BHAVSAR, K. and PRABHU, R. 2019. Investigations on sensitivity enhancement of SPR biosensor using tunable wavelength and graphene layers. *IOP conference series: materials science and engineering* [online], 499, article number 012008. Available from: https://doi.org/10.1088/1757-899x/499/1/012008
Originally presented at 4th International conference on structural nanocomposites (*NANOSTRUC 2018*), 23-24 May 2018, Berlin, Germany.

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2019

IOP Conference Series: Materials Science and Engineering

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To cite this article: K Bhavsar and R Prabhu 2019 *IOP Conf. Ser.: Mater. Sci. Eng.* **499** 012008

4th International Conference on Structural NanoComposites (NANOSTRUC2018) IOP Publishing
IOP Conf. Series: Materials Science and Engineering **499** (2019) 012008 doi:10.1088/1757-899X/499/1/012008

Investigations on sensitivity enhancement of SPR biosensor using tunable wavelength and graphene layers

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Abstract. Surface plasmon resonance (SPR) is a well-known, rapid and sensitive technique used for probing the biomolecular interactions in real time. Several new approaches have been suggested to improve the sensitivity of SPR sensors over the last two decades. Recently, there have been few reports on using graphene on a metal film based SPR sensor in order to improve the sensitivity. The role of incident light wavelength and graphene layers in sensitivity enhancement is unclear. This paper reports computational investigations on sensitivity enhancement of SPR biosensor using tunable wavelength and graphene layers. The reflectivity of p-polarized incident light has been calculated using the N-layer model for the most common Kretschmann configuration. Sensitivity enhancements over a conventional angular interrogated SPR sensor have been calculated within the wavelength range 600 -1600 nm and up to ten graphene layers. Results indicate that the sensitivity can be enhanced by the increasing the graphene layers on conventional gold coating based SPR biosensor. Sensitivity enhancement is highly dominated by the wavelength of interrogation used in this design. By tuning the wavelength and graphene layers sensitivity of the graphene-based SPR biosensor can be increased.

1. Introduction

The Surface Plasmon Resonance (SPR) is a rapid and sensitive technique used for probing the biomolecular interactions in real-time [1]. Potential of this technique is due to its very high sensitivity towards the change in refractive index of sensing medium, which occurs through adsorption or binding of biomolecules and their concentration. Typical conventional SPR biosensors include a thin metal film coated on a prism isolating the sensing medium from the prism. Most commonly, a thin gold film is used in SPR sensors because of the stable optical and chemical properties and as it supports the propagation of surface plasmon polaritons (SPP) in the visible wavelength range [1]. However, adsorption of biomolecules on the gold surface is very poor which limits the sensitivity of the SPR biosensors. Several new approaches have been suggested to improve the sensitivity of SPR sensors over the last two decades using different configurations and materials [2-4].

Graphene, a single layer of carbon atoms arranged in a honeycomb structure, is emerging as the most popular material of the decade which is under intense research [5,6]. Graphene has a very high surface-to-volume ratio and strong binding/adsorption affinity towards biomolecules due to its carbon ring structure from π-π stacking interactions [7]. Graphene-based electrochemical sensor has also been reported higher sensitivity for the detection of pharmaceutical drugs [8]. Recently, there have been few reports on using graphene on a metal film to improve the sensitivity [9]. Graphene offers several advantages over the conventional SPR sensing. The very high surface–to-volume ratio offered by graphene is expected to give higher adsorption efficiency compared to gold. Also, the adsorption of biomolecules on graphene is higher because of the carbon ring-based structure providing π-π interactions [7] and can be integrated with microfluidic chip based SPR sensors [10]. But, the role of wavelength on the sensitivity of the graphene-based SPR biosensors has not been investigated. Factors such as penetration depths of the electric field into the dielectric and the metal, propagation length of surface plasmon polaritons depend on the wavelength of incidence light and therefore, the wavelength of incident light plays a very crucial role in the design of SPR sensors [11]. Herein, we report computational investigations on sensitivity enhancement of SPR biosensor using tunable wavelength and graphene layers. The reflectivity of the p-polarized incident light has been calculated using the N-layer model for the most common Kretschmann configuration in the range of 600-1600 nm and up to 10 layers of graphene. Obtained results show that graphene layer increases the sensitivity of the conventional SPR sensor, irrespective of the wavelength of light within the range. However, wavelength-based sensitivity enhancement results show that wavelength plays the dominant role in sensitivity enhancement in this sensor design configuration. By tuning the wavelength and graphene layers, a sensitivity of the graphene-based SPR biosensor can be further increased.

2. Theory

Figure 1 shows the graphene surface plasmon resonance sensor configuration, where the first layer is SF11 glass prism with refractive index n_1. The second and third layers are gold and graphene coatings followed by a sensing aqueous medium. An incident light beam propagating through the prism undergoes total internal reflection at the prism-gold layer interface, generating an evanescent wave. This generated evanescent wave penetrates through the 50 nm gold layer and propagates in the x-direction. The magnitude of propagating wave vector in the x-direction can be expressed as [12],

$$k_x = \frac{2\pi n_1}{\lambda}\sin\theta \tag{1}$$

Propagation vector of surface plasmon involves the refractive index of gold, n_2 and the sensing medium, n_3 because the wave propagation at the metal-surrounding medium interface occurs partly in both the material. Therefore, the surface plasmon propagation vector, k_{sp} can be defined as [12],

$$k_{sp} = \frac{2\pi}{\lambda}\sqrt{\frac{n_2^2 n_3^2}{n_2^2+n_3^2}} \tag{2}$$

The SPP can be excited by adjusting the incident angle θ, so that the propagation vector of the evanescent field, k_x, matches with the k_{sp}. Therefore, when this condition satisfies $k_x = k_{sp}$, reflected light intensity drops sharply. The reflectivity curve at this resonance condition referred as SPR curve and the angle corresponding to reflectivity minimum referred as SPR angle. The reflectivity of the p-polarized incident light has been calculated using the N-layer model for the most common Kretschmann configuration [13]. An angular interrogated reflectance of the structure has been calculated using a transfer matrix method [14].

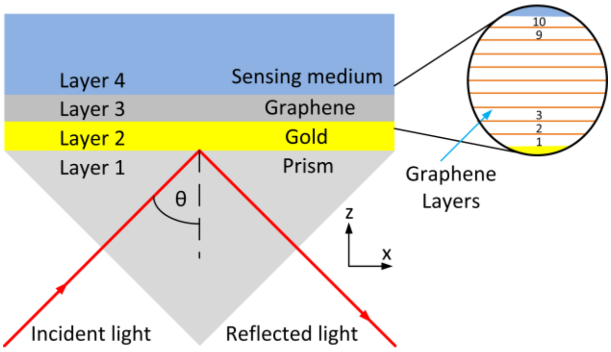

Figure 1. A schematic diagram of graphene-based SPR sensor in Kretschmann configuration.

3. Results and discussions

Reflectance has been calculated for a conventional SPR sensor (L = 0) and a graphene biosensor (L=1 to 10) for the incident p-polarized light, where L is the number of graphene layers. Various parameters used for the calculation are listed in table 1. To analyse the effect of graphene layers on the SPR curve, reflectivity calculations have been carried out for the number of graphene layers, L = 1 to 10. Figure 2(a) shows the calculated reflectance as a function of an angle of incidence. SPR curve shows that an increase in the number of graphene layers causes the shift to the higher plasmonic angles and broadening of the SPR curve. The observed effect can be attributed to the change in thickness and increased absorption of light by the graphene layers where each layer of graphene absorbs 2.3% of light [15].

Table 1. List of parameters used to calculate the reflectance of the graphene-based SPR sensor.

Wavelength	Prism [16]	Gold [17]			Graphene [15,18]		
λ(nm)	n_1	n_2	k_2	d_2(nm)	n_3	k_3	d_3(nm)
633	1.7786	0.1834	3.4332	50	3.0	1.1491	0.34
700	1.7718	0.1310	4.0624	50	3.0	1.2707	0.34
800	1.7646	0.1535	4.9077	50	3.0	1.4523	0.34
900	1.7596	0.1744	5.7227	50	3.0	1.6338	0.34
1000	1.7559	0.2277	6.4731	50	3.0	1.8153	0.34
1550	1.7434	0.5241	10.742	50	3.0	2.8138	0.34

Adsorption or binding of biomolecules and their concentration changes the refractive index near the metal-dielectric (sensing medium) interface. This change in refractive index can be measured as the shift in the SPR angle. Therefore, sensitivity can be assessed based on the change in SPR angle upon a change in refractive index and can be defined by, $S_{RIU}^{L} = \Delta\theta^{L}/\Delta n,$ where RIU is the refractive index unit. Consider that the adsorption of a biomolecule which causes the change in refractive index (Δn = 0.005) resulting in a shift in the SPR angle, $\Delta\theta^{o}$ = 0.352 and therefore, sensitivity can be expressed as $S_{RIU}^{0} = \Delta\theta^{o}/\Delta n$ = 70.4 for a conventional SPR sensor (L = 0). A shift of $\Delta\theta^{1}$ = 0.355 has been observed for a monolayer graphene coated SPR sensor leading to the sensitivity $S_{RIU}^{1} = \Delta\theta^{1}/\Delta n = 71$. In order to analyse the sensitivity enhancement over a conventional SPR sensor, $\Delta S_{RIU}^{L} = S_{RIU}^{L} - S_{RIU}^{0}$ has been calculated as a function of the number of graphene layers. Sensitivity enhancement has been plotted as a function of graphene layers, L = 1 to 10, as $\Delta S_{RIU}^{L}/S_{RIU}^{0}$ as shown in figure 2(b) at 633 nm. Results indicate that increasing the graphene layers has increased the sensitivity. The observed sensitivity enhancement can be attributed to the optical properties of graphene [14].

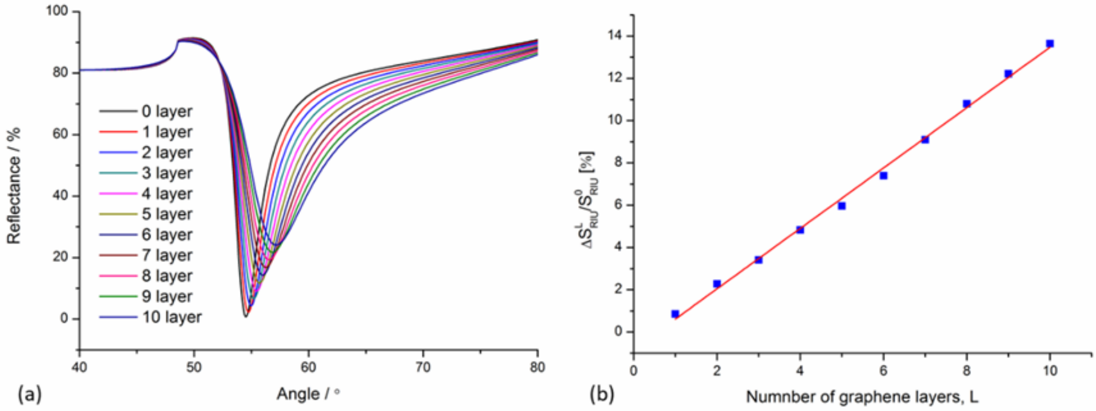

Figure 2. Reflectivity curve of the graphene-based SPR sensor with increasing number of graphene layers L at λ = 633 nm. (b) Sensitivity enhancement $\Delta S_{RIU}^{L}/S_{RIU}^{0}$ with graphene layers over a conventional SPR biosensor.

In order to analyze the wavelength effect on graphene-based SPR sensor, relative sensitivity enhancements over the conventional SPR sensor have been calculated for various wavelengths. Figure 3(a) shows the calculated relative sensitivity enhancement as a function of graphene layers. Results show that for all the incident light wavelengths in the range of 600-1600 nm, sensitivity enhancements were observed with increasing number of graphene layers. However, there is no significant enhancement observed when wavelength was increased to 1550 nm. The observed sensitivity enhancement can be attributed to the optical constant of the graphene. Further, sensitivity has been evaluated as a function of wavelength with the number of graphene layers. Figure 3(b) shows the plot of sensitivity versus incident light wavelength for the number of graphene layers. It was observed that increase in the wavelength from 600 nm to 1600 nm decreases the sensitivity. However, irrespective of the wavelength, each additional graphene layer causes the increase in the sensitivity up to 10 layers. Obtained results suggest the sensitivity enhancement was highly dominated by the interrogated light wavelength. The dominance effect was due to the optical properties of the base metal gold where the imaginary part of the dielectric constant of gold increases with decreasing wavelength.

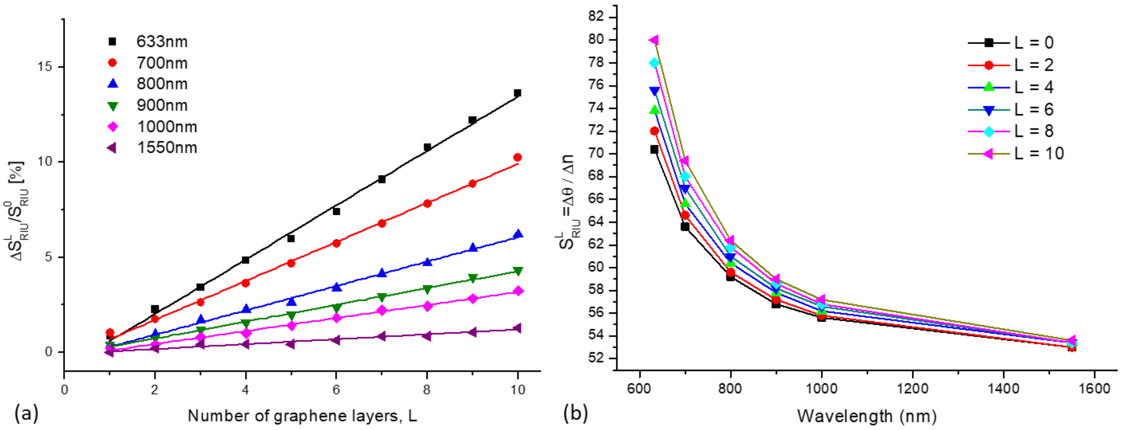

Figure 3. (a) Relative sensitivity enhancement $\Delta S_{RIU}^L/S_{RIU}^0$ with number graphene layers at various incident light wavelengths and (b) calculated sensitivity as a function of wavelength with graphene layers.

4. Conclusion

Investigations on the sensitivity enhancement of SPR biosensor has been carried out using an angular interrogated method. Computational results show that graphene increases the sensitivity of the conventional SPR sensor in the range of 600-1600 nm. Relative sensitivity enhancement has been calculated (up to 10 graphene layers) over a conventional SPR sensor. Obtained results show that increase in the number of graphene layers enhances the sensitivity. Further, wavelength-based sensitivity study shows that by tuning the wavelength, sensitivity of the graphene-based SPR biosensor can be increased and the sensitivity enhancement is mainly dominated by the wavelength of interrogation for the graphene-based SPR biosensor in this design. These investigations have opened up new possibilities for the real-time monitoring of highly sensitive biomolecular interactions studies using graphene and wavelength of interrogation tunability.

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