Abrupt phase change in graphene-gold SPR-based biosensor

Nasrin Bouzari¹, Jafar Mostafavi Amjad²,³, Ramin Mohammadkhani¹,⁴, and Peyman Jahanshahi³

¹ Department of Physics, Faculty of Science, University of Zanjan, 45371-38791, Zanjan, Iran
² Institute for Advanced Studies in Basic Sciences (IASBS) No. 444, Prof. Yousef Sobouti Blvd. P. O. Box 45195-1159, Zanjan, Iran
³ Nobleo Technology B.V., Heggeranklaan 1, 5643BP Eindhoven, The Netherlands
⁴ Authors to whom any correspondence should be addressed.

E-mail: n_bouzari@znu.ac.ir, mostafavi@iasbs.ac.ir, rmkhani@znu.ac.ir and peyman840@gmail.com

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Abstract

The performance of surface plasmon resonance (SPR) sensors can be different depending on which characteristic of the SPR sensor the amplitude or the phase is monitored. The phase sensitivity strongly depends on the geometry and the optical properties of the system. The existence of sharp changes in the phase spectrum variations is found as the thickness of SPR-supporting gold (dgold) varies around a critical thickness (dg). In addition, the simulation results indicate that the phase sensitivity is divided into two regions so that phase sensitivity Sϕ for region dgold ≤ dg is greater than region dgold > dg. It is demonstrated in condition of dgold ≤ dg, the phase sensitivity has a strong jump when the sensing medium refractive index lies within a certain interval, while the amplitude sensitivity has a monotonic shape. The phase analysis from another aspect exhibits that the phase maximum difference Δϕmax towards the blank sample is sensitive to refractive index in a continuous interval. As a result, the phase detection interval is tunable by varying the gold thickness, which potentially is important for medical, biology and chemistry applications.

1. Introduction

Sensors based on SPR are powerful tools for real-time supervising of interactions in medicine, biology and chemistry analysis due to the enhancement of the surface sensitivity and accurate detection of the sensing medium molecules’ reaction [1–4]. Surface plasmons (SPs) are collective oscillations of free electrons at the metal-dielectric interface [5]. Coupling of the incident light with SPs leads to the formation of a Surface plasmon polariton (SPPs), which propagate along the metal-dielectric interface and decays exponentially in a direction perpendicular to the interface [6, 7].

Because of practical nature properties of gold metal such as stable, superior performance and good resistance to oxidation and corrosion is chosen as an active metal in the conventional SPR [8]. The most advantages of the use graphene layers can be pointed to large surface to volume ratio and the enhancement of biomolecular absorbance compared with gold, so a number of graphene layers are generated onto an optimized gold thin film to enhance the sensitivity of the SPR sensor [9–11]. Titanium is used as a supplementary adhesive layer to ensure strong contact between gold thin film and substrate glass [12, 13].

In these sensors, the detection methods are performed based on the scanning of the wavelength and the angle of incident light. Under a resonance angle or wavelength of light incidence, the photon energy is transferred to a plasmon propagating over the interface of metal-dielectric and the intensity of reflected light reaches to minimum value [14–16]. Such amplitude-sensitive are useful for studies of many interactions, including relatively large molecules such as protein and DNA. Due to a physical limit in the detection of low molecular weight analytes by different sensor implementation with the wavelength or angular spectrum, the phase properties of light reflected under SPR reveal an important role in the detection [1, 17].

In the study of the phase detection, the existence of a sharp phase jump under the some characterization of sensor such as the certain thickness and dielectric function of SPR-supporting metal [18–20]. The maximum value of phase jump and its curve strongly is depended on the refractive index (RI) of sensing medium [21, 22].
Generally, several methods have been developed for SPR phase investigation, including polarimetry, heterodyne detection, spatial phase modulation interferometry, temporal phase modulation interferometry and phase-shift interferometry [23–26].

In this study, we consider a Kretschmann configuration, including prism, titanium, gold, graphene and sensing medium. Owing to that the phase variations strongly affiliates to the shape, geometry and optical properties of the structure, any slight change in them leads to the variation in phase spectrum. It is presented that by varying the gold thickness \( d_g \) around the critical thickness \( d_c \), a sharp change occurs in the phase spectrum. According to the phase jump evens at the matched angle \( \theta_{\text{SPR}} \), it is further demonstrated that the maximum variation of phase with respect to the sensing medium refractive index \( \text{phase sensitivity}, S_j \) is divided into two regions \( d_g > d_c \) and \( d_g \leq d_c \) so that \( S_j(d_g > d_c) \) is greater than \( S_j(d_g < d_c) \).

2. Characterization of sensor in terms of phase and amplitude

The primary structure of the proposed SPR sensor as shown in figure 1 is consisted from five-layer prism, titanium, gold, graphene and sensing medium. Each medium is subscribed by a thickness \( d_k \), permittivity \( \varepsilon_k \) and permeability \( \mu_k \).

The total reflectivity of the system is calculated based on Fresnel theory which for multilayer structure can be developed using transfer matrix method [27]. According to this method, the reflectance coefficient for p-polarized light can be given as follows:

\[
M = \prod_{k=2}^{N-1} M_k = \begin{bmatrix} M_{11} & M_{12} \\ M_{21} & M_{22} \end{bmatrix},
\]

\[
M_k = \begin{bmatrix} \cos \beta_k & -i \sin \beta_k / q_k \\ -i q_k \sin \beta_k & \cos \beta_k \end{bmatrix},
\]

(1)

where, \( N \) is the number of layers, \( \beta_k \) and \( q_k \) are the optically admittance and the phase factor, respectively that are characterized with the refractive index of prism \( n_1 \) and incident light angle \( \theta_\text{in} \) are represented as:

\[
q_k = \frac{1}{\varepsilon_k} (\varepsilon_k \mu_k - n_1^2 \sin^2 \theta_\text{in})^{1/2}, \quad \beta_k = \frac{2\pi}{\lambda} d_k \varepsilon_k q_k.
\]

(2)

The total reflectivity for p-polarized incident light is given by:

\[
r_p = \frac{(M_{11} + M_{22}q_N)q_1 - (M_{21} + M_{22}q_N)q_1}{(M_{11} + M_{22}q_N)q_1 + (M_{21} + M_{22}q_N)q_1},
\]

(3)

where, \( q_1 \) and \( q_N \) are the phase factor of prism and sensing medium, respectively.

By converting the equation (3) to polar form, the phase sensitivity that is defined as the ratio between the phase change and the refractive index variation of the Nth layer (sensing medium \( n_s \)) can be obtained as below:

![Figure 1. Schematic diagram of 2D material-based SPR sensor.](image-url)
Because of the SPR highly sensitive to the variation of intensity amplitude, angle and spectrum width, we use the sensitivity $S_{IAW}$ that have introduced in our previous work [15] as following:

$$r_p = |r_p| \exp(i\varphi), \quad S_p = \max\left(\left|\frac{\partial \varphi}{\partial n_i}\right|\right)$$

here, $S_A$, $S_I$ and $\Delta_I$ denote the angular sensitivity, the intensity-amplitude sensitivity and the spectrum width, respectively. As mentioned in reference [28] the phase information improves detection with respect to the intensity one. In addition, it is found that with regard to refractive index change, the variations of the $S_p$ has a complex behavior compared to the $S_{IAW}$ ones. One can see that the $S_p$ shows an abrupt change towards $n_i$, which strongly depends on the gold thickness. Investigation of phase detection from another aspect is clearly determined the maximum phase change $\Delta \varphi_{\text{max}}$ is sensitive to a continuous interval of $n_i$, whereas the amplitude sensitivity with respect to $n_i$ changes smoothly. Profiting from the abrupt change in $S_p$ or continuous change in $\Delta \varphi_{\text{max}}$ one can achieve a much better sensitivity.

3. Results and discussion

To compare the amplitude and phase sensitivities, we consider a graphene-gold SPR-based configuration with the fixed thicknesses of titanium and graphene 3 nm and 1.7 nm, respectively [15]. To investigate the effect of gold thickness on phase spectrum and its amplitude sensitivity, the thickness of gold is swiped from 30 nm to 55 nm with step size of 5 nm. In order to see the typical phase response of the system, the refractive index in the sensing layer ($n_s$) varies from 1 RIU to 1.633 RIU at an optimized wavelength of 850 nm that can deliver the best sensitivity performance.

Figure 2. (a) The reflection spectrum of $d_g = 40$ nm versus $\theta_r$ for various refractive indices of sensing medium $n_s$. (b) Dependence of amplitude sensitivity $S_{IAW}$ on different gold thickness.

Figure 3. (a) The phase spectrum of SPR sensor for different values of $n_s$ and the gold thickness of 40 nm, which shows the phase change evolution towards $n_s$. (b) For region of $d_g \leq d_c$, the abrupt phase change occurs in the phase sensitivity (red curve) at $n_{sA}$ and $n_{sB}$ compared to the amplitude sensitivity (blue curve).

$$S_{IAW} = \frac{1}{\Delta n} (S_I + S_A),$$
In order to detect the amplitude sensitivity and its comparison with phase sensitivity, the reflection spectrum curves of SPR sensor versus of \( \theta \) in for various gold thickness extracted, as an example in figure 2 (a), the reflection spectrum of 40 nm gold thickness has been plotted. As shown in figure 2 (b), the logarithm of amplitude sensitivity in terms of \( n_s \) delivers a same behavior for all the gold thicknesses. It is clearly seen from this figure that with increasing of the \( n_s \), first the sensitivity value decreases monotonically and then increases.

The optical phase detection of SPR sensor has been investigated experimentally and theoretically [29–31]. Their results show a strong dependence on sensor film thicknesses. According to their results the phase spectrum shows a same behavior for all metal thicknesses and sensing medium refractive indices. More accurate investigation of the phase detection indicates a different behavior with respect to previous works. Our simulation results show at a critical thickness of gold film, an abrupt phase change occurs in the phase spectrum. This novelty is high worthwhile in phase detection of SPR sensors.

Figure 3 (a) shows a typical phase response plot with regard to refractive index change for the \( d_g = 40 \) nm. As is observed for the sensing medium refractive indices in the interval \( n_A = 1.370 \) to \( n_B = 1.405 \) the evolution of the phase change with regard to varying \( n_s \) is clearly identified. According to figure 3 (b), the abrupt phase change causes the value of phase sensitivity at \( n_s \) strongly enhances. The appearance of local sharp peaks in \( S_j \) promises to provide a more sensitive transduction to refractive index changes (red curve in figure 3 (b)), in while the sensor performance is insensitive to amplitude measurement \( S_{IAW} \) in these points (blue curve in figure 3 (b)).

In order to examine the effect of gold thickness on sensor performance, we consider two regions \( d_g > d_c \) and \( d_g \leq d_c \) that the critical thickness \( (d_c) \) is 40 nm. In the case of \( d_g \leq d_c \), the behavior of \( S_j \) is 35 nm is the same as the thickness of 40 nm but only the peak values of \( S_j \) are shifted to \( n_A = 1.145 \) and \( n_B = 1.440 \), respectively. Further reduce the thickness to 30 nm explicitly indicates a different functional compared to \( d_g = 40 \) nm. As shown in figure 4 (a), the behavior of phase spectrum is the same as the shape of step function (SSF) for all \( n_s \) and the phase sensitivity has only a single sharp peak at \( n_{sc} = 1.450 \) (see figure 4 (b)). As shown in figure 5 (a), in condition of \( d_g > d_c \) the phase spectrum curves are modified away from SSF. Owning to figure 5 (b) there is no sharp peak in \( S_j \) curve, which as a result the phase sensitivity reduces towards previous case.
In the experimental measurements, before injection liquid samples inside the chamber the phase changes of the chamber must be determined. Usually for the study of evolution of phase change, the phase sensitivity of the system is calculated via the conventional relationship in equation (4). In this equation the sensitivity is found through a maximum value of phase difference between two consecutive phase spectrum. To better understand from the phase detection we introduce a different approach to phase interpretation. In this approach the chamber phase spectrum is used as the blank spectrum and the phase changes are measured with respect to it as follow:

\[ \Delta \varphi_{\text{max}} = \max(|\varphi(n_s) - \varphi(n_0)|), \]  

(6)

here, \(n_0\) is the refractive index of blank sample which the air is considered as blank. In figure 6, the \(\Delta \varphi_{\text{max}}\) in terms of the \(n_s\) for various gold thickness has been extracted. For \(d_g \leq d_s\), the \(\Delta \varphi_{\text{max}}\) has a maximum with certain detection width, while for \(d_g > d_s\) has a uniform behavior. The detection width of SPR sensor can vary with regard to the gold thickness.

The \(S_j\) method the detection in the limited between \(n_{A} \) and \(n_{B}\) is determined by two sharp peaks, whereas the detection with later technique (\(\Delta \varphi_{\text{max}}\)) occurs in a continuous interval. Therefore, by controlling the gold thickness and using two methods, \(S_j\) and \(\Delta \varphi_{\text{max}}\), the detection of experimental samples can be determined with better accuracy.

4. Conclusion

Phase measurements of the SPR sensors have been well modified and proven to provide highly sensitive to the geometry and the optical properties of the sensor structure. The phase sensitivity (\(S_j\)) based on phase difference between two adjacent phase spectrum shows a better sensitivity in the region of \(d_g \leq 40\) nm. It is found that for \(d_g = 30\) nm a single peak appears at \(n_{A} = 1.450\). For \(d_g = 35\) nm two peaks occur at \(n_{A} = 1.145\) and \(n_{B} = 1.440\), the peaks shift to \(n_{A} = 1.370\) and \(n_{B} = 1.405\) in \(d_g = 40\) nm. In the region of \(d_g > 40\) nm the \(S_j\) does not exhibit any sharp peak. The maximum phase difference (\(\Delta \varphi_{\text{max}}\)) with respect to the blank sample (\(n_0\)) occurs in a continuous detection width of \(n_s\). For \(d_g = 30\) nm, the \(\Delta \varphi_{\text{max}}\) has continuously maximized at interval between \(n_s = 1.065\) and \(n_s = 1.633\). The detection width is limited to \(n_{A} = 1.145\) and \(n_{B} = 1.440\) in \(35\) nm gold thickness. The narrower detection width evens for critical gold thickness of \(40\) nm in the interval \(n_{A} = 1.370\) to \(n_{B} = 1.405\). Overall, by controlling the gold thickness and using two methods, \(S_j\) and \(\Delta \varphi_{\text{max}}\), the detection of experimental samples can be determined with high accuracy which is applicable in medical, biology and chemistry.

ORCID iDs

Jafar Mostafavi Amjad @ https://orcid.org/0000-0002-0147-1299
Ramin Mohammadkhani @ https://orcid.org/0000-0002-8542-1183
References

[1] Wang J, Lin W, Cao E, Xu X, Liang W and Zhang X 2017 Sensors 17 2719
[2] Jahanshahi P, Zalnezhad E, Sekaran S D and Adikan F R M 2014 Sci. Rep. 4 3851
[3] Zeng S, Baillargeat D, Ho H P and Yong K T 2014 Chem. Soc. Rev. 43 3426–52
[4] Jahanshahi P, Wei Q, He Z, Ghomeishi M, Sekaran S D and Mahamd Adikan F R 2017 Bioengineered 8 239–47
[5] Chen Y and Ming H 2012 Photonic Sens. 2 37–49
[6] Maier S A 2007 Plasmonics: Fundamentals and Applications (Springer Science & Business Media)
[7] Arora P, Talker E, Mazurski N and Levy U 2018 Sci. Rep. 8 9060
[8] Maurya J, Prajapati Y, Singh V, Saini J and Tripathi R 2016 Opt. Commun. 359 426–34
[9] Zeng S, Hu S, Xia J, Anderson T, Dinh X Q, Meng X M, Coquet P and Yong K T 2015 Sensors Actuators B 207 801–10
[10] Verma R, Gupta B D and Jha R 2011 Sensors Actuators B 160 623–31
[11] Szunerits S, Maalouli N, Wijaya E, Vilcot J P and Boukherroub R 2013 Anal. Bioanal. Chem. 405 1435–43
[12] Aouani H, Wenger J, Gérard D, Rigneault H, Devaux E, Ebbesen T W, Mahdavi F, Xu T and Blair S 2009 ACS Nano 3 2043–8
[13] Kushwaha A S, Kumar A, Kumar R and Srivastava S 2018 Photonics and Nanostructures-Fundamentals and Applications 31 99–106
[14] Fu H, Zhang S, Chen H and Weng J 2015 IEEE Sensors J. 15 5478–82
[15] Jafari S, Amjad J M, Mohammadkhani R and Jahanshahi P 2018 Mater. Res. Express 5 125021
[16] Ouyang Q, Zeng S, Jiang L, Hong L, Xu G, Dinh X Q, Qian J, He S, Qu J and Coquet P 2016 Sci. Rep. 6 28190
[17] Kabashin A, Evans P, Pastkovsky S, Hendren W, Wurtz G, Akinsson R, Pollard R, Podolskiy V and Zayats A 2009 Nat. Mater. 8 867
[18] Wu L, You Q, Shan Y, Gan S, Zhao Y, Dai X and Xiang Y 2018 Sensors Actuators B 277 210–5
[19] Aytik K Uludağ University Journal of The Faculty of Engineering 23 117–32
[20] Huang Y, Ho H, Wu S, Kong S, Wong W and Shum P 2011 Opt. Lett. 36 4092–4
[21] Abeles F 1976 Surf. Sci. 56 237–51
[22] Kuo W K, Huang N C, Weng H P and Yu H H 2014 Opt. Express 22 22968–73
[23] Kashif M, Bakar A, Arsad N and Shaari S 2014 Sensors 14 15914–38
[24] Huang Y, Ho H, Wu S and Kong S 2012 Advances in Optical Technologies 2012 1–12
[25] Kuo W K, Syu S H, Lin P Z and Yu H H 2016 Appl. Opt. 55 903–7
[26] Deng S, Wang P and Yu X 2017 Sensors 17 2819
[27] Cherifi A and Bouhafs B 2017 Photonic Sens. 7 199–205
[28] Huang Y, Ho H P, Kong S K and Kabashin A V 2012 Ann. Phys. 524 637–62
[29] Nelson S, Johnston K S and Yee S S 1996 Sensors Actuators B 35 167–91
[30] Shen S, Liu T and Guo J 1998 Appl. Opt. 37 1747–51
[31] Gwon H R and Lee S H 2010 Materials Transactions 51 1150–5