the studied hole arrays has to be affected by other parameters such as the gold film thickness and the hole morphology. The gold film thickness is determined by the reaction time of the electroless deposition process and can be easily controlled. The chosen reaction conditions led normally to a gold film thickness of approximately 120 nm. Most of the fabricated hole arrays had gold film thicknesses of 129 ± 10 nm

but for the disordered nanostructures which showed unusual transmission properties gold film thicknesses of either 102 ± 20 nm (bright blue) or 175 ± 18 nm (black) were obtained (determined by AFM). However, the gold film thickness is known to have an influence on the transmission efficiency but does not change the position of the transmission maxima. In contrast variations in the hole shape can have an effect on the optical properties of the hole array.⁴ At least SEM images of the hole array labelled in bright blue show considerable deviation from a circle (figure S4).

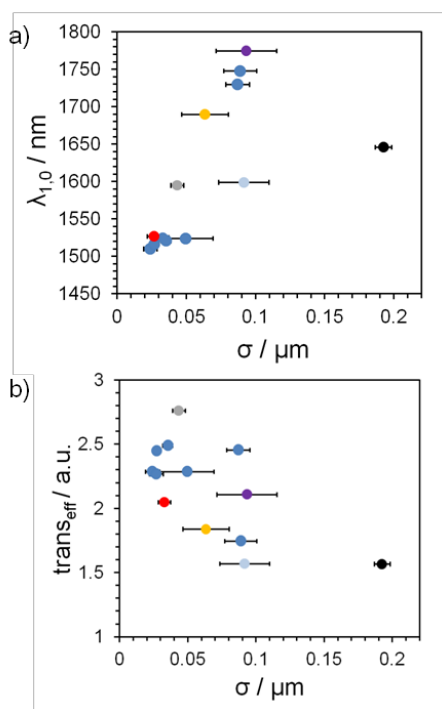


Fig. 5 Dependence of the optical properties of fabricated hole arrays on their degree of order: a) Position of the (1,0) Au/glass resonance. b) Transmission efficiency.

In general the overall transmission of hole arrays in metallic films may involve coupling between the incident light, SPP modes, LSP modes and cavity modes that ultimately lead to a wavelength dependent transmission enhancement.³⁸⁻⁴⁰ In order to support the hypothesis that a reduced efficiency of SPP excitation is responsible for the drop in the transmission efficiency transmission spectra were measured at oblique incidence. If SPP play a major role in the transmission process an angle dependent dispersion of the transmission maxima is expected. For highly ordered hole arrays an additional peak splitting is expected as the degeneracy of certain SP-modes is lifted.⁴¹ Transmission processes governed by cavity as well as localized surface plasmon modes are in contrast expected to be almost unaffected by the angle of incidence.

In figure S5 angle depended transmission spectra of a highly ordered hole array (a) and hole array with a low degree of order (b) are displayed. The spectra clearly show the

involvement of SPPs in the transmission of light through the hole arrays. For both ordered and disordered hole arrays a red shift is observed with increasing angle. In the ordered case additional peaks occur for oblique incidence as expected from the grating coupling equation¹:

$$k_{\text{sp}} = k_{\parallel} \pm iG_1 \pm jG_2,$$

where k_{sp} is the surface plasmon wave vector, $|k_{\parallel}| = (2\pi/\lambda_0)\sin\theta$ is the component of the incident light in the plane of the grating and $|G_1|=|G_2|= 4\pi/(3^{1/2}L)$ are the grating momentum wave vectors of a hexagonal array. A variation of the angle of incidence θ results in the excitation of different SP modes as it can be seen by peak shifts in the transmission spectra shown in figure S4.

Numerous publications are concerned with the use of hole arrays as sensors.^{21,42,43} As colloidal lithography might represent a simple and cheap mean to fabricate such arrays it is important to ask how the sensing performance depends on the lattice order. To determine the sensitivity of the fabricated hole arrays with different degrees of order they were immersed in solvents of varying index of refraction (1,1,2-trichloro-1,2,2-trifluoroethane, tetrachloroethylene, toluene, cyclohexane and acetone) and their transmission spectra were collected at normal incidence. The dependence of the (1,0) gold/glass peak position on the index of refraction was then used to obtain the sensitivity of the structures. We used tabularized NIR refractive indices and least square fitted a Sellmeier function to the data set. The index of refraction was then calculated using this function for the region of interest to obtain accurate values. The sensitivity of the hole arrays was determined by plotting the position of the (1,0) gold/glass resonance vs. the refractive index of the solvent and calculating the slope of the resulting linear dependence. Surprisingly no correlation between the degree of order of the investigated hole array sensor and its sensitivity could be observed (figure 6).

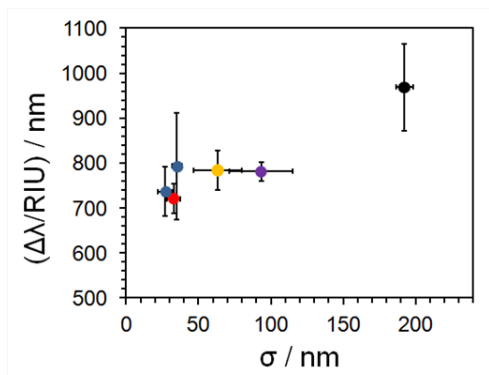


Fig. 6 Sensitivity of hole arrays as a function of their degree of order.

The values fluctuated around a mean sensitivity of 796 ± 81 nm/RIU. Thus, when using hole arrays as sensors the lattice order plays a minor role. However, the transmission minimum in the transmission spectra of hole arrays in metallic films is

more sensitive to refractive index changes⁴⁴ and therefore should be considered for the evaluation of the sensor performance. The respective transmission minimum can only be resolved in well-ordered hole arrays. Hence, optical sensors based on hole arrays with a high degree of order do have advantages over less ordered hole arrays because the highly ordered structures offer more optical features for the sensitive detection of refractive index changes.

Conclusions

To summarize, hole arrays in gold films with different degrees of order were fabricated by using solely chemical methods such as colloidal lithography, silanization, gold nanoparticle and electroless gold deposition. The degree of order of the hole arrays was varied by changing the process parameter for the colloidal mask formation and determined by analyzing SEM images. Correlation of the degree of order of the hole arrays with their transmission properties showed that a lower degree of order led to an increased lattice constant of the hole array and consequently to a shift of the transmission maxima to longer wavelengths. The transmission efficiency was not determined by the degree of order of the investigated hole arrays in gold films. However, transmission spectra of highly ordered hole arrays are highly reproducible allowing for an optical quality control of the fabrication process. The sensitivity of the hole array sensors is not necessarily influenced by the degree of order of the hexagonal lattice but depends on the spectral feature used in the sensing experiment. All these observations encourage the use of colloidal lithography for the fabrication of plasmonic sensors on large areas.

Acknowledgment

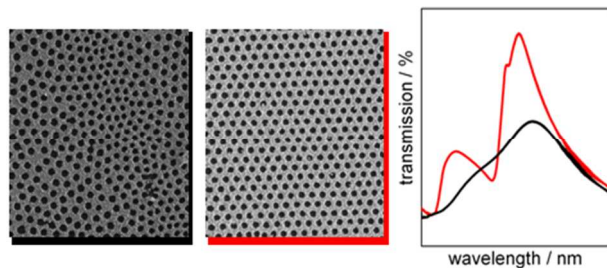
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TOC Entry



Periodic hole arrays in gold films showing extraordinary transmission of light are fabricated using solely chemical methods. The degree of order of the hole arrays has a strong impact on their transmission properties which can be utilized for a spectral quality control of the produced plasmonic sensors.