Published in final edited form as:

Nanoscale. 2015 March 7; 7(9): 4226–4233. doi:10.1039/c4nr06586g.

Polarization interferometry for real-time spectroscopic plasmonic sensing

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Abstract

We present quantitative, spectroscopic polarization interferometry phase measurements on plasmonic surfaces for sensing applications. By adding a liquid crystal variable wave plate in our beam path, we are able to measure phase shifts due to small refractive index changes on the sensor surface. By scanning in a quick sequence, our technique is extended to demonstrate real-time measurements. While this optical technique is applicable to different sensor geometries — *e.g.*, nanoparticles, nanogratings, or nanoapertures — the plasmonic sensors we use here consist of an ultrasmooth gold layer with buried linear gratings. Using these devices and our phase measurement technique, we calculate a figure of merit that shows improvement over measuring only surface plasmon resonance shifts from a reflected intensity spectrum. To demonstrate the general-purpose versatility of our phase-resolved measurements, we also show numerical simulations with another common device architecture: periodic plasmonic slits. Since our technique inherently measures both the intensity and phase of the reflected or transmitted light simultaneously, quantitative sensor device characterization is possible.

Introduction

Surface plasmon resonance (SPR) is often used for biological and chemical sensing due to its extreme sensitivity to index of refraction changes at the interface of a metal and a dielectric medium^{1–8}. While many geometries, devices, and illumination methods have been used, typical SPR sensing measurements yield only intensity information in the form of a reflection, transmission, or scattering spectrum^{5,7–9}. To gain more information, such as the phase of the plasmon¹⁰, or to improve sensitivity, a more complicated optical system is often required, for example with interferometric techniques^{11–24}, spectroscopic ellipsometry^{25–29}, the addition of magnetic materials for magneto-optical SPR sensing³⁰, or the addition of gain media for detection with plasmon laser systems³¹. Among these, interferometric techniques are useful not only for sensing, but also for more complete device characterization. However, these techniques often involve split-beam paths with complicated

optics^{10,17,23,24}, are typically restricted to only one laser wavelength^{10–17,32}, or require complex on-chip plasmonic interferometers^{22,33,34}. Spectroscopic ellipsometry techniques can also be used for sensing, but require oblique illumination angles and generally require specialized equipment^{25–27}. In order to obtain both quantitative phase and intensity information across a broad wavelength spectrum for biosensing or imaging applications, a simpler measurement technique is desirable, especially one that can be performed in real-time.

Liquid crystal variable wave plates (LCVWPs) are simple optical components that, under computer control, are capable of inducing phase shifts between light of different linear polarizations or converting the polarization state of an incident beam. In previous works on SPR imaging and beyond, LCVWPs have been applied as correcting agents for time-varying and spatially inconsistent light sources^{32,35,36}, mechanical vibrations and phase drift³², grating interferometers³⁷, the measurement of negative refractive index materials^{11,12}, and as phase-measurement tools within a Kretschmann configuration³⁸. In this work, we employ a LCVWP as the critical component in a common-path polarization interferometer setup combined with a standard optical microscope and spectrometer for measuring real-time phase shifts due to refractive index changes over a wide range of wavelengths simultaneously. The addition of a LCVWP for quantitative phase measurements and real-time sensing can, in principle, be used with a wide variety of plasmonic nano-structures and geometries. In this regard, here we experimentally analyze one particular device structure while also presenting proof-of-concept numerical solutions for another device architecture, as shown in Figure S1. Thus, the installation of a LCVWP for plasmonic sensing promises general-purpose versatility.

Common geometries for SPR sensing include the Kretschmann configuration^{1,2,7,9}, scattering or reflection from nanoparticles^{3–5,7} or plasmonic gratings^{1–3,5,39}, and transmission through nanohole arrays^{5,7–9,18,19,40–48}. A key advantage of the Kretschmann configuration is a decoupling of the light path and the sensing medium, *i.e.* where both the incident and reflected light do not directly pass through the sensing medium. Unfortunately, the Kretschmann configuration involves large incident angles, cumbersome optics and alignment, and does not lend itself to high-resolution imaging with large numerical aperture (N.A.) microscope objectives for multiplexing^{9,49}. These issues are also apparent in spectroscopic ellipsometry measurements. To address this, several alternative sensing geometries have been developed, as mentioned above, but often do not simultaneously maintain both of the advantages of normally incident illumination (for high-resolution SPR imaging and multiplexing) and detection that are decoupled from the sensing medium. Previously, we presented buried grating devices that offer one solution to these issues⁴⁹. The devices are produced using template stripping⁵⁰ and show adaptability with tunable plasmonic resonances in a reflection-mode geometry. In contrast to transmission-based plasmonic sensors, the “backside” optical illumination and collection capability allows measurements of turbid and opaque liquids. Because of these advantages, in this current paper, we chose to use the buried backside structures to examine the versatility of our new measurement technique. In other words, we present here both a new measurement technique as well as an SPR sensing platform that together are capable of real-time refractive index

sensing with quantitative phase and intensity information in a common-path, normally-incident, reflection-mode geometry that decouples any microscope optics from the sensing liquid. Beyond using these buried grating structures for our phase-resolved sensing experiments, a more detailed study can be found in our previous publication⁴⁹.

Materials and Methods

Experimental Setup

Our setup consists of an inverted microscope, a pair of linear polarizers, a LCVWP, and an imaging spectrometer (Figure 1). This technique demonstrates normal incidence reflection-mode data collection using white light common-path polarization interferometry, which is less sensitive to alignment and ambient vibrations than more common beam splitting interferometric techniques. This method overcomes several weaknesses of previously developed plasmonic phase detection techniques such as: laser illumination that introduces speckle and makes imaging more difficult, Kretschmann prism coupling and spectroscopic ellipsometry with oblique angles of illumination^{1,2,9,25–27}, and Michelson interferometry and other beam splitting techniques using free space optics that are particularly sensitive to vibrations and require precise alignment^{10,17,23}. Our measurement system contains simple optics (polarizers and a wave plate) that can be aligned and implemented with relative ease into a standard microscope and spectrometer setup using white light illumination. Rather than tracking an angle of incidence or a spectral resonance peak or dip, we track the real-time phase delay between two orthogonal polarizations near a sharp phase feature by rapidly scanning the LCVWP and obtaining data over a wide range of optical wavelengths simultaneously. It is possible to measure the quantitative phase delay caused by the plasmon resonance because our linear grating structure only excites plasmon resonances with one polarization — the orthogonal polarization is used as our phase reference. The experimental phase information was then compared to full-field electromagnetic modeling results using COMSOL Multiphysics™ and analyzed with Jones matrix calculations. Finally, it should be noted that this phase measurement technique can be applied more generally in reflection or transmission mode geometries to a wide variety of plasmonic sensing devices, *e.g.* other grating designs, nanorods, slits, apertures, elliptical nanoholes⁴⁷, or even to a standard spectroscopic Kretschmann configuration with white light. For example, see Supplementary Information and Figure S1 for modeling of our measurement system using transmission through a periodic slit array.

Plasmonic Structure

While other geometries are possible (Figure S1), the particular devices we used in this paper are described in our previous work⁴⁹ and further in the Supplementary Information. The final form (Figure 2a) consists of an ultrasmooth gold layer (root mean square (RMS) roughness <0.5 nm) with gold gratings buried in an adhesive substrate. This smooth surface is particularly good for sensing with self-assembled monolayers or lipid membranes. Indeed, a surface roughness on the order of only 1–2 nm RMS can cause interference in the self-organized assembly of lipid membranes and can reduce protein mobility^{9,51–53}. A scanning electron micrograph (SEM) of the grating structures imaged through the ultrasmooth gold layer is shown in Figure 2b. The reflected light spectral resonances of our sensor can be

tuned by varying the period of the grating and the width of the grating lines as shown in Figures 2c.

Numerical Simulations

Previous characterization of buried grating structures described several plasmonic resonances^{41,49,54}. Specifically, the dips present in the reflection spectrum corresponded to three different resonances: a grating resonance on the sensing “upper” side of the gold film; a grating resonance on the “buried” substrate side of the gold film; and a central resonance corresponding to a “coupled” propagating (sensing side) and localized (substrate side) mode with short field penetration on the sensing side. This resonance was not found to yield the most sensitivity to refractive index changes on the upper gold surface due to its localized nature^{25,49}. However, it has been shown that large phase features are present near diffractively coupled localized SPRs, which is advantageous for our experiment^{25,26,55}. A typical experimental reflection spectrum for a grating of period 410 nm and line width of 160 nm is shown in Figure 3a. We also performed finite-element method (FEM) modeling with COMSOL MultiphysicsTM software (further described in the Supplementary Information) from which we can reproduce a reflection spectrum (Figure 3b) that agrees well with the experimental data presented in Figure 3a. The “upper” side and “buried” side resonances were located at 593 nm and 757nm, respectively, while the “coupled” resonance was at 671 nm. A simulated reflected phase (Figure 3c) and a field intensity map (Figure 3d, Figure S2) are also shown. While the exact spectral positions of the peaks and dips are within $\sim 2 - 20$ nm in experiment vs. simulation, all the main features of the experimental spectra are accounted for. At the location of the “coupled” plasmon mode at 671 nm there is a strong phase feature that only appears with transverse-magnetic (TM) illumination. It is this phase feature that is tracked for sensing applications. Illumination with transverse-electric (TE) polarization does not excite plasmons and is therefore used as our phase reference.

Experimental Techniques

Our measurement system is based around an inverted microscope (Nikon) in reflection-mode with a white light (tungsten halogen) source and a 5x objective (N.A. = 0.13). The objective aperture was closed as small as possible to have near-normally incident light. The first polarizer, located inside the microscope's illumination path, was positioned at 45 degrees. The second polarizer was positioned at 45 degrees after the sample, external to the microscope, and immediately before the spectrometer. The key element that allowed the measurement of phase differences between the TE and TM polarizations was the addition of a LCVWP (Thorlabs LCC1223-A, 350-700 nm, slow axis vertical). With correct alignment of the fast and slow axes of the device, the LCVWP could be used to induce a phase delay between the TE and TM polarizations after reflection off of the sample. Since the phase delay produced by the LCVWP could be scanned over one full wave of retardance and used to effectively cancel the TE vs. TM phase delay introduced by the plasmonic gratings, quantitative TE (no plasmonic resonance) vs. TM (plasmonic resonance) phase information could be retrieved from the sample. The retardance of the LCVWP was modulated with an applied voltage and calibrated across a range of wavelengths. A complete voltage scan on the LCVWP typically ranged from 0.5 V to 3.5 V. Therefore, coupled with an imaging

spectrometer (Horiba) and a CCD camera (Apogee), our setup measured both the reflected intensity and TE vs. TM phase delay from the sample over a range of wavelengths. Finally, since our experiments were automated with homemade LabVIEW software, scanning the LCVWP and recording the reflection spectra was performed relatively quickly for real-time sensing experiments. To the best of our knowledge, a LCVWP has not been used before in this manner for real-time plasmonic sensing experiments.

Results and Discussion

Experimental data collected with LabVIEW software was analyzed within a MATLAB script using the following equations¹¹:

$$\Delta I = \frac{I_{\max} - I_{\min}}{2}$$

$$I_0 = \frac{I_{\max} + I_{\min}}{2}$$

$$\varphi = \arccos \left[\frac{1}{\Delta I} (I - I_0) \right]$$

where I is the signal intensity (as a function of the LCVWP voltage) and ϕ is the reflected phase. $I_{\max}$ occurs where the total phase delay between the TE and TM polarizations due to the sample, the intermediate optics, and the LCVWP amounts to 2π radians. $I_{\min}$ occurs where the total phase delay is π radians. The intensity maximum ($I_{\max}$) and minimum ($I_{\min}$) points are thus used to center the data between +1 and -1, and the *arccos* function is used to determine the full reflected phase profile (Figure S3c). When analysis was performed over the full wavelength range, a two-dimensional phase map was produced for both the flat gold (Figure 4a) surface and the buried grating structures (Figure 4b). Additionally, the spectrum from the flat gold was used to calibrate the LCVWP and for data normalization. Since our spectrometer was set up in an imaging format, a spectrum was saved simultaneously for both the plasmonic grating (Figure S3a) and a nearby flat gold surface region for each voltage applied to the LCVWP. The data could also be analyzed at one particular wavelength of interest as the applied voltage changed (Figure S3b,c). Here in our MATLAB analysis, the voltage applied could be translated to phase using the flat gold calibration data obtained from the LCVWP. A cosine fit function was then used across phase and normalized intensity to extract a relative phase offset. At each wavelength, the difference in the grating phase and the gold phase yielded the phase delay (*i.e.* TE vs. TM retardance) from the buried grating patterns. Figure 4c shows the resulting phase delay spectrum due to the buried gratings with water on the sensing surface.

COMSOL modeling was used to simulate these structures, and the following Jones calculus⁵⁶ was used to model the polarization optics of our system outlined in Figure 1:

$$F = \left\| \frac{1}{2} \begin{pmatrix} 1 & 1 \\ 1 & 1 \end{pmatrix} \begin{pmatrix} e^{i\phi_{wp}} & 0 \\ 0 & 1 \end{pmatrix} \begin{pmatrix} e^{i(\phi_{TE}-\phi_{TM})} & 0 \\ 0 & 1 \end{pmatrix} \frac{1}{\sqrt{2}} \begin{pmatrix} 1 \\ 1 \end{pmatrix} \right\|^2,$$

where F is the field signal and ϕ_{wp} is information input from the experimental results of light reflecting off the flat gold region (Figure 4a). This compensates for the dispersive nature of the LCVWP and the birefringence of any intermediate optics of the system. ϕ_{TE} and ϕ_{TM} are direct outputs from the COMSOL simulation results. When the same algorithm used to analyze the experimental data is applied to F as computed above, simulated phase maps are generated. Figure 4d shows a simulated solution identical to the experimental result for light reflecting off the flat gold regions, which was expected. The COMSOL model yields $\phi_{TE} - \phi_{TM} = 0$ for flat gold (at normal incidence), so the sample matrix becomes the identity matrix. The phase information shown in Figure 3c is ϕ_{TM} for the period 410 nm, grating line width 160 nm structure and was analyzed along with ϕ_{TE} to generate the simulated results (Figure 4e) shown alongside our experimental results in Figure 4b. The simulated phase delay between the TE and TM polarizations due to our buried gratings is shown in Figure 4f alongside the experimental spectrum of Figure 4c. Comparing experiments and theoretical calculations shows reasonable agreement since the calculations capture all the relevant spectral features. However, the simulated phase feature that we are tracking is relatively sharp and therefore a small shift between experiment and theory could shift our simulation “peaks” to experimental “dips” or vice versa. However, such a small shift could easily be due to slight differences in the grating dimensions (bump height, period, duty cycle, or rounded edges).

To use this measurement technique in the context of plasmonic sensing, we determined our device's sensitivity to refractive index changes with simulations and experiment. Simulations were performed with both water ($n=1.333$) and a glycerol solution (8.65 wt.%, $n=1.3432$) on the sensing surface, and as previously discussed, the reflected spectra were used to determine the phase delay between the TE and TM polarizations due to the changing refractive index at the surface (Figure 5a). A red shift of $\lambda = 1.4$ nm was observed for the phase feature of interest. We then compared these simulation results to real-time experimental data.

Real-time refractive index sensing experiments were performed by recording multiple reflection spectra over 20 steps from 0.5 V to 3.5 V for each scan series. Midway through the 54 total scans in time, a glycerol solution (8.65 wt. %, $n = 1.3432$) was introduced, replacing the pure deionized water ($n = 1.3328$). Each scan was analyzed as before to yield the phase delay spectrum. The spectra from the first water scan and the first full glycerol solution scan are shown in Figure 5b. Some smoothing over wavelength was performed before the phase feature position was extracted by a local quadratic fit as shown in Figure 5b. The abrupt change from water to the glycerol solution can be clearly seen at about 150 seconds (Figure 5c). The mean peak wavelengths of water and the glycerol solution are plotted, respectively, in blue and red and have values of 661.2 nm and 663.1 nm, which translates to a shift of $\lambda = 1.9$ nm. To demonstrate the further utility of our measurement technique, we also extracted the reflected intensity spectra from the real-time scans in order

to track the intensity dip at ~ 660 nm (further details in Supplementary Information). As with the phase spectra, water and glycerol solution intensity spectra are shown in Figure 5e. In Figure 5e, the mean peak wavelengths of water and the glycerol solution are plotted, respectively, in blue and red and have values of 657.1 nm and 655.3 nm, which translates to a shift of $\lambda = 1.8$ nm. Analyzing the data in this way offers another advantage: Phase-sensitive measurements measure signals near an intensity minimum, leading to increased noise. Here, however, the introduction of a scanning LCVWP allows us to measure both intensity and phase information simultaneously.

For further quantitative comparison of our buried grating structure using both the phase and intensity tracking capabilities of this current technique, we determined the feature full width at half maximum (FWHM, for calculation details, see Supplementary Information) and calculated both the sensitivity (λ/n) and the figure of merit ($\text{FOM} = (\lambda/n) / \text{FWHM}$)^{6,25,27,40,42,57}. This was done for both the phase and intensity tracking real-time sensing results. The sensitivity of the intensity dip was 173 nm/RIU, and the FOM was found to be 8.0 for a feature FWHM of 21.7 nm. On the other hand, the sensitivity of the phase dip was found to be 183 nm/RIU with the FOM determined to be 11.2 for a feature FWHM of 16.4 nm. These results demonstrate the capability of our phase detection technique to improve on the sensitivity of our buried grating devices without losing any of the intensity spectral information. Since the experimental phase feature has a smaller FWHM and a slightly higher sensitivity, the sensing FOM is improved, in this case, by about 39%.

While our sensitivity and FOM calculations are consistent with literature and comparable to other plasmonic sensors^{6,27,42}, further optimization is desirable and possible⁵⁸. In our case, the buried surface of the sensor is still an as-deposited rough metal film (in contrast to the ultrasmooth sensing surface), which could account for a loss of sensitivity (*i.e.* broadening the resonance features). Further tuning of the buried grating structure dimensions, or the use of another class of plasmonic structures, could yield sharper phase features along with a greater sensitivity. These might include nanoparticle arrays that have been shown to demonstrate narrow collective plasmon resonances^{25,26,55} or other structures that exploit Fano resonances³⁹. In addition, a higher-powered light source would prove useful, as it would allow faster measurements with less noise and a higher resolution spectrometer grating for increased resolution. Finally, the wavelength range overlap of our LCVWP (maximum of about 700 nm) and gold as a good plasmonic metal (minimum mid-500 nm) was relatively small compared to the desired range for ease of resonance tunability. Optimizing these parameters for a larger allowable observation range would add greatly to the flexibility of this measurement technique. As an additional direction, further FOM analysis could be performed with the help of recent work by comparing the differences between bulk refractive index changes (as shown here) and local surface refractive changes that occur in other biosensing experiments^{59–62}.

Conclusions

In conclusion, we demonstrated a versatile spectroscopic polarization interferometry scheme that, to the best of our knowledge, has not yet been applied to real-time plasmonic sensing.

By using a LCVWP element in the beam path of a white light spectroscopy and polarization interferometer setup, we were able to measure quantitative phase and intensity information that was useful for real-time plasmonic sensing and found that the phase feature exhibited a higher FOM. Our setup was also used to more fully characterize the buried grating devices that have potential for high-throughput plasmonic biosensing, imaging, and possible work with materials that would benefit from extremely flat surfaces. In addition, our sensing technique is not restricted to any particular device or plasmonic geometry, but can be used in combination with various grating-like structures in reflection or transmission mode geometries, with LSPR and SPR sensing devices, or even in a Kretschmann configuration while obtaining quantitative phase information without the loss of any reflected intensity information.

Supplementary Material

Refer to Web version on PubMed Central for supplementary material.

Acknowledgments

L.M.O. acknowledges support from the National Institutes of Health (NIH) biotechnology training grant (T 32 GM008347) and the National Science Foundation (NSF) Graduate Research Fellowship Program (00039202). D.A.M. acknowledges support from the NIH biotechnology training grant (T 32 GM008347). T.W.J. acknowledges support from the University of Minnesota doctoral dissertation fellowship. N.C.L. acknowledges support from NSF Award CHE-1306642. Device fabrication was performed at the Minnesota Nano Center at the University of Minnesota under support received from the NSF through the National Nanotechnology Infrastructure Network (NNIN). Computational modeling using COMSOL Multiphysics™ was performed through the University of Minnesota Supercomputing Institute.

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Figure 1.

The measurement system. Elements internal to the inverted microscope are outlined in the dashed box. White light polarized at 45 degrees is incident on the backside of the sample, and a change in phase of the reflected transverse-magnetic (TM) polarized light, relative to the transverse-electric (TE) light, occurs due to surface plasmon resonances. The reflected light then exits the microscope and undergoes a known TE vs. TM shift in phase due to the liquid crystal variable wave plate (LCVWP, slow axis vertical, 0 degrees). Finally only the light polarized at 45 degrees is allowed to pass through the second polarizer and to the spectrometer. Data is collected by saving a spectrum, changing the voltage applied to the LCVWP (and therefore changing the phase shift), and saving another spectrum, *etc.* A scan through the applied voltage yields a two dimensional mapping of our data. As long as the applied voltage scans through an intensity maximum and minimum (phase minimum and maximum, respectively) at each wavelength of interest (550 nm – 750 nm), this setup will yield quantitative reflected phase information.

Figure 2.

The backside SPR device with buried gratings. (a) Device schematic. The grating patterns are buried/submerged in optical adhesive, and when template stripped, reveal an ultrasmooth sensing surface offering a SPR sensing scheme where both the incident and reflected (collected) light is decoupled from the sensing media. (b) A post-template stripping scanning electron micrograph (SEM) of a grating with period 420 nm and line width of 120 nm. Inset shows zoomed in view. Both scale bars are 1 μm . (c) A micrograph of an array of line gratings. The arrows point in the direction of increasing period and width of lines patterned with electron beam lithography. Scale bar 400 μm .

Figure 3.

A buried grating structure with period 410 nm and line width 160 nm. (a) Experimental reflection spectrum normalized to the plain gold surface. (b) Simulated reflected intensity spectrum (also normalized to the gold surface) and (c) the reflected phase spectrum of the TM and TE modes. The phase feature of interest is marked by a red circle and only appears for the TM mode. (d) A field intensity map of the grating structure at the “coupled” mode resonance (671 nm) denoted by the red circle in (b). Finite-element method simulations were performed with COMSOL MultiphysicsTM with water on the sensing surface.

Figure 4.

Experimental phase maps for (a) the flat gold region and (b) the grating region. (c) The experimental phase delay between the TE and TM polarizations due to the plasmonic gratings. All other phase shifts and dispersion effects of the experimental system and its optics have been removed via (a) (d-f) The simulated equivalents of (a-c).

Figure 5.

Real-time sensitivity measurements. (a) The simulated phase delay between the TE and TM polarizations for water and a glycerol solution (8.65 wt. %, $n = 10^{-2}$ RIU) on the same grating as in Figure 3. (b) The experimental equivalent of (a) for a similar grating used in a real-time sensing experiment. MATLAB was used to analyze the data, and the wavelength location was determined for the minimum phase values in each scan series using a quadratic fit of the dip and is plotted in (c). A clear change from water to the glycerol solution can be observed, resulting in a 1.92 nm shift in the peak wavelength position. (d) The simulated TM intensity spectra for both water and the glycerol solution. (e) The real-time intensity spectra for both water and the glycerol solution due to the incident light polarized at 45 degrees. (f) The clear change in part (c) is also seen from the intensity spectra, resulting in a wavelength shift of 1.86 nm.