Sensitivity Optimization of Plain Silver Surface Plasmon Resonance Imaging Sensor

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Abstract. Plain silver surface plasmon resonance imaging (SPRi) sensor has been studied extensively due to its high sensitivity and desirable stability in liquid environments. To further enhance sensitivity performance of the sensor, angular sensitivity, angular slope and depth-width ratio (DWR) of SPR curve, and imaging sensitivity are evaluated at different thickness combinations of the gold and silver films respectively. In this work, the angular slope of SPR curve is found to be the critical factor to the optimized imaging sensitivity of plain silver SPRi sensor. In the comparative study, the above parameters of the plain silver SPR sensor, single gold film and bimetallic SPR sensors are compared. Plain silver SPRi sensor is proved to be of the highest imaging sensitivity, which is 4.08 and 1.18 times imaging sensitivity of the single gold film and bimetallic SPR sensors separately.

Keywords. plain silver SPRi structure, thickness optimization, angular slope.

1. Introduction
Surface plasmon resonance imaging (SPRi) sensors have been widely explored as a label-free and real-time monitoring technique in several areas of applications, such as chemistry, biotechnology, medicine and so on[1-6]. One of the most common configurations in the technique is the Kretschmann configuration, in which an expanded, collimated transverse magnetic (TM) polarized light beam travels through SPR setup at a fixed incident angle, and reflection change is monitored by a charge-coupled device (CCD) detector array to provide refractive index information of analyte[2,7]. An ideal SPRi sensor should possess high sensitivity, capability of high-throughput measurements, and reasonable stability[8-10]. Among varieties of metals in the SPRi configuration, single gold film is commonly used in the applications for its pronounced chemical stability and ease of structure fabrication[2-7]. In comparison, silver-based structures, featuring much higher sensitivity and throughput of SPRi, are a more attractive choice when a storage time up to 3 months is reached in the gold-silver-self assembled monolayer (SAM) structure of plain silver SPRi sensor[11-13]. Different from the protective layer in bimetallic SPRi sensors[14-17], the gold film in the plain silver SPRi sensor functions as an adhesion/nucleation layer of the silver film[11,18-20]. Due to its limited thickness, the gold film does not alternate plasmonic propagation of the plain silver SPRi sensor significantly, thus the sensor demonstrates a narrower full width at half maximum (FWHM) of SPR curve and higher imaging sensitivity than the bimetallic configurations[11,20, 21].

To further optimize sensitivity performance of the plain silver SPRi sensor configuration, three factors need to be evaluated. The first is angular sensitivity, which is sensitivity between SPR resonance angle shift and refractive index unit (RIU) change of analyte. The second is angular slope, i.e. the slope between the reflectivity change and its corresponding SPR resonance angle shift. According to Campbell’s work, sensitivity of SPRi sensor is determined by these two factors[22]. The last one is
depth-width ratio (DWR), which is defined as ratio between depth and FWHM of the SPR curve[23]. A SPRi sensor featuring high throughput of detection requires small region of interest (ROI) of each measurement channel, however, decrease in the ROI size results in a lower resolution, which deteriorates sensitivity performance of SPRi sensor[24]. In this case, DWR of SPR curve need to be enhanced in the optimization because of its inverse ratio relation to resolution[25]. Besides the above factors, functionality of the gold film should also be considered in the sensitivity optimization process due to its contribution to the stability. The gold film thickness should be small to minimize alternating plasmonic properties of the sensor, but also sufficient to provide desirable adhesion and smoothness of the silver layer[14].

In this paper, we investigated the plain silver SPRi sensor for high sensitivity by optimizing thicknesses of gold and silver films in the configuration theoretically. We evaluated effect of the angular sensitivity and angular slope on sensitivity performance of the sensor separately, and found that the latter one is the key factor of promoting SPRi sensitivity. We also calculated DWR and explored possibility of achieving highest SPRi sensitivity and highest DWR simultaneously. Lastly, we compared SPRi sensitivity, DWR of SPR curve, field enhancement at metal/dielectric interface of the plain silver SPRi sensor with single gold film and bimetallic SPRi sensors. The plain silver SPRi sensor demonstrated 4.08 and 1.18 times imaging sensitivity of the single gold film and bimetallic SPRi sensors separately after the above optimizations.

2. Method

In our study, angular spectrum of the plain silver SPRi sensor in figure 1 a was simulated as Eq.(1)[13,26], where the metal films can be considered as independent layers, and the prism and the analyte are seen as the incident and emergent medium respectively.

\[
\eta_i = \frac{n_i}{\cos \theta_i}, \delta_i = \frac{2\pi}{\lambda} n_i \delta_i \cos \theta_i, \ Y = \frac{H_y}{E_y} (i = 1,2,3,4)
\]

\[
E_0 \left[ \begin{array}{c} 1 \\ Y \\ \frac{B}{C} \end{array} \right] = \left[ \begin{array}{ccc} \cos \delta_i & \frac{1}{\eta_i} \sin \delta_i & 1 \\ j \eta_i \sin \delta_i & \frac{1}{\eta_i} \cos \delta_i & 1 \\ \eta_i \beta & 1 \end{array} \right] \left[ \begin{array}{c} 1 \\ Y \\ \frac{B}{C} \end{array} \right] E_0 (j = \sqrt{-1})
\]

\[
R = \left| \frac{\eta_i B - C}{\eta_i B + C} \right|^2
\]

\[
R_{norm} = \frac{R}{R_{max}} \times 100\%
\]

Where \( \lambda \) is the incident wavelength, \( d_i, n_i, and \theta_i \) are the thickness, refractive index and incident angle of each sequenced medium respectively. \( R_{norm} \) is normalized reflectivity of the simulated SPR angular spectrum[22]. The lower indices 0 to 4 represent the five layers in the plain silver SPRi sensor, namely, the prism, the gold layer, the silver layer, the SAM layer and the analyte respectively. Sensitivity \( S_{imaging} \) of the plain silver SPRi sensor can be expanded into two terms in the following.

\[
S_{imaging} = \frac{dR_{norm}}{dn} = \frac{d\theta_R}{dn} \times \frac{dR_{norm}}{d\theta_R}
\]

Where \( \theta_R \) is SPR resonance angle of the spectrum. In Eq.(2), the first term denotes the angular sensitivity of SPRi sensor, yet the second term is the slope between the reflectivity change and SPR resonance angle shift, which we define as angular slope in the following work. In the following calculations of \( dR_{norm} \), we chose the angle corresponding to 30% normalized reflectivity as incident angle[27].

3. Results and Discussion
3.1. Optimization of Plain Silver SPRi Sensitivity

In the following simulations, incident light wavelength is 633nm. Refractive indices of the prism, silver, gold, Octane-1-thiol SAM and analyte at room temperature are 1.78, 0.05 + 4.483i, 0.14 + 3.697i, 1.45 and 1.333 respectively[13,28,29]. Thickness range of the silver film in the configurations of Figure 1 is 35-65nm, while thicknesses of the chromium and SAM films are 2.5nm and 1.3nm respectively[13, 30]. In the plain silver SPRi sensor, thickness range of the gold film is 1-5nm, which has been reported to be sufficient for the adhesion of the silver film in practical use[19].

\[
\text{Figure 1. Schematic diagrams of (a) plain silver SPRi sensor, (b) bimetallic SPRi sensor and (c) single gold film SPRi sensor.}
\]

Figure 2a shows that angular sensitivity distributes around 59 degree/RIU and varies less than 0.5% through all the gold and silver thickness combinations. The results show that the effective refractive index at silver/SAM/analyte interfaces in the plain SPRi sensor is mainly determined by the silver film of sufficient thickness[2,25,31,32]. In contrast, the angular slope in figure 2b shows a high value region where the silver film thickness ranges from 60nm to 65nm. The highest value of the angular slope is 459.314 %/degree, where thickness of the gold and silver film are 1nm and 61nm respectively. Similarly, the highest value of DWR, 365.503 %/degree, occurs at the abovementioned combination of gold and silver film thicknesses in figure 2c. Furthermore, the imaging sensitivity in figure 2d is calculated according to Eq. (2) and showing a high value region similar with the angular slope result. The highest value of the imaging sensitivity is 27559.040 %/RIU, where thickness of the gold and silver film are 1nm and 61nm respectively. The above results indicate that the angular slope of SPR curve is the main factor determining imaging sensitivity of the plain silver SPRi sensor according to Eq. (2).
Figure 2. (a) Angular sensitivity, (b) angular slope, (c) DWR and (d) imaging sensitivity of plain silver SPRi sensor.

In the following comparative study of sensitivity optimization, the bimetallic and single gold film SPRi sensors are considered. In study of the bimetallic SPRi sensor, Figure 3a shows that angular sensitivity increases from around 60 degree/RIU to more than 65 degree/RIU when the gold film thickness becomes larger at all the values of the silver film thicknesses. The results show that the effective refractive index at gold/SAM/analyte interfaces in the bimetallic SPRi sensor is mainly determined by the gold film of sufficient thickness\cite{2,25,31,32}. In contrast, the angular slope in Figure 3b shows the highest value of the angular slope as 388.017 %/degree, where thickness of the gold and silver film are 1nm and 59nm respectively. Similarly, the highest value of DWR, 306.789 %/degree, occurs at the abovementioned combination of gold and silver film thicknesses in Figure 3c. Furthermore, the imaging sensitivity in figure 3d is calculated according to Eq. (2) and showing a high value region similar with the angular slope result. The highest value of the imaging sensitivity is 23281.169 %/RIU, where thickness of the gold and silver film are 1nm and 59nm respectively. The above results indicate that the optimized imaging sensitivity of the plain silver SPRi sensor is 1.18 times of the bimetallic SPRi sensor.
Figure 3. (a) Angular sensitivity, (b) angular slope, (c) DWR and (d) imaging sensitivity of bimetallic SPRi sensor.

Figure 4a shows that angular sensitivity varies around 66 degree/RIU at all the values of the gold film thicknesses in the single gold film SPRi sensor. In contrast, the angular slope in figure 4b shows the highest value of the angular slope as 102.067 %/degree, where thickness of the gold film is 58nm. Similarly, the highest value of DWR, 63.982 %/degree, occurs at the abovementioned gold film thickness in figure 4c. Furthermore, the imaging sensitivity in figure 4d is calculated according to Eq. (2) and showing a high value region similar with the angular slope result. However, the highest value of the imaging sensitivity is 6749.257 %/RIU, where the gold film thickness is 57nm. Deviation between the thicknesses corresponding to the highest angular slope and imaging sensitivity can be explained as the angular sensitivity difference between the two thicknesses. The above results indicate that the optimized imaging sensitivity of the plain silver SPRi sensor is 4.08 times of the single gold film SPRi sensor.
Figure 4. (a) Angular sensitivity, (b) angular slope, (c) DWR and (d) imaging sensitivity of single gold film SPRi sensor.

4. Conclusions
In this paper, we reported a sensitivity optimization method of plain silver SPRi sensor. In the method, angular sensitivity, angular slope and DWR of SPR curve at different combinations of gold and silver film thicknesses are calculated respectively, and the angular slope is found to be critical to the imaging sensitivity optimization. In the further comparative study, the above parameters and imaging sensitivity of the plain silver SPR sensor, single gold film and bimetallic SPR imaging sensors are compared. Plain silver SPR sensor is proved to be of the highest imaging sensitivity, which is 4.08 and 1.18 times imaging sensitivity of the single gold film and bimetallic SPRi sensors separately.

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