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2014 Nanotechnology 25 055203

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Optical properties of ultrafine line and space polymeric nanogratings coated with metal and metal–dielectric–metal thin films

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Received 26 August 2013, revised 1 December 2013

Accepted for publication 19 December 2013

Published 9 January 2014

Abstract

Noble metal and metal–dielectric–metal ultrathin films were deposited on the surfaces of ultrafine polymeric nanogratings, which were fabricated using nanoimprint lithography. Experimental results showed dramatic differences of the surface morphologies for single metal and triple metal–dielectric–metal films deposited on flat and corrugated polymeric surfaces. The effect of the surface morphology on the optical properties was hence investigated and analyzed under linearly polarized light. The surface plasmon resonances of single metal and triple metal–dielectric–metal films deposited on polymeric nanograting surfaces were also characterized based on the Kretschmann prism-coupling method. The single metal and triple metal–dielectric–metal films deposited on polymeric nanograting surfaces are important for the study of photon–plasmon interactions (i.e. couplings and conversions) at the interfaces between a nanograting and metal films.

Keywords: grating, surface roughness, surface plasmon

(Some figures may appear in colour only in the online journal)

1. Introduction

The interaction of light with nanostructured materials, particularly those containing noble metals, can produce a variety of unique and useful optical properties. Examples include extraordinary optical transmission [1, 2], negative refractive index [3–5], and super-resolution optical imaging [6–11]. The origins of these optical phenomena can be traced to the excitation and propagation of surface plasmons in the nanostructured metal/dielectric interfaces. The strong confine-

ment of light associated with surface plasmon resonances has led to the development of various subwavelength photonic components, such as waveguides [12–16], switches [17–19], filters [20–26], lenses [27–32], and spasers [33–37].

Gratings have been used to efficiently couple free-space light to surface plasmons by bridging the momentum gap between them [38, 39]. Conversely, surface plasmons can also enhance the grating diffraction [40–45]. Interactions at the interface between a grating and a metal nanostructure are fundamentally interesting and important. For example, subwavelength metal–dielectric–metal (MDM) gratings have been exploited to demonstrate optical magnetic

⁵ These authors contributed equally to this work.

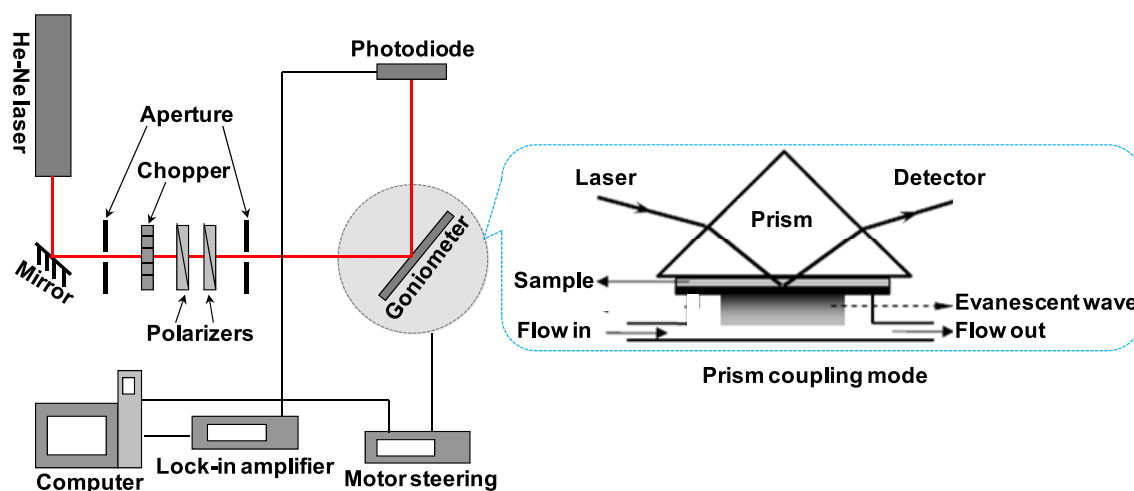


Figure 1. Schematic of experimental setup based on the Kretschmann configuration. The magnified part shows the detailed layout with integration of a flow cell for refractive index sensing.

resonances [46–50]. Therefore, the grating represents an inherently information-rich system since surface plasmon signals appear not only in the directly reflected and transmitted light, but also in the various diffracted orders [51]. In addition, the plasmonic resonance is highly tunable on the basis of the size and shape of the grating surface. Indeed, varying the amplitude, shape, or pitch of the grating profile has a dramatic effect on the plasmonic resonances [52–55].

In this paper, we will study and compare the surface morphologies and their effect on the optical properties for single-layer Au and triple-layer Au-SiO₂-Au thin films deposited on flat and corrugated polymeric surfaces. Their surface plasmon resonances are also characterized based on the Kretschmann prism-coupling method.

2. Experiments

2.1. Nanograting fabrication

The detailed fabrication of the polymeric nanogratings can be found elsewhere [56]. In brief, an organic material (Transpin HE-0600, Molecular Imprints, Inc.) was first spun onto the surface of a double-side polished quartz substrate at two-step spin speeds, 1800 rpm for 3 s and 3000 rpm for 30 s, and baked at 195 °C for 5 min to obtain a 65 nm thick planarization layer. A liquid acrylate imprint resist, poly(methyl methacrylate) (PMMA), was subsequently dispensed across the surface of the sapphire substrate and then imprinted using a quartz mold via ultraviolet illumination. Finally, the mold was separated from the substrate, leaving behind an exact inverse replica of the mold pattern. The quartz mold, with the size of 65 mm × 65 mm and 10 mm × 10 mm active patterned area, featured 50 nm line and space (L&S) structures (duty ratio of 1) with a height of 100 nm and a pitch of 100 nm. This imprint process can be repeated across the substrate areas to obtain several imprint fields on the substrate.

2.2. Metal and metal–dielectric–metal film deposition

Once the imprinted nanograting samples were ready, a 3-nm-thick Ti adhesion layer and a 30-nm-thick Au layer were subsequently deposited on one PMMA nanograting by electron-beam evaporation (Denton Vacuum Explorer) at room temperature. On the other PMMA nanograting, subsequent Ti-Au-SiO₂-Au (3 nm/30 nm/30 nm/30 nm) layers were deposited under the same conditions. To minimize the roughness introduced by metal deposition, a low evaporation rate was chosen, of 0.5 nm s^{−1}.

2.3. Optical characterization

The surface morphologies of the nanogratings were characterized using scanning electron microscopy (SEM). Optical transmittance of the samples was measured under a linearly polarized broadband light source at room temperature using an inverted optical microscope (Olympus IX 71) integrated with a monochromator (Acton SP2300). We used a 20× objective lens combined with a variable aperture to select a small detecting area and to collect the optical signal as well. The polarization of the incident light can be set in any direction with the accuracy of ~1°.

As for the sensing test, we used the prism-coupled surface plasmon resonances based on the Kretschmann configuration [57], as shown in figure 1. In brief, a p-polarized He–Ne laser (633 nm) modulated by a frequency chopper was used to excite the surface plasmons. The light was reflected off the sample surface, and its intensity was measured by a photodiode detector connected to a lock-in amplifier. The sample holder and the detector were controlled by two coaxial goniometers, and they rotated in a $\theta/2\theta$ mode in an angular scan. An LaSFN9 prism ($n = 1.8449@633$ nm) was used in order to shift the SPP resonance at the Au/aqueous solution interface to not too high angles. The sample was pressed against a Viton O-ring to form a sealed cavity, which was integrated with a flow cell for the index sensing test. A

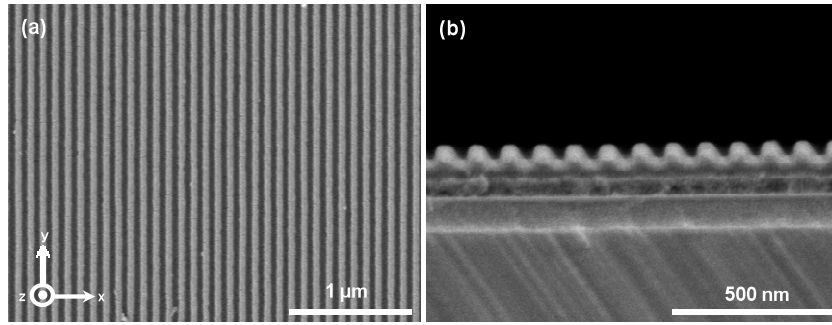


Figure 2. SEM images showing the top (a) and cross-section (b) views of the imprinted PMMA nanogratings.

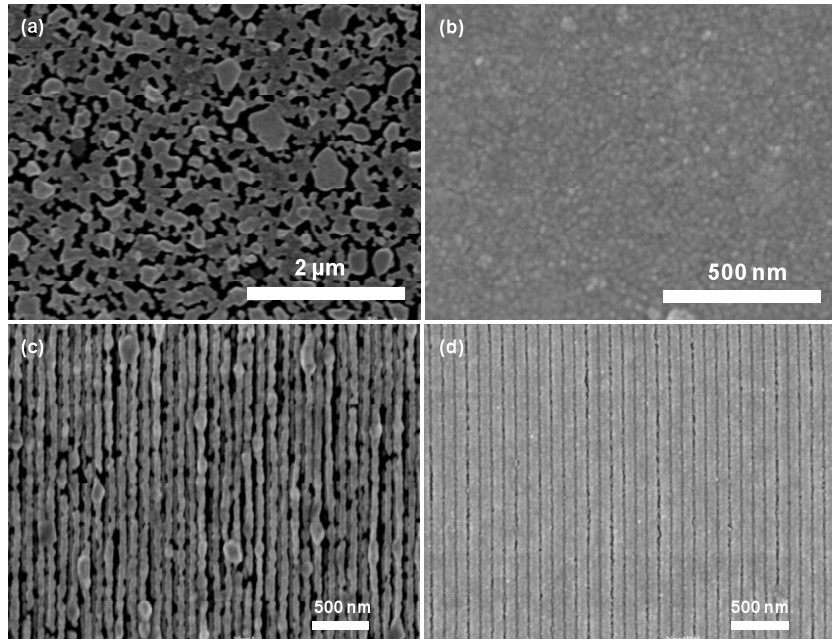


Figure 3. Surface morphologies of single-layer Au ((a) and (c)) and triple-layer Au-SiO₂-Au ((b) and (d)) deposition on a flat PMMA surface and a corrugated PMMA nanograting surface, respectively.

peristaltic pump was used when introducing the aqueous solution into the flow cell. Refractive index sensing was carried out by exposing the sample surface to aqueous solutions of glycerol at different concentrations (0%, 10%, 20%, 30% and 60% by weight, respectively).

2.4. Optical simulation

To model the optical properties of the PMMA nanogratings with Au and Au-SiO₂-Au films, we carried out finite-difference time-domain (FDTD) calculations with commercial software (Lumerical). The whole structure was simulated with periodic (x -direction) and perfectly matched layer (PML) (y - and z -directions) boundary conditions. The mesh size of the simulation space was 1 nm (Δx) $\times$ 1 nm (Δy) $\times$ 1 nm (Δz). We injected a plane wave with polarization direction along the x -axis from the bottom of the quartz substrate. The dispersion of gold was based on the Johnson and Christy model [58] in the material library of the software. The refractive index of PMMA was derived by fitting the experimental data using a

three-coefficient Cauchy model and written as $n(\lambda) = A + B/\lambda^2 + C/\lambda^4$, where $A = 1.488$, $B = 2.898 \times 10^{-3} \mu\text{m}^2$, and $C = 1.579 \times 10^{-4} \mu\text{m}^4$.

3. Results and discussion

Figure 2 shows typical SEM images of the PMMA nanogratings after nanoimprint lithography. A clear L&S pattern was achieved. The pitch (the sum of the widths of a trench and a ridge) of the L&S pattern is 100 nm. The duty ratio of line to space is ~ 0.9 , which is slightly smaller than that of the quartz template since the photopolymerization of PMMA generally induces shrinkage in volume.

After the deposition of Au and Au-SiO₂-Au films, the surface morphologies were checked again using SEM, as shown in figure 3. We can see dramatic changes of surface morphologies compared to original ones in figure 2. For the sake of discussion in the following, we term single-layer Au and triple-layer Au-SiO₂-Au films deposited on flat PMMA surfaces as M-film and MDM-film systems, while

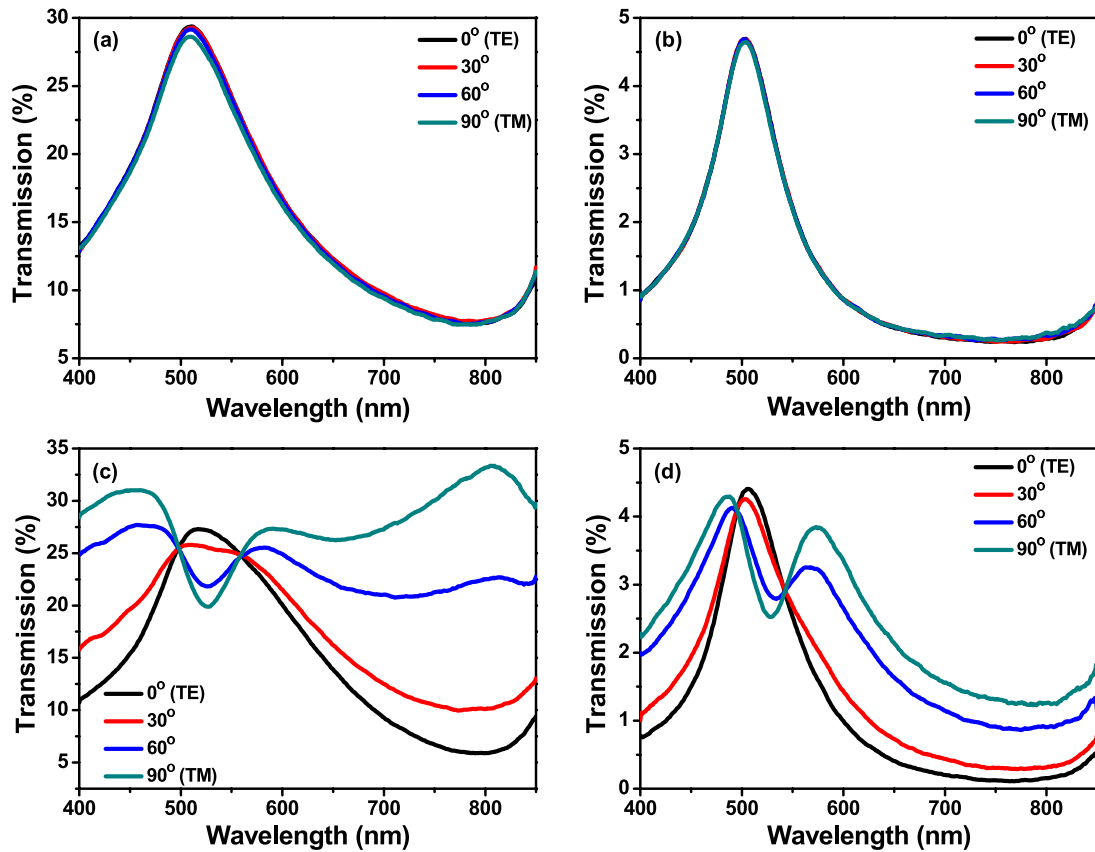


Figure 4. Optical transmission of M-film (a), MDM-film (b), M-grating (c) and MDM-grating (d) systems, respectively, under normally incident light with different polarizations.

on corrugated PMMA nanograting surfaces as M-grating and MDM-grating systems, respectively. As shown in figure 3(a), only a semicontinuous thin film is formed for the M-film system since the gold has poor affinity to PMMA films and grows in the Volmer–Weber mode [59–62]. Although the Ti adhesion layer enhances the gold affinity to the PMMA surface, the Ti layer does not completely cover the whole surface of the PMMA film due to its ultrathin deposition. Therefore, gold still has a high chance to directly contact the PMMA surface. This could be the partial reason that the Au film is still flake like. This leads to a rough film with large scattering loss and, hence, additional damping loss. However, the presence of surface roughness can also facilitate the excitation of SPPs. In contrast, for the MDM-film system, the surface roughness has been greatly improved, and grains are much smaller since the thin SiO₂ layer improves the affinity of gold and serves as a planarization layer as well. As a result, more continuous and much smoother films are formed, as shown in figure 3(b). Similar phenomena have been observed in M-grating and MDM-grating systems, as shown in figures 3(c) and (d).

Optical transmittance of the samples was measured using a broad band light beam with different polarizations. For the M-film and MDM-film systems (figures 4(a) and (b)), we only observe a single transmission peak at ~500 nm regardless of polarizations of the incident light and Au layers. This transmission peak arises from the electron transition and recombination between the filled d-bands and the Fermi

level in the conduction band of gold films [63–65]. It is interesting that the spectral linewidth, i.e., the full width at half maximum (FWHM), of the transmission peak for the MDM-film system (80 nm) becomes much narrower than that for the M-film system (137 nm), which could be attributed to less interfacial electron scattering in the MDM-film system. These experimental results also confirm that the localized surface plasmons are hardly excited in our wavelength range of interest for the two optical systems even though the gold films are semicontinuous (for the M-film system) or particle like (for the MDM-film system). Figures 4(c) and (d) show the measured transmission for the M-grating and the MDM-grating systems. We can see from figures 4(c) and (d) that there still exists only one transmission peak for TE polarization denoting the interband electron transitions since the TE-polarized incident light cannot excite the surface plasmon in our optical systems. We note that the spectral linewidth of the transmission peak for the M-grating system becomes much broader than that for the M-film system, while the spectral linewidth stays almost the same for both MDM-film and MDM-grating systems. The broadening of the spectral linewidth in the M-grating system could arise from much stronger interfacial electron scattering since the M-grating system has a much rougher surface compared to the M-film system. As the incident light polarization changes from transverse electric (TE) to transverse magnetic (TM), a clear trough appears at ~527 nm on the spectra for both M-grating and MDM-grating systems. This trough is caused

by the surface plasmon excitation. For TM-polarized light, the troughs become lowest. It is worth noting that under the TM-polarized light illumination, another transmission peak appears at the wavelength of ~ 800 nm in the M-grating system due to the excitation of localized surface plasmons. From the SEM image of the M-grating system, it can be seen that some elongated, isolated gold particles with long axis along the grating lines are formed. Their transverse localized surface plasmons can be excited using the TM-polarized light and hence enhance the transmission. In contrast, in the MDM-grating system, much smoother and more continuous MDM films are formed and localized mode surface plasmons are hardly excited. Therefore, no additional peaks appear above 600 nm in the spectra. We also note that on one hand, the Ti adhesion layer may cause plasmon damping loss, hence broadening of the surface plasmon resonances; on the other hand, it also improves the surface morphologies, especially the surface roughness, which hence enhances the surface plasmon resonances. Therefore, the adhesion layer has a compromise effect on damping loss and resonance. Very recently, the plasmon damping effect caused by the adhesion layer has attracted much attention, and various alternatives have been proposed to overcome the damping issue [66, 67]. We believe that the surface plasmon resonances in our M-grating and MDM-grating systems will become sharp by minimizing the damping loss.

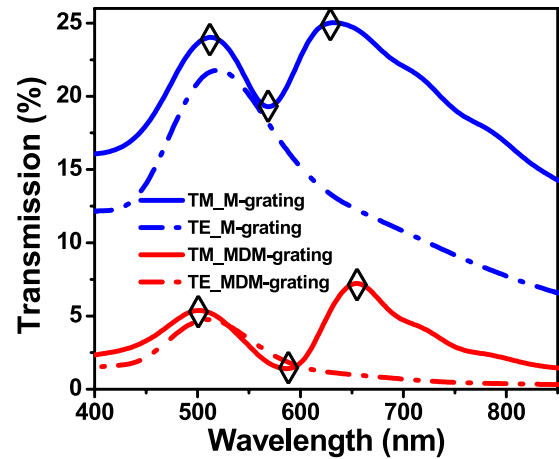


Figure 5. Simulated transmission of M-grating and MDM-grating systems under TE and TM polarized light illumination.

We further carried out the FDTD simulation for our M-grating and MDM-grating systems. The simulation results are shown in figure 5. We can see that the simulation curves are in reasonable agreement with the experimental results (figures 4(c) and (d)). There is only a difference between simulation and experiment for the M-grating system where a transmission peak at ~ 800 nm was observed experimentally due to the excitation of localized surface plasmons. However,

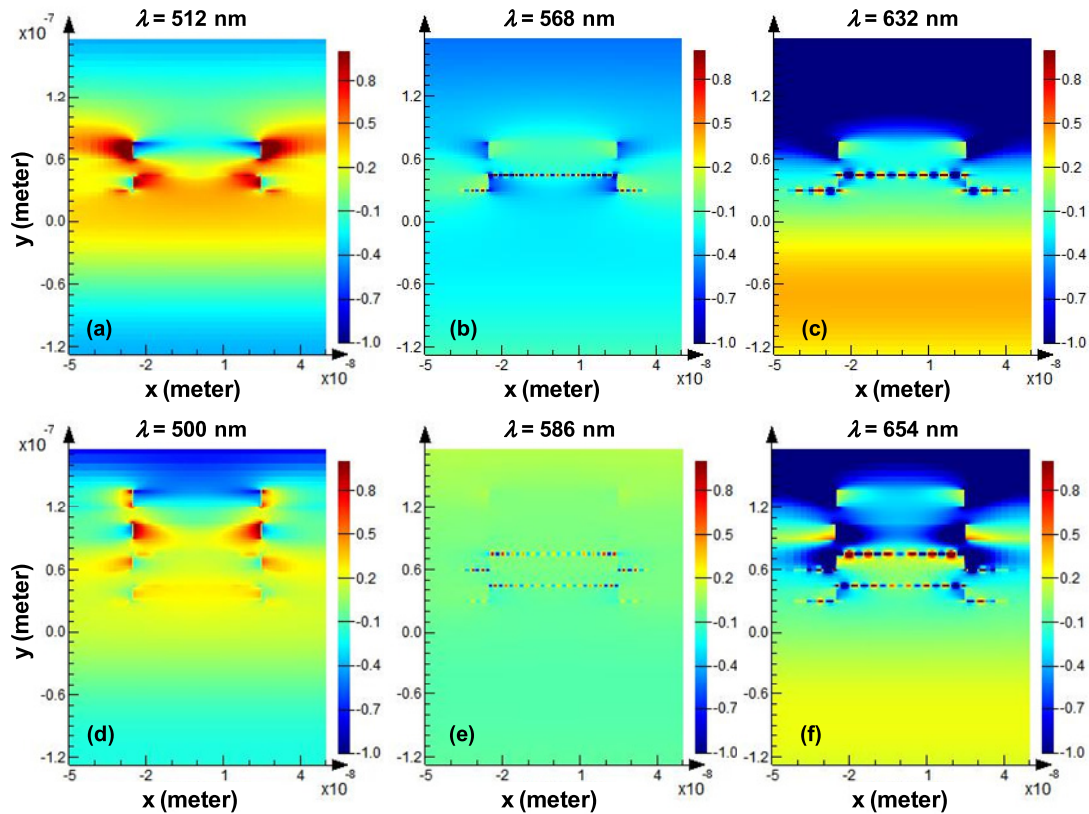


Figure 6. Electric-field distributions at three typical positions denoted as '◇' in figure 5 for M-grating ((a)–(c)) and MDM-grating ((d)–(f)) systems under TM-polarized light illumination.

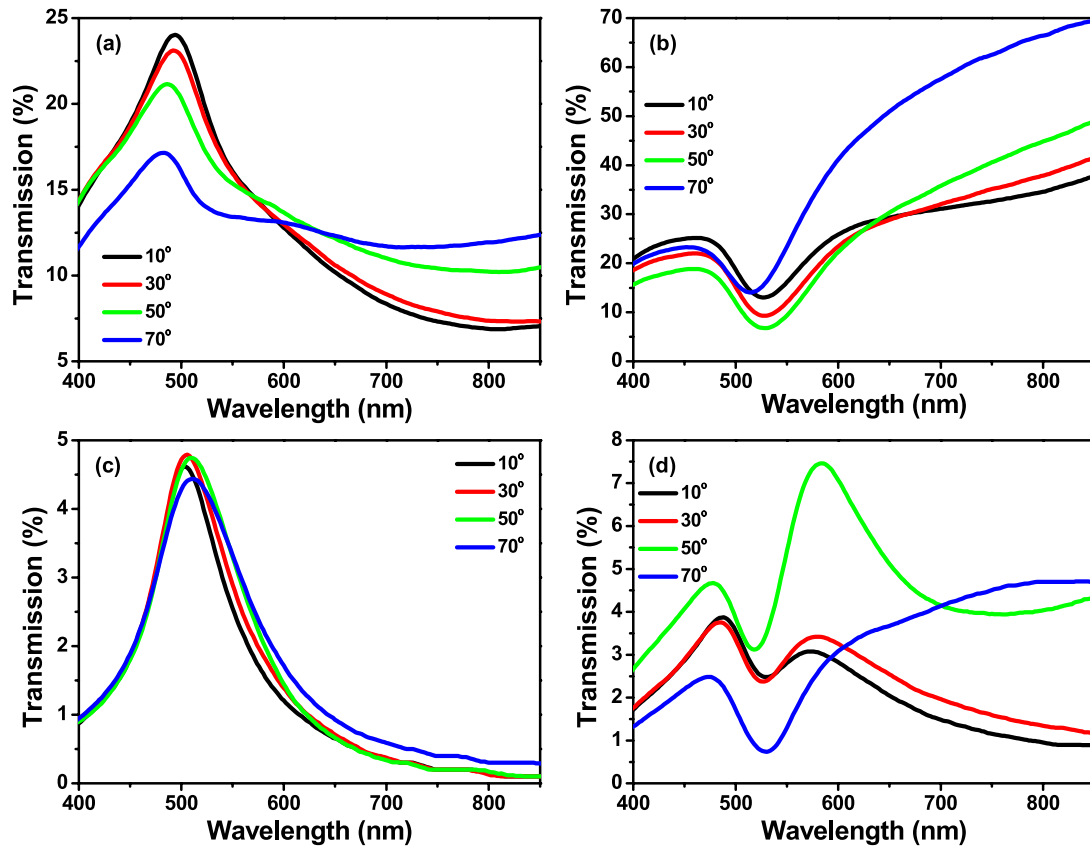


Figure 7. Angle-dependent optical transmission of M-grating ((a) and (b)) and MDM-grating ((c) and (d)) systems under TE ((a) and (c)) and TM ((b) and (d)) polarized light, respectively.

we did not observe this transmission peak in our simulation since the thin gold film deposited on the PMMA nanograting surface was set perfectly continuous and smooth and hence no localized surface plasmons were excited. We further mapped the electric-field distributions at three typical positions in figure 5 for the M-grating and MDM-grating systems under TM-polarized light illumination, as shown in figure 6. From figure 6, we can see that at the peak positions, obvious light resonances are formed inside both M-grating and MDM-grating systems, while at the dip position, no clear resonance is observed in either system. A closer look at the electric-field distributions at two peak positions shows that different resonance modes are formed inside both systems. In figures 6(a) and (d), the electric fields on the upper and lower gold films are in-phase, from which one can infer that there is an anti-symmetric charge distribution on the gold surfaces; while in figures 6(c) and (f), the electric fields on the upper and lower gold films are anti-phase, which means a symmetric charge distribution on the gold surfaces.

In general, gold-coated gratings demonstrate incident angle-dependent optical transmission at specific wavelengths associated with a matching of the grating wavevector with that of SPPs at the metal/dielectric interfaces [68–70]. We therefore investigate the angle-dependent transmission of our M-grating and MDM-grating systems under TM-polarized light, as shown in figure 7. We can see that both M-grating and MDM-grating systems demonstrate the angle-independent

transmission in terms of peak or dip positions. The ultrafine subwavelength features of nanogratings could be the possible reason for the angle-independent transmission. This angular insensitivity in plasmon excitation will make it easier to integrate our systems with other measurement systems.

Our M-grating and MDM-grating systems are potentially useful for surface plasmon resonance spectroscopy and microscopy since the grating permits momentum matching between the incident light and the surface plasmon wave. In addition, the systems can be conveniently integrated with other system components, such as microfluidic channels, coupling ports and reaction chambers, without additional complications or extra costs. In this regard, we carried out a surface plasmon resonance sensing test using our M-grating and MDM-grating systems. The surface plasmon coupling efficiency of the grating coupler for the M-grating and the MDM-grating systems was compared, as shown in figure 8. In both cases, there is no clear feature in the reflectivity for TE-polarized incident light, while both reflectivity curves exhibit clear minima for TM-polarized incident light, which correspond to the excitation of surface plasmons. However, the M-grating system shows much higher coupling efficiency than the MDM-grating system. The low coupling efficiency for the MDM-grating system might be attributed to the destructive interference after multiple reflections on the metal–dielectric interfaces [71]. With specially engineered film thickness, the coupling efficiency could be greatly

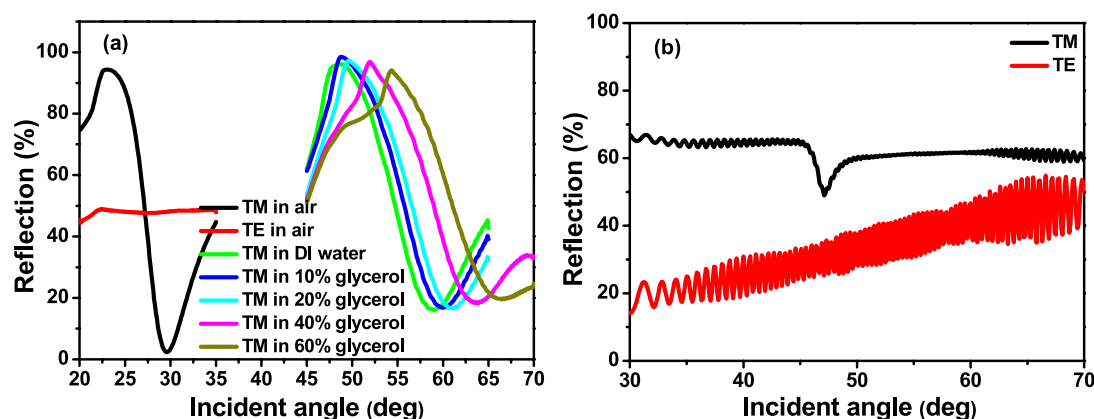


Figure 8. Surface plasmon resonance reflection curves of M-grating (a) and MDM-grating (b) systems for TM and TE polarized light. SPR refractive index sensing test is also shown in (a) for glycerol solutions with different concentrations.

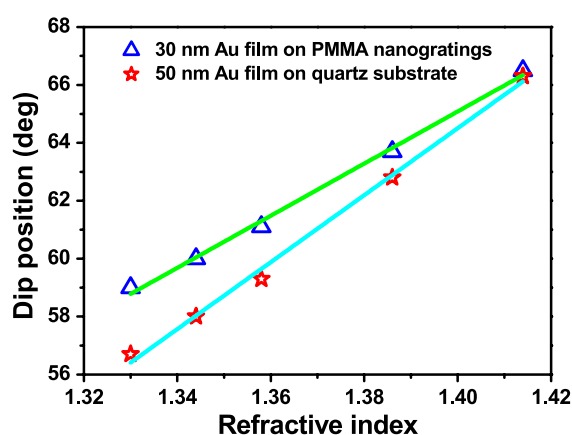


Figure 9. Evolution of reflection dip positions as a function of refractive index of glycerol solutions with increased concentrations.

enhanced due to the constructive interference after multiple reflections. We further checked the sensing performance using the M-grating system. Figure 8(a) shows the changes of the surface plasmon resonance spectra monitored as a function of glycerol concentration in deionized water. It can be seen from figure 8(a) that with the increase of the glycerol concentration, i.e., the increase of the refractive index of the medium, the reflectivity minima shift from 59° to 66.5° . The experimental data were further linearly fitted in figure 9 to determine the sensitivity, which is defined in units of incident angle shift at the reflectivity minima per refractive index unit (RIU). It is worth mentioning that the refractive indices of glycerol solution at different concentrations were calculated by the mass fraction (i.e., the concentration by weight) of glycerol in water. The refractive indices of glycerol and water were set to be 1.47 and 1.33, respectively. By calculating the slope of the fitted line, the M-grating system exhibits the incident angular sensitivity of $89^\circ/\text{RIU}$, which is comparable to the optimum sensitivity of $114^\circ/\text{RIU}$ based on a 50 nm gold film on a quartz substrate. This high angular sensitivity benefits from the corrugated surface, which effectively increases the loading efficiency of glycerol molecules.

4. Conclusion

In summary, we have studied the surface morphologies and optical properties of M-film, MDM-film, M-grating and MDM-grating systems. The M-film and M-grating systems showed semicontinuous and rough surfaces, while the MDM-film and MDM-grating systems have more continuous and much smoother surfaces. As a result, these morphological differences affect their optical properties, which have been confirmed from the transmission spectra under incident light with different polarizations. In addition, experimental results show that the M-grating system is promising for index sensing applications, with the angular sensitivity of $89^\circ/\text{RIU}$. The M-grating and MDM-grating systems are also important as a platform to investigate photon-plasmon interactions (i.e. photon-plasmon couplings and conversions) at the interfaces between nanogratings and metal films. The MDM-grating system has a much more complex coupling processes than the M-grating system, which is potentially useful for engineering the optical magnetic resonances in metamaterials.

Acknowledgments

This work was financially supported by the Joint Council Office (JCO) of the Agency for Science Technology and Research (A*STAR), under the grant No. 12302FG012. H T Dai also thanks the funding support from the National Natural Science Foundation of China under grant No. 61177061.

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