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Multi-layer Si-Based Surface Plasmon Resonance Structure for Absorption Sensing

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ABSTRACT

A multi-layer Si-based surface plasmon resonance (SPR) sensing structure, consisting of a silicon coupling prism, an intermediate SiO_2 layer, a gold film, and a sensing medium, is considered. Such structure makes possible an excitation of two angularly separated surface plasmon polariton modes over both sides of the gold film. We examine the response of the system in the case of the absorption sensing, which is simulated by the gold thickness change. Both

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calculations and experimental data show 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 over the gold/sensing medium interface, which is employed in most conventional SPR schemes. The proposed internal plasmon-based absorption sensor structure can be used for studies of optical absorption layers and for colloidal Au-enhanced SPR sensing of ultra-small (bio)-chemical agents.

Key Words: Surface plasmon resonance (SPR); Silicon; Colloid gold; Multi-layer silicon.

INTRODUCTION

Among a variety of optical techniques, surface plasmon resonance (SPR) has become a widely accepted analytical instrument, used in different fields such as materials science of ultrathin films[1] and biosensing for real-time characterization of reversible binding interactions between biological macromolecules.[2,3] Most SPR sensors use the Kretschmann–Raether geometry,[4] in which a thin sensing layer is immobilized on a gold film (~50 nm), deposited on a glass prism. *p*-Polarized light, directed through the prism and then reflected from the gold film, exhibits a resonant dip of reflected intensity at a certain incidence angle (wavelength) due to the plasmon excitation over the interface between the gold film and the adjacent sensing medium. The angular[5,6] and wavelength[7] positions of the dip and the phase of light[8–10] are extremely sensitive to a refractive index of a thin (~300 nm) sensing layer near the gold. This enables to characterize thin films and record in real time bio- and chemical interactions resulting in the film thickness (refractive index) change (for review, see Refs.[2,3]). However, conventional SPR transduction principle 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.[11] In this case, the SPR system operates similarly to the SPR absorption sensor,[12,13] which is frequently used for studies of optical absorption coatings with nonzero 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.[11,13]

We have recently introduced near-IR-based SPR sensing schemes on a silicon platform,[14,15] with the anticipation of the ease of miniaturization and multi-channel integration of the SPR technique applying Si-based methods for microfabrication. Silicon-based schemes displayed quite different regularities of plasmon excitation and polarity of sensing response, while the relatively high sensitivity and an enhanced probe depth (1–2 μm) advantaged the remote sensing of large objects. Using different combined silicon/dielectric layer/gold structures and taking advantage of a relatively high refractive index of Si ($n \sim 3.75$) in comparison with most dielectrics, we also managed to excite an additional "internal" plasmon polariton mode over the layer/gold interface.[16] 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. In this article, we examine the potential of the combined Si-based multi-layer structures for absorption sensing. The sensing response of external and internal plasmon modes is compared, while the adsorption is simulated by the increase of the thickness of SPR-supporting gold layer.

EXPERIMENTAL

The SPR coupling system consisted of a silicon prism, dielectric layer, and a gold film, as shown schematically in Fig. 1. Gold films were deposited by electron beam evaporation technique on a SiO_2 coating, which was thermally grown on a 0.5-mm thick silicon wafer (*N*-type, $\rho > 10\,\Omega\,cm^2$, Silicon Quest, Santa Clara, CA). In addition, for comparative tests we used conventional Kretschmann–Raether geometry with gold films deposited directly on the silicon wafer. Both systems were then placed in the immersion contact with a base of a semi-cylindrical silicon prism (Silicon Quest) with the aid of a high refractive index immersion liquid (Cargille Labs., Cedar Grove, NJ), which provided a good optical and mechanical contact with the silicon multilayer structure. As we showed in Patskovsky et al.,[15] the presence of immersion contact of the silicon prism with the wafer did not change conditions of plasmon excitation and obtained dependencies. The gold film thickness was varied in different experiments from 15 to 35 nm. The SiO_2 layer thickness was also

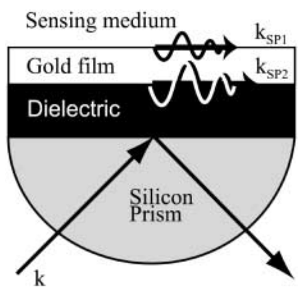

Figure 1. Schematic of the SPR coupling structure (silicon prism/SiO_2 layer/gold film/tested medium) used in the experiment and calculations.

varied from 580 to 1110 nm. The coupling system was connected to a flow cell (empty or filled with distilled water, depending on the aqueous or gaseous tested medium).

The SPR coupling system with the flow cell 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 with variable wavelengths, obtained by passing white light through a monochromator. Light reflected from the coupling system was analyzed by detectors, whose characteristics determined the dynamic range of the spectral measurement from 193 to 1700 nm. The experiments were performed with a fixed wavelength ($\lambda = 1200$ nm). The precision of the angular measurements was 0.005°.

THEORETICAL ANALYSIS

Conditions and parameters of plasmon excitation in dielectric multi-layer structures were studied by many groups (for review, see, e.g., Ref.[1]). It is known that two plasmon polariton modes can be simultaneously excited in the system prism/dielectric layer/gold/dielectric medium if the refractive index of the prism is higher than that of the dielectric layer. In this case, two plasmon modes exist at both sides of the gold film, as shown schematically in Fig. 1. It should be noted that the structure of Fig. 1 is known as long-range surface plasmon (LRSP) scheme, since it was used for the excitation of long-range plasmons. These long-range plasmons are characterized by low losses and appear under the coupling of two plasmon modes in conditions of relatively thin gold film and close refractive indices of the dielectric layer and of the tested dielectric medium (symmetric systems).[17,18]

In contrast, in this study we consider an essentially asymmetric structure since the refractive index of the SiO_2 layer is much higher than that of the tested medium ($n = 1.33$ or $n = 1$). Conditions and parameters of plasmon excitation have been determined using Fresnel's formulas using a matrix method.[19] For comparison, reflectivity curves were calculated for both multi-layer geometry (Fig. 1) and conventional Kretschmann–Raether geometry. In the analysis, the metal layer adsorption on the gold surface is simulated by the increase of the thickness of the SPR-supporting gold layer.

RESULTS AND DISCUSSION

Figure 2 presents calculated angular reflectivity curves in the multi-layer Si-based structure for the cases of gaseous (a) and aqueous (b) tested media. The reflective curves contained two minima corresponding to the excitation of external and internal surface plasmon polariton modes. For both gaseous and aqueous tested media, the dip related to the external plasmon was achieved at lower incident angles. For example, for the air medium the external polariton mode provided the SPR dip at 16.5–16.8°, while the internal one at 24.8–26°. Similarly, for the aqueous medium the relevant values for external and internal polaritons were 22.4–22.5° and 24.8–27°, respectively.

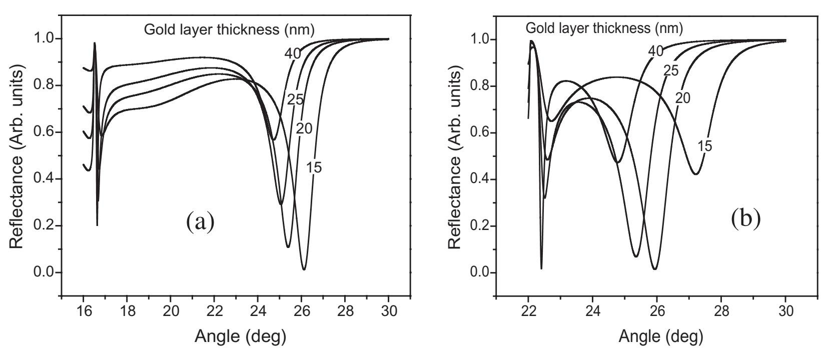

Figure 2. Calculated angular reflectivity curves in the $Si/SiO_2/Au$ structure for configurations of gaseous (a) and aqueous (b) tested media. Different curves correspond to different thicknesses of the gold film. The data are given for the pumping wavelength $\lambda = 1200$ nm and the thickness of the SiO_2 layer $h = 580$ nm.

As shown in Fig. 2, both minima 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. 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. The data for the SPR minimum positions collected from the angular reflectivity curves are summarized in Fig. 3. This figure also presents experimental points collected from our measurements with ellipsometry. 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 nonuniform film deposition and a formation of discrete islands.[20]

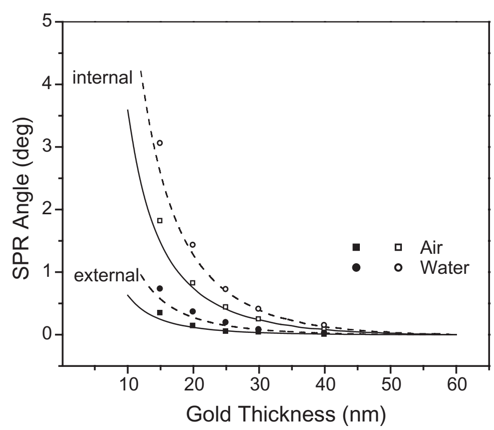

Figure 3. Angular sensing response of the external (conventional structure) and internal (multi-layer structure) plasmon modes for gaseous (solid line) and aqueous (dashed line) tested media. Experimental data are indicated by square and circle signs for gaseous and aqueous media, respectively. The data are given for $\lambda = 1200$ nm, $h = 580$ nm.

It is known that schemes with intensity interrogation are often preferable for absorption-based SPR sensing in comparison with the angular interrogation ones.[11–13] Figure 4(a) shows the sensing response in such a scheme, with the reflected intensity in the SPR minimum R_{min} as a function of the gold thickness. The internal plasmon related reflectivity curves slightly differ for gaseous and aqueous tested media, whereas this difference is essentially absent in the case of the external plasmon. Nevertheless, as in the case of the angular interrogation (Fig. 2), the internal plasmon appeared to be much more sensitive to the thickness increase in comparison with the external one. For a fixed SiO_2 layer thickness of 580 nm, the minimum of reflected intensity for the internal plasmon was achieved at a much smaller thickness of 15–20 nm (for the external plasmon this minimum takes place at the thickness of 40 nm). Another advantage of the multi-layer system includes the possibility for a fine adjustment of the intensity minimum position on the R_{min} (gold thickness) curve by an appropriate selection of the SiO_2 layer thickness, as illustrated in Fig. 4(b). This enables to select the most sensitive slope of the curve for concrete parameters of used materials and thus improves the flexibility of the sensor to dynamical range adjustments. Notice that most dependencies and optimizations of this research were obtained for a fixed wavelength of the pumping light ($\lambda = 1200$ nm). Figure 5 generalizes optimizations of the SiO_2 intermediate layer for an arbitrary wavelength and for three different thicknesses of the gold film. As shown in the figure, the general trend is an increase of the optimal SiO_2 layer thickness with an increase of the wavelength.

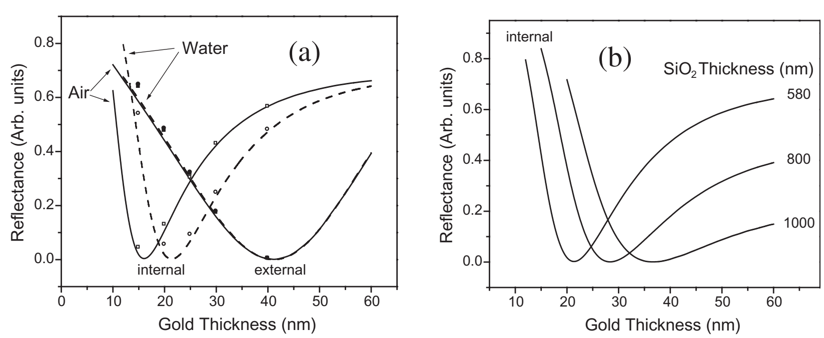

Figure 4. (a) Calculated reflected intensity at a minimum of SPR curve R_{min} as a function of the gold layer thickness for external and internal plasmons. The data are given for $\lambda = 1200$ nm, $h = 580$ nm; (b) calculated reflected intensity R_{min} as a function of the SiO_2 layer thickness.

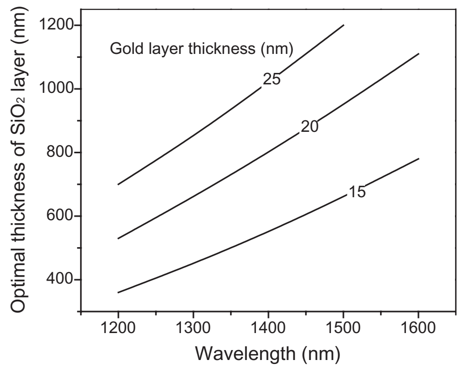

Figure 5. Calculated optimal SiO_2 layer thickness as a function of pumping wavelength. Different curves correspond to different thicknesses of the gold film.

CONCLUSION

Conditions of excitation and absorption sensing characteristics of surface plasmon polaritons in the combined silicon prism/SiO_2 layer/gold film structure have been investigated. We show that this structure makes possible the excitation of internal and external plasmons over both sides of the gold film and optimized the sensing response of two plasmons. The internal plasmon was found 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[11] and studies of properties of absorbent coatings on gold.[12,13]

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