Silicon-based surface plasmon resonance sensing with two surface plasmon polariton modes

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Surface plasmon resonance (SPR) sensing on a silicon-based platform is considered. We have studied properties of SPR in a combined silicon–dielectric layer–gold film–sample medium structure and established conditions of the simultaneous excitation of two plasmon polariton modes that provide narrow and well-separated minima of the reflected intensity. It has been shown that the external mode over the gold–sample medium interface demonstrates a highly sensitive response to a change in the refractive index of the sample medium, whereas the internal mode over the dielectric–gold interface is almost insensitive to medium parameters. We propose that the internal mode can be used as an effective reference zero point for miniature and portable SPR-based systems designed for field and multichannel sensing. © 2003 Optical Society of America

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1. Introduction

Over the past decade surface plasmon resonance (SPR) biosensors have been widely employed in life and environmental sciences for a real-time and label-free characterization of reversible binding interactions between biological macromolecules.[1,2] In conventional SPR biosensors, a thin biological film is immobilized on the surface of a gold film (~50 nm), which is deposited on a glass prism. *P*-polarized visible light, directed through the prism and then reflected from the gold film, exhibits a resonant dip of reflected intensity at a certain light incident angle (wavelength) that is due to plasmon excitation.[3,4] The resonant conditions are dependent on the refractive index of the thin layer near the gold surface (within a distance of approximately 300 nm for visible light), and any change of the biological film thickness that is due to specific binding interactions can be followed by measurement of angular,[5–7] wavelength,[8,9] or phase[10–12] characteristics of the reflected light.

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We have recently shown that SPR sensing can be implemented on a purely silicon platform with silicon as the coupling material.[13,14] By sensing with IR pumping light in the 1100–2300-nm range, silicon-based SPR schemes displayed quite different regularities of plasmon excitation and polarity of sensing response, which was attributed to essentially different behavior of dispersion characteristics of silicon in comparison with glass. In addition, silicon-based schemes showed relatively high sensitivity and potential applications for SPR sensing of relatively large objects (the probe depth of these schemes reached 1–2 μm). The design of sensing on a silicon platform is especially attractive with respect to the ease of miniaturization and multichannel integration of the SPR technique, key requirements for remote monitoring applications. The expectation is based on the fact that methods for microfabrication and circuit integration are well developed for silicon. We reason that some additional opportunities for sensing could be obtained by use of combined silicon–dielectric–gold structures, implying a relatively high index of silicon prism n_p in comparison with that of an intermediate dielectric layer (n_d). It is known that similar dielectric structures with $n_p > n_d$ allow for the excitation of two plasmon polariton modes over both sides of the gold film.[15] However, the two modes usually provide relatively broad and superimposed minima in the case of a purely glass (dielectric) platform since refractive indices of most dielectrics do not strongly exceed that of the sample medium ($n > 1.33$). In particular, these modes can be used in

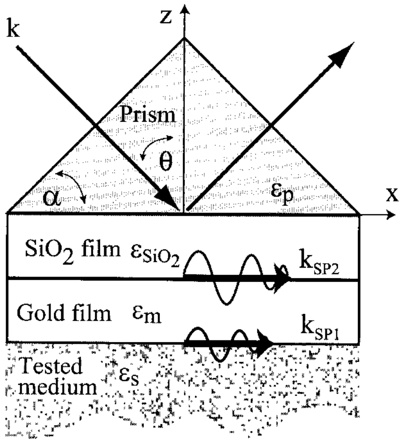

Fig. 1. (a) Schematic of the four-layer system (silicon prism–dielectric film–gold film–tested medium) used in the experiment and calculations.

conditions of mutual coupling,[16] which is known to improve the sensor performance somewhat.[17] In contrast, silicon is a high refractive-index material ($n > 3$),[18] providing the potential for the separation of minima for most standard dielectric coatings (SiO_2 and Si_3N_4) on silicon and the appearance of two independent channels for sensing. In this paper we study the excitation of surface plasmons in combined Si-based structures and properties of plasmons in this geometry. We also discuss potential applications of the combined structures to improve the stability and precision of sensing schemes.

2. Theoretical Framework

We used a model of plasmon oscillations in the Kretschmann–Raether arrangement[19] consisting of a silicon prism, a gold film and a tested medium, as shown in Fig. 1. We also consider a parallel dielectric layer between silicon and gold to examine the influence of its parameters on plasmon excitation. We obtained the resonance conditions by matching the projection of the wave number of the incident beam on surface k_x to the surface plasmon wave number k_{SP} at a specific combination of pumping frequency ω and angle of incidence θ_{SPR}:

$$n_p \frac{\omega}{c} \sin \theta_{SPR} = k_{SP}. \quad (1)$$

The wave number of plasmon k_{SP} over the interface of metal and dielectric with dielectric constants ε_m and ε_s is derived with parameters of the involved media[19]:

$$k_{SP} \approx \frac{\omega}{c} \left[\frac{\varepsilon_m(\omega)\varepsilon_s(\omega)}{\varepsilon_m(\omega) + \varepsilon_s(\omega)} \right]^{1/2}. \quad (2)$$

Equation (1) can be solved to provide pumping wavelength λ and θ_{SPR}, two key parameters for plasmon excitation. In the Kretschmann–Raether prism geometry, the surface plasmon is excited over the interface of the gold film with the tested medium, as shown in Fig. 1. An appropriate combination of dielectric prism and intermediate layer between the prism and the gold makes possible an excitation of surface plasmon on the opposite side of the gold film.[15] In this case, the intermediate layer should have lower refractive index n_d in comparison with the prism material ($n_d < n_p$) and an appropriate thickness. In principle, the excitation of a similar mode might be extended for a prism made of a semiconductor material such as silicon, taking into account that silicon has a relatively high real part of a refractive index (~3.45–3.6 in the IR range[18]). However, the clarification of this supposition requires a detailed consideration of dispersion characteristics of silicon, which is quite different in comparison with dielectrics[13,14] and their correlation with characteristics of all the other materials involved. In our calculations, the dispersion characteristics of silicon were obtained from the approximation of experimental dependencies reported by Herzinger *et al.*[18] Dispersion properties of gold in visible and IR light were taken from the data of Innes and Sambles[20] and Johansen *et al.*[21] We examined air and water as two typical examples of tested media. The dispersion relation for water was taken from Harvey *et al.*,[22] with a correction factor that is due to weak water absorption taken from the data of Kou *et al.*[23] We tested different standard coatings (SiO_2 and Si_3N_4) on silicon as intermediate layers. The dispersion characteristics of these layers were obtained by direct ellipsometric measurements in an appropriate wavelength range.

3. Experimental

The experiments were carried out with a Si-based coupling system shown schematically in Fig. 1. The coupling system was connected to a flow cell (empty or filled with distilled water, depending on the aqueous or gaseous tested medium). The silicon prisms (p type, $R > 20\ \Omega$ cm, Almaz Optics, Marlton, N.J.) with $\alpha = 16.6°$ and $\alpha = 22.4°$ were specially designed for experiments with the gaseous and aqueous tested medium, respectively. With such prisms, it is feasible to achieve an incident light beam on the silicon–gold interface at an angle close to θ_{SPR}, the estimated value. Gold films were deposited on a 0.5-mm-thick silicon wafer or on SiO_2 and Si_3N_4 coatings on the wafer (Silicon Quest International, Santa Clara, Calif.), which was then placed in contact with the prism. The gold film thickness was 35 nm.

The SPR coupling system (with or without the flow cell) was placed upon a rotary block of a variable-angle spectroscopic ellipsometer (J. A. Woollam, Lincoln, Nebr.) to allow for a 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 that we obtained by passing white light 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 to 1700 nm. The experiments were performed with a configura-

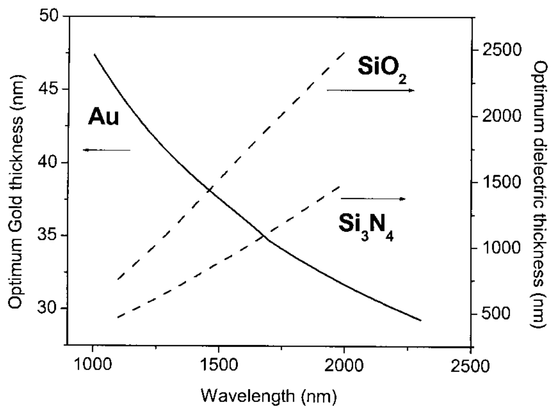

Fig. 2. Optimal thicknesses of the gold film and the SiO_2 and Si_3N_4 dielectric films as a function of wavelength for 35-nm gold film.

tion of a fixed wavelength with the precision of angular measurements of 0.005°.

4. Results and Discussion

The calculated results and experimental data confirmed the possibility of simultaneous excitation of two surface plasmon polariton modes with a silicon platform and IR pumping light, if the thicknesses of the dielectric coating and the gold film are optimized. The optimization of the gold film thickness was performed by Fresnel formulas with a matrix method[24] to produce minimal reflected intensity in the SPR dip related to the plasmon at the gold–tested medium interface (external plasmon). As shown in Fig. 2, the main trend was the decrease of the optimal gold thickness with an increase in λ. For example, the optimal thickness changed from 45 to 30 nm when λ increased from 1100 to 2300 nm. A 35-nm-thick gold film was selected for our experiment to provide relatively low reflected intensity in the total wavelength range of interrogation. For each gold film thickness, one can select an appropriate thickness of the dielectric coating to result in minimal reflectivity of the second SPR dip corresponding to the plasmon at the gold–coating interface (internal plasmon). In particular, Fig. 2 demonstrates the wavelength dependence of optimal thicknesses of SiO_2 and Si_3N_4 layers for the fixed gold thickness of 35 nm. In contrast to gold, the optimal thicknesses of dielectric layers increased when the wavelength increased and were of the micrometer scale.

Figure 3 presents typical angular reflectivity curves in the Si–SiO_2–Au structure from the theoretical (dotted curve) and experimental data (solid curve) for (a) gaseous and (b) aqueous sample media. As presented by the experimental curves, the angles relate to the prism–gold interface, whereas a light refraction at the entrance to the prism was taken into account as a correction factor. Essentially, the main trend of the theory was well confirmed by the experimental data and the calculated and measured reflectivity curves were close to each other. The reflective curves contained two minima that correspond to the excitation of

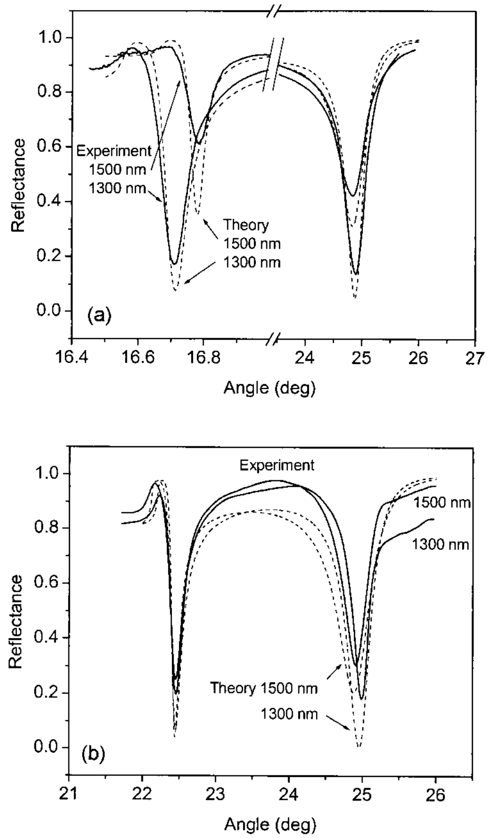

Fig. 3. Typical angular reflectivity curves in the Si–SiO_2–Au structure for configurations of (a) gaseous and (b) aqueous sample media. The broken and solid curves represent the calculated and experimental data, respectively.

external and internal surface plasmon polariton modes. For both gaseous and aqueous tested media, the dips related to the two modes did not superimpose, whereas the dip related to the external plasmon was achieved at lower incident angles. For example, for the air medium the external polariton mode provided a dip at $\theta_{SPR} \cong 16.5$–16.8°, whereas the internal one at $\theta_{SPR} \cong 24.8$–24.9°. Similarly, for the aqueous medium the relevant values for external and internal polaritons were 22.4–22.5° and 24.8–25°, respectively.

The data for the SPR minimum position collected from the angular reflectivity curves are summarized in Fig. 4 to illustrate the resonant conditions for a simultaneous variation in the wavelength and the angle of incidence. The SPR minimum angle and wavelength can be generated from these plots by taking a cut parallel to the *Y* or *X* axis. As shown in Fig. 4(a), in the gaseous medium, the pumping wavelength increased with an increase in the resonant angle θ_{SPR} for the external plasmon, whereas the opposite trend was noted for the internal plasmon. The positive slope of the $\theta_{SPR}(\lambda)$ curve is a characteristic of the silicon prism. As we have shown previously, glass prisms used in most SPR systems resulted in a directly opposite trend.[14] In an aqueous milieu, the behavior of SPR dispersion curves for the external plasmon became more complicated [Fig.

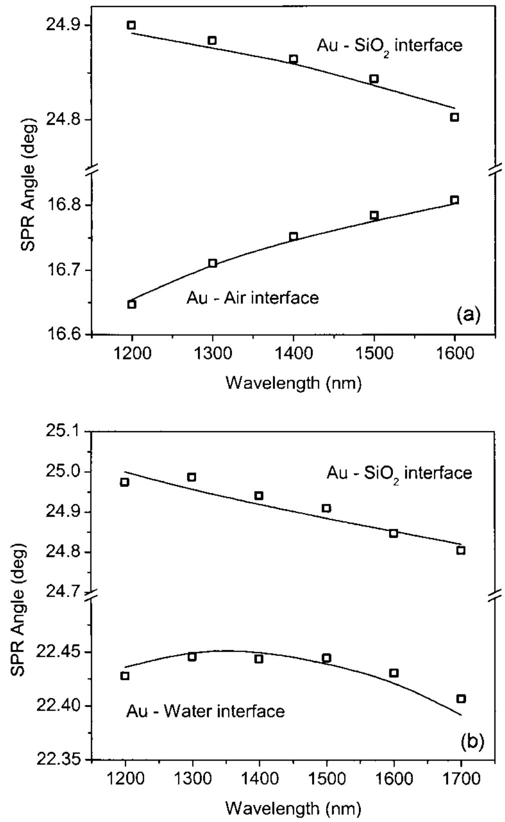

Fig. 4. SPR dispersion curves in the Si–SiO_2–Au structure for configurations of (a) gaseous and (b) aqueous sample media. The symbols represent the experimental data, the curves depict the results of the calculations.

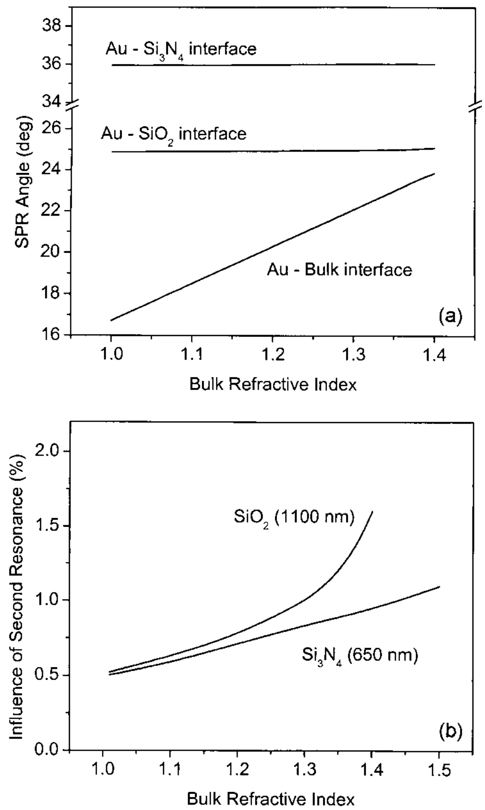

Fig. 5. Angular sensing response of the external and internal plasmon polariton modes to a change in refractive index n_s of the tested medium: (a) the Si–SiO_2–Au and Si–Si_3N_4–Au structures and (b) relative percentage of change.

4(b)]. Indeed, the resonant angle for the external plasmon initially increased with an increase in the wavelength to reach a maximum value at $\lambda = 1400$ nm and then decreased with a further increase in λ.

The position of the minimum related to the internal plasmon was almost identical for gaseous and aqueous sensing media. In brief, the internal plasmon was almost insensitive to the refractive index of the tested medium. For a correct analysis, we separately studied the effect of parameters of the tested medium on the position of the minimums. Figure 5(a) demonstrates the position of minimums related to both plasmons as a function of the refractive index of the tested medium. The refractive-index change caused a significant shift of the resonant angle for the external plasmon, whereas this angle was almost constant for the internal plasmon. As shown in Fig. 5(b), the shift of the resonant angle θ_{SPR} of the internal plasmon with respect to the external one was less than 1.5% for the SiO_2 coating and less than 1% for the Si_3N_4 coating, which 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 biochemical 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 in refractive index. Note that the detailed sensing characteristics of this mode were studied in our previous study.[14] 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) has an equal effect on the excitation of both modes, we propose that the internal mode can be used as an effective zero-point reference for biological and chemical sensing.

In a real sensing experiment, the presence of such an independent reference zero point enables us 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 movable stages. However, in the case of Si-based SPR technology, we imply mainly 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 a 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 or no), the presence of the zero point becomes absolutely necessary. One of the examples is a 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 on the angle of the slide installation but independent of the refractive-index changes, enables us to fix a zero point without any high-precision stage and then to 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 a sensing in the multichannel regime by the use of the same slide. The presence of the zero point makes possible corrections to the system calibration on the nonuniformity of biolayer thickness in every channel. It should be added 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 undoubtedly be used with microsensors.

5. Conclusions

Characteristics and conditions of excitation of surface plasmon polaritons in a combined silicon prism–dielectric layer–gold film–sample medium structure have been studied. We have shown conditions of a simultaneous excitation of two surface plasmon polariton modes on opposite sides of gold film. The first external surface plasmon polariton mode, excited over the interface of the gold film with the tested medium, is sensitive to the properties of the tested medium. The second internal mode, excited over the gold–dielectric layer interface, however, is almost insensitive to the properties of the tested medium. We propose that the internal mode can be used as a reference zero point in miniature and portable SPR-based systems for remote monitoring applications.

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