Optical transmission of corrugated metal films on a two-dimensional hetero-colloidal crystal

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Abstract: The near infrared transmission of corrugated metal films deposited on hetero-colloidal crystals is investigated. The transmission response of the quasi-three-dimensional (quasi-3D) metal film is modified by controlling the nominal thickness of a dielectric layer pre-deposited on the top surface of the colloidal crystal to form a new hetero-colloidal crystal. An extraordinary optical transmission (EOT) phenomenon could be presented in such metallodielectric (MD) architectures. We have found that the main transmission peak is suppressed as the thickness of the intercalated dielectric layer is increased. We propose that the observed EOT is a result of constructive interference between a localized sphere-like plasmon mode and an index-guided eigen mode mainly confined in the colloidal crystal, which is confirmed by our numerical simulations. Based on the MD microstructures, a distinct plasmon sensitivity response difference is achieved, which indicates potential applications for biochemical sensing.

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OCIS codes: (120.7000) Transmission; (240.6680) Surface plasmons.

References and links

1. Introduction

In the past decade, thin perforated metal films have attracted increasing interest since the first report of extraordinary optical transmission (EOT) [1] through arrays of subwavelength holes on metal films [2–8]. The EOT phenomenon is generally acceptable as a result of propagating surface plasmons (SPs) in perforated metal films, where SPs on one side of the metal films are excited by the incident light, then evanescently tunnel to the exit side through the building up of strong electromagnetic fields above the apertures, and are finally re-emitted into optical far field [8–10]. After extensive studies, it is found that various geometrical factors, such as symmetry [11,12] and periodicity of the structure, the aspect ratios and shape of the holes [1–3,7,8,13], aperture area [4,9], thickness of the metal film [14,15], and adhesion layer materials [5], can affect the EOT in different ways. Recent studies have revealed that EOT phenomenon can be further manipulated by controlling the interference between localized and propagating SP modes [16–21]. So far, a number of applications based on the EOT phenomenon have been suggested and demonstrated, such as wavelength selective optical filters, sensors, near-field microscopy, surface enhanced Raman spectroscopy, etc [2,3,8,22–25].

In addition to the study of optical properties of planar perforated metal films, periodically corrugated metal films have been reported experimentally to show the EOT effect [26–32]. A corrugated metal film without tiny holes can show a narrow and strong transmission peak, which can be treated as surface-plasmon-assisted resonant tunneling of light through a corrugated metal film rather than light penetration through tiny holes array [32]. The metal films could be prepared in various ways including focused ion beam and multi-step lithographic methods. More recently, instead of using modern or complex nanofabrication techniques, the metallic architecture can be easily prepared in a relatively large area by depositing a metal film on the surface of colloidal crystals [33,34]. In this way, the metal film is spatially corrugated with a quasi-three-dimensional (quasi-3D) nature following the spherical surface of colloidal substrate. It should be noted that in order to observe the EOT effect in the template metal architectures, a critical metal thickness is required in order to form a conducting network on the surface of the colloidal crystal [26]. The present authors have demonstrated both experimentally and theoretically that a removal of the colloidal substrate can lead to a four times increase of the sensitivity to the change of the environmental refractive index, which could make the quasi-3D metallic structure very useful in sensing [30].

However, the interpretation of the origin that lead to the EOT effect in such a metal-on-sphere architectures is still under discussions though great efforts have been made by researchers in recent studies. The propagating Bragg or Bragg-like plasmon modes was used to interpret the mechanism of the main transmission peak [27] and the supported modes in sphere arrays were also found to be of utmost importance for the transmission mechanism by Landström et al [28]. The interesting evolution from index-guided modes to localized SPs modes and extended SP modes with different metal coating thickness has been used to interpret the anomalous infrared transmission of gold films on two-dimensional (2D) colloidal crystals by Zhan et al [26]. In the silver-coated two-dimensional colloidal crystals, localized cavity SP modes are suggested to be more likely relevant to the mechanism of transmission enhancement by Farcau et al [35]. In order to demonstrate the modification of the photonic crystal properties induced by the corrugated metal film, two main factors have been shown to

affect the transmitted light intensity in the recent review by Romanov et al [10]. The two main factors are (i) the overlap of SPs and index guided modes, and (ii) the probability for the light, which in back coupled from SPs to the electromagnetic radiation, to propagate along the incidence direction. As a result, the interpretation of the physical mechanism is still under consideration, and a further study is thus needed. More importantly, understanding the transmission mechanism is especially crucial for exploiting such low-cost metal-on-sphere architectures in subwavelength optics, nanophotonics and biochemical sensing.

In this paper, we have investigated the near infrared transmission of periodically modulated thin metal films with a high corrugation, which are prepared by depositing a thin metal film on a monolayer of polystyrene (PS) microspheres. In order to further understand the mechanism of EOT through the highly corrugated metal films, we rely on the introduction of an amorphous silica (a-SiO$_2$) layer deposited on the two-dimensional (2D) PS monolayer beads to form a PS-SiO$_2$ hetero-colloidal crystal. In addition to displaying transmission resonances as the simple metal-on-sphere architectures [26–30], these metalodielectric (MD) microstructures show a main transmission peak that can be controlled by varying the thickness of the dielectric layer, thus providing an additional approach to tune the characteristics of EOT in highly corrugated metal films. More importantly, we propose that the EOT in corrugated metal films is a result of interference between sphere-like plasmon modes localized at the outer metal interface and index-guided eigen modes in the colloidal crystal monolayer. Our measurements are in good agreement with our numerical simulations, which confirm the change of the transmission characteristics versus the variation of the thickness of the a-SiO$_2$ layer.

2. Sample preparation and optical characterization

The schematic geometry of the MD microstructures is depicted in Fig. 1(a). First, a large-area 2D hexagonal-close-packed (HCP) colloidal crystal consisting of PS microspheres was prepared on the quartz substrate as the primary template using our recently reported method [34]. An a-SiO$_2$ dielectric layer with controllable thickness ($h$) was then plasma sputtered on the surface of the PS colloidal crystal to form a dielectric cap on each PS microsphere (here denoted as hetero-colloidal particles). Finally, a thin gold film with a thickness of 40 nm was deposited on the surface of the hetero-colloidal crystal by vacuum deposition. Figures 1(b) and 1(c) show the scanning electron microscope (SEM, FEI Philips XL-30) images of two typical samples without and with the intercalated a-SiO$_2$ layer. The diameter of template PS microsphere is $D = 1.6 \mu$m, and four samples with various values of $h = 0.15, 0.22, 0.28, 0.35$ in unit of $D$ were prepared, which are evaluated from the cross section SEM image analysis of the metal-coated hetero-colloidal particles (see below). The zero-order transmission spectra were measured at normal incidence in the near infrared spectrum from $1.0 \mu$m to $2.6 \mu$m, using a commercial Fourier-transform infrared spectrometer (FTIR, Nicolet 6700) equipped with a polarizer. In the experiments, light incident along $z$ axis is polarized along $x$ axis, as schematically shown in Fig. 1(a). The optical spot size of the incident beam on the samples was about 0.8 mm. The numerical aperture of our optical setup is estimated to be less than 0.01. All transmission spectra have been normalized to the transmittance of a pure quartz substrate.
3. Results and discussion

3.1 Pure dielectric microstructures

Figure 2(a) shows the measured transmission spectra for the hetero-colloidal crystals composed of 2D PS colloidal crystal deposited by a-SiO$_2$ layer with different thickness. For the pure PS colloidal crystal which means $h = 0$, there are two main transmission dips observed around $\lambda_1 = 1.944$ $\mu$m and $\lambda_2 = 1.621$ $\mu$m, denoted as G1 and G2. These two pronounced dips basically correspond to the photonic eigen modes of the monolayer dielectric periodic microstructures, which are excited as resultant of strong coherent coupling of incident light [36–39]. When the thickness of the a-SiO$_2$ layer on the top of PS colloidal crystal template continues to increase, there is only an imperceptible change in its spectral position for the G1 mode, whereas the G2 mode shows a continuous red-shift [Fig. 2(c)].

To well understand the optical properties of the pure dielectric microstructures, numerical simulations are performed using the finite difference time domain method [40]. In these models, the distributions of the a-SiO$_2$ layer are approximated as follows. Each PS sphere is assumed half-coated by an a-SiO$_2$ nanocap with a semi-ellipsoidal outer shape to mimic the relatively thick layer of the a-SiO$_2$ layer on the top of the PS spheres. A periodic boundary condition for the unit cell is adopted and the computational domain is terminated with a perfect matching layer [30]. The dielectric constant of PS microsphere and a-SiO$_2$ film is assumed to be $\varepsilon_1 = 2.46$ and $\varepsilon_2 = 2.13$, respectively. The coordinate is chosen such that the periodic microstructures lie on the xy plane, as shown in Fig. 1(a) and light is incident along z axis with its polarization along x axis. The calculated transmission spectra for the hetero-colloidal crystals with different a-SiO$_2$ layers are summarized in Fig. 2(b). It is seen that the calculations based on the models reproduce the measured optical features. In particular, the calculations predict a weak dependence of the G1 mode as well as a noticeable red-shift of the G2 mode as function of the increasing nominal thickness of the a-SiO$_2$ layer [see Fig. 2(c)].
Fig. 2. Measured (a) and calculated (b) transmission spectra for the pure dielectric hetero-colloidal crystals with different a-SiO$_2$ layer thicknesses from $h = 0$ to 0.15D, 0.22D, 0.28D, 0.35D. G1 and G2 indicate the two main dips for the pure dielectric microstructures. For clarity, the individual spectra are offset by 10% from one another. (c) Measured (solid line) and calculated (dashed line) wavelength of G1 (solid squares) and G2 (hollow squares) modes for the pure dielectric hetero-colloidal crystals as functions of $h$. The lines connecting the data points are guides to the eye.

### 3.2 MD microstructures

Figure 3(a) shows the measured transmission spectra for the MD microstructures prepared using the hetero-colloidal crystals as the substrates. In contrast to the pure dielectric structures, all the MD microstructures show a series of transmission peaks [26–30]. It is interesting to note that these peaks always occur at wavelengths very near the transmission minima in the corresponding hetero-colloidal crystal, indicating a close relation between the excited modes in the pure dielectric and the MD microstructures. A significant change in the transmission spectra upon the introduction of a thin a-SiO$_2$ interlayer is that the intensity of P1 mode at $\lambda_1 = 2.064 \, \mu$m for the metal films formed on the bare PS colloidal crystal is
significantly decreased, even for a small value of $h = 0.15D$, but the wavelength of P1 mode has been almost unchanged with the increase of $h$.

![Graph](image)

**Fig. 3.** Measured (a) and calculated (b) transmission spectra for the MD microstructures with different SiO$_2$ layer thicknesses from $h = 0$ to $0.15D$, $0.22D$, $0.28D$, $0.35D$. P1 and P2 denote the two obvious peaks of the microstructures. For clarity, the individual spectra are offset by 5% from one another. (c) Measured (solid line) and calculated (dashed line) wavelength of P1 (solid squares) and P2 (hollow squares) modes for the MD microstructures as functions of $h$. The lines connecting the data points are guides to the eye.

A second important phenomenon is that a quite different characteristic is observed for the neighboring subpeak at $\lambda_2 = 1.711 \mu m$, namely P2 mode. For example, this mode shows a continuous red-shift in its spectral position when the a-SiO$_2$ interlayer thickness is increased, but its intensity shows only a small change. The spectral positions of the transmission peaks P1 and P2 for the corrugated MD architectures are summarized in Fig. 3(c). Again note that their wavelength dependences are similar to the spectral dependences of the optical modes that are responsible for the transmission dips (G1 and G2) in the pure hetero-colloidal crystals.
We have also performed 3D numerical simulations to calculate the transmission spectra of the MD microstructures. In the models, the Au cover layer is assumed to have a thickness of 40 nm on the top of the a-SiO$_2$ nanocap layer and 10 nm at the rim. To mimic the Au connections between adjacent Au bowls, Au bridges are assumed and modeled as Au semi-tubes with a uniform 100 nm thickness and an outer radius of 290 nm [30]. The array of the islands [Figs. 1(a) and 1(c)] deposited on the silica substrate during the evaporation is not taken into account since it makes negligible positive contribution to the observed transmission [26]. Although the distributions of the a-SiO$_2$ and Au layers are both simplified, these models are shown to capture the most important spectral features of the MD microstructures. The permittivity of gold is described by the Drude model,

$$
\varepsilon_{Au} = 1 - \frac{\omega_p^2}{(\omega + i\omega_c)^2}
$$

with the plasma frequency $\omega_p = 8.99$ eV and the collision frequency $\omega_c = 0.0269$ eV [30].

The theoretical calculations of the transmission spectra for the corrugated MD microstructures are plotted in Fig. 3(b). The wavelengths of the two main peaks are summarized in Fig. 3(c). From Fig. 3(b), it is found that the experimentally observed transmission features, particularly for the two dominant peaks of the MD microstructures, are reproduced based on our calculation models. For example, with the increase of the a-SiO$_2$ layer, the dramatic decrease of P1 peak and the insensitivity of the P2 peak amplitude are confirmed in the calculations. Furthermore, the calculated wavelengths of the P1 and P2 peaks as a function of $h$ are well consistent with the experimental observations. The remaining discrepancies, especially at shorter wavelength in the measured spectra, most likely arise from the fabrication tolerances in the experiments. The consistency between the simulations and the measurements suggests that the models we have proposed can be quite good approximations to the MD microstructures and that we can make further field analysis based on these models.

4. Field distribution calculations of hetero-colloidal crystals and MD microstructures

Previous studies [26–30] have shown that for $h = 0$, the two main transmission peaks in the MD microstructures are located near the wavelength of the eigen modes of the colloidal crystal templates, only with a slight shift in their spectral positions. In this work, it is observed experimentally and confirmed numerically that the G1 and P1 modes (also G2 and P2 modes) are located very close to each other in the spectra, and even show the same evolution tendency by increasing the a-SiO$_2$ layer thickness from 0 to $0.35D$. In order to reveal the underlying physics of these resonance modes, electrical field distributions are plotted. Figure 4 shows the calculated electrical field amplitude distributions at the cross-sectional $xz$ plane. Figures 4(a)-4(f) are presented for G1 and G2 modes of the pure dielectric hetero-colloidal crystals and Figs. 4(g)-4(l) are displayed for P1 and P2 modes of the MD microstructures.

Taking an overview of the field distributions of G1 mode shown in Figs. 4(a)-4(c), considerable field intensity is found to be distributed within the PS microsphere, which is considered as the contribution of the photonic eigen mode of the 2D PS colloidal crystal. With $h$ increasing from $0.22D$ to $0.35D$, significant decrease of the field distribution in the PS sphere is observed in Figs. 4(b)-4(c), which also confirmed the strong decrease of the transmission intensity in Fig. 2(a). Owing to the main field confined inside the sphere, the position of G1 mode shows negligible shift with the increased coating a-SiO$_2$ layer as shown in Fig. 2(c). In Figs. 4(d)-4(f), the field distributions of G2 mode show obvious changes. With $h$ increasing from 0 to $0.35D$, the main field distribution moves from the air area near the interface of the sphere and glass substrate to the intercalated a-SiO$_2$ layer. This results from the obtained leaky channel for the high-order eigen mode of the PS colloidal crystal by the coating a-SiO$_2$ layer. Owing to the environmental change by the main field distribution moving into the dielectric layer, the position of G2 mode shows obvious red-shift as shown in Fig. 2(c).
Fig. 4. Calculated $|E|^2$ distributions of the pure dielectric hetero-colloidal crystals with G1 (a-c) and G2 (d-f) modes and the MD microstructures at the resonance P1 (g-i) and P2 (j-l) modes for $h$ from 0 to 0.22\(D\) and 0.35\(D\), respectively. The right column shows the SEM images of the corresponding MD microstructures.

Compared with the G1 and G2 modes in Figs. 4(a)-4(f), the changed field distribution pattern of P1 and P2 modes may result from the reshaping because of the metal coating layer. As for the P1 and P2 modes of the MD microstructures, taking an overview of the field distributions is shown in Figs. 4(g)-4(l), in each case the fields are mostly confined on the top surface of the corrugated metal film with nodes (zero intensity point). Such field patterns are characteristics of the hexapole sphere-like plasmon mode supported in metallic half-shell arrays [41]. Our previous theoretical work has clearly demonstrated that a monolayer of HCP metallic complete or broken shells could support void-like, localized sphere-like, and delocalized Bragg-type plasmons [41,42]. The presence of these plasmon modes has also been confirmed in our recently experimental study on a 2D array of cavity-controllable metallic colloids [43]. In particular, since the sphere-like plasmon mode usually has a broad band feature, it could be interfered with other localized and delocalized modes [41].

Meanwhile, considerable field amplitude of P1 mode is found to be concentrated within the PS microsphere [Fig. 4(g)], similar to the G1 mode [Fig. 4(a)]. As $h$ increasing from 0 to 0.35\(D\), similar field distribution patterns are observed with main field distribution still keeping inside sphere and without obvious leaky energy into the a-SiO$_2$ layer, which show similar evolution to the G1 mode and drop a hint that the transmission resonance P1 is closely
related to the supported eigen mode of the hetero-colloidal crystals. From these mixed field distributions added with the experiment and calculation spectra results, we could claim that the transmission resonance P1 must be a result of the coupling between the localized hexapole sphere-like plasmon mode and the eigen mode of the hetero-colloidal crystal.

As for the P2 mode, with $h$ increasing from 0 to 0.35$d$, obvious field distribution emerges in the a-SiO$_2$ layer, indicating a great difference from P1 mode. For $h = 0$, except the strong field distribution on the top surface of corrugated metal film, the remaining weak field distribution around the sphere surface is similar to that of the G2 mode as shown in Fig. 4(d). With $h$ increasing, obvious field distribution occurs in the a-SiO$_2$ layer as almost the same evolution of G2 mode. For the same reason, the transmission P2 should also be attributed to the coupling mechanism between the localized hexapole sphere-like plasmon mode and the high order eigen mode of the hetero-colloidal crystal.

Next, we now show that the above analysis can also be used to explain why the P1 mode is continuously suppressed with increasing the thickness of the a-SiO$_2$ layer, which in turn further strengthens the above analysis and provides additional clues to reveal the origin of the EOT resonance P1. In such complex MD microstructures, the intercalated a-SiO$_2$ layer actually plays a critical role. From the point of view of the mode coupling, the a-SiO$_2$ dielectric layer is a gap between the corrugated metal film and the hetero-colloidal particle. Obviously, thicker a-SiO$_2$ layer makes the corrugated metal film move further away from the PS colloidal crystal, resulting in weaker coupling between the sphere-like plasmon mode and the eigen mode of the PS colloidal crystal. Indeed, as shown in Figs. 4(g)-4(i), P1 is continuously suppressed with increasing the thickness of the a-SiO$_2$ layer.

From the point of view of the waveguide, the deposition of a-SiO$_2$ onto the PS spheres acts as the cladding layer, which causes an increase of the refractive index in the microstructures, since the air around the pure microsphere is replaced by the a-SiO$_2$ dielectric layer. As seen in Fig. 2 and Fig. 3, such change in refractive index causes a tiny red-shift for the transmission dip appearing around 1950 nm (G1 mode), while a remarkable red-shift for the transmission dip around 1650 nm (G2 mode). Now that the presence of a-SiO$_2$ layer has an almost neglected effect on the G1 mode (the lowest order eigen mode of PS colloidal crystal), the a-SiO$_2$ layer acts only as a character of gap. Therefore, due to weaker coupling, the transmission P1 mode should be expected to be continuously suppressed with increasing the thickness of a-SiO$_2$ layer. On the other hand, the G2 mode is a high order eigen mode with its fields simultaneously distributed within the a-SiO$_2$ layer. This part of field distribution within the a-SiO$_2$ layer can obtain strong coupling to the sphere-like plasmon mode. This could partially counteract the weakened coupling between sphere-like plasmon mode and G2 mode, and the intensity of the P2 mode is thus almost unchanged with the increase of the a-SiO$_2$ thickness.

In addition, an interesting dielectric environmental response is observed in these MD microstructures. In our previous work, we studied the sensing effects based on plasmonic crystals prepared by depositing a thin gold layer onto a 2D colloidal crystal [29,30]. In Fig. 5, the measured transmission spectra for the MD microstructures surrounded by various dielectric matrices of different refractive index are presented. For $h = 0$, only a very small red-shift for these two peaks is observed, as shown in Fig. 5(a). However, the red-shift of P2 is much larger than that of P1 when the a-SiO$_2$ layer is inserted with $h = 0.28d$, as shown in Fig. 5(b).

Figure 5(c) summarizes the wavelength shifts of the main peaks for both MD microstructures as a function of the environmental refractive index. From the slope of the linear fitting, a sensitivity factor defined as the wavelength shifts per refractive index unit change (RIU) $m = \Delta\lambda/\Delta n$ is obtained. With respect to P1, a sensitivity of 179 nm/RIU ($h = 0.28d$) is observed, which is nearly equal to the one of 167 nm/RIU for the MD microstructure with $h = 0$. However, a greatly enhanced sensitivity of 374 nm/RIU is observed for P2 with $h = 0.28d$, showing more than twice to that of P1 with $h = 0$ or 0.28$d$. 

#164162 - $15.00 USD Received 6 Mar 2012; revised 29 Mar 2012; accepted 2 Apr 2012; published 5 Apr 2012 (C) 2012 OSA 9 April 2012 / Vol. 20, No. 8 / OPTICS EXPRESS 9224
which obviously originates from the different response between P1 and P2. This greatly different sensitivity response degree indicates great potential applications for biochemical sensing. The distinct optical response can be mainly attributed to the different plasmon resonance modes with their distinctive field distributions as discussed above.

Fig. 5. Measured transmission spectra for the MD microstructures immersed in different environment media: air (black line, $n = 1.0$), ethanol gas (green line, $n = 1.22$), ethanol liquid (red line, $n = 1.36$), and iso-Propyl alcohol liquid (blue line, $n = 1.38$) with $h = 0$ (a) and $h = 0.28D$ (b). (c) Plot of the main peaks shifts versus refractive index of the P2 (red circles) and P1 (black squares) of $h = 0.28D$, and P1 (green triangles) of $h = 0$.

5. Conclusion

In conclusion, we have reported a study on the near infrared EOT of corrugated gold films, which are prepared by coating PS colloidal crystals with a-SiO$_2$ layer, followed by a further deposition of thin gold films onto the top-most surface. The original main transmission peak of the corrugated gold film is found to be continuously suppressed with increasing the thickness of a-SiO$_2$ layer. Modeled transmission spectra show a good agreement with the measured ones. Further simulations confirm that the underlying mechanism is a result of interference between sphere-like plasmon modes localized mostly at the metal outer interface and eigen modes in the colloidal crystal film. This study will be helpful to understand the nature of EOT through the quasi-3D corrugated metal films, and to promote exploiting such low-cost and easily fabricated metallic structures in subwavelength optics, nanophotonics, and molecular sensing. The resonance peaks shifts versus RIU changes show a distinct plasmon sensitivity response difference, indicating great potential applications for biochemical sensing.

Acknowledgments

This work is supported by the State Key Program for Basic Research of China (No. 2012CB921501), the National Natural Science Foundation of China (Nos. 11174137, 11104136, 11021403, 10804044, 11104136), the Fundamental Research Funds for the Central Universities (No. 1115020403). Partial support from Priority Academic Program Development (PAPD) is also acknowledged.