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Temperature-dependent sensitivity of surface plasmon resonance sensors at the gold–water interface

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ABSTRACT

Instrumental performance and sensitivity of surface plasmon polariton or resonance (SPR) sensors are crucially affected by ambient temperature fluctuations. Apart from temperature-induced opto-mechanical displacements, resonance conditions and associated output quantities vary, due to thermo-physical properties of optical components, like prism, semi-transparent metal-film and aqueous analyte solution. The variation of instrumental sensitivity S as function of environmental temperature has been exploited experimentally in the temperature region $275\,\mathrm{K} < T < 320\,\mathrm{K}$. A compact, robust commercial SPR device has been used, operating in the angular interrogation mode. At temperature $< 300\,\mathrm{K}$, S^{θ} steadily deteriorates from 120°/RIU to 30°/RIU. For comparison, the thermal device characteristics also has been evaluated theoretically within the range $273\,\mathrm{K} < T < 370\,\mathrm{K}$ for both, angular interrogation mode (AIM) and wavelength interrogation mode (WIM). Fresnel's equation system and established analytical sensitivity expressions have been elaborated, and differences assigned to simplifications in the analytical form. An appropriate thermo-physical data set of experimentally verified optical materials parameters $n(\lambda, T)$ and $\varepsilon(\lambda, T)$ for all, BK7 glass prism, gold metal film, and aqueous analyte has been used. A singularity has been identified in the simulations near the freezing point of water, while a soft transition appears in the experiment. Towards higher device temperatures at $300\,\mathrm{K} < T < 370\,\mathrm{K}$,$S^{\theta,\lambda}$ decreases weakly. The effect is more pronounced at shorter wavelength $\leq 550\,\mathrm{nm}$, and in the wavelength interrogation mode. A steady increase towards higher T was observed for the SPR-line broadening parameter in the AIM, but a distinct maximum resolved at 305 K for wavelength interrogation.

1. Introduction

The resonant optical excitation and propagation of coherent charge density oscillations at the metal–dielectric interface is a well-known physical effect, denoted as the surface plasmon polariton or resonance (SPR) [1,2]. Since Turbadar's early work [3], the SPR phenomenon has been identified as a highly sensitive tool for thin film characterization and other applications. Initially, Liedberg et al. [4] used the sensing principle for gas detection, followed by numerous applications, ranging from biochemical binding analysis to environmental monitoring [5–7]. The technical complexity of state of the art SPR devices, considered as high precision optical instruments and integrated with a microfluidic system, puts serious restrictions on their use, where special care is required for reliable operation [8,9]. Being considered as a general rule for almost all physical sensors, temperature has a pronounced impact on the performance of SPR sensors. The large physical size and significant thermal mass of most commercial SPR instruments makes experimental observations a demanding issue, where it appears very difficult to fully identify the origin of any temperature effects.

A typical SPR sensor in the attenuated total reflection (ATR) configuration comprises a set of three basic optical components as: a glass prism, a semi-transparent metal (gold) film and the adjacent analyte (water). The resonance can be optically excited by p-polarized light under specific boundary conditions and tracked with two operation modes: via wavelength interrogation, where the entrance angle is maintained and the wavelength changed, or by angular interrogation, where the entrance wavelength is maintained, and the input angle changed. Commercial instruments employ angular interrogation, originally based on the Kretschmann configuration [10], where the use of a one- or two-dimensional digital camera for image capture avoids any moving parts in the instrumental design. Due to well-established thermo-physical properties of the implemented optical materials (optical prism,

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gold film, aqueous analyte) the variation of the optical resonance condition with temperature can be treated in a physically accessible way.

Likewise, the mounting geometry of all optical components of the instrumental housing is thermally affected, in relation with their specific thermal expansion coefficients and local temperatures. Thus all, location and emission/transmission characteristics of the (LED) light source, lenses, optical chip and chip holder, glass prism, index matching gel, camera and camera-holder do not retain fixed geometric positions, emission wavelength or sensitivity, but are vulnerable to minute thermo-mechanical displacements, usually on micrometer scaling. This leads to small- not necessarily fully reversible- but generally poorly defined distortions of the optical propagation path, along with a deteriorating effect onto resonance conditions. Instrumental sensitivity to temperature fluctuations increases with the technical complexity, usually required for high-resolution instruments. All of these thermal effects superimpose, and usually cause a temperature-induced drift of the output signal.

Temperature compensation and regulation approaches have been developed to cope with this problem [11,12]. A theoretical model of the achievable sensitivity at elevated *T* has been reported earlier [13,14] excluding, however, thermal effects resulting from the glass prism and aqueous analyte. The utilization of temperature effects onto the SPR resonance as a tool for remote temperature sensing has been evaluated recently, and includes fiber-optic SPR spectrometry [15,16]. Experimental results were shown by Chiang et al. [17,18] via phase measurement of a silver/silicon junction. However, reliable experimental verifications that include the achievable figures of merit of a SPR sensor have not been reported.

In this work, an attempt has been made to experimentally and theoretically address the influence of temperature onto the sensitivity of SPR instrumentation. Experimental data have been recorded within the temperature region $276\,\mathrm{K} < T < 333\,\mathrm{K}$, using a compact commercial SPR evaluation kit [20,22], connected to an aqueous solution. The experimental findings have been supported by theoretical analysis of angular wavelength and interrogation SPR-sensing modes. There has been some early speculation about the existence of a singularity related to the vanishing denominator in the sensitivity expression [21,23], where:

$$S_{P\theta} = \frac{\mathrm{d}\theta}{\mathrm{d}n_a} = \frac{\varepsilon_{mr}\sqrt{-\varepsilon_{mr}}}{(\varepsilon_{mr}+n_a^2)\sqrt{\varepsilon_{mr}(n_a^2-n_p^2)-n_p^2n_a^2}} \qquad (1)$$

with $\varepsilon_m = \varepsilon_{mr} + \mathrm{i}\varepsilon_{mi}$ considering $\varepsilon_{mi} \ll \varepsilon_{mr}$.

Both, an established analytical sensitivity formula (1) and numerical results, derived from an appropriately defined Fresnel's equation system in a 3-layer matrix representation have been employed, comprising a glass prism, semi-transparent gold film and aqueous solution. However, it should be noted that these models are not fully equivalent, since the analytical approach disregards the complex part of the metal dielectric function. Eventually, on bases of the present data, figures of merit of an SPR-based temperature sensor can be been elaborated for both modes.

2. Experimental

The SPREETA evaluation kit, operating exclusively in the angular interrogation mode, has been employed for the experimental investigation, where the simple and robust design allows for reliable investigations of temperature effects. The disposable sensor element integrates a LED light source with emission at a wavelength of 830 nm, a polarizer, the sensing surface, a reflecting mirror and a one-dimensional array light detector into a single, molded polymer structure. The compact device of approximate size of 3 cm × 4 cm × 1 cm was fully dipped into a water-filled, thermally isolated Dewar container. The experimental set-up is illustrated in Fig. 1, where a peristaltic pump has been used for analyte transport to the SPREETA sensing surface.

Experiments have been performed during the slow cool down phase at ($\mathrm{d}T/\mathrm{d}t \approx 0.4\,\mathrm{K/min}$), from hot water ($\approx 350$ K) to ambient *T*, and during the warm-phase from an ice–water mixture to ambient temperature around 300 K. The relatively small thermal mass of the SPREETA device allowed sufficiently fast approach to thermal equilibration. The refractive index variation Δn has been obtained by admission of a diluted, 0.05 molar NaOH solution to the sensor at the desired temperature. Teflon tubes were used for analyte transport, fed through the Dewar to maintain the desired temperature. The temperature variation of the absolute refractive index of the weak NaOH-solution corresponds to plain water, thus the temperature variation $\Delta n(T)$ can be neglected. The experiments have been performed by first calibrating the instrument with a dry cell recording at given sensor temperature *T*, then pure water solution has been admitted, followed by the NaOH-solution to establish the Δn step. The initial value of the refractive index variation has been confirmed independently, using refractometric reading. The associated angular variations of the resonance angle $\Delta\theta$ have been taken from the instrumental output readings with high accuracy.

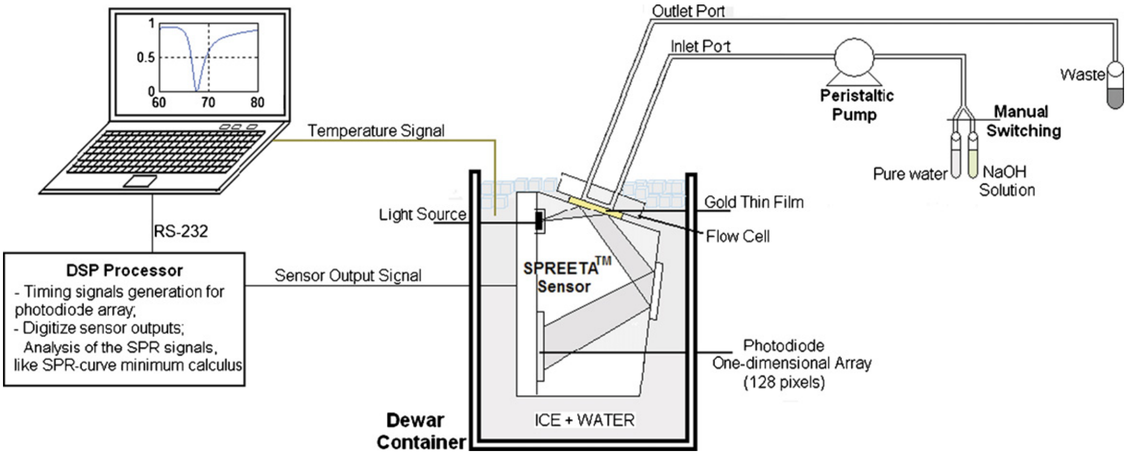

Fig. 1. Schematic diagram of the experimental set-up, where a peristaltic pump has been used for analyte (pure water or NaOH solution) transport to the SPREETA sensor, which is immersed into a ice–water mixture. Output sensor signal is connected to a control and processing system with a DSP processor and general-purpose computer. SPREETA sensor internal elements, DSP processor functions and the temperature signal are also indicated.