# Sensing properties of surface plasmon resonance in different multi-layer Si-based structures

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## ABSTRACT

The progress in the development of Si-based Surface Plasmon Resonance sensing technology is reported. This technology uses multi-layer structures with a gold film and a silicon prism in the Kretschmann-Raether geometry and makes potentially possible the miniaturization and integration of the sensor device on a silicon-based microplatform. We show conditions of the simultaneous excitation for two plasmon polariton modes over both sides of the gold film using different intermediate layers, between the high-refractive index silicon prism and the gold, and examine their response in configurations of the conventional and nanoparticle-enhanced sensing. The system has been calibrated in real – time measurements of protein (Concanavalin A) adsorption.

**Keywords:** surface plasmon resonance, silicon, dispersion, infrared, protein adsorption.

## 1. INTRODUCTION

Surface Plasmon Resonance (SPR) technology is now actively employed for a direct, label-free study of biological recognition and binding events[1,2]. The conventional SPR technology uses Kretschmann-Raether arrangement[3] with SPR-supporting gold film and a glass prism. However, this glass-based technology imposes severe limitations on the miniaturization of sensor schemes. Therefore, SPR sensors are generally implemented as cumbersome laboratory units[4-7], although a certain miniaturization of the sensor design can be achieved by the use of a fiber glass technology[8] or through compact optical designs[9,10].

As an alternative approach for the sensor miniaturization, we have recently proposed a concept of the SPR sensor on a purely silicon platform[11-15]. The miniaturization prospects are based on the advanced development of the methods for silicon microfabrication that can significantly facilitate the miniaturization and integration of the sensor transducer, emitter, detector, and processing electronics on this platform. In addition, the Si-based technology makes possible the formation of microfluidic systems and multi-channel arrays on the same platform. Our studies revealed quite different regularities of the SPR production with a silicon prism (e.g., the polarity of sensing response could be opposite to the case of the glass-based technology). Such difference was attributed to essentially different behaviors of dispersion characteristics of silicon compared to glasses. Nevertheless, silicon-based schemes showed a relatively high sensitivity and good abilities for sensing of relatively large objects.

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We also studied conditions of SPR production in different combined Si-based structures[14,15]. In this paper, we consider an example of such combined structure (Si prism/$SiO_2$ coating/gold film/ sample medium) and examine the sensing response of the system in configurations of the conventional and nanoparticle-enhanced sensing.

## 2. RESULTS AND DISCUSSION

### 2.1 Methods and materials

Within the theoretical framework, we have developed software based on the model of surface plasmon excitation in multi-layer systems (detailed description of the model was given elsewhere[12]). In particular, we examined a system, consisting of a Si prism, gold layer and a sample gaseous or aqueous medium with refractive indices of 1 or 1.33, respectively. In addition, we considered an intermediate dielectric layer ($SiO_2$, $Si_3N_4$) between the gold and the prism.

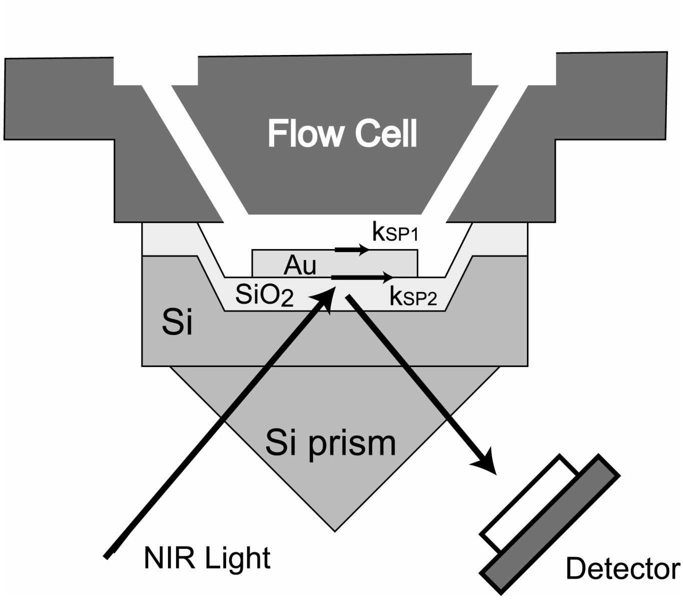

Figure 1: Schematic of the combined Si-based SPR system, which was used in the experiments

To verify the concept, we carried out tests in the Kretschmann-Raether prism arrangement consisting of a silicon prism and a gold film, as shown in Fig. 1. The gold film was deposited on the prism or on a 0.5-mm thick silicon wafer or on $SiO_2$ coatings on the wafer, which was then placed in intimate contact with the silicon prism. Two silicon prisms (FZ, p-type, R>20 Ω·cm, Almaz Optics, West Berlin, NJ) with a base angle of $\alpha = 16.6°$ and $\alpha = 22.4°$, respectively, were custom made for our study. Such prisms conditioned the incidence of the laser beam onto the silicon/gold interface at angles close to the resonance ($\theta_{SPR}$) obtained from theoretical calculations. The gold layer thickness (40 nm) was selected to provide a relatively low reflected light intensity with SPR sensing in the range of 1100-1700 nm. The gold film was in contact with a flow cell (empty or filled with deionized water, depending on whether the sensing medium is air or liquid). The SPR coupling system was placed onto a rotary block of a variable angle spectroscopic ellipsometer (Woollam VASE® ellipsometer, J.A. Woollam, Lincoln, NE) to allow for a very fine variation of the angular prism position with respect to the optical path of the ellipsometer. The system was illuminated by monochromatic p-polarized light of variable wavelength, obtained by passing a white light source through a monochromator. The light reflected from the coupling system was analyzed by a detector, whose characteristics determined the dynamic range of the spectral measurement from 193-1700 nm. The experiments were performed in a configuration of a fixed wavelength or incident angle. The precision of angular and spectral measurements was 0.005° and 0.1 nm, respectively.

### 2.2 Si-based SPR with two surface plasmon polariton modes: conventional sensing

We found that the proposed combined structure, shown in Fig. 1, made possible the simultaneous excitation of two surface plasmon polariton modes, over the dielectric/gold interface (internal plasmon) and over the gold/sample medium interface (external plasmon), if the thicknesses of the dielectric coating and the gold film were optimized (Fig. 2a). The optimization of the gold film thickness was performed by Fresnel's formulas using a matrix method to produce minimal reflected intensity in the SPR dip related to the plasmon at the gold/tested medium interface (external plasmon). A 35-nm thick gold film was selected in our experiments to provide relatively low reflected intensity in the total wavelength range of interrogation, as shown in Fig. 2(a). Fig. 2(b) presents typical angular reflectivity curves in the Si/$SiO_2$/Au structure from the theory (dotted line) and experimental data (solid line) for the aqueous sample medium. Essentially, the main trend of the theory was well confirmed by the experimental data and the calculated and measured reflectivity curves were very close to each other. The reflective curves contained two minima corresponding to the excitation of external and internal surface plasmon polariton modes. One can see that the dip related to the external plasmon was achieved at lower incident angles ($\theta_{SPR} \cong 22.4$-$22.5°$) compared to the internal plasmon ($\theta_{SPR} \cong$ 24.8-25°).

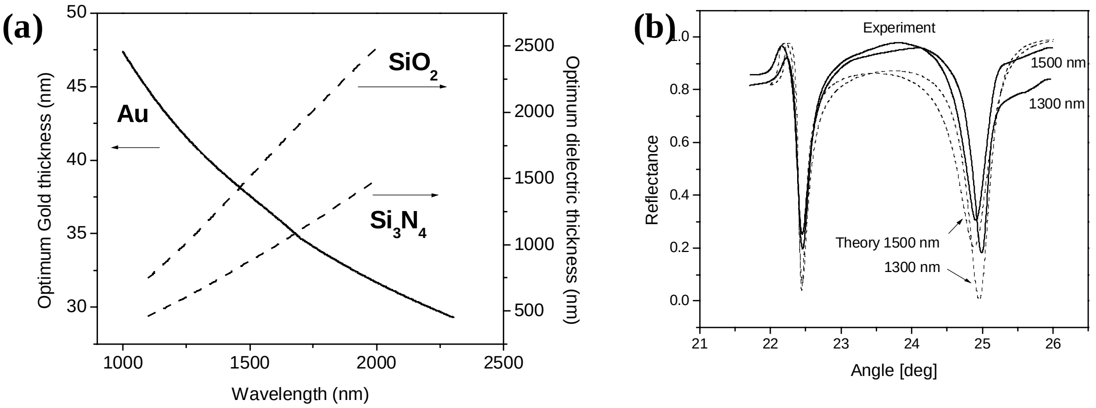

Figure 2 (a) Optimal thickness of the gold film as a function of the wavelength. Optimal thickness of $SiO_2$ and $Si_3N_4$ dielectric films as a function of the wavelength for 35 nm gold film; (b) Typical angular reflectivity curves in the Si/$SiO_2$/Au structure for configurations of aqueous tested media. The broken and solid lines present the calculated and experimental data respectively.

The proposed combined structure was tested in a configuration of the conventional SPR biosensing, in which a change of the biolayer thickness on gold due a binding reaction is recorded. In our model, the process was simulated by the increase of the thickness of a model dielectric film on gold with a fixed refractive index ($n_s$ = 1.42). This situation corresponds to typical conditions of SPR sensing with most biomaterials. For a correct analysis, we separately studied the effect of parameters of the tested medium on the position of the minimums. Fig. 3(a) demonstrates the position of minimums related to both plasmons as a function of the refractive index of the tested medium. The change of the refractive index caused a significant shift of the resonant angle for the external plasmon, while for the internal plasmon this angle was almost constant. As shown in Fig. 3(b), the shift of the resonant angle $\theta_{SPR}$ of the internal plasmon with respect to the external one was less than 1.5% for $SiO_2$ coating and less than 1% for $Si_3N_4$ coating. It means that the internal plasmon was hardly affected by any change in the properties of the sample medium. It should be noted that the presented range of refractive index variation covers both bio- and chemical sensing.

Thus, we have observed quite different behavior of two angularly separated modes under the refractive index change. The external mode, conventional for SPR sensors, demonstrates a highly sensitive response to any change of the refractive index. In contrast, the internal mode is almost insensitive to parameters of the sample medium. Since any variation of external conditions (e.g., misalignment of the angle of incidence) might have an equal effect on the excitation of both modes, we propose that the internal mode can be used as an effective reference zero point for biological and chemical sensing.

In sensing experiments, the presence of such an independent reference zero point will enable to simplify calibration and adjustment procedures and to improve the precision of measurements even for stationary laboratory systems with the use of expensive imaging equipment and high-precision moving stages. However, with Si-based SPR technology, we mainly imply the development of inexpensive and portable micro SPR sensors, taking into account that the advanced state of development of the methods for silicon microfabrication can significantly facilitate the miniaturization and integration of the sensor transducer, emitter, detector, and processing electronics on a single silicon-based chip. Since these portable sensors should not contain expensive parts such as high-precision stages and should basically have a simplified sensing parameter (e.g. in terms of yes/no), the presence of the zero point becomes mandatory. One of such examples is rapid field sensing of dangerous toxic agents with the use of biological substances immobilized on demountable slides. The presence of the internal plasmon mode, whose dip is dependent of the angle of the slide installation, but independent of the refractive index changes, enables to fix a zero point without any high-precision stage and then collect the information signal from the external plasmon-related dip (e.g., the relative position of the dip with respect to the zero point). Another important example is sensing in the multi-channel regime with the use of the same slide. The presence of the zero point makes possible corrections of the system calibration on the non-uniformity of biolayer thickness in every channel. In should be noted that in contrast to purely glass (dielectric) schemes, the proposed combined Si-based platform utilizes standard commercially available microelectronic structures such as thermally grown $SiO_2$ or deposited $Si_3N_4$ coatings on silicon. These structures are absolutely compatible with methods for Si microfabrication and can be undoubtedly used with microsensors.

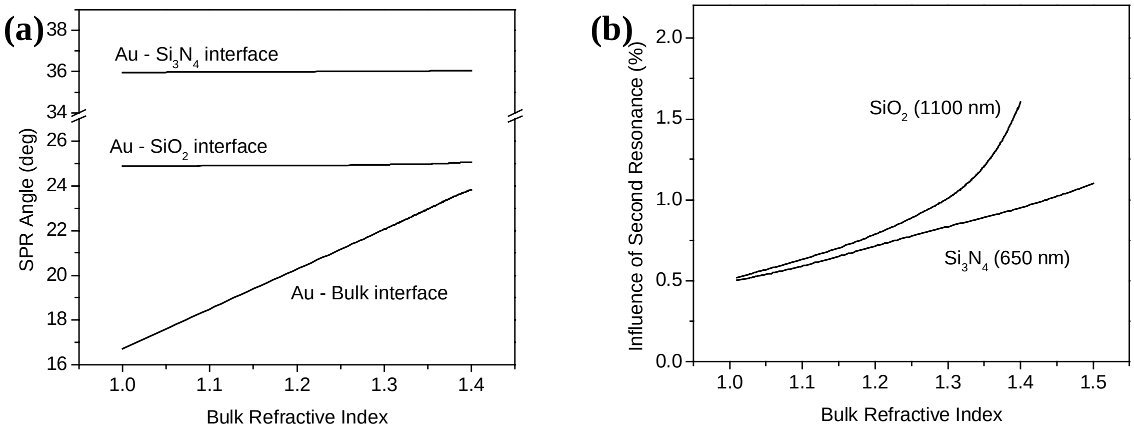

Figure 3: Angular sensing response of the external and internal plasmon polariton modes in the $Si/SiO_2/Au$ and $Si/Si_3N_4/Au$ structures (a) and their percent relation (b) to a change of refractive index $n_s$ of the tested medium

### 2.3 Si-based SPR with two surface plasmon polariton modes: absorption sensing

The conventional SPR transduction principle, based on the refractive index monitoring, becomes less efficient when changes of refractive index are extremely small, as e.g., in cases of protein complexation or an adsorption of ultra-small biological agents such as low-molecular weight drugs. To enhance sensing response in such situations, it has been proposed to use colloidal Au nanoparticles as markers of objects of interest[16]. In this case, the SPR system operates similarly to the SPR absorption sensor[17,18], which is frequently used for studies of optical absorption coatings with non-zero imaginary part of the refractive index (carbon, metals). The adsorption of even a small quantity of an absorbent material on the gold surface leads to an effective plasmon wave damping and consequently the decrease of the reflected intensity at the resonance point. For metal coatings the absorption sensing is known to be simulated with a good precision by an increase of the SPR-supporting film thickness[16,18]

In our study, we studied the response of the proposed combined Si-based structure to the nanoparticle-enhanced sensing. The adsorption was simulated by the increase of the thickness of SPR-supporting gold layer. Fig. 4 shows the response of the internal and external plasmon polariton modes to the thickness increase. To correctly compare the thickness responses of two plasmons, we recalculated all data for the external plasmon using the conventional Kretschmann-Raether geometry without the intermediate $SiO_2$ layer. This enabled to exclude possible deviations of the dependences for this plasmon due to electromagnetic coupling effects. One can see that the minima, corresponding to both internal and external plasmons, shifted to smaller angles when the thickness of the gold film increased. However, it is clear that the shift was much stronger for the internal plasmon. The increase of the thickness from 15 to 25 nm led to the shift of the minimum related to internal-related plasmon by 1.1° for gaseous and 2.3° for aqueous medium, whereas the relevant values for the external plasmon were 0.25 and 0.4°, respectively. This gives four- to six-fold gain in sensitivity for the internal mode in comparison with the external one. Note that our calculations with Fresnel's equations were in good agreement with the experimental results and the calculated and measured data were relatively close to each other. A slight increase of the data deviation at small thicknesses $h < 20$ nm is apparently related to the increase of film roughness due to the non-uniform film deposition and a formation of discrete islands[19].

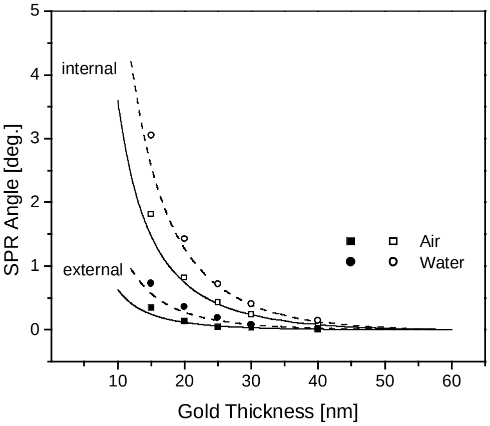

Figure 4 Angular sensing response of the external (conventional structure) and internal (multi-layer structure) plasmon modes for gaseous (solid line) and aqueous (dashed line) tested media. Experimental data are indicated by square and circle signs for gaseous and aqueous media, respectively. The data are given for $\lambda = 1200$ nm, $h = 580$ nm.

Thus, the internal plasmon appears to be much more sensitive to the absorption sensing, suggesting that sensing characteristics of this plasmon can be promising for colloidal Au-nanoparticle-enhanced biosensing[16] and studies of properties of absorbent coatings on gold[17,18].

## 2.4 Si-based SPR with two surface plasmon polariton modes: tests with biological materials

The proposed Si-based SPR structure was calibrated in real-time measurements of the protein adsorption on gold. In the experiments, we used Concanavalin A ((2cna.pdb), a plant-based sugar-binding protein (lectin), which was placed in a solution of the Phosphate buffered saline (PBS, 0.01 M, pH 7.2, 0.9% NaCl, 0.001 M CaCl2, 0.05% NaN3).

Our system appeared to be sensitive enough to detect the adsorption process. As shown in Fig.5, the adsorption of Concanavalin led to the increase of the SPR resonant angle. The higher was the concentration of the protein, the stronger was the increase of the resonant angle. In particular, the replacement of the PBS by 0.06 mg/ml solution of Concanavalin resulted in the resonant angle shift of 0.07 deg that corresponded to the increase of absolute refractive index by $n_s = 0.0035$ from our calculations. Further increase of the concanavalin concentration up to 0.12 mg/ml led to a larger shift of the resonant angle to 0.133 deg., corresponding $n_s = 0.007$. Note that in spite of a relatively small angular variation (about 0.133 deg.), the signal noise ratio was very high and much lower variations of the protein concentration could be measured. Different tests are now in progress to determine detection limits of the proposed Si-based system.

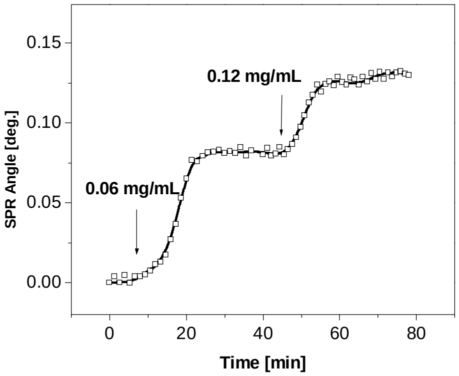

Figure 5. Time response of SPR sensor to physical adsorption of Concanavalin.

## 3. CONCLUSIONS

We showed the possibility of a simultaneous excitation of two surface plasmon polariton modes over the opposite sides of the gold film polaritons in the combined silicon prism/dielectric layer/gold film structure. The internal mode appeared to be almost insensitive to the change of the refractive index of the sensing medium for the optimal gold thickness, suggesting that this mode can be used as a reference sensing point for multi-channel remote monitoring applications. On the other hand, we found that the “internal” plasmon mode over the $SiO_2$/gold interface appears to be at least 4-6 times more sensitive than the “external” one to nanoparticle-enhanced SPR sensing .

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