Polarization-dependent sensing of a self-assembled nanohole using biaxial nanohole arrays

F. Eftekhari,1,a R. Gordon,1 J. Ferreira,2 A. G. Brolo,2 and D. Sinton3
1Department of Electrical and Computer Engineering, University of Victoria, Victoria, British Columbia, Canada V8P 5C2
2Chemistry Department, University of Victoria, Victoria, British Columbia, Canada V8P 5C2
3Department of Mechanical Engineering, University of Victoria, Victoria, British Columbia, Canada V8P 5C2

(Received 25 March 2008; accepted 3 June 2008; published online 23 June 2008)

We demonstrate surface plasmon resonance (SPR) sensing based on the polarization-dependent extraordinary optical transmission through a biaxial nanohole array. The biaxial array has two periodicities in a single array that can be individually probed by varying polarization. Here, the SPR polarization-spectral dependence is demonstrated for the detection of a self-assembled monolayer for four sets of biaxial array periodicities. By monitoring the polarization dependence of transmission through the nanohole arrays with biaxial periodicity, surface-sensitive refractive index induced intensity variations may be separated from other effects such as absorption, scattering, and intensity fluctuations, while using a single wavelength source. Biaxial sensing is useful for ongoing microfluidic integration of nanohole SPR, where the light source is transmitted through a microfluidic channel. © 2008 American Institute of Physics. [DOI: 10.1063/1.2949682]

Surface plasmon resonance (SPR) has been used widely in sensor applications including drug discovery1 and biosensing.2,3 The inherent dependence of resonant surface plasmons on local refractive index changes at the surface of a noble metal is the physical mechanism explored in SPR sensing. Commercial SPR systems generally operate in total internal reflection mode using the Kretschmann geometry, where the reflection minima shift is monitored as a function of angle or wavelength.4 Alternatively, arrays of nanoholes in gold films provide an attractive strategy for SPR-based sensing. Nanohole SPR benefits from a collinear optical geometry, dense integration, and the possibility of multiple sensing elements, which enables multiplexed sensing integrated in a microfluidic environment.5 The optical coupling between nanohole array surface absorbed molecules has been observed as a dramatic transmission resonance change, ranging from the visible6,7 to the terahertz8 regimes. Initial demonstrations of a nanohole array based SPR sensing have shown a sensitivity of 400 nm/RIU,5 which is an order of magnitude lower than obtained from commercial devices based on the Kretschmann configuration. Recent innovations to nanohole SPR have allowed for significant improvements in both the sensitivity9–11 and limits of detection.12 In parallel, several strategies for microfluidic integration of nanohole SPR for a variety of sensing applications are underway.9,13–15 Other than SPR sensing, subwavelength hole arrays in metal films have been explored for enhanced spectroscopy, such as IR-absorption spectroscopy,16,17 enhanced Raman spectroscopy,18–20 and fluorescence detection.21–23

For dense and cost-effective microfluidic integration of SPR nanohole sensing, it is desirable to use a single wave-length laser diode source and either a photodiode or detector array to detect transmission. It is more straightforward to integrate a laser/detector pair than a broadband light source and spectrometer at each array. The intensity change that comes from a SPR shift is then used to detect molecular absorption. The drawback of this approach is that intensity changes from absorption, reduced transmission and optical scattering in the microfluidic channel, and intensity fluctuations (at the source or detector) cannot be isolated from the intensity changes used for SPR sensing; in short, the spectral information is lost. To regain some of the spectral diversity, it is possible to integrate several different periodicity arrays in a single microfluidic channel,13 and these may be used for real-time detection using a laser source and a two-dimensional (2D) detector array.14 One array may show increased transmission, while another array may show reduced transmission. This is useful to correct for intensity fluctuations that are not associated with the SPR sensing (as described above). In addition, having multiple array periodicities allows for an extended dynamic range in refractive index detection while using a fixed wavelength (nontunable and inexpensive) optical source. The major drawback of having multiple periodicity arrays is that each array senses a different local region of the chip.

Here we demonstrate the use of a biaxial array for SPR detection to provide the benefits of having two periodicities in a single array. Extraordinary transmission through nanohole array with unsymmetrical periodicity (biaxial array)24 and large-scale biaxial arrays of nanoholes25 have been shown to exhibit polarization dependency. Different enhanced optical transmission resonances of the biaxial nanohole array are probed rotating the polarization. The incidence light is polarized along x-direction to excite the transmission resonance of periodicity a and along y-direction for periodicity b. We demonstrate the polarization dependence of the SPR shifts for several biaxial arrays with different periodicities. We transmit the polarized light from a broadband source and measure the transmission spectrum. For a particular wavelength, one linear polarization shows an increased intensity, while the other shows a decreased intensity, which allows separation of SPR sensing resonance effects from spurious polarization-independent changes in the intensity. In

aElectronic mail: eftekhar@ece.uvic.ca.
addition, the two different periodicities of the biaxial array can be used to extend the dynamic range of refractive index detection from a single array.

It is well known that the $x$-polarization of the electric field excites a SP that propagates in the $x$-direction when scattering off of the holes, and $y$-polarization excites a $y$-direction SP.\textsuperscript{26,27} For these SPs, the resonance wavelength is approximately related to the array periodicity by the SP dispersion relation and the Bragg condition. The usual expression given for this resonance (for example, see Ref. \textsuperscript{28}) is modified for the case of the biaxial array as

$$\lambda_{\text{max}(i,j)} = \frac{ab}{\sqrt{j^2b^2 + j^2a^2}} \sqrt{\frac{\varepsilon_g \varepsilon_m}{\varepsilon_d + \varepsilon_m}}$$

where $a$ is the periodicity of the array $x$-direction, $b$ is the periodicity along the $y$-direction, $i$ and $j$ are integer mode indices, $\varepsilon_m$ is the dielectric constant of the metal, and $\varepsilon_d$ is the dielectric constant of the interface medium.

Figure 1 shows a scanning electron microscope image of a typical biaxial nanohole array. The nanohole arrays were fabricated by focused ion beam milling of a 100 nm optically thick commercially coated gold film on a glass slide with a 5 nm thick chromium adhesion layer. We measured the surface roughness using atomic force microscopy and found short-range height variations between 0.5 and 1 nm, which is a reasonable surface quality to minimize random SP scattering. The biaxial arrays were fabricated and imaged using a FEI 235 dual-beam focused ion beam and field emission scanning electron microscope. The gallium ion beam was set to 30 KeV for milling and a beam current of 50 pA. The 200 nm diameter nanoholes were fabricated in two different periodicity arrangements, the first set has 20 nm difference in $x$- and $y$-aligned periodicities ($a$ and $b$) where in the second set this parameter has been changed to 40 nm. Since the 20 nm difference did not provide sufficient spectral diversity, here we present the results for the 40 nm arrays only. The smallest fabricated array periodicity is shown to emphasize the biaxial nature of these arrays.

The broadband optical spectrum from a halogen source was collimated and focused on to each array at normal incidence using a 40X microscope objective. The area of focus of the incident light was larger than the area of each array.

The zeroth order transmitted light was collected using a fiber-coupled (200 $\mu$m core) UV-visible spectrometer at a distance 5 mm from the sample. A polarizer was placed before the sample to obtain the $x$- and $y$-polarized incident light, as defined with respect to the lattice, as shown in Fig. 1. The recorded transmission was normalized to the halogen source spectrum for each polarization.

The slides containing the biaxial arrays were first cleaned prior using a piranha solution [3:1 (v/v) sulfuric acid:H$_2$O$_2$] and an ultrasonic bath. After being characterized optically, the slide was immersed in a 1 mM ethanoic solution of 11-mercaptoundecanoic acid (MUA) for 24 h.\textsuperscript{29} MUA is well known to attach to gold surfaces to form an organized self-assembled monolayer. The slides were washed with ethanol and dried using a pure nitrogen stream. The normal transmission spectra were again measured. Following these measurements, the slides were cleaned once again, the MUA monolayer removed, and a transmission spectrum was obtained to ensure the repeatability of the results.

Figure 2 shows the transmission spectra of white light through an array of $520 \times 480$ mm$^2$ periodicity before and after surface modification with MUA. The incident light was polarized along $x$- and $y$-directions. The bare gold shows a $(1,0)$ resonance peak mode of gold-air interface at 632 nm for $x$-polarized incident light (for periodicity 520 nm) and a $(0,1)$ resonance at 604 nm for the $y$-polarization (for periodicity 480 nm). The resonances from the glass-gold interface are suppressed due to the lossy chromium adhesion layer. After the metallic surface was modified with a monolayer of MUA, a resonance shift was observed for both the $x$ and $y$ incident light polarizations, as shown with the dashed curves in Fig. 2. The shift in the SPRs are associated with the changes in the effective dielectric constant at the metallic interface due to the MUA adsorption.

Figure 2 demonstrates the principle of polarization-dependent biaxial sensing. The first important observation is that the dashed curves and the solid curves intersect at a
particular wavelength. This means that a single wavelength source at the intersection wavelength would not be able to detect an intensity change from the MUA absorption and so it could not be used for SPR sensing. With the additional polarization diversity, while the one polarization may show no intensity change, the other polarization still shows an intensity change.

To benefit from having polarization diversity while operating at a single wavelength, it is desirable to select a wavelength of operation between the (1,0) and (0,1) resonance peaks. As a result, a spectral shift from molecular surface absorption will result in a transmission intensity increase for one polarization and a corresponding decrease for the other polarization. For example, Fig. 2 shows a possible wavelength of operation for the laser source at 620 nm with a thin vertical line. For this wavelength, the intensity along the y-polarization (for periodicity 480 nm) is increased by 10.1% after the absorption of MUA, while the intensity along the x-polarization (for periodicity 520 nm) is decreased by 15.4%. Table I summarizes the results for different biaxial arrays with operation wavelength varying from 560 to 790 nm.

As a future experiment, we plan to integrate biaxial arrays into a microfluidic platform including a single wavelength laser source and polarization selective optics to monitor molecular adsorption to a single array in real time. By comparing the two orthogonal polarization intensities, a differential signal will be achieved. The main advantage of this technique is that spurious laser intensity changes that are present in both polarizations will become separated from the changes coming from the SPR shift provoked by surface modification. Hence, it is not necessary to do comparison measurements on two discrete arrays where a separate control array is required.

In conclusion, we have demonstrated a nanohole array SPR sensor based on the polarization dependence of optical transmission through a biaxial array. The biaxial array benefited from having two periodicities in a single array that could be individually addressed by varying the polarization. Thereby, the usual spectral diversity of spectrometer-based sensing was replaced with polarization diversity while using a single wavelength laser source and a single array. This will allow for decoupling of the desired intensity variations of the analyte surface adsorption from other spurious polarization-independent intensity variations that may arise from optical absorption or scattering in the microfluidic channel, reduced or increased transmission through the nanohole arrays, and intensity fluctuations at the source or detector. In addition, the biaxial structure allows for a broader dynamic range in refractive index detection from the distinct (1,0) and (0,1) resonances, while using only a single wavelength optical source. These results will aid in the ongoing development of nanohole SPR sensors for integration within the microfluidic environment.

The authors would like to thank Karen L. Kavanagh, at the Nanomaging Facility of Simon Fraser University, for assistance with nanofabrication. Operating funding for this work was provided through an NSERC Strategic Grant with the BC Cancer Agency, and Micralyne Inc. Infrastructure funding was provided by CFI and BCKDF.

<table>
<thead>
<tr>
<th>Periodicity (nm)</th>
<th>(\lambda_{\text{operation}}) (nm)</th>
<th>(\Delta I_x) %</th>
<th>(\Delta I_y) %</th>
</tr>
</thead>
<tbody>
<tr>
<td>420 × 380</td>
<td>560</td>
<td>−4.5</td>
<td>+5.1</td>
</tr>
<tr>
<td>520 × 480</td>
<td>620</td>
<td>−15.4</td>
<td>+10.1</td>
</tr>
<tr>
<td>620 × 580</td>
<td>700</td>
<td>−20.8</td>
<td>+13.6</td>
</tr>
<tr>
<td>720 × 680</td>
<td>790</td>
<td>−19.5</td>
<td>+11.7</td>
</tr>
</tbody>
</table>

1M. A. Cooper, Nat. Rev. Drug Discovery 1, 515 (2002).

TABLE I. Percentage transmission intensity change after the absorption of MUA for biaxial arrays of different periodicities. For each array, the operation wavelength is chosen between the (1,0) and (0,1) resonance peaks and the transmission changes for the x- and y-polarizations are given for that wavelength.