Angle Shifting in Surface Plasmon Resonance: Experimental and Theoretical Verification

W M Mukhtar¹, P Susthitha Menon¹, S Shaari¹, M Z A Malek² and A M Abdullah²

¹Institute of Microengineering and Nanoelectronics, Universiti Kebangsaan Malaysia
43600 UKM Bangi, Malaysia
²Advanced Materials Research Centre, Lot 34, Jalan Hi-Tech 2/3, Kulim Hi-Tech Park, 09000 Kulim Kedah, Malaysia

E-mail:wmaisarah2101@yahoo.com, susi@eng.ukm.my, sahbudin@eng.ukm.my, zahid@sirim.my, makarimi@sirim.my

Abstract. This paper discussed a sensing property of the SPR sensor to detect changes in refractive index of the dielectric medium. The resonant angle shifting was observed as the dielectrics medium was changed from air to SiO₂ thin film. The effect of a free space wavelength to the excitation of SPP was investigated by employing laser sources with wavelengths transmission of 545nm and 632.8nm. In comparison with 545nm of wavelength transmission, we revealed that He-Ne laser source with wavelength of 632.8nm is suitable to produce a strong SPR signal due to its high Q-factor. To avoid misinterpretation between the destructive interference and SPR phenomenon, we proposed a simple theoretical approach using momentum conservation principle which concerning the wavevector values to validate the experimental results. By ignoring the imaginary part of the dielectric function of gold, we proved that this theoretical approach is still acceptable due to the excellent agreement between the theoretical and simulation approaches.

1. Introduction
Recently, researches in surface plasmon resonance (SPR) become a major interest in biomedical sensing application. The biosensing techniques are motivated by numerous applications in medical diagnostics and single molecule detection. SPR is an optic method to detect the small change of the refractive index on the metal surface [1, 2]. Many works have been conducted to improve the sensitivity and stability of the SPR sensor.

SPR phenomenon is represented by a sharp dip of curve which represents the minimum reflectance. A high Q-factor of SPR curve implies that the plasmons are strongly confined. The Q-factor is influenced by the thin film thicknesses, types of metal used, structures of nanoparticles, thicknesses, types of metal used, structures of nanoparticles, deposition techniques, value of the free space wavelength, quality of substrates and the coupling methods [3-12]. Nonetheless, it is important to differentiate between the existences of SPR and destructive interference where both phenomena are interpreted as an absorption dip in the reflectance function. Consequently, with the support of a theoretical analysis by using plasmonic related equations such as Fresnel equation, Drude model analysis and Maxwell equations; the SPR phenomenon can be recognized [13-16].

Published under licence by IOP Publishing Ltd
In this paper, we seek to determine the SPR sensing characteristics using our custom made modified optical waveguiding assembly by monitoring the angle shifting phenomenon. We believe that this research output can be exploited gainfully in many sensing applications due to its sensitive response to the change of refractive index of the dielectric medium. A significant theoretical approach for the verification of the SPR phenomenon using a momentum conservation principle by matching the component of wavevector along the surface plasmon propagation interface, \( k_s \), with the wavevector of surface plasmon, \( k_{spp} \) has been discovered.

2. Theory

Surface plasmon is the localized charge density oscillations that occur in the interface between a metal and a dielectric medium. These oscillations propagate along the boundary between a thin metal film and a dielectric medium. The relationship of the surface plasmon wave vector (\( k_{spp} \)) between the metal and dielectric medium is given as

\[
k_{spp} = k_o \frac{\varepsilon_{metal} \varepsilon_{dielectric}}{\varepsilon_{metal} + \varepsilon_{dielectric}}
\]  

(1)

where \( k_o \) is the free space wave vector of the optical wave which can be calculated as \( k_o = \frac{2\pi}{\lambda_o} \), \( \varepsilon_{metal} \) and \( \varepsilon_{dielectric} \) are respectively the dielectric functions of metal and the dielectric medium. During SPR, the energy of the incident light can be strongly coupled from photons onto the surface plasmon wave which decays via heat dissipation along the propagation path. The relationship between \( k_x \) and angle of incident light can be expressed as follows:

\[
k_x = k_o n_{glass} \sin \theta_{inc}
\]  

(2)

where \( n_{glass} \) is the refractive index of the glass prism and \( \theta_{inc} \) is the angle of incidence [17]. The conditions for the surface plasmon excitation at the interface between the metal and dielectric layers in a glass-metal-dielectric are given by

\[
k_x = k_{spp}
\]  

(3)

Resonance is achieved by matching the projection of the wave vector of the incident light in the direction of the interface and wave vector of the surface plasmon oscillations as expressed in Eq. (3). Using a prism with dielectric constant value larger than 1 with the incident angle is larger than the critical angle, value of \( k_x \) can be determined. As the incident light satisfies the resonance condition, a strong absorption dip in the reflectance can be observed.

3. Methodology

Herein, we investigated the distinct resonance condition associated with the excitation of surface plasmons for different types of samples, namely single layer of Au (Au-air) and Au-SiO\(_2\) (Au layer deposited prior SiO\(_2\) layer). We fixed the thickness of SiO\(_2\) and gold layer to 45nm and 50nm, respectively. Gold layer was sputtered on a borosilicate glass slide (RI: 1.503) using direct current (DC) sputtering technique; meanwhile SiO\(_2\) layers was sputtered by radio frequency (RF) sputtering technique. The thin film thicknesses were determined using reflectometer (Brand: Filmetrics). We applied a curve fitting method with 96% of accuracy to obtain the thicknesses of the films. Prior to thin film sputtering, the substrate was cleaned by acetone in an ultrasonic bath for 15 min and rinsed with ethanol and deionized water, before dried with a nitrogen stream.

The SPR phenomenon was created using our custom made modified optical waveguiding assembly. He-Ne laser sources with different transmission wavelengths were employed, namely 545nm and 632.8nm. In SPR, it is sufficient to consider only \( p \)-polarized waves because no solutions exist for the case of \( s \)-polarization. Since the linearly polarized lasers were used in this experiment, the \( p \)-polarization state was obtained by rotating the position of laser into 90°. It is worth mentioning that the \( p \)-polarization state of the incident light can be achieved by observed the reflected light without the metal coated layer on the glass slide to obtain the critical angle and the Brewster angle.
Once the TM polarization state was confirmed, the excitation of SPP was accomplished by illuminating the thin film surface normally with a focused laser beam using an angular interrogation technique. The focusing of linearly polarized beam was realized by coupled the light incident from monochromatic \( p \)-polarized He-Ne laser (Brand: Thorlabs) using a convex lens (Brand: Thorlabs). The reflected light intensity from the metal-coated prism was measured by photodetector (Brand: Newport). The intensity will go through a minimum when the coupling with the plasmon wave occurs. To excite surface plasmon polaritons (SPP), we applied a prism coupling technique so that the phase matching between \( k_{\text{spp}} \) and \( k_x \) can be achieved. By employed Kretschmann configuration, the microscope glass slide and the half-cylinder prism were coupled using optical couplant gel which can reduce Fresnel reflection and the difference in the index of refraction between the glass slide and prism. Figure 1 depicts the schematic illustration of Kretschmann configuration for the SPP excitation.

\[
\text{Figure 1. Illustration of SPR phenomenon which can be achieved by matching the projection of the wavevectors, } k_i \text{ and } k_{\text{spp}}.
\]

For the experimental results satisfaction, we ran a simulation using WINSPALL 3.02 simulator programme to investigate the accuracy of our experimental results with the simulated one. The theoretical study was performed to satisfy the principle of momentum conservation by considering two types of wavevectors, namely \( k_i \) and \( k_{\text{spp}} \). The behaviour of \( \lambda_{\text{spp}} \) which is always less than the free space wavelength \( \lambda_0 \) was investigated. In this paper, we set the dielectric functions of gold as \( \varepsilon_i = -11.6+1.2i \) and \( \varepsilon_i = -6+2.2i \) for the transmission wavelength of 632.8nm and 545nm, respectively based on a plot of the dielectric constant from the paper of Johnson and Christy which is an extended work from Drude model [19]. For simplicity, we assume that the imaginary parts of the dielectric functions are small as compare with the real parts, so that they may be neglected [19]. By considering only the real parts, we investigated the SPP waves that propagate along the interface, which is between the metal thin film and the dielectric (i.e air and SiO\(_2\)). The losses in the plasmon’s propagation which associated with the electron scattering were omitted due to the ignorance of the imaginary parts of the dielectric function.

4. Results

Prior observation of the SPR phenomenon, it is important to confirm the characteristic of light propagation in \( p \)-polarization state. The light reflectance behaviour for the combination of bare microscope glass slide and the prism using \( p \)-polarized laser results an excellent agreement with the theoretical as illustrated in figure 2 [20]. The critical angles for laser sources with wavelengths of 632.8nm and 545nm are 38.5° and 43°, respectively. Since the excitations of SPP occur above the critical angles, we expected that the location of SPR dips should be beyond these angles.
4.1 Investigation of the angle shifting phenomena with the increment of refractive indices of the dielectrics medium

By using our custom made modified optical waveguiding assembly, the shifts of incident angles were investigated as the dielectrics medium were changed from air to SiO$_2$. In this experiment, we set the refractive indices values of the dielectrics medium namely air and SiO$_2$ as 1.00 and 1.47 respectively. Figure 3(a) illustrates the characteristics of SPP with wavelength transmission of 545 nm. A strongly shifted of SPR dips from 45.0° to 55.0° with the increment of minimum reflectance from 0.03 to 0.15 are clearly seen as the dielectric was replaced with SiO$_2$. Evidently, the Q-factor is increased with the increment of light transmission wavelength to 632.8nm as depicted in figure 3(b). With the additional layer of SiO$_2$ on top of the gold layer, the resonant angles shifted from 43.0° to 56.4°, as well as the minimum reflectances which increased from 0.13 to 0.28.

For a clarification purpose, we performed a simulation using WINSPALL 3.02 simulator developed by Knoll Group, Max-Plank Institute. This simulator programme is based on a normalized Fresnel equation. Both experimental and simulated results show a good verification as proven in figure 3 and figure 4. The high Q-factors were obtained with the employment of a light source with transmission wavelength of 632.8nm. Figure 4(a) reveals the shifting of resonance angle from 47° to 71° as the refractive index of the dielectric increased from 1.00 to 1.47 with the transmission wavelength of 545nm. As the transmission wavelength changed to 632.8nm (figure 4(b)), the location of resonant dip is shifted from 44.6° to 55.4° without any effect to the reflectance.
The angles shifting which occur due to the changes in refractive index of the dielectric are an important indicator in SPR sensing application. Apart from the experimental and simulation approach, we also performed a theoretical study using equation (1) - (3) to verify the experimental results. Table 1 shows the comparison of angle shifting using three types of methods, namely theoretical, simulation and experimental. Whilst the transmission wavelength of 632.8nm used, the experimental result demonstrated a good agreement with the theoretical and simulation with small percentage difference between them. Despite that, the angle shifting for the transmission wavelength of 545nm resulted a large percentage different between experimental and both theoretical and simulation.

![Figure 4(a). Angle shifting as the dielectric changed from air to SiO$_2$ using 545nm wavelength transmission (simulation)](image1)

![Figure 4(b). Angle shifting as the dielectric changed from air to SiO$_2$ using 632.8nm wavelength transmission (simulation)](image2)

| Method      | Angle shifting, $\Delta \theta$ (°) | 545nm | 632.8nm |
|-------------|-------------------------------------|-------|---------|
| Theoretical | 25.9                                | 10.0  |         |
| Simulation  | 24.0                                | 10.8  |         |
| Experimental| 10.0                                | 13.4  |         |

4.2 Effect of wavevector value, $k_x$ and $k_{app}$ in determining the SPP excitation

Value of the wavevector is the crucial part in SPR study in order to determine the occurrence of SPP excitation. By considering the wavevector, we can simply make a verification either the SPR phenomenon is occurred or not. For any given energy $\hbar \omega$, the wavevector $k_x$ is always larger than the wavevector of light in free space, $k_0$ [18]. Evidently, this reveals that the SPP on a planar interface cannot be excited by light at any frequency that propagates in free space. In this paper, the values of $k_0$ obtained are 0.00993 and 0.01153 using 632.8nm and 545nm of light wavelength transmission, respectively. As depicted in Table 2, $k_x>k_0$ which proves the potential of SPP excitation in this experiment. Table 2 lists value of $k_x$ and $k_{app}$ during the SPR phenomena using the transmission wavelengths of 545nm and 632.8nm with the employment of different dielectric medium. For both wavelength transmissions under the Au-air configuration, the value of $k_x \cong k_{app}$, which fulfil the principle of momentum conservation. Nevertheless, as the dielectric changes to SiO$_2$ with the transmission wavelength of 545nm, the momentum is not conserved with the fact that $k_x<k_{app}$. This reveals the inaccuracy of the obtained result for 545nm wavelength as the dielectric was replaced with SiO$_2$. 

![Table 1: Value of angle shifting as types of dielectric change from air to SiO$_2$](image3)
Table 2. Value of wavevector along the propagation direction, k, and SPP wavevector, k_{spp}, for different transmission wavelength of laser source

| Metal-dielectric | λ₀=545nm | λ₀=632.8nm |
|------------------|-----------|------------|
| Au-air           | 0.012     | 0.011      |
| Au-SiO₂          | 0.016     | 0.023      |

5. Discussions

The generation of the SPR signal must satisfy the TIR condition where the excitation of SPP is above the critical angle. By considering figure 3, the SPR curves are located between 43° to 57°, meanwhile the critical angles obtained are at 38.5° and 43° for the transmission wavelength of 632.8nm and 545 nm, respectively. So, it can be concluded that the existence of absorption dips obtained are due to the SPP excitation. SPP signal strength can be measured by observing the Q-factor of the SPR curves. High Q-factor represents a strong signal of SPPs excitation and vice versa. Figure 3(b) illustrates a high Q-factor curve which reveals the suitable wavelength to excite strong SPR signal is 632.8nm as supported by the simulation result (figure 4(b)).

With the replacement of the dielectric medium from air to SiO₂, the angle shifting should be observed due to the change in refractive index. If we recap the calculation of k_{spp} using equation (1), the imaginary part of the gold dielectric function was omitted for the simplicity purpose. Although the imaginary part is ignored, the good verification between theoretical and simulated results has validated that this approach is acceptable as proven in Table 1. As captured in figure 3 and figure 4, the angles shifting between the experimental and simulation results show the excellent agreement with small percentage differences. However, the minimum reflectance obtained using both methods are slightly different which reveals an argument between the experimental and simulated results. The explanation for this problem is due to the value of the gold dielectric function used during the simulation. Note that the SPR phenomenon is mostly affected by metal characteristics as mentioned in the first section of this paper. Apart from the thin film thickness, the metal dielectric functions also affected the depth of the absorption dip. Since the dielectric function of gold used in this simulation is an ideal value, it is worth to conclude that the experimental value of the dielectric function is slightly different with the ideal one. This leads to the instability of results between the experimental and the simulation approaches.

Owing to the similar characteristics of the absorption dips in reflectance between the destructive interference and the SPR phenomenon, it is critical to distinguish both of them. By conducting a simple theoretical analysis based on the conservation of momentum principle, we compare the wavevector values of k, and k_{spp} for both transmission wavelengths. This principle must be satisfied in order to generate the SPP. With the employment of a prism coupling technique, the wavevector k is always larger than the wavevector of light in free space, k₀. The main purpose of the prism coupling is to increase the wavevector, k, in order to match it with k_{spp}. Value of k_{spp} is obtained by considering the dielectric functions of gold and dielectric mediums (air and SiO₂). We determine value of k using an angular interrogation technique by varies the incident angles until the sharp dip is observed. For the confirmation of the SPR phenomenon, the principle of momentum conservation must be obeyed which is k_{spp} ≈ k. As projected in Table 2, the SPR phenomena are clearly observed with the employment of air as the dielectric medium. An excellent validation between k and k_{spp} proves the occurrence of the SPP excitation. Conversely, with the appointment of 545nm laser source and SiO₂ layer as a dielectric medium, the wavevector for both k and k_{spp} does not obey the principle of momentum conservation, where k_{spp}>k. By considering the experimental and simulated results as captured in figure 3(a) and figure 4(a), the resonant angles for both Au-SiO₂ configurations are different which reveals that the SPP excitation was not occurred. We concluded that the dip observed in figure 4(a) using SiO₂ layer as the dielectric is due to the destructive interference. According to the simulated results as illustrated in
figure 4(a), the SPR resonance of Au-SiO$_2$ thin film should be occurred at the incident angle of 71°, not at 55° as proposed experimentally.

6. Conclusions
In conclusions, we found that our custom made modified optical waveguiding assembly is capable to be used in SPR sensing. A good respond to detect changes in refractive index of the dielectric medium shows the sensing properties based on the SPP excitation. High Q-factor resulted from the transmission wavelength of 632.8nm reveals that strong SPR signal can be created using this wavelength as compare with 545nm. We prove the importance of the principle of momentum conservation for the confirmation of SPP excitation.

Acknowledgements
The authors would like to acknowledge the support of Universiti Kebangsaan Malaysia and the Malaysian Ministry of Higher Education (MOHE) for funding this work under grant ERGS/1/2012/STG02/UKM/02/2, Advanced Materials Research Centre (AMREC) Kulim, Kedah for the thin film sputtering facilities and Universiti Sains Islam Malaysia (USIM)-MOHE for the scholarship.

References
[1] Lavine B K, Westover D J, Oxenford L, Mirjankar N and Kaval N 2007, Microchem J 86 147
[2] Lin C W, Chen K P, Hsiao C N, Lin S and Lee C K 2006, Sens and Act B, 113 169
[3] Umar A A and Oyama M 2006, Appl Surf Sci 253 2933
[4] Feng W Y, Chiu N F, Lu H L, Shih H C and Yang D 2008 Surface Plasmon Resonance Biochip Based on ZnO Thin Film for Nitric Oxide Sensing, 30th Annual International IEEE EMBS Conference, Canada, pp. 5757-5760
[5] Lyon L A, Musick M D, Smith P C, Reiss B D, Pena D J and Natan M J 1999 Sens and Act B, 54 118
[6] Schmid A H, Stanca S E, Thakur M S, Thampi K R and Suri C R 2006 Sens and Act B, 113 297
[7] Chen X, Pan M and Jiang K 2010 Microelectron Eng 87 790
[8] Chowdhury M H, Ray K, Geddes C and Lakowicz J R 2008 Chem Phys Lett. 452 162
[9] Maarof A I, Cortie M B and Smith G B 2005 J Opt A-Pure Appl Op. 7 303
[10] Thirstup C, Zong W, Borre M, Neff H, Pedersen H C and Holzhuetter G 2004 Sens and Act B, 100 298
[11] Kim J B, Zou Y, Kim Y D, Kim J J and Hwangbo C K 2011 Thin Solid Films. 520 1451
[12] Brahma R and Krishna M G 2008 Nucl Instrum Meth B. 266 1493
[13] Neff H, Zong W, Lima A M N, Borre M and Holzhuter G 2006 Thin Solid Films 496 688
[14] Islam A S and Kouzani A Z 2011 Variable incidence angle localized surface plasmon resonance graphene biosensor, Proceedings of the 2011 IEEE/ICME, China, pp. 58-63.
[15] Shandilya S, Tomar M, Sreenivas K and Gupta V 2010 J Lightwave Technol 28 3004
[16] Kuo C H and Moghaddam M 2008 IEEE T Antenn Propag 56 1133
[17] Pun S H, Lam W W, Ho H P and Zhang Y T 2002, A preliminary study on optical measurements of glucose concentration using a surface plasmon resonance system Proceedings of the IEEE-EMBS Special Topic Conference on, China, pp. 68-70.
[18] Novotny L and Hecht B 2007, Principles of Nano-Optics (Cambridge: Cambridge University Press)
[19] Johnson P B and Christy R W 1972, Phys. Rev. B. 6 4370
[20] Saleh B E A and Teich M C 2007, Fundamentals of Photonics (New Jersey: Wiley)
[21] Barnes W L 2006 J. Opt. A: Pure Appl. Opt. 8 S87