# **Influence of the Metal Film Thickness on the Sensitivity of Surface Plasmon Resonance Biosensors**

## SANONG EKGASIT,\* CHUCHAAT THAMMACHAROEN, FANG YU, and WOLFGANG KNOLL

Sensor Research Unit, Department of Chemistry, Faculty of Science, Chulalongkorn University, Bangkok 10330, Thailand (S.E., C.T.); and Max-Planck-Institut für Polymerforschung, Ackermannweg 10, D-55128 Mainz, Germany (F.Y., W.K.)

The influence of the metal film thickness (i.e., the chromium adhesion promoting film and the gold film) on the sensitivity of surface plasmon resonance (SPR) signals (i.e., resonance angle shift and reflectance change) towards the thickness variation of the nonabsorbing dielectric film is investigated. The sensitivity of reflectance change decreases when a thick chromium film or a thin gold film is employed. Its linear range becomes narrower as the thickness of the metal films increases. The sensitivity and linear range of the resonance angle shift are not affected by the thickness variation of the metal films. The phenomena were theoretically explained based on the attenuated total reflection (ATR) generated evanescent field at the prism/metal interface and the SPR-generated evanescent field at the metal/dielectric interface.

Index Headings: Surface plasmon resonance; SPR; Metal film; Sensitivity; Evanescent field.

### **INTRODUCTION**

Surface plasmon resonance (SPR) spectroscopy is a powerful affinity biosensor for quantitative analysis of interactions at the surface of the noble metal film. The technique exploits the surface plasmon wave propagating along the surface of the thin metal film for probing refractive index and/or thickness variation of the thin dielectric film attached to the metal surface.<sup>1-3</sup> The highly surface sensitive nature of the SPR-based biosensors is derived from the unique characteristic of the SPR-generated evanescent field at the metal/dielectric interface under the total internal reflection condition. The evanescent field is strongest at the metal/dielectric interface due to the resonance coupling between the incident radiation and the surface plasmon wave. The evanescent field decays exponentially into both the metal film and the dielectric media. The rapid decay of the evanescent field makes SPR-based biosensors very sensitive to thickness and/or refractive index changes of the thin dielectric film attached to the metal surface.<sup>1-6</sup>

Surface plasmon resonance is extensively employed as a biosensor for monitoring specific interactions at interfaces (i.e., enzyme–substrate, antigen–antibody, receptor– ligand, and drug–protein interactions) and as a highly sensitive technique for monitoring physicochemical phenomena (i.e., chemical reactions, absorption, degradation, and protein hybridizations) associated with thin dielectric films. The physicochemical phenomena at the metal surface induce dielectric constant and/or thickness changes of the functionalized dielectric film. The changes shift the resonance condition of the surface plasmon wave, which can be observed experimentally as SPR curve shifts. The linear relationship between the SPR signals (i.e., the reflectance at an angle slightly lower than the resonance angle<sup>7–10</sup> or at the resonance angle<sup>11–15</sup>) and the refractive index and/or thickness of the dielectric film enables SPR spectroscopy for quantitative analysis of the interactions.<sup>2–5</sup> By monitoring the SPR signals as a function of time, the kinetics of the binding phenomena or progress of the interactions can be studied in real time.<sup>7–15</sup>

In the SPR biosensor chip fabrication, a thin film of a transition metal (i.e., Cr, Ti, or W) is generally employed as an adhesion promoter between the noble metal film and the glass substrate. A thin adhesion promoting film up to a few nanometers thick is normally coated onto the glass substrate prior to the deposition of an  $\sim$ 50 nm thick noble metal film.<sup>16-20</sup> The thin transition metal film not only improves the adhesion but also enhances the stability of the noble metal film. The noble metal film without a thin adhesion promoting layer cannot withstand harsh chemical treatment (i.e., cleaning by a strong oxidizing agent) or becomes unstable under potential cycling in voltammetric experiments.<sup>6</sup>

This paper shows that the linear response and sensitivity of the SPR signals are governed by the SPR-generated evanescent field at the metal/dielectric interface and the attenuated total reflection (ATR) generated evanescent field at the prism/metal interface. The influences of the thickness of the chromium adhesion promoting film and the gold film on the sensitivity and linearity of the SPR signals will be theoretically explained based on the evanescent field profile within the metal film.

#### THEORY

The SPR reflectance  $R(\theta)$  of a multilayer can be expressed in terms of the dielectric constants of the materials in the sensor architecture and the evanescent field by<sup>21,22</sup>

$$R(\theta) = 1 - A(\theta)$$
  
=  $1 - \left(\frac{2\pi}{\lambda}\right)^2 \frac{1}{k_{zP}(\theta)} \sum_{j=1}^N \left[\int_{z_j}^{z_{j+1}} \operatorname{Im}(\hat{\varepsilon}_j) \langle E_z^2(\theta) \rangle \, dz\right]$ (1)

where  $\theta$  is the angle of incidence,  $A(\theta)$  is the *absorptance*,  $\lambda$  is the wavelength of the coupled radiation,  $\hat{\varepsilon}$  is the complex dielectric constant of the *j*th layer, and  $\langle E_z^2(\theta) \rangle$  is the mean square evanescent field at a distance *z* from the prism/metal interface. *N* is the number of layers in the sensor architecture with the metal film next to the prism as the first layer.  $k_{zP}(\theta)$  is the *z*-component of the

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<sup>\*</sup> Author to whom correspondence should be sent. E-mail: sanong.e@ chula.ac.th.

wavevector in the prism.  $k_{zP}(\theta)$  can be expressed in terms of the *x*-component of the wavevector  $k_{xP}(\theta)$  by

$$k_{zP}(\theta) = [(2\pi/\lambda)^2 \varepsilon_P - k_{xP}^2(\theta)]^{1/2} \text{ with}$$
$$k_{xP}(\theta) = (2\pi/\lambda) [\varepsilon_P \sin^2 \theta]^{1/2}$$

 $\varepsilon_P$  is the dielectric constant of the prism. The detailed derivations of the reflectance and the evanescent field are given elsewhere.<sup>21–23</sup>

For SPR of nonabsorbing dielectrics, the absorption of the metal film is the only source for the attenuation of the reflectance. If the metal film consists of two or more layers (i.e., a chromium adhesion promoting film and a gold film), the reflectance can be expressed in terms of the optical constants of the metals by<sup>22</sup>

$$R(\theta) = 1 - \left(\frac{2\pi}{\lambda}\right)^2 \frac{1}{k_{zP}(\theta)}$$

$$\times \left[\int_0^{d_{Cr}} \operatorname{Im}(\hat{\varepsilon}_{Cr}) \langle E_z^2(\theta) \rangle \, \mathrm{d}z + \int_{d_{Cr}}^{d_{Cr}+d_{Au}} \operatorname{Im}(\hat{\varepsilon}_{Au}) \langle E_z^2(\theta) \rangle \, \mathrm{d}z\right] \qquad (2)$$

where  $d_{Cr}$  and  $\hat{\varepsilon}_{Cr}$ , respectively, are the thickness and complex dielectric constant of the chromium film, while  $d_{Au}$  and  $\hat{\varepsilon}_{Au}$  are those of the gold film.

Although the optical properties of the nonabsorbing dielectrics do not appear in the equations, their influence does exist in the observed SPR curves. The nonabsorbing dielectric does not contribute to the reflection loss but governs the resonance condition. The resonance angle increases without a significant change of the reflectance minimum as the thickness and/or refractive index of the nonabsorbing dielectric film increases.<sup>21,22</sup>

#### **EXPERIMENTAL**

LaSFN9 glass wafers ( $20 \times 20 \times 2.5$  mm, Schott Glas, Germany) were cleaned and coated with an  $\sim$ 50 nm thick gold film via a commercially available thermal evaporation instrument (Edwards FL400, England) at a deposition rate of 0.1 nm/s under an ultra-high-vacuum condition. One of the wafers was coated with an 0.5 nm thick chromium film prior to the deposition of the gold film. The self-assembled monolayer (SAM) was fabricated by immersing the gold-coated wafers in a thiol solution (500 µM of 11-mercaptoundecanole in absolute ethanol) over night at room temperature. The prepared substrates were rinsed thoroughly with absolute ethanol, blow-dried with dry nitrogen, and kept under an argon environment until being used. Conventional angle-scanned SPR experiments with a right-angled prism were performed at room temperature (21  $\pm$  2 °C) with water as a semi-infinitely thick nonabsorbing dielectric substrate. Detailed descriptions of the measurement procedure are given elsewhere. 21, 22

#### RESULTS

For an SPR experiment under the Kretschmann-Raether ATR setup, the surface plasmon resonance phenomenon takes place under the total internal reflection condition where the angle of incidence is greater than the critical angle  $\theta_{c}$ . According to the angle-scan SPR curve in Fig. 1A, the onset of the total internal reflection phenomenon is indicated by the abrupt increment of the reflectance at 47.37° while surface plasmon resonance is observed at 56.70°. Due to the resonance coupling between the incident radiation and the surface plasmon wave, the evanescent field in the metal film has two origins: a weak ATR-generated evanescent field at the prism/metal interface and a strong SPR-generated evanescent field at the metal/dielectric interface.<sup>22</sup> The evanescent field amplitudes in Fig. 1C indicate that the SPR-generated evanescent field governs the reflectance near the resonance angle while the ATR-generated evanescent field governs that far away from the resonance angle. At an angle slightly above the critical angle, a relatively constant and high reflectance is observed. The high reflectance in this region is due to the small absorption of the gold film associated with the weak ATR-generated evanescent field. As the angle increases, an onset of the surface plasmon resonance is observed. The reflectance is attenuated to a minimal value as the incident angle reaches the resonance angle. The small reflectance in this region is due to the high absorption of the gold film associated with the strong SPR-generated evanescent field. Although the reflectance is directly related to the evanescent field, as shown in Eq. 1, the resonance angle is slightly greater than the angle with maximum evanescent field at the metal/dielectric interface (see Fig. 1). This difference is due to the decay characteristic of the SPR-generated evanescent field in the metal film where the field decays with the angle of the field maximum tailing towards the greater angle.22

The shaded area in Fig. 1 indicates the angular region with a relatively constant slope  $\Delta R/\Delta \theta e$ . Under the employed sensor architecture, the region covers approximately 0.9°. Beyond this region, a nonlinear relationship between the reflectance and the incidence angle is observed. Since the resonance condition is strongly dependent on the optical property of the dielectric medium attached to the gold film, the physicochemical phenomena at the interface that induce the refractive index and/or thickness variation thus shift the resonance angle. If the dielectric media are not absorbing, the resonance angle shifts without a significant change in the curve shape and the reflectance minimum.<sup>22</sup> As a result, by monitoring the reflectance at an angle slightly smaller than the resonance angle (i.e.,  $\theta e_{Observe}$ )<sup>7-10</sup> or by monitoring the resonance angle shift,11-15 the physicochemical phenomena at the interface can be followed in real time. According to Fig. 1, the angular region with the constant slope corresponds to the region with the minimum ATR-generated evanescent field. This implies that, within this angular region, the metal film near the prism/metal interface has very small contribution to the reflection loss of the SPR curve.

Figure 2 shows experimentally observed SPR curves without and with a 0.5 nm thick chromium film. Although the reflectance in the SPR-dominated regions of both curves is very similar, the presence of the thin chromium film can be noticed from the ATR-dominated region.

It is well known that the dielectric constant of the met-



FIG. 1. (A) SPR curve; (B) absorptance (solid line) and reflectance at the air/prism interface (broken line); and (C) the ATR-generated evanescent field at the prism/metal interface on the metal side (at  $z = 0^+$ ) and SPR-generated evanescent field at the metal/dielectric interface on the metal side (at  $z = d_{Au}^-$ ). The shaded area indicates the angular region with relatively constant slope  $\Delta R/\Delta \theta e$ . The simulation parameters are shown. The reflectance and absorptance are corrected for the reflection at the air/prism interface.

al film changes with its thickness due to electron scattering at the film boundary. However, for simplicity of the simulation and the evaluation of the influence of the film thickness, the optical constant of the metal film is assumed constant and is independent of the metal film thickness. As shown in Fig. 3, reflectance in the ATR- dominated region of the sensor chip without a chromium film is relatively constant. The reflectance in the ATRdominated region of the sensor with chromium, on the other hand, decreases as the thickness of the chromium film increases. This is due to the absorption of the chromium film associated with the ATR-generated evanescent



FIG. 2. Experimentally observed SPR curves from sensor chips without a chromium film (open circles) and with a 0.5 nm thick chromium film (open squares). The Fresnel fits are superimposed on the observed SPR curves. The simulation parameters with water as an ambient substrate ( $\varepsilon_{water} = 1.778$ ) are shown. The complex dielectric constant of chromium is obtained from Ref. 26.



FIG. 3. (A) SPR curves; (B) absorptance of gold and chromium films; (C) the ATR-generated evanescent field (at  $z = 0^+$ ) and the SPR-generated evanescent field (at  $z = d_{Au}^-$ ); and (D) the  $A_{Cr}/A_{Au}$  ratio at chromium film thicknesses of 0.0, 0.5, 1.0, 1.5, 2.0, 2.5, and 3.0 nm. The simulation parameters are shown.

field. Although the ATR-generated evanescent field is very weak and does not change significantly as the thickness of the chromium film increases (Fig. 3C), absorption of the chromium film can be noticed. Due to the high absorption index of the chromium film, its presence can be detected with a film only a few nanometers thick.<sup>21,24–27</sup> Unlike the ATR-generated evanescent field, the SPR-generated evanescent field decreases substantially as the thickness of the chromium film increases. According to Fig. 3B, the absorption of the gold film decreases with a slight decrease of the angle with absorption maximum while the increased absorption of the chromium film shifts the resonance angle to a greater value. Although the increased absorption of the chromium film near the resonance angle cannot compensate for the decreased absorption of the gold film (due to the decreased evanescent field), it does increase the resonance angle. It should be noted that the large decrement of the ATR-generated evanescent field in Fig. 3C is associated with the change in the sensor architecture (i.e., from prism/gold/dielectrics to prism/chromium/gold/dielectrics).

Figure 4 shows SPR curves, the reflectance observed at  $\theta_{Observe}$ , and the resonance angle as the thickness of the dielectric film increases. The linear change of the re-

flectance is observed when the thickness increment is not too high. If the thickness increment is too high, the reflectance at  $\theta e_{Observe}$  is out of the linear region (i.e., the region within the shaded area in Figs. 1 and 3). With the dielectric constant of the dielectric film  $\varepsilon_{\text{DielectricFilm}} = 2.25$ , an onset of the deviation of the reflectance (at  $\theta e_{Observe} =$ 55.9°) from linearity is observed when the thickness increment is greater than  $\sim$ 5 nm. The slope  $\Delta R / \Delta d_{\text{DielectricFilm}}$ of the  $R-d_{\text{DielectricFilm}}$  plot equals 0.049 RU/nm in the linear region. For the sensor architecture with a 1 nm thick chromium film, Fig. 4B, the reflectance is observed at  $\theta e_{Observe} = 56.0^{\circ}$  (the slightly greater  $\theta e_{Observe}$  compensates the increased resonance angle when the chromium film is present). Although the onset of the nonlinearity of the reflectance change is observed at approximately the same thickness of the dielectric film as that of the system without a chromium film, the slope of the  $R-d_{\text{DielectricFilm}}$  plot is smaller ( $\Delta R / \Delta d_{\text{DielectricFilm}} = 0.045 \text{ RU/nm}$ ). For the 3 nm chromium film, Fig. 4C, an onset of the nonlinearity is observed at approximately the same dielectric film thickness,  $\sim 5$  nm at  $\varepsilon_{\text{DielectricFilm}} = 2.25$ . However, the slope of the  $R-d_{\text{DielectricFilm}}$  plot is smaller ( $\Delta R/\Delta d_{\text{DielectricFilm}}$ = 0.040 RU/nm). The observed phenomena correspond to the smaller slope  $\Delta R/\Delta \theta e$  within the angular region



FIG. 4. The SPR curve, the resonance angle (dotted lines), and the reflectance monitored at  $\theta e_{\text{Observe}}$  (solid lines) as the thickness of the nonabsorbing dielectric film increases. Thickness of the chromium film: (A) 0 nm; (B) 1 nm; and (C) 3 nm. The simulation parameters are shown.

where the reflectance shift is monitored (see the shaded area in Fig. 3A). This implies that sensitivity of the reflectance change monitored at  $\theta e_{Observe}$  decreases as the thickness of the chromium film increases.

According to Fig. 3B, as the angle is decreased below the resonance angle, the absorption of the chromium film shows a U-shape variation. The contribution of the chromium film is not constant over the angular region. The influence of the chromium film becomes stronger as its thickness increases. The U-shape contribution of the chromium film results in the S-type curve shape in the  $R-d_{\text{DielectricFilm}}$  plots. Although the S-type curve shape is not obvious in Fig. 4B due to the small absorption of the thin chromium film, the influence of chromium absorption is obvious in the sensor chip with a thicker chromium film.

In contrast to the  $R-d_{\text{DielectricFilm}}$  plot, the constant slope of the  $\theta e_{\text{SPR}}-d_{\text{DielectricFilm}}$  plots ( $\Delta \theta e_{\text{SPR}}/\Delta d_{\text{DielectricFilm}} = 0.186$ degree/nm at  $\varepsilon_{\text{DielectricFilm}} = 2.25$ ) indicates that the chromium film does not have any influence on the sensitivity of the resonance angle shifts.

A similar phenomenon is also observed when a gold film of different thickness is considered. Under the employed complex dielectric constant ( $\hat{\varepsilon} = -12.70 + i1.40$ ), the optimal thickness of the gold film is 45.63 nm. As shown in the shaded area of Fig. 5A, an SPR curve with a steep slope together with the minimal reflectance minimum is observed when an optimally thick gold film is employed. When a gold film with a thickness less than the optimal value is employed, a broader SPR curve with a greater reflectance minimum, a greater resonance angle, and a less steep slope near the resonance angle are ob-

served. When a gold film with thickness greater than the optimal value is employed, an SPR curve with a slightly smaller resonance angle and a greater reflectance minimum is observed. The SPR curve shape does not change significantly from that with the optimal gold thickness (Fig. 5A). These phenomena are attributed to the SPRgenerated evanescent field, see Fig. 5B. The field at the metal/dielectric interface is greatest when the optimally thick gold film is employed. The SPR-generated evanescent field decreases when the gold film is thicker or thinner than the optimal value. The slope within the shaded region becomes less steep when the gold film is thinner than the optimal thickness. The slope is slightly greater as the thickness of the gold film is increased beyond the optimal thickness. The angle with the field maximum is slightly decreased as the thickness of the gold film increases. Although the angle at the field minimum of the ATR-generated evanescent field shifts slightly towards the greater angle as the thickness of the gold film increases, the field amplitude at the resonance angle does not change significantly.

Due to the slightly increased slope  $\Delta R/\Delta \theta$ e within the shaded angular region in Fig. 5A, a slightly greater sensitivity of the reflectance change at  $\theta e_{Observe}$  towards the thickness variation of the dielectric film is expected when a thick gold film is employed (see Fig. 6). The slope of the  $R-d_{DielectricFilm}$  plots increases as the thickness of the gold film increases (i.e.,  $\Delta R/\Delta d_{DielectricFilm} = 0.0319$ , 0.0464, 0.0478, and 0.0500 RU/nm, respectively, for  $d_{Au} = 40.63$ , 45.63, 50.63, and 55.63 nm). However, the linear range of the  $R-d_{DielectricFilm}$  plot is slightly decreased as the thickness of the gold film is sincreased beyond the



FIG. 5. (A) The SPR curves and (B) the ATR-generated evanescent fields and the SPR-generated evanescent fields at various thicknesses of the gold film (40.63, 45.63, 50.63, and 55.63 nm). The inserted tables show the corresponding resonance angle and the angle with the maximum SPR-generated evanescent field. The arrows indicate the direction of the thickness increment. The simulation parameters are shown.



FIG. 6. The SPR curve, the resonance angle (dotted lines), and the reflectance monitored at  $\theta e_{Observe}$  (solid lines) as the thickness of the nonabsorbing dielectric film increases. Thickness of the gold film: (A) 40.63 nm; (B) 45.63 nm; (C) 50.63 nm; and (D) 55.63 nm. The simulation parameters are shown.

optimal thickness. This is due to the weaker SPR-generated evanescent field and the U-type curve shape of the ATR-generated evanescent field (see Fig. 5B).

Although the resonance angle decreases as the thickness of the gold film increases, the constant slope of the  $\theta e_{\text{SPR}}-d_{\text{DielectricFilm}}$  plots in Fig. 6 ( $\Delta \theta e_{\text{SPR}}/\Delta d_{\text{DielectricFilm}} = 0.186$  degree/nm at  $\varepsilon_{\text{DielectricFilm}} = 2.25$ ) indicates that the gold film does not have any influence on the sensitivity of the resonance angle shifts.

#### DISCUSSION

The constant slope of  $\theta e_{SPR}$ - $d_{DielectricFilm}$  plots in Figs. 4 and 6 is due to the independent nature of the evanescent field maximum from the thickness of the metal film. Under the employed conditions, the resonance angle increases slightly as the thickness of the metal film increases. The reflectance monitored at  $\theta e_{\text{Observe}}$  depends strongly on the thickness of the metal film. The sensitivity of the reflectance change (indicated by the slope  $\Delta R/\Delta d_{
m DielectricFilm}$ ) towards the variation of the dielectric film thickness decreases as the thickness of the chromium film increases. The sensitivity also decreases as the thickness of the gold film decreases. The decreased sensitivity is associated with the weaker SPR-generated evanescent field within the observed region (i.e., the shaded areas in Figs. 3 and 5). The absorption with Utype curve shape of the chromium film is responsible for the narrower linear range of the  $R-d_{\text{DielectricFilm}}$  plots. Although the slope of the SPR curve within the shaded region does not change significantly, the decreased SPRgenerated evanescent field, as the thickness of the gold film is increased beyond the optimal thickness, narrows the linear range of the  $R-d_{\text{DielectricFilm}}$  plots.

Although the linear range of the  $\theta e_{SPR} - d_{DielectricFilm}$  plot is much greater than that of the  $R-d_{\text{DielectricFilm}}$  plot, the experimental operation of the latter is inherently more robust since it does not involve the angular scan (i.e., near the resonance angle). Thus, a system with fast changes can be followed in real time by monitoring reflectance change at a fixed angle  $\theta e_{\text{Observe}}.$  The narrow linear range of the  $R-d_{\text{DielectricFilm}}$  plot can be overcome by changing the  $\theta e_{Observe}$  to a greater angle when nonlinearity is reached. The linear range for the reflectance shift can be estimated from the observed angle-scan SPR curve. The modification of the  $\theta e_{Observe}$  can be programmed and executed as the defined reflectivity is reached.<sup>12</sup> The linearity of the  $R-d_{\text{DielectricFilm}}$  plot is retained at the new  $\theta e_{Observe}$  since the SPR curve shifts without a significant change of the curve shape and reflectance minimum as the thickness of the nonabsorbing dielectric increases.

#### CONCLUSION

Although the ATR-generated evanescent field is very small compared to the SPR-generated evanescent field,

the large imaginary part of the complex dielectric constant of the thin chromium adhesion promoting metal film makes its absorption significant. The progress of the interaction monitored by the reflectance change, although having advantages for following rapid phenomena, suffers from the dependence of the reflectance on the metal film thickness. The sensitivity and linear range of the reflectance change depend strongly on the metal film thickness. The sensitivity and linear range of the resonance angle shift towards the thickness variation of the nonabsorbing dielectric, on the other hand, are not affected by the metal film thickness.

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