AUTHOR(S): BHAVSAR, K., PRABHU, R. and POLLARD, P.

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Ultrasensitive graphene coated SPR sensor for biosensing applications

K. Bhavsar, R. Prabhu*, P. Pollard
IDEAS Research Institute, Robert Gordon University, Aberdeen, UK

ABSTRACT

Surface plasmon resonance (SPR) is a 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. Most of them are based on creating or patterning nanostructures/nanomaterials in order to enhance the sensitivity. Graphene offers several advantages due to its special optical and structural properties. Herein, we propose a new angular interrogated dual wavelength based differential detection approach for graphene based SPR sensing to increase the sensitivity. Reflectivity of the p-polarized incident light has been calculated using the N-layer model for the most common Kretschmann configuration. Sensitivity of the SPR with and without graphene layers has been calculated for single and dual wavelength based approaches. Computational results show that the proposed graphene SPR sensor has $(1 + 0.4\,L)\,\eta$ times higher sensitivity than the conventional gold thin film based SPR sensors. Further, increasing the number of graphene layers, L, improves the sensitivity. Where, η represents the enhanced sensitivity due to increased binding/adsorption of biomolecules on graphene over a gold thin film. Sensitivity analysis has been carried out for a refractive index $(\Delta n) = 0.005$ with L = 1 to 10.

Keywords: Surface plasmon resonance, graphene, optical sensors, plasmonic sensors

1. INTRODUCTION

Surface plasmon resonance (SPR) is an optical technique emerging as an essential analytic tool to study the biomolecular interactions. The potential of this technique is the very high sensitivity towards the change in refractive index of sensing medium, which occurs through adsorption or binding of biomolecules and their concentrations. 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 it supports the propagation of surface plasmon polaritons (SPP) in visible wavelength range[1]. However, adsorption of biomolecules on gold 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[2,3]. Most of them are based on creating nanoparticles[4], nanowires[5], nanorings[6] nanoholes[2] and nanoslits[7] on the metal surface to enhance the localized E-field and therefore, it is quite challenging to have control over their optical properties[8].

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[9-12]. 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[10,13,14]. Recently, there have been a few reports on using the graphene on thin metal film based SPR sensor in order to improve the sensitivity[15]. 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[16]. Small mechanical vibrations and temperature variations become limiting factors in monitoring slower adsorption processes at very high resolution and sensitivity[17]. In such cases, this may be overcome by using a reference signal. In most cases the SPR signal from the adsorption and binding events near the metal-solution interface are affected by any change in the bulk solution. Angular interrogation mode and dual wavelength based detection approach could avoid such problems by using another signal from longer (near infrared) wavelength. The E-field penetration depth of longer wavelengths is high; therefore, signal can penetrate longer into the bulk solution and allows differentiating surface and bulk effects[18].

Herein, we have exploited a graphene coated SPR biosensor to enhance the sensitivity of conventional SPR biosensors. The effect of graphene on the sensitivity of conventional SPR sensors has been analysed for a single wavelength based differential detection approach. Results on the sensitivity enhancement with increasing the number of graphene layers have been presented and discussed. Reflectivity of the p-polarized incident light has been calculated using the N-layer

*r.prabhu@rgu.ac.uk

model for the most common Kretschmann configuration. Sensitivity of the SPR with and without a graphene layer has been calculated for a single and dual wavelength based differential approaches. Computational results show that the proposed graphene SPR biosensor using the dual wavelength based differential approach has higher sensitivity than the conventional graphene based SPR biosensor and it increases as the number of graphene layers increases. The proposed sensor could possibly eliminate/minimize the problems of thermal drift, mechanical vibrations, noise and bulk solution refractive index change.

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. A propagating light through the prism undergoes total internal reflection at the prism-gold layer interface, generating an evanescent wave. This generated evanescent wave penetrates through the 50nm gold layer and propagates in the x direction. The magnitude of propagation vector in the x direction can be expressed as[19],

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

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[19],

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

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. Reflectivity of the p-polarized incident light has been calculated using the N-layer model for the most common Kretschmann configuration[20].

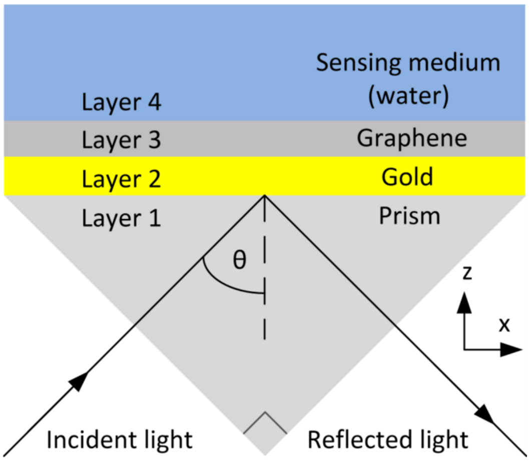

Figure 1. A schematic diagram of graphene based SPR sensor in Kretschmann configuration.

Using a transfer matrix method, the reflectivity calculation has been carried out for N-layered structure, where the m^{th} layer of thickness d_m, has a complex refractive index $n_{m,c} = n_m - ik_m$. The interference matrix of m^{th} layer can be expressed as[21],

$$M_m = \begin{bmatrix} M_{11} & M_{12} \\ M_{21} & M_{22} \end{bmatrix} = \begin{bmatrix} cos\beta_m & -i\ sin\beta_m/q_m \\ -iq_m sin\beta_m & cos\beta_m \end{bmatrix} \quad (3)$$

Where,

$$q_m = \frac{(\varepsilon_m - {n_1}^2 sin^2\theta)^{1/2}}{\varepsilon_m} \quad (4)$$

$$\beta_m = d_m\left(\frac{2\pi}{\lambda}\right)(\varepsilon_m - {n_1}^2 sin^2\theta)^{1/2} \quad (5)$$

The total interference matrix of the whole N-layered system can be obtained by[21],

$$M = \prod_{m=1}^{N} M_m$$

Reflectance, R, of the N-layer stack can be obtained by[21],

$$R = \left|\frac{(M_{11}+M_{12}q_N)q_1-(M_{21}+M_{22}q_N)}{(M_{11}+M_{12}q_N)q_1+(M_{21}+M_{22}q_N)}\right|^2 \quad (6)$$

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 incidence p-polarized light, where L is the number of graphene layers. Various parameters used for the calculation are listed in table 1. Adsorption or binding of biomolecules and their concentration changes the refractive index near the metal-dielectric (sensing medium) interface. This change in refractive index modifies the propagation constant of SPP and can be measured as shift in the SPR angle. Therefore, sensitivity can be assessed based on the change in SPR angle upon change in refractive index and can be defined by, $S = \Delta\theta_{SPR}/\Delta n$. For the further sensitivity calculations in this paper, $\Delta\theta_{SPR} = \Delta\theta$. For a graphene coated SPR sensor, sensitivity with number of graphene layers can be defined by, $S^L = \Delta\theta^L/\Delta n$, where L is the number of graphene layers. A unique structural property of graphene allows the higher and strong adsorption of biomolecules compared to the gold surface[16]. The enhanced adsorption efficiency of graphene, referred to as η, over the conventional SPR sensors can be related to the sensitivity enhancement as, $S_{graphene} = \eta \times S_{conventional}$, where, $\eta > 1$. In order to access the effect of graphene on the SPR curve, the optical properties of the graphene needs to be known. The complex refractive index, n_3, of graphene is expressed as[22]:

$$n_3 = 3.0 + i\frac{C}{3}\lambda \quad (7)$$

where, $C \approx 5.446\ \mu m^{-1}$ is the opacity constant[23], and λ is the wavelength in μm. A single layer of graphene has a thickness of 0.34 nm and hence, the thickness of L layers of graphene can be given by $d_3 = 0.34L$[22].

Table 1 List of parameters used to calculate the reflectivity of the graphene coated SPR sensor.

Wavelength	**SF11 Prism**[24]	**Gold**[25]			**Graphene**[22,23]		
λ(nm)	n_1	n_2	k_2	d_2(nm)	n_3	k_3	d_3(nm)
633	1.7786	0.18344	3.4332	50	3	1.14911	0.34L
808	1.7642	0.15598	4.9741	50	3	1.46679	0.34L

Figure 2 shows the reflectivity curve for conventional and monolayer graphene coated SPR before and after adsorption of biomolecules. Consider that the adsorption of a biomolecule causes the change in refractive index ($\Delta n = 0.005$) which in turn causes the shift towards the larger SPR angle. For example, adsorption of a biomolecule causes 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. A shift of $\Delta\theta^1 = 0.355$ has been observed for a monolayer graphene coated SPR sensor leading to the sensitivity $S_{RIU}{}^1 = \Delta\theta^1/\Delta n = 71$. The SPR angle shift and sensitivity results indicate that the graphene coated SPR sensor has a higher sensitivity.

To analyse the effect of multi-layers of graphene on the sensitivity, reflectivity calculations have been carried out for the number of graphene layers, L = 1 to 10. A single layer of graphene absorbs 2.3% of light and each additional layer absorbs the same amount of light[23]. Therefore, as increase in the number of graphene layers causes the shift to the higher plasmonic angles and broadening of the SPR curve. 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 3. Results indicate that increasing the graphene layers has increased the sensitivity.

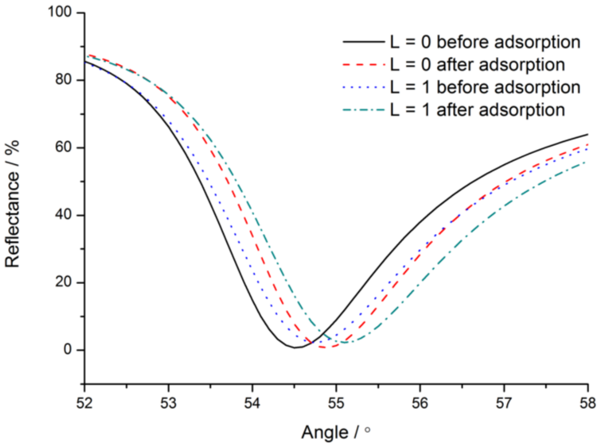

Figure 2. Reflectivity curve of the SPR sensor with and without a monolayer graphene before and after the adsorption of biomolecules.

The observed sensitivity enhancement can be attributed to the optical properties of graphene. The refractive index of graphene at 633 nm is $n_3 = 3 + i1.1491$. Therefore, the dielectric constant of graphene is $\varepsilon_3 = 7.6796 + i6.8946$. An increase in the number of graphene layers modifies the SPP in such a way that change in the SPR angle led to enhanced sensitivity. Graphene has a refractive index of $n_3 = 3 + i1.46679$ at 808 nm. Therefore, the dielectric constant of graphene is $\varepsilon_3 = 6.8485 + i8.8008$ which indicates that graphene is a dielectric material at 808 nm. Therefore, the angular interrogated dual wavelength based differential signal detection using graphene coated SPR biosensor can provide substantial increase in the sensitivity and will minimize the measurement errors.

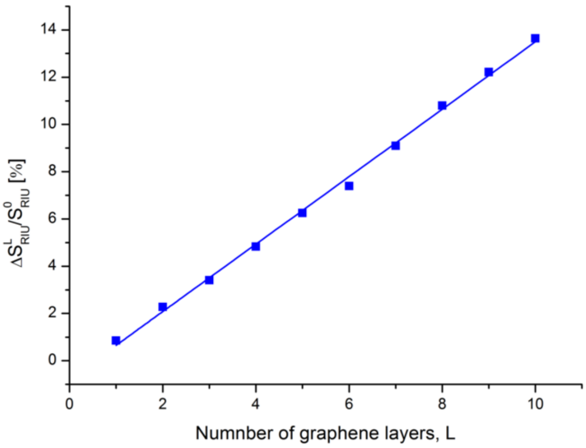

Figure 3. Sensitivity enhancement $\Delta S_{RIU}^{L}/S_{RIU}^{0}$ with grapheme layers over a conventional SPR.

Figure 4(a) shows the proposed detection configuration for the graphene coated SPR biosensor, where the gold thin film (50nm) coated on the SF11 glass prism has been divided into two regions, sensing area and reference area. The sensing area has been coated with graphene layers varying from L = 1 to 10. Laser diodes with emission wavelengths of 633 nm and 808 nm have been used to excite the surface plasmon. Reflected signals from sensing area, A (633nm) and B (808nm), and reference area, C (633nm) and D (808nm), have been detected on CCD camera simultaneously. The shift in the SPR angles have been calculated for differential signal[17], (A - B)/(A + B) and (C - D)/(C + D), respectively, before and after the adsorption of biomolecule.

The SPR angle shift resulting from the adsorption of biomolecule has been calculated as $\Delta\theta^L = (\Delta\theta_A - \Delta\theta_B)/(\Delta\theta_A + \Delta\theta_B)$ and $\Delta\theta^0 = (\Delta\theta_C - \Delta\theta_D)/(\Delta\theta_C + \Delta\theta_D)$, where, L = 1 to10. The sensitivity enhancement of this new approach has been calculated in the same way, where $\Delta S_{RIU}{}^L = S_{RIU}{}^L - S_{RIU}{}^0$ has been calculated as a function of the number of graphene layers. The sensitivity enhancement over the conventional SPR sensor, $\Delta S_{RIU}{}^L/S_{RIU}{}^0$, has been plotted as a function of graphene layers, L = 1 to 10, as shown in figure 4(b). Results indicate that an increase in the number of graphene layers can provide increased sensitivity. For 10 layers of graphene, the sensitivity enhancement $\Delta S_{RIU}{}^L/S_{RIU}{}^0$ can be as high as 40%. The observed sensitivity enhancement can be attributed to the graphene optical properties. However, increasing the graphene layers will broaden the SPR curve and may create difficulties in the detection, therefore, we have restricted the work to the 10 layers of graphene.

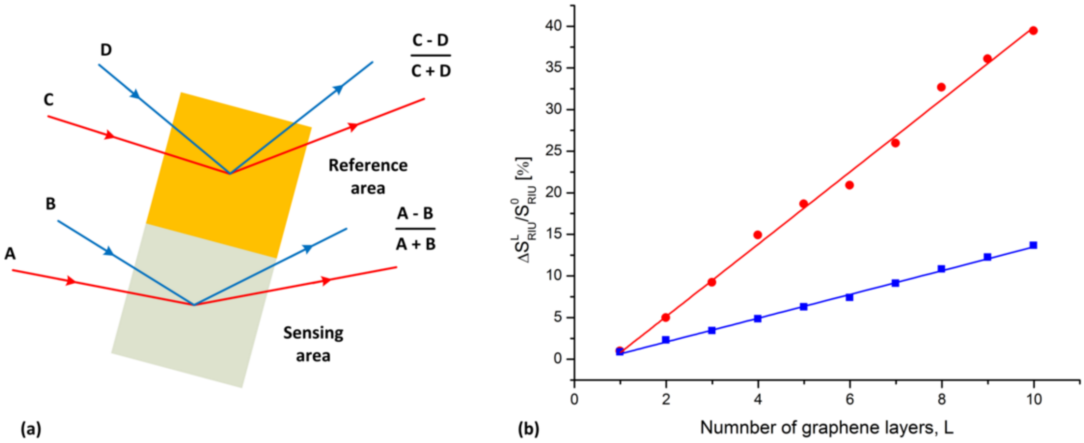

Figure 4 (a) Shows the setup for the sensitivity analysis of angular interrogated dual wavelength based differential SPR sensor. (b) SPR sensitivity enhancement $\Delta S_{RIU}{}^L/S_{RIU}{}^0$ as a function of graphene layers for conventional and the proposed graphene based SPR biosensors.

4. SUMMARY

An angular interrogated dual wavelength based differential detection approach has been proposed using a graphene based SPR biosensor to achieve the ultra-high sensitivity. Proposed graphene coated SPR biosensor has shown increased sensitivity by (1+ 0.4 L) η times. Consider that graphene can adsorb 2 times (η = 2) more biomolecules, the sensitivity enhancement for L=10 will be a factor of 10. The increased sensitivity can be attributed to the properties of the graphene and the proposed detection approach. In addition to the higher sensitivity, the proposed sensor is less sensitive to noise signals and compensates for thermal drift, mechanical vibrations and bulk solution refractive index changes. The proposed sensor presented here can be relatively simple to realize in practice.

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