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Diffraction-Based Tracking of Surface Plasmon Resonance Enhanced Transmission Through a Gold-Coated Grating

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Supporting Information

ABSTRACT: Surface plasmon resonance enhanced transmission through metal-coated nanostructures represents a highly sensitive yet simple method for quantitative measurement of surface processes and is particularly useful in the development of thin film and adsorption sensors. Diffraction-induced surface plasmon excitation can produce enhanced transmission at select regions of the visible spectrum, and wavelength shifts associated with these transmission peaks can be used to track adsorption processes and film formation. In this report, we describe a simple optical microscope-based method for monitoring the first-order diffracted peaks associated with enhanced transmission through a gold-coated diffraction grating. A Bertrand lens is used to focus the grating’s diffraction image onto a CCD camera, and the spatial position of the diffracted peaks can be readily transformed into a spectral signature of the transmitted light without the use of a spectrometer. The surface plasmon peaks appear as a region of enhanced transmission when the sample is illuminated with p-polarized light, and the peak position reflects the local dielectric properties of the metal interface, including the presence of thin films. The ability to track the position of the plasmon peak and, thus, measure film thickness is demonstrated using the diffracted peaks for samples possessing thin films of silicon oxide. The experimental results are then compared with calculations of optical diffraction through a model, film-coated grating using the rigorously coupled wave analysis simulation method.

Coupling of light with nanostructured objects leads to a variety of unique and potentially useful optical phenomena. Some of the more interesting examples involve the coupling of light to nanostructured metal surfaces, which can lead to what is known as enhanced or extraordinary optical transmission. The origins of enhanced transmission through metal films can be traced to the excitation of surface plasmons (SPs) in the nanostructured metal interface. The high sensitivity of these SPs to the local dielectric conditions at the metal interface can be exploited in sensor development. Examples of nanostructure-based plasmonic sensing include nanostructures consisting of nanohole arrays, single nanometric holes, nanoslit arrays, and various grating-type and diffractive nanostructures.

A variety of fabrication strategies can be used to create nanostructured optical elements ranging from electron beam lithography to colloidal nanoparticle lithography. Beyond these specialized methods, one can exploit the features of commercially available diffraction gratings as nanostructured elements. Indeed, optical sensors and SP-based sensing platforms that exploit gratings have become increasingly popular. Gratings represent an inherently information-rich substrate due to SPs appearing not only in the directly reflected and transmitted peaks, but also in the various diffracted orders. In addition, the SP response is highly tunable on the basis of the size and shape of the grating surface. Indeed, changing the amplitude, shape, or pitch of the grating profile has a dramatic effect on the details of SPs. Thus, this substrate represents a highly flexible and tunable platform for sensor development.

We and others have previously demonstrated that a diffraction grating constructed from a commercial DVD supported SP-enhanced light transmission when coated with a thin metal film. The observed enhanced transmission consists of narrow peaks in the visible spectrum, whose central wavelength can be tuned by simple rotation of the grating. In the work presented here, we describe a simple optical microscope-based method for monitoring the first-order diffracted peaks associated with enhanced transmission through a gold-coated diffraction grating. We illustrate how peaks associated with SP excitation can be observed by tracking the light transmitted through the ±1 diffracted orders. Diffracted light is monitored by using a Bertrand lens to focus the grating’s diffraction image onto a CCD camera. The spatial position of the diffracted peaks are then transformed through a simple calibration procedure into a spectral signature of the transmitted light without the use of a spectrometer. The ability to track the position of the plasmon peak and, thus, measure film thickness using the diffracted light is demonstrated for thin films of silicon oxide. The experimental results are then compared with calculations on the basis of an optical model of the grating interface as determined using the rigorously coupled wave analysis simulation method.

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EXPERIMENTAL SECTION

Materials and Reagents. Absolute ethanol and nitric acid were purchased from Sigma Aldrich (St. Louis, MO). All chemicals and reagents were used as received. Deionized water with electrical resistivity greater than 18 MΩ·cm was used during rinsing and cleaning procedures (NANOPure, Barnstead, Dubuque, IA). Recordable digital versatile discs (DVD-R, 4.7GB) were purchased from Inkjet Art Solutions (Salt Lake City, UT). Gold (99.999%) and tungsten wire baskets were purchased from Ted Pella, Inc. (Redding, CA). Silicon monoxide (SiO) with purity of 99.9% was purchased from GERAC (Milwaukee, WI).

Grating Construction. Two different gratings were used in this work. The first was a commercial holographic transmission grating with a 1000 nm pitch (Edmund Optics). The second was prepared from a commercial DVD-R and coated with a thin (~40 nm) layer of gold. Preparation of the metal-coated grating has been described previously (details in the Supporting Information). SiO films were formed on the gold grating via vacuum evaporation under conditions similar to gold coating (Supporting Information). Film thicknesses and composition were confirmed using atomic force microscopy (AFM) imaging, ellipsometry, and infrared reflection absorption spectroscopy (IRRAS) (details of methods in the Supporting Information).

Optical Characterization. Optical transmission measurements were performed using an optical microscope (Olympus model B41) in transmission mode with a broadband, white light source. A schematic of the optical train (Scheme 1) illustrates the major components. The light source consisted of a 150 W tungsten-halogen bulb with the standard infrared filter removed. Control of the incident light polarization (with respect to the grating direction) was achieved using a linear polarizer between the light source and the aperture diaphragm. Light was focused onto the sample using a condenser lens. The sample was mounted to a mechanical translation stage for xyz movement. A 100× microscope objective was used to focus the sample image into the observation tube. The microscope’s detector consisted of either a CCD camera (Thorlabs) or a fiber-optic spectrometer (Ocean Optics). Collection of the sample’s diffraction image was achieved by inserting a Bertrand lens into the observation tube. The Bertrand lens focuses the sample’s Fourier image, which is located at the rear focal plane, onto the microscope’s imaging plane to allow capture of optical diffraction data with the CCD detector. Subsequent data analysis was performed using ImageJ.14

Optical Modeling. The optical response of the film-coated grating was modeled using the rigorously coupled wave analysis (RCWA) method. Details of the method and the form of its implementation used here can be found in several publications.15 Briefly, diffraction efficiencies were calculated for both transverse magnetic (TM) and transverse electric (TE) incident light as a function of wavelength. Calculations were performed using a
custom-built code written in Matlab (further details in the Supporting Information). The grating geometry used in the model calculations was based upon fitting experimental AFM measurements of the DVD-R profile (Supporting Information: Figure S.2). Upon the basis of these results, a sawtooth profile was used with a pitch of 670 nm and an amplitude of 120 nm. Refractive index values for the various materials included published values for gold16 and SiO.17 The polycarbonate substrate was modeled using the Sellmeier equation.18

**RESULTS AND DISCUSSION**

An image of a holographic transmission grating, as observed through an optical microscope using a 100× objective, is shown in Figure 1A. The periodicity of the ridges in the image reflects the 1000 nm pitch of the grating. An image of the optical diffraction pattern from this grating can be observed by inserting a Bertrand lens into the microscope’s observation tube.13 A color version of the diffraction image (Figure 1B) exhibits three dominant features. A white, circular spot appears at the center of the image. This spot represents light that is directly transmitted through the sample, otherwise referred to as the zeroth-order spot. Two elliptical spots appear to the right and left of the central spot. These features are due to light that is diffracted by the grating and are associated with the +1 (right) and −1 (left) diffracted orders (Scheme 1). Although the zeroth-order peak appears white when viewed by eye or as imaged with a color CCD camera, the plus/minus peaks disperse the light with blue light (shorter wavelengths) appearing nearest to the center and red light (longer wavelengths) appearing at the outer edges. The distances of the ±1 diffracted spots from the zeroth-order spot are proportional to the reciprocal of the grating pitch. The 1000 nm pitch for this grating gives diffracted spots that are located at ±1 μm−1. Using the same magnification objective, a smaller grating pitch would produce ±1 diffracted spots that are located further from the zeroth-order spot (due to a larger diffracted angle). The diffracted angle can be described by the grating equation,

\[ \sin \theta_i + \sin \theta_m = \frac{m \lambda}{\Lambda} \]  

where \( \theta_i \) is the angle of incidence, \( \Lambda \) is the grating pitch, \( \lambda \) is the wavelength, \( m \) is the diffracted order, and \( \theta_m \) is the angle of the diffracted spot of order \( m \). In a collinear mounting (\( \theta_i = 0 \)), the position \( L \) of the diffracted spots on the diffraction image (Figure 1B) can be described by

\[ L = D \left( \frac{m \lambda}{\Lambda} \right) \]

where \( L \) is the measured distance from the zeroth-order spot, and \( D \) is a constant associated with the magnification level. Equation 2 shows that the location of the diffracted spots moves farther away from the zeroth-order spot with decreasing pitch and increasing diffracted orders. In addition, the location of the colors in the diffracted spot tracks with their wavelengths, with longer wavelengths appearing at larger distances from the origin. The dispersed light appearing in the ±1-order spots in this diffraction image allows the spectral signature of a sample to be measured by simply determining the intensity as a function of position in the captured image. With proper calibration, the intensity versus pixel location in the image can be converted into intensity versus wavelength (vide infra).

![Figure 2. Optical diffraction images (insets) and transmitted intensity profiles for DVD-R gratings: (A) uncoated grating p-polarized, (B) 40 nm Au-coated grating s-polarized, and (C) 40 nm Au-coated grating p-polarized. The SP peak is denoted by an asterisk in part C.](image)

To excite SPs at the gold/air interface, we chose to use a commercial DVD-R as the grating source. The DVD-R represents an inexpensive grating whose pitch (∼670 nm) coincidentally has a value that is appropriate for exciting SPs in a thin metal film when using a collinear optical configuration (\( \theta_i = 0 \)).26 Thus, the DVD-R geometry is ideally suited for SP transmission (or reflection) measurements with an optical microscope.

The diffraction image of an uncoated DVD-R (Figure 2A) exhibits features similar to the transmission grating in Figure 1, with an intense zeroth-order peak at the image center and the ±1-order peaks to the left and right of the image center. A horizontal intensity profile along the center of the diffracted spots shows a large intensity for the zeroth-order peak and broad features for the ±1-order peaks. Notably, the diffraction image is independent of polarization (s or p) when exposed with direct (\( \theta_i = 0 \)) illumination. Coating the grating with 40 nm of Au attenuates the transmitted light intensity and produces several new features as well as significant differences between s- and p-polarized light. The zeroth-order peak for s-polarized light is attenuated, and the ±1 diffracted peaks are substantially weaker, especially at longer wavelengths (Figure 2B). This is due to absorption from the thin, gold film. The response to p-polarized light shows a similar attenuation, but with an additional, strong transmission in the plus/minus first-order peaks at longer wavelengths (denoted by an asterisk in Figure 2C). This new transmission peak is due to excitation of a SP at the metal/air interface on the grating.7e
resulting spectra for the three cases shown in Figure 2 are depicted in Figure 3. The uncoated DVD (dotted line) shows a broad intensity profile between ∼400 and 750 nm, which is consistent with the shape of light produced by the tungsten-halogen light source. The intensity of the light from the uncoated sample drops sharply at ∼780 nm, which is a result of the diffracted spot reaching the edge of the image window. This wavelength range can be extended to larger values by using a higher magnification objective (150 or 200×). The spectra from the Au-coated sample using s-polarized (dashed line) and p-polarized (solid line) light exhibit the expected features. The s-polarized spectrum is broad with a peak near 550 nm, consistent with a green transmitted color of a thin gold film. The p-polarized light tracks the s-polarized spectrum at small wavelengths, but then exhibits a very large transmission peak centered at ∼700 nm. This transmission peak is due to excitation of a SP at the gold/air interface. Notably, due to the asymmetric nature of this grating (air/gold/polycarbonate), a SP is also excited at the gold/polycarbonate interface, but due to the higher refractive index of the polycarbonate substrate, this resonance is located in the near-infrared region (∼1100 nm) and not observable in this data (vide infra).

A comparison of the experimental results with those derived from an optical simulation of the grating interface can be used to assist in data interpretation and to identify notable spectral features. The RCWA method was used to simulate the transmission and reflection of the various diffracted orders (Scheme 1) through a model grating (vide supra). Predicted transmission spectra were determined for TM and transverse electric TE light using the model grating profile with a 40 nm gold layer. Results for the zeroth- and first-order diffraction efficiencies are shown. For both TM0 (p-polarized) and TE0 (s-polarized) (Figure 4A), a peak is observed near 500 nm, as expected for a thin gold film. The TE0 result shows no other notable features, whereas the TM0 exhibits an intense enhancement near 700 nm, which is the result of SP excitation. Prior measurements of directly transmitted light through a gold-coated DVD-R showed spectra nearly identical in shape to what appears in Figure 4A (see Figure 3B in ref 7e). The predicted diffraction efficiencies for the +1-order peak (Figure 4B) are also consistent with the experimental results, with TE1 showing only a broad peak near 500 nm and TM1 exhibiting an intense SP peak near ∼700 nm. The primary difference between the model (Figure 4B) and experimental results (Figure 3) for the +1-order peak is that the experimental data shows more light transmission near 500 nm than the prediction. This could be due to minor differences in the grating shape, gold thickness, or limitations in the experimental interface.
optics, such as the nonlinearity of the light source. Nevertheless, the significant features (notably the presence of the SP peak) are consistent with both results.

To demonstrate the ability to track adsorption/film formation on the gold surface using these diffracted peaks, a series of SiO films were coated onto the grating. SiO was vapor-deposited onto the grating at thicknesses of 0, 10, 20, and 30 nm, as determined by a quartz crystal thickness monitor. The composition of the SiO films was confirmed using IRRAS. Features characteristic of the Si—O—Si stretching vibration (denoted by “#”) were seen with a sharp peak at ∼1100 cm⁻¹ that increased in magnitude with increasing film thickness (Figure 5A). In addition, a broad, although rather weak, signature associated with the OH stretching vibration from Si—OH (denoted by an asterisk) is observed between 3000 and 3600 cm⁻¹. A plot of the intensity of the Si—O peak at 1100 cm⁻¹ versus film thickness shows a clear, linear trend, which is consistent with a linearly increasing film thickness (Figure 5B).

The impact of the SiO films on the optical response of the gold-coated grating is illustrated in Figure 6. A series of slices showing the right half of the diffraction images from each sample are shown. The images depict a portion of the diffraction image starting at the zeroth-order peak and including the complete +1-order peak. The −1 peak looks similar to the +1, but is not shown for clarity. The transmission depicted by the +1 peak for s-polarized light shows a broad, shallow band. With increasing SiO thickness, this band increases in intensity, but it remains fixed in position. In contrast, the p-polarized light shows two dominant features in the +1 peak. For the 0 nm SiO sample, the left portion of the +1 peak is a shallow, broad transmission peak similar to what is in the s data; however, the right portion of the +1 spot shows a larger peak, which is associated with an enhanced transmission that is caused by the formation of a SP at the gold/air interface. With the deposition of a SiO film, the broad, lower-wavelength peak increases in magnitude in a fashion similar to the s-polarized result. In addition, the SPR peak is seen to both broaden slightly and shift to longer wavelengths as the SiO thickness increases from 0 to 10, 20, and 30 nm. In the 30 nm case, the plasmon peak has shifted nearly out of the field of view.

A quantitative view of the spectra associated with the +1 diffracted peaks in Figure 6 are depicted in Figure 7 after converting the intensity-versus-pixel location to transmittance-versus-wavelength. As was evident in the diffraction images, the s-polarized light displays a broad transmission peak centered around 500 nm (denoted as peak 1). With increasing film thickness, the magnitude of the transmission peak in this region increases. This increase in transmission can be most readily explained by considering the SiO film as an antireflective coating. The presence of the SiO film on the gold surface reduces reflection at that surface, which serves to increase the amount of light that is transmitted through and, subsequently, measured at the detector. The spectra determined for the p-polarized transmission also show an increase in the light transmitted at smaller wavelengths (peak 1), which is also a result of this antireflective effect. In addition, the spectrum for p-polarized light clearly shows the strong enhanced transmission peak due to SP resonance at ∼700 nm (peak 2) for the 0 nm SiO sample. The 10 nm SiO sample shows a slight attenuation and broadening of the SPR transmission peak and a red shift of the peak position. The peak magnitude continues to decrease, and the peak position red shifts for the 20 and 30 nm films, although the longer wavelength region of both peaks is truncated by the edge of the image window (vide supra). Thus, the SPR peak red-shifts with increasing film thickness, just as would be expected. An additional feature also appears for the 20 and 30 nm SiO films. Peak 3 appears as a shoulder on peak 1 for the 20 nm film and then becomes more clear for the 30 nm film. This additional peak is also a SP peak, although one originating from a second-order diffracted peak on the back side of the grating (the gold/polycarbonate interface).
The sensitivity of this diffraction-based approach for SPR detection of film thickness is consistent with other grating-based SPR detection methods. A quantitative comparison of the peak shifts in the experimental data show a sensitivity of ~1.4 nm peak shift/nm film thickness for the thinnest SiO layers and an increasing sensitivity to nearly 5 nm peak shift/nm film thickness for the 30 nm film (Figure S4, Supporting Information). This increase in sensitivity ($S$) is a direct function of the fact that peak shifts for grating-based SPR sensing are proportional to the wavelength ($S \propto \lambda_{peak}$), at which the peaks appear. Thus, longer-wavelength peak positions have a greater sensitivity and give a larger wavelength shift for an equivalent change in refractive index. Details of these sensitivity calculations as well as comparison of various SPR-based sensing methods have been previously described.7,11c

Figure 8 depicts simulation results for the model DVD grating with SiO films of several different thicknesses. The directly transmitted light associated with s-polarized light (transverse electric, zeroth order: $TE_0$) is shown in Figure 8A. The simulation results are consistent with those obtained experimentally. A broad peak is observed with a maximum near 500 nm (peak 1). Increasing the thickness of the SiO layer in the model system results in an increase in transmission. Again, this increase can be attributed to an antireflective effect associated with the SiO layer, which increases the transmitted light.

The predicted transmission with p-polarized light (transverse magnetic zeroth order: $TM_0$) in Figure 8B exhibits two dominant peaks in the absence of a SiO film. The peak at 1 was just described, and a second peak appears at ~700 nm (peak 2). Peak 2 is an enhanced transmission peak that is due to the excitation of a SP at the gold/air interface. The location of this peak can be readily calculated by considering the momentum matching condition between the wavevector of the SP ($k_p$) with that of the incident p-polarized light interacting with the diffraction grating ($k_{gr}$), as given in eq 3

$$k_p = \frac{2\pi}{\lambda_0} \sqrt{\frac{\varepsilon_{M,ED}}{\varepsilon_{M} + \varepsilon_{D}}} = \frac{2\pi}{\lambda_0} \sqrt{\varepsilon_{D} \sin \theta_0 + m^2} = \frac{2\pi}{\lambda}$$

where $\varepsilon_{D}$ is the real part of the metal’s dielectric constant, and $\varepsilon_{D}$ is the dielectric constant of the neighboring material (air or polycarbonate). At an incident angle of $\theta = 0^\circ$, this equality may be satisfied by several different conditions. With a grating pitch of $\Lambda = 670$ nm, for example, the first diffracted order ($m = 1$) will satisfy this momentum matching condition at a gold ($\varepsilon_{M}$)/air ($\varepsilon_{D}$) interface at $\lambda_{sp} \sim 687$ nm. As a plasmon peak at the gold/air interface, its location is impacted by the local dielectric conditions existing at that interface. The presence of a thin film will cause this peak to red shift due to the increasing dielectric constant associated with that layer (increasing effective $\varepsilon_{D}$). Indeed, the calculation supports this red shift in the position of peak 2 after the addition of a thin film represented by 10 and 20 nm SiO layers. The calculated shift in peak position is ~1.4 nm wavelength shift per nanometer of film at small film thicknesses and increases to almost 6 nm peak shift per nanometer film thickness for the 30 nm film, which is consistent with expectations.7,11c

With the 20 nm SiO film, a third peak emerges (peak 3) in the calculation and appears as a shoulder on peak 1. This is also a SP, but it is associated with the gold/polycarbonate interface at the back side of the DVD grating. The position of this peak can be found by solving eq 3 using the gold/polycarbonate dielectric constants ($\varepsilon_{D} \sim 2.5$) and $m = 2$, to give $\lambda_{sp} \sim 581$ nm. Another SP is excited at the gold/polycarbonate interface that is associated with the $m = \pm 1$ or first diffracted orders. However, this peak appears at ~1100 nm, so it is at higher wavelengths than what is measured in this work.

The predicted values for the first-order diffracted peak behave in a manner consistent with what was seen with the experimental results in that the SP peaks also red shift with increasing film thickness. Figure 8C plots the diffraction efficiency for the first-order diffracted peak for transverse magnetic illumination ($TM_1$). An intense peak appears at ~700 nm, and this peak shifts toward longer wavelengths with the addition of thicker SiO films. Notably, a direct comparison between the peak positions and peak shifts as observed experimentally (see Figure S4 of the Supporting Information) show that both the data and modeling results exhibit a similar peak position and peak shifts for increasing film thicknesses.

It should be noted that the SPs that exist at the back side (gold/polycarbonate) of the grating sense little of what occurs at the front side (gold/air) of the grating, since the decay length of the SP within the gold is ~25 nm under these conditions. More extensive analysis of the modeling results allows one to compare the behavior of peaks appearing at both the back and front side of the grating, and indeed, they are related. In fact, the appearance of
SPs at one side of the grating can often be traced to the passing off of an order from the other side of the grating, which creates an evanescent wave and thus excites a SP. Although this behavior indicates that SPs form at several different conditions at the front and back side of the grating, because of the short SP decay lengths within the gold film, only those at the gold/air interface show a significant response to thickness changes in a thin film forming at the front side of the grating. More importantly, the peaks from the gold/air interface are the dominant features in both the experimental and simulated spectra.

CONCLUSIONS

Grating-based coupling strategies for surface plasmon resonance sensing represent a simple, yet highly sensitive, method for tracking adsorption and thin film formation. In this work, we have demonstrated how film formation on a grating based upon a commercial DVD-R can be monitored using a simple optical microscope setup. In fact, the ability to use a Bertrand lens to image the diffracted spots associated with the grating allows one to monitor the transmission peaks associated with SPs at the gold/air interface are the dominant features in both the gold and back side of the grating, because of the short SP decay lengths at the front and back sides of the metal surface.

ASSOCIATED CONTENT

Supporting Information. Additional information as noted in text. This material is available free of charge via the Internet at http://pubs.acs.org.

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