THE EFFECT OF BILAYER GRAPHENE ON SENSITIVITY OF SURFACE PLASMON RESONANCE BIOSENSOR

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ABSTRACT

In this paper, the effect of bilayer graphene on sensitivity of surface plasmon resonance (SPR) biosensor is numerically presented. It shows that the zero reflection at the resonance angle occurred by choosing proper thickness for gold and graphene layers. This research analyzes light reflection in angular modulation with a fixed wavelength (λ=633 nm) of incident light regarding to variation in thickness of gold layer underlying bilayer graphene. In comparison to the conventional SPR sensors, graphene based sensor gives a larger local change in the refractive index near the sensor surface. The light reflection coupled into a SPR mode propagating along a gold-graphene layer is calculated and compared to a conventional SPR sensor with varied gold thicknesses.

Keywords—surface plasmon resonance, biosensor, bilayer graphene.

1. INTRODUCTION

Surface plasmons (SPs) are waves that propagate along the surface of a noble metals such as gold, copper and silver in visible range. The SP waves at a metal-dielectric interface is applicable as kind of robust and label-free electrochemical biosensor which called surface plasmon resonance (SPR) biosensor [1]. The SPR biosensor shown as a very effective optical detection for absorption of biomolecules [2, 3].

The SP propagation constant is changed by variation in the refractive index at the metal surface. Therefore, both the light and SP wave coupling condition possibly change and observed. Classification of SPR sensor depends on coupling wavelength, coupling angle, and change in intensity, phase, or polarization [4].

Figure 1 shows that a thin noble metal layer is sandwiched between two dielectrics in a conventional surface plasmon resonance sensor. Unfortunately the sensitivity of the sensor is restricted due to the weak biomolecule adsorption of gold or silver. Oxidation of the metal surface further reduces the sensitivity dramatically. Numerous techniques have been investigated to improve sensitivity in SPR biosensor such as metallic nanoslits, metal nanoholes and nanoparticles in buffered solution [5-10]. The accurate control of the optical properties and geometry of nanostructure still remains challenging. The surface plasmons properties can be changed by functionalizing of the metal surface with biomolecular recognition elements (BRE). This is an alternative to enhance biomolecule adsorption efficiency on the metal surface.

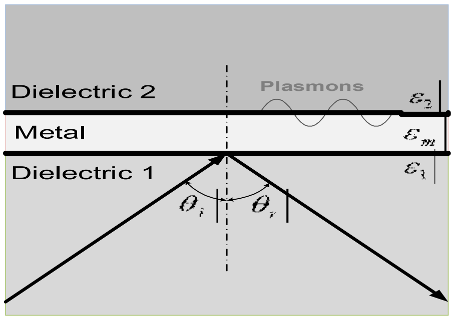


Figure 1. Excitation of surface plasmon at metal-dielectric interface

Coating graphene on the top of metal layer as a BRE is seen as an effective way to improve sensitivity. Several researchers investigated the multilayer graphene based SPR sensor, which typically used 50 nm gold layer but the effect of gold thickness on the light reflection was highly neglected ref. This work describes comparative sensor studies conducted on characteristics of the reflection curve regarding to the coating bilayer graphene on gold film in conventional SPR sensor.

2. DESIGHN CONSIDERATION AND THEORETICAL MODEL

In recent years, graphene on Au has been fabricated and shows stable adsorption of biomolecule with carbon-based ring structures [11-13]. In comparison with a conventional SPR sensor graphene provides a greater change of refractive near the metal surface. In addition a grapheme coating on the gold surface improves the surface plasmon polariton (SPP) propagation constant and prevents oxidation. The optimal thickness of gold layer to have surface plasmon excitation in Kretschmann configuration in visible range is 50 nanometers. Due to dielectric properties of graphene, the thickness of the gold layer should be optimized to get the best response when the bilayer graphene coated on top of the Au layer.

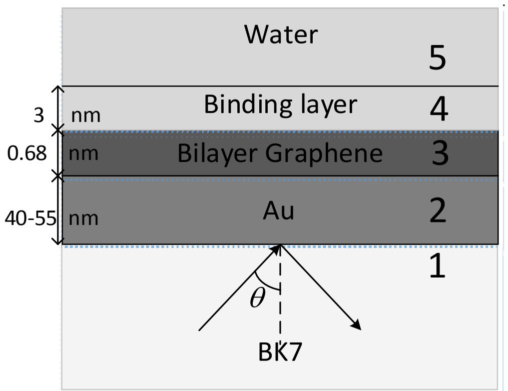


Figure 2. Simple schematic of Kretschmann configuration for gold- bilayer graphene SPR biosensor.

The set up for proposed biosensor is illustrated in figure 2, where the bilayer graphene covers a gold thin film. The other side of gold layer is in contact with BK7 glass. Considering the intensity of light reflected from a N-layer system for a transverse-magnetic incident wave, the total reflection, R, is given by [14]:

$$R=\left|\frac{(M_{11}+M_{12}q_N)q_1-(M_{21}+M_{22}q_N)}{(M_{11}+M_{12}q_N)q_1+(M_{21}+M_{22}q_N)}\right|^2 \quad (1)$$

$$M_{ij}=\left(\prod_{k=2}^{N-1}M_k\right)_{ij} \qquad ,i,j=1,2 \quad (2)$$

$$M_k=\begin{bmatrix}\cos\beta_k & -i\sin\beta_k/q_k\\ -iq_k\sin\beta_k & \cos\beta_k\end{bmatrix} \quad (3)$$

$$q_k=\frac{\sqrt{\varepsilon_k-n_1^2\sin^2\theta}}{\varepsilon_k} \quad (4)$$

$$\beta_k=d_k\left(\frac{2\pi}{\lambda}\right)\sqrt{\varepsilon_k-n_1^2\sin^2\theta} \quad (5)$$

The k_{th} layer, where k is from 2 to $N-1$, has a thickness of d_k and local dielectric function ε_k. The scenario considered uses a gold film with bilayer graphene (d_3) as the BRE. At an initial stage, binding layer of DNA hybridization with 3 nm thickness are modeled as a homogeneous layer with a refractive index of 1.462 in a water medium and the refractive index of water is 1.33 respectively. This values gradually increases with the double-stranded DNA (ds-DNA) corresponded to the refractive index of 1.53 [12].
Graphene can be used as a gapless material or the one have small and large optical gaps. A mixture of graphene with conventional plasmonic nanodevices may offer ultrasensitive chemical sensors and biosensors. It expects that graphene has a very high quantum effectiveness for light–matter interactions [15]. Furthermore, its optical and electrical properties can be altered by doping and gating in conventional plasmonics devices based on noble metals.
Recently, the dielectric function of graphene in the visible range was estimated, which can be useful for accurate prediction of the optical behavior of graphene structures. In our calculation, the bilayer graphene is presumed to be homogeneous and its thickness is equal to d_3=0.68 nm.
Recent studies on transmission of light through graphene membranes revealed a universal opacity constant of graphene (wavelength independent) [16]. By using the Fresnel coefficients calculation framework the refractive index in the visible spectrum is obtained from [17, 18]:

$$n_{Graphene}=3+i(1.8153\times10^6)\lambda_0 \quad (6)$$

where λ0 is the free space wavelength.
The π-stacking interaction between carbon-based hexagonal structure of graphene with carbon-based ring biomolecule such as single-stranded DNA is the key factor for high adsorption efficiency of graphene. The impermeability of graphene is another reason to functionalize gold surface by graphene layer which is protect gold surface from oxidation [19, 20].

The sensitivity (S) can be defined by relation between the sensor output, θ, angle of incidence light, and the moles of biomolecules in the water, M [21]:

$$S=\frac{\Delta\theta}{\Delta M}=\frac{\Delta\theta}{\Delta n}\times\frac{\Delta n}{\Delta M}=S_nE \quad (7)$$

Where Δn is the change in refractive index of biding layer.
The graphene surface is a better absorber of biomolecules, due to the π-stacking interactions between graphene's hexagonal cells and the carbon-based ring structures in biomolecules [22, 23]. The enhanced adsorption efficiency of biomolecules is given by:

$$E_{Graphene}=A.E_{conventional} \quad \text{(where A>1)} \quad (8)$$

A is coefficient of adsorption efficiency. The exact value of adsorption efficiency requires experimental measurement.

3. RESULT AND DISCUSSION

Figure 3 shows the reflection, transmission and absorption via MATLAB simulation for a gold-graphene structure. The free electrons at metal surface can be excited by p-polarized incident light. It depicts that the SPR occurs in total internal reflection condition. So the SPR angle is always greater than critical angle. It is worth considering that a binding layer with refractive index 1.462 is applied on top of the bilayer graphene.

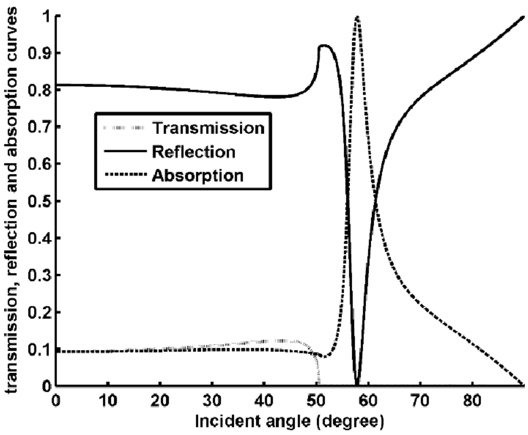
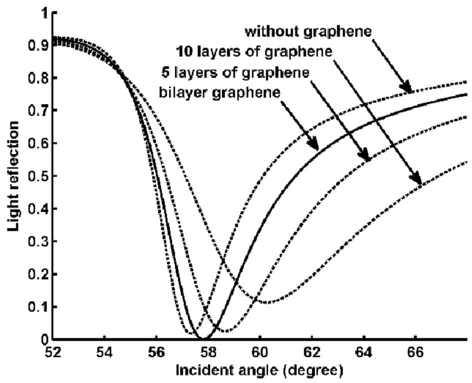
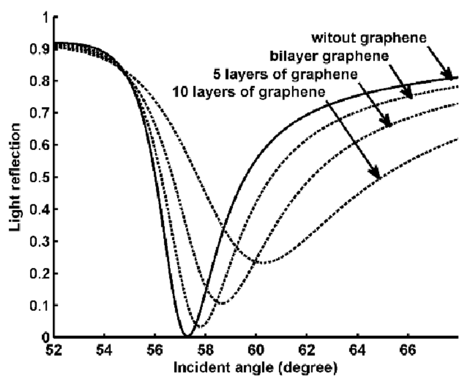


Figure 3. Reflection, transmission and absorption of light in Kretschmann structure by P-polarized incident light for 45 nm gold underlying bilayer graphene.



a)



b)

Figure 4. SPR curves for multilayer graphene on top of the a) 45 nm and b) 50 nm gold.

The angle at which the minimum reflection (also referred as SPR dip) occurs is known as resonance angle. Other researchers concluded that with an increase in graphene layers on top of 50 nm gold thickness, the SPR curve become wider and the minimum reflection at resonance angle increases respectively as shown in figure 4.b [11]. Figure 4.a illustrates the SPR curve for 45 nanometer gold thickness. The solid line curves indicates the ideal SPR dip with zero reflection for 50nm and 45nm gold. The results are simulated with 2, 5 and ten different graphene layers on the top of gold. These graphs shows that, the SPR curve shifts rightwards and broadens with an increased graphene layer. However the minimum reflection at resonance angle increases gradually for 50 nm gold thin film unlike for 45nm where the minimum reflection at resonance angle is first decreased for first few graphene layers, but then increased showing unpredictable result in SPR dip. The zero reflection at resonance angle occurs for 45 nm gold by applying bilayer graphene which is depicted in figure 4.a by solid black line.

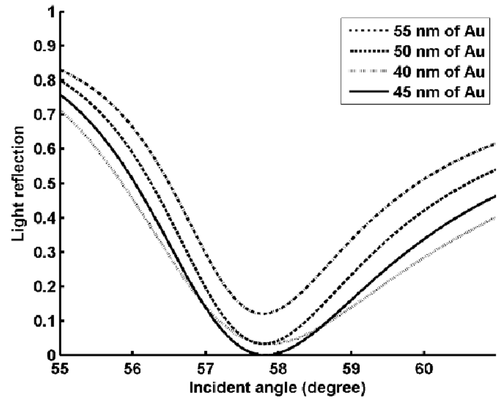


Figure 5. Reflection of light for different gold thicknesses in gold-bilayer graphene SPR biosensor.

It is illustrated in figure 5 that the variation of gold thickness mostly effects on light reflection value at resonance angle. It shows that the SPR angle is slightly depends on gold thickness. The sharpest SPR curve along with the zero reflection at resonance angle occurred by coating the bilayer graphene on 45 nanometers of gold film.

The SPR curves for 45 and 50 nm of gold coating bilayer graphene shows better response as compared to the other thicknesses of gold layer underlying bilayer graphene. In 40 nm gold, the resonance angle and minimum reflection is as same as the SPR angle and reflection to that of 50 nm gold but with wider SPR curve. We analyzed the sensitivity of gold-bilayer graphene by using 45 and 50 nm of gold due to their better SPR curve depicted in figure 5.

The sensitivities among bilayer graphene on gold and conventional gold substrates with two different thicknesses of gold layer is studied by considering a change in the SPR angle. This change occurred with the increase in refractive index of the binding layer in agreement to the adsorbed analytes. Not only this it had but the refractive index of water changes itself as well due to the presence of analytes solution in it.

Due to the graphene properties, the adsorption efficiency, E, enhances as graphene layer is covered on the gold thin film. Beside this the application of the graphene layer will modify the sensitivity to refractive index change as was reported by Wu et al [11].

The SPR curves for two different thicknesses of gold film in conventional biosensor and the gold-bilayer graphene biosensor for He-Ne laser incident light (λ=633 nm) is simulated via MATLAB to analyze the sensitivity to refractive index change. The structure include prism (n_1= *1.723*) | Au (d_2= *45, 50 nm*, n_2= *0.1726 + i3.4218*) | bilayer graphene (d_3= *0.68 nm*, n_3= *3 + i 1.149106*) | binding layer (d_4=*3 nm*, n_4= *1.462*) | water (n_5= *1.33*), assuming the same refractive index change in binding layer Δn_4=0.068 and water Δn_5=0.005 after adsorption of biomolecules in both conventional and graphene based structure.

Based on the N-layer model using transfer matrix, SPR curves are simulated for the conventional biosensor using 50 nm gold as the metal layer and the gold-bilayer graphene biosensor. The resonance angle calculated in SPR curve before and after the adsorption of biomolecules, assuming that the same refractive index change is Δn_4= 0.068 for 3 nm of binding layer. The SPR curve by adding bilayer graphene on top of the 50 nm gold film is shifted up and rightward compare to conventional 50 nm gold. But it shifted down and rightward compare to conventional structure for 45 nm gold respectively. It is an interesting result that in conventional SPR biosensor, the value of minimum reflection at resonance angle for 50 nm gold is smaller than that of the 45 nm gold but in gold-bilayer graphene structure, the value of minimum reflection at resonance angle for 50 nm gold is greater than the 45 nm gold. The resonance angle (SPR angle) for conventional structure and graphene based structure is slightly change by variation of gold thickness. The minimum reflection at resonance angle in conventional structure is changed slightly for different gold thickness but it changed dramatically in graphene based structure considering the gold thickness variation.

The biomolecules adsorption cause a SPR shift towards a larger SPR angle due to an increase in the refractive index of sensing medium. For example, a 0.38 SPR angle shift due to biomolecule adsorption in conventional SPR biosensor give the 5.588 value for sensitivity to refractive index change with the use of 50 nm gold. Furthermore a shift of 0.39 and 5.735 sensitivity to refractive index change by coating bilayer graphene on 50 nm gold. The results are summarized in Table 1 where the sensitivity with bilayer graphene on 45 nm gold almost double as compared to that for 50 nm gold with reference to the conventional SPR biosensor.

Table 1: sensitivity enhancement by using bilayer graphene on 45 and 50 nm gold thin film.

Au [nm]	Graphene [nm]	θ_{SPR} [deg] Before adsorption	θ_{SPR} [deg] After adsorption	$\Delta\theta$	S_n	$\frac{\Delta S_n}{S_n^0}$ (%)
50	0	57	57.38	0.38	5.588	------
	0.68	57.49	57.88	0.39	5.735	2.63 %
45	0	57.04	57.42	0.38	5.588	------
	0.68	57.51	57.91	0.4	5.882	5.5 %

It is found that coating bilayer graphene on different thickness of gold film can modify the sensitivity. The sensitivity enhancement can be as high as 2.63% for bilayer graphene on 50 nm gold and 5.5% for 45 nm gold. Based on our calculations, it indicates that the sensitivity is enhanced for 50 nm gold thickness by the factor of (1+0.0263)*A*, where *A* is a coefficient of adsorption efficiency. It has been reported that A can reach up to a value of 4 [11], giving a 4.1052 times increase in sensitivity for bilayer graphene and 4.22 times for 45 nm gold. So by comparing the sensitivity for different gold thicknesses, we can conclude that by using 45 nm Au-bilayer graphene biosensor, the sensitivity can be enhanced by about 3% as compared to the same structure of biosensor with 50 nm gold thickness.

The major outcome for this simulation is the effect of bilayer graphene on sensitivity of SPR sensor. It should be noted that adding more graphene layers on top of the gold layer with any thicknesses will broaden the SPR curves, which may cause difficulties in a SPR measurement. So there is a thickness limitation to use graphene on top of the metal layer.

4. CONCLUSION

This paper presented sensitivity enhancement considering zero reflection at resonance angle for Au-bilayer graphene SPR biosensor. The shift of plasmon dip can be controlled by changing the thickness of gold layer with respect to the increased number of graphene layers in order to sensitivity improvement. Based on the numerical results, it is confirmed that the SPR angle is slightly depends on gold thickness but it is increased dramatically with increasing of graphene thickness. The variation of gold thickness mostly effects on minimum reflection at resonance angle. We conclude that even if the 50 nm gold in conventional structure has a better response with zero reflection compare to 45 nm gold but by covering bilayer graphene on top of gold film, the sensitivity to refractive index change in 45 nm gold is greater than the 50 nm gold.

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