Surface plasmon resonance features of corrugated gold films: wavelength interrogation mode for exhaled gas detection

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Abstract. The characterization of a surface plasmon resonance sensor operating in the grating mode has been explored theoretically and experimentally. Wavelength interrogation mode was exploited at specular reflection in the gas phase for thin gold films, deposited onto a corrugated polymer substrate by sputtering. Some tests using water vapor were performed and the achievable responsivity $S_{gm}$ at specular reflection was determined experimentally to be 87 nm/RIU and the limit of detection of $13.2 \times 10^{-3}$ RIU was calculated. The good agreement between experimental and theoretical results confirms the correctness of the methodology and the feasibility of the proposed sensing system.

1. Introduction

Surface plasmon resonance (SPR) sensors are highly versatile optical tools and widely used for unlabeled real time monitoring of biochemical interactions in an aqueous environment [1, 3]. SPR sensors are applied to a variety of research disciplines that range from genomics, proteomics, drug discovery and development to medical diagnostics. In this study, the suitability of a specially designed SPR sensor for human gas exhaled sensing is explored.

The phenomenon SPR accounts for an exceptional surface sensitivity to changes of the refractive index [7], of the surrounding dielectric phase. Coupling to and resonant interaction of the SP-wave with an incoming photon, requires that the SP-wave vector $k_{sp}$ (eq.1), matches to the wave vector of the incident light $k_{ph}$, corresponding to energy-momentum conservation. To augment $k_{ph}$, light propagation must occur within a dielectric material, where the refractive index $n > 1$. Under conditions, where the incident light beam propagates through vacuum or gas, with $n \approx 1$, the reflective surface must be spatially modulated through a corrugated surface profile, to establish appropriate momentum transfer. The former condition is known as the attenuated total reflection configuration, or Kretschmann set-up, the latter denoted as the grating mode (GM). The classical SPR sensor configuration, also known as the Kretschmann configuration, whose the incident light is reflected from the film and leaves the prism, utilizing attenuated total reflection (ATR) conditions. In the GM, light propagates at the opposite side, within gas or vacuum and is either specularly reflected at a corrugated metal film ($m = 0$), or diffracted into higher order ($m \geq 1$). A sketch of the geometry is outlined in Figure 1 who shows the type of grating studied, which has its profile similar to a sawtooth wave. The incident light
beam, p-polarized, with a fixed angle of $40^\circ$ and spanning several wavelengths characterizes the wavelength interrogation study (WIM).

$$k_{sp} = \frac{2\pi}{\lambda} \left( \frac{\varepsilon'_m \varepsilon_d}{\varepsilon'_m + \varepsilon_d} \right)^{1/2}$$  \hspace{1cm} (1)

where $\lambda$ is the wavelength of the incident light, $\varepsilon'_m$ is the real part of the relative permittivity of the metal and $\varepsilon_d$ is the permittivity of the dielectric.

**Figure 1.** Geometry of the device grating. The thin metallic layer shows the periodic grating. P-polarized light has the electric field component parallel to the grooves of the grating. The reflectance conditions at the grating surface for GM-WIM condition is showed.

For the GM mode, the light beam, p-polarized, coming directly from the source strikes the surface of the metal grating. P-polarized means that the electric field is parallel to the plane of incidence, while S-polarized means that the electric field is perpendicular to this plane. In this case, a material with good optical properties will not be necessary, the surface plasmons wave (SPW) being produced via coupling in the grating. The grating boosts the incident wave through the grating moment vector, which is expressed by [5]:

$$k_{ph} = \kappa_x + m\kappa_g$$  \hspace{1cm} (2)

where $\kappa_x$ denotes the $x$ component of the surface wave vector, $m$ are orders of diffraction (positive or negative integers), $\kappa_g = 2\pi/\Lambda$ is the vector of the diffraction grating and $\Lambda$ the periodicity. Once the resonance conditions are satisfied, vector of the wave of plasmons $k_{sp}$ is coupled to the vector $k_{ph}$ and both propagates in the same frequency, thus $k_{ph} = k_{sp}$.

In this work the construction of a SPR sensor system based on the periodic grating was approached. Simulations and practical experiments were performed in order to determine the sensitivity and limit of detection for the device built.

**2. Methodology**

An attempt is made for the first time to characterize the grating mode under spectrally broadband SPR excitation conditions. The used mode was Grating Mode-Wavelength Interrogation Mode (GM-WIM). The device was fabricated in an optical diffraction grating, composed of a polymer and a metallic thin film, and has been used how study tool. Figure 4, shows the grating profile; the device comprises a 50 nm thin sputter deposited gold film, exhibits a maximum grating amplitude of 50 nm, and a periodicity of nearly 500 nm.
Simulations of the scenario were performed in the COMSOL software as well as practical experiments, which validate the results obtained from this tool. The software tool allows to study this type of SPR simulation for different types gratings, since it is based on the direct solution of electromagnetic field equations. Due the waveform presented of the grating hasn’t sinusoidal profile, shown in Figure 4, a Fourier series expansion was performed and thus the first harmonic was used for simulation, as shown in Figure 2. In the simulation the structure was built with only one period of the grating, however, with periodic configuration. The piece has a multilayer structure containing the substrate and the metal grating. The upper region of the grating consists of the dielectric, which used the air, since the incidence occurs directly on the metal surface. The incident light beam was configured with P polarization, whose electric field is parallel to the plane of incidence. The structure used for simulation was created following the parameters of the Table 1. Computation results for propagation of the electromagnetic wave in sinusoidal corrugated surface provides the ratio (Ip/Is) between electromagnetic fields of the reflected wave.

Table 1. Parameters used in the computational study.

| Parameter            | Value          |
|----------------------|----------------|
| Periodicity (\(A\)) | 478 (nm)       |
| Height of the structure | 500 (nm) |
| Width of the structure | 478 (nm) |
| Height of the metallic layer | 50 (nm) |
| IR of air            | 1              |
| IR of substrate (BK7) | 1.52           |
| Incident angle       | \(\theta_{\text{in}}\) \(^{(\circ)}\) |
| Wavelength           | \(\lambda\)    |
| Frequency            | \(3 \times 10^{8}/\lambda\) |

Figure 2. Simulated structure for GM-WIM conditions. The waveform of the grating is reproduced with the first harmonic resulting from the Fourier series expansion. The bluish region shows the deposited metal grid and the substrate. The variation of the electric field strength for a p-polarized incident light beam, given in V/m, is seen in the colored region.

The experimental device (Figure 3) was made in the laboratory with the deposition of a metallic layer of 50 nm, through the process of sputtering. The metal chosen to constitute the metal grating was gold, which according to [9], due to its excellent characteristics for excitation of the plasmons \(\varepsilon(\lambda)\) is the major metallic materials used in SPR applications.

Figure 3. Device used in the experiments. The device has two regions with similar gratings, which can be used for light incidence.
A photographic image of the optical set-up is shown in Figure 5. It comprises a non-polarized white light, a collimating lens, a polarizer and a compact optical spectrometer. The optical source used in the experiment is a stabilized tungsten-halogen light source providing a constant-intensity, 10 mW blackbody (blackbody spectrum spans both in the visible and near-infrared regions) radiation spectrum between 360 and 2600 nm. In both situations the incident angle of the light was of 40° and ambient temperature of 23°. The spectrometer captures the intensity of light reflected by the grating at two different times, being the reference curve with the light s-polarized (Is) and the curve resulting from the excitation of the plasmons p-polarized (Ip) light. The spectral position of the resonance is extracted from the reflectance ratio Ip/Is of the s- and p-polarized components.

The software used is a tool created to process the data obtained from the spectrometer, whose capture occurs through the USB connection. Once all components are correctly positioned, the software is initialized to plot the SPR curves and the sensorgram, making a pixel × λ relation. Some parameters such as curve smoothing, integration time and minimum detector algorithm can be changed from a graphical interface, to obtain a stable signal. The SPR curve is generated from the ratio between signals captured with different polarizations, and the sensorgram determines the change in the minimum of this curve as a function of the refractive index, with reference initially to the index of refraction of air.

**Figure 4.** SEM and TEM images of the corrugated surface

**Figure 5.** SEM and TEM images of the corrugated surface
3. Results

Experimentally recorded Ip/Ip (s/p) intensity ratio as function of wavelength, insets show p and s-polarized spectra. Theoretically calculated p/s intensity ratio, as function of wavelength in for an incident angle of 40°. Figures 4 and 5 exhibit a grating resonance in the GM-WIM for $m = 0$ along with the associated responsivities given in the inset, numerically obtained values for $S_{\lambda}^{\text{gm}} = \frac{\Delta R}{\Delta n_A}$ ($\lambda_R$ and $n_A$ denote the resonance wavelength and the refractive index of the analyte, respectively) are marginally smaller than those calculated.

![Experimental and theoretical results](image)

**Figure 6.** Experimental and calculated results as function of wavelength for an incident angle of 40°.

The temporal evolution and shift of the resonance minimum, generated upon exposure of the grating surface to a flash of condensing exhaled air, taken from a minimum hunt algorithm and processed in real time, is shown in the WIM-sensorgram of Figure 7. The flow of exhaled air at $38\pm 2^\circ C$ condenses on the Gold surface at $23^\circ C$ to a nanometer thin, quickly desorbing multi-layer of water molecules. Its maximum thickness was independently verified by fast laser ellipsometry (Sentec GmbH) to $110\pm 10$ nm. The digitally processed SP-output signal is a change of the refractive index (RIU). This quantity is proportional to the film thickness [7]. To extract the SP-sensor responsivity $S_{\lambda}^{\text{gm}}$ in the gas-phase, the RIU-value of a known protein film with known thickness and refractive index [8] is re-scaled to that of a condensed water film with known thickness on the gold layer, comprising a refractive index of 1.33.

The sensorgram, displaying the variation of the resonance wavelength as function of time to adsorption from the gas phase, is illustrated in Figure 7. At $t = 20$ s, $t = 48$ s and $t = 79$ s (see Figure 7), the grating surface was briefly exposed to exhaled water vapor. The data set illustrates the effect of rapid vapor condensation onto and desorption from its surface, comprising a rather short time span of 3-5 s. The maximum achievable wavelength change was 2.2 nm. After a fast
initial vapor condensation, water molecules are desorbing at a similar rate [8]. The identical gas adsorption experiment has been performed on the same gold film, albeit analyzing the reflected beam by means of a laser ellipsometer, comprising a response time of 2 s. The responsivity $S_{\lambda}^{GM}$ was estimated to 87 nm/RIU. The limit of detection as taken from the sensorgram is $13.2 \times 10^{-3}$ RIU. It is important to point out that such small responsivity value results from the thin film of condensed exhaled air, which would increase by a factor 4-5 in case of a homogeneous adjacent analyte phase and thickness of several hundred nm.

Conclusions

This work shows the design of an SPR sensor system based on a periodic structure to detect humans gases exhaled. A minimal difference is found among the methods used, however, it can be justified by two factors: the deposition is not perfectly linear, as it is considered in the software, and the smoothing of the profile obtained through the Fourier series first harmonic. Therefore, it is possible to affirm that there are an agreement between experimental and theoretical results confirms the correctness of the methodology and the feasibility of the proposed sensing system.

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