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AN ENHANCED SENSITIVE GRAPHENE-BASED SPR BIOSENSOR WITH ANGULAR MODULATION

Hamid Toloue A. T. and Anthony Centeno Nano Ikohza
Malaysia- Japan International Institute of Technology Universiti Teknologi Malaysia Kuala Lumpur, Malaysia
E-Mail: h.toloue@gmail.com

ABSTRACT

This paper theoretically presents an improved sensitive surface plasmon resonance (SPR) biosensor using multilayer graphene with angular modulation. Metal thin film functionalization with graphene leads to an enhanced sensitive biosensor. This is due to pi-stacking interaction between carbon-based hexagonal structure of graphene and carbon-based ring biomolecules which increase biomolecule adsorption in the graphene layers. In comparison to conventional SPR sensors this produces a large change in the local refractive index at the sensor surface. The light reflection coupled into a SPR mode propagating along a silver-graphene interface is calculated and compared to a conventional silver-based SPR biosensor. The comparison result shows the improvement in sensitivity of biosensor.

Keywords: surface plasmon resonance, biosensor, graphene, silver.

INTRODUCTION

In the last two decades there has been much investigation and improvement of optical biosensors and biochips. Such instruments hold much potential for different types of application in areas such as proteomics, pharmacogenomics, medical diagnostics, environmental monitoring, food safety, agriculture and security demonstrated by recent scientific and technological advances. Consequently, a wide variety of biosensors based on different detection techniques has been studied [1-3].

A unique technology is presented by a kind of optical biosensors which is label free. It is possible to make direct observation of molecular interaction in real-time. Binding-induced refractive index variations are measured by optical label free biosensors and they are typically based on metal-dielectric waveguides such as surface plasmon resonance (SPR) biosensor [4].

SPR sensor is fundamentally based on surface plasmon (SP) waves. SP waves propagate along the surface of noble metals such as gold, copper and silver at the metal-dielectric interface in the visible range of light spectrum. In a conventional SPR sensor, a thin noble metal film is sandwiched between two dielectrics, as shown in Figure-1. Silver and copper surfaces generally oxidize quickly and gold is a weak biomolecule absorber. Weak molecular adsorptions of metal and oxidation layer on top of the metal surface are two main reasons which restrict the sensitivity of the sensor.

SPR sensors can be classified by coupling wavelength, coupling angle, and intensity, phase, or polarization changes. A laser wave excites SP wave in the SPR sensors based on angular interrogation. The strength of coupling between the SP wave and the incident wave can be evaluated and measured for several angles of incident light. The strongest coupling of the angle of incident light which has minimum reflection is used as the output of sensor [5].

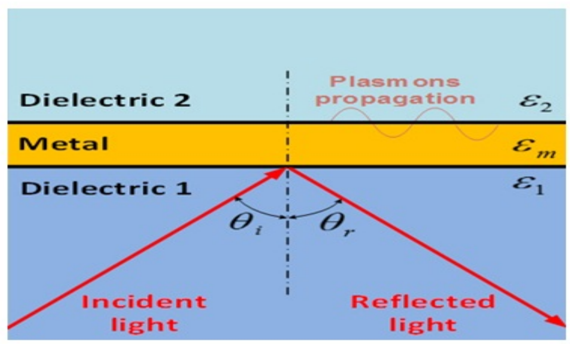

Figure-1. Optical excitation of surface plasmon in dielectric-metal-dielectric structure.

The vast majority of the electromagnetic field of SPs is concentrated in the dielectric which plays the role of the sensing medium. The propagation constant of the SPs is highly sensitive to changes in the relative electric permittivity, or equivalently, the refractive index of dielectric.

The SPR biosensor is known as a very effective optical detection for absorption of biomolecules [6]. This is due to the great change in the excitation angle of SPs which made by local variation of refractive index in sensing medium near the sensor surface.

Numerous techniques have been investigated to improve sensitivity in SPR biosensor such as metallic nanoslits, metal nanoholes and nanoparticles in buffered solution [7, 8]. 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.

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Optical Properties of Graphene in Visible Spectrum

Two dimensional crystals and hybrids such as graphene are now rapidly developing from pure science to technology. Graphene is evolving as a possible alternative to conventional optoelectronic, plasmonic and nanophotonic materials. Graphene could play a significant role in new generation of multilayer optical devices consisting of almost all kinds of optical materials such as dielectrics, semiconductors, semimetals, metals [9]. A mixture of graphene with conventional plasmonic nanodevices may offer ultrasensitive chemical sensors and biosensors. It expects that graphene has very high quantum effectiveness for light–matter interactions. Furthermore, its optical and electrical properties can be altered by doping and gating in conventional plasmonics devices based on noble metals.

Recent studies on transmission of light through graphene membranes revealed a universal opacity constant of graphene (wavelength independent) [10]. By using the Fresnel coefficients calculation framework the refractive index in the visible spectrum is obtained from [11]:

$$n_{Graphene} = 3 + i(1.8153 \times 10^{6})\lambda_0 \quad (1)$$

where λ0 is the free space wavelength.

Biosensing application could improve by several properties of graphene such as high adsorption of biomolecule due to π-stacking interactions, constant absorption in visible to the infrared (IR), SP with high field concentration in IR, low small molecule permeability offering passivation [12, 13].

THEORETICAL MODEL

In this study, a graphene sheet on top of the silver thin film is considered as a BRE which is a good molecule absorber and impermeable to molecules as small as helium. Impermeability of graphene is an important factor to prevent silver surface from oxidation. In recent years, graphene on Au and Ag has been fabricated and shows stable adsorption of biomolecule with carbon-based ring structures [14, 15]. In comparison with a conventional SPR sensor, graphene provides a greater change of refractive index near the metal surface. In addition a graphene coating on the silver surface improves the surface plasmon polariton (SPP) propagation constant.
Considering the intensity of light reflected from a N-layer system shown in Figure-2 for a transverse-magnetic incident wave, the total reflection, R, is given by [16].

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

$$M_{ij} = \left(\prod_{k=2}^{N-1} M_k \right)_{ij}, \; i, j = 1, 2 \quad (3)$$

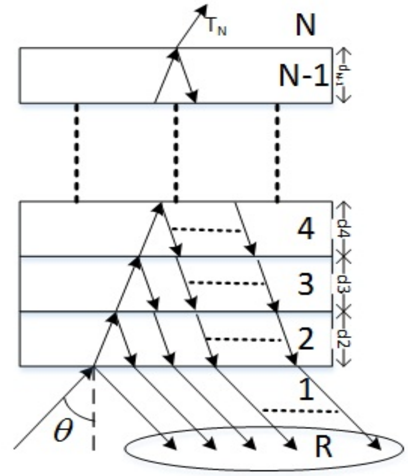

Figure-2. Light reflection for N-layer system.

$$M_k = \begin{bmatrix} \cos\beta_k & -i\sin\beta_k / q_k \\ -iq_k \sin\beta_k & \cos\beta_k \end{bmatrix} \quad (4)$$

$$q_k = \frac{\sqrt{\varepsilon_k - n_1^2 \sin^2\theta}}{\varepsilon_k} \quad (5)$$

$$\beta_k = d_k \left(\frac{2\pi}{\lambda} \right) \sqrt{\varepsilon_k - n_1^2 \sin^2\theta} \quad (6)$$

The kth layer has local dielectric function εk and a thickness of dk where k is from 2 to N-1. In this study we considered a fixed wavelength of 633 nm which is for He-Ne laser. The calculations were carried out for the dielectric function of silver using a Drude-Lorentz model. The scenario considered uses a 56 nm silver thin film with multiple layers of graphene (d4) as the BRE. Thickness of each graphene layer is 0.34 nm. Biomolecule adsorption on sensor surface causes a small local change in water near to the sensor surface. This local change is modeled for 100 nm depth from sensor surface to the sensing medium. This binding layer assumed to have a refractive index of 1.335 in a water medium and the refractive index of water is 1.33.

The set up for silver-graphene SPR biosensor is illustrated in Figure-3, where the graphene layer covers a silver thin film. The other side of silver layer is in contact with titanium as an adhesive layer on top of the SF10 glass. Thickness of the titanium layer is 3 nm and the refractive index of this layer is 2.7+i3.76.

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 [17]:

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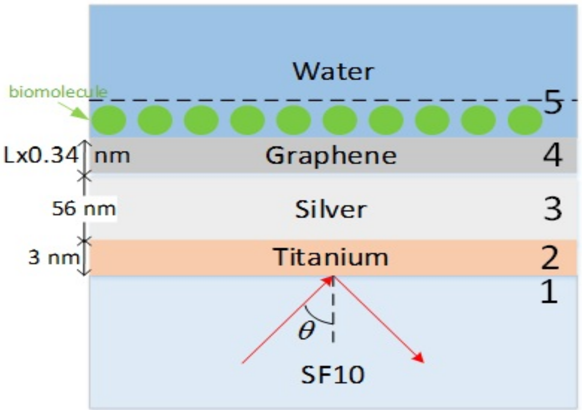

Figure-3. Schematic of silver-graphene SPR biosensor with an adhesive layer.

$$S = \frac{\Delta\theta}{\Delta M} = \frac{\Delta\theta}{\Delta n} \times \frac{\Delta n}{\Delta M} = S_n E \qquad (6)$$

Where Δn is the change in refractive index at the sensor surface.

The enhanced adsorption efficiency of biomolecules by using graphene is given by $E_{Graphene} = A.E_{conventional}$ (where A>1). We should notice the actual value of adsorption efficiency need to be derived from experimental result. The adsorption efficiency is increased by coating graphene on top of the silver surface.

By considering Eq. (7), the total sensitivity will be improved by increasing sensitivity to refractive index change (S_n) for silver-graphene substrate. The local change in refractive index near to sensor surface is assumed to be same (0.005 for 100 nm depth) in conventional and graphene-based structures. It means the sensitivity can be enhanced only if the shift in SPR angle by adding biomolecules on sensor surface in graphene-based is greater than conventional structure.

RESULTS AND DISCUSSIONS

The numerically simulated SPR curves (red graphs) for the conventional biosensor based on silver (solid line) and gold (dashed line) before biomolecule adsorption are shown in Figure-4. The green curves on the other hand show the light absorption and blue graph indicates the transmission of light, respectively. A minimum reflection in red curve is due to the excitation of the SPP. As shown, the SPR occurred in total internal reflection. There is no transmission of light for all the incident angles bigger than 50.7 degree. SPR curve for silver substrate is sharper than gold substrate. Furthermore, the SPR angle and full width at half maximum (FWHM) for silver substrate is less than that of gold substrate. These make silver a much better and more responsive sensor than gold.

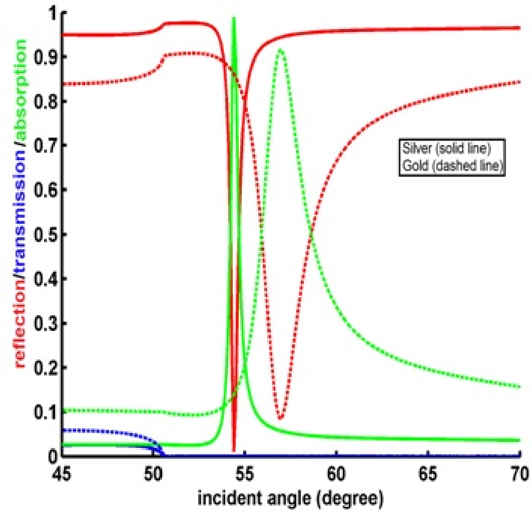

Figure-4. Reflection (red), transmission (blue) and absorption (green) of incident light for gold (dashed line) and silver (solid line) thin films in SPR biosensor.

Figure-5 shows the simulation result of six different SPR curves for the silver-based SPR biosensor with variation in thickness of silver thin film prior to biomolecules adsorption. Silver thickness ranging from 46nm to 59nm with the interval of 3nm in between was applied on the sensor. It was observed that the sharpest SPR curve with zero reflection in SPR angle was obtained for 56 nm of silver.

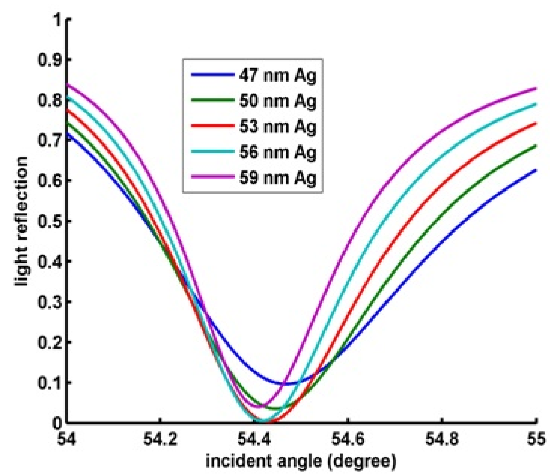

Figure-5. Reflection of light in conventional silver SPR sensor based on Fresnel equation.

By adding the biomolecules on top of the silver surface, refractive index of local area near to the silver surface will be changed causing a shift in the angle of the minima as shown in Figure-6. The incidence angles at minimum point are known as SPR angle.

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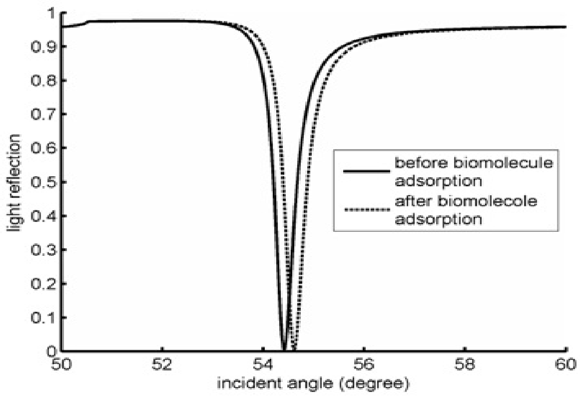

Figure-6. SPR curve before (solid line) and after (dashed line) adding biomolecules in conventional silver-based structure.

It is observed the change in refractive index only causes the shift in SPR angle to the right side of the graph. There are not any other changes in light reflection curve after adding biomolecules because the refractive index of sensing medium is a real number and does not have any imaginary part.

The effect of multilayer graphene in SPR curve is calculated, based on transfer matrix for N-layer Fresnel equation, as shown in Figure-7. It is clearly illustrated that by adding more graphene layers on top of the silver surface, the SPR curve will be broaden, resulting in less sensitivity [18]. Therefore the maximum thickness of the graphene layer to get the desired output should be noticed. The results summarized in Figure-8 shows that the sensitivity to refractive index change enhanced with an increase in number of graphene layers. This is due to greater shift of resonance angle by increasing graphene layers. It occurred because of the larger change in refractive index at sensing medium near to the graphene surface.

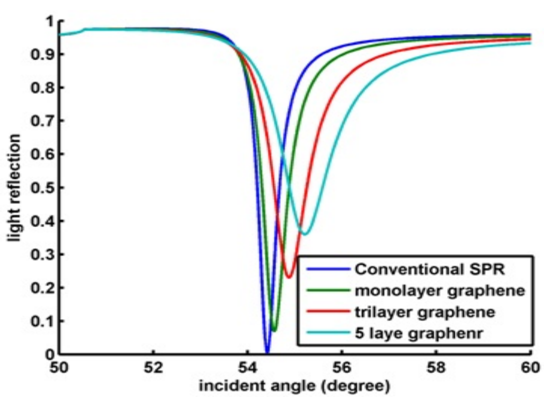

Figure-7. SPR curves for conventional structure and multilayer graphene-based structure.

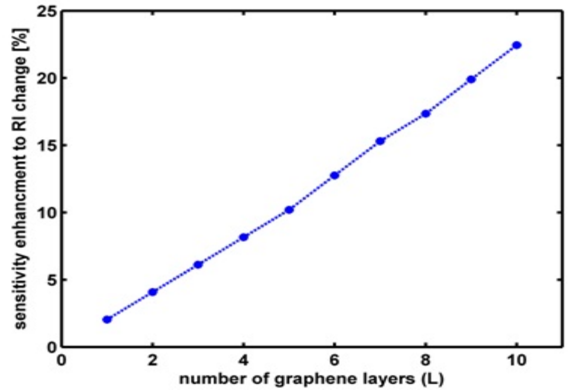

Figure-8. Enhancement in sensitivity to refractive index change for multilayer graphene based SPR biosensor.

The calculations indicated that the sensitivity to refractive index is enhanced by 22.5% for 10 layer of graphene. The sensitivity to local variation in refractive index near to sensor surface can be obtained by the following equation $S_n = 1 + 0.0204N$, where N is the number of graphene layers. The equation is only valid up to 5 layers of graphene. This is due to linearly increment as observed in Figure-8.

CONCLUSIONS

Simulations of the sensitivity for a silver-graphene SPR biosensor have been presented by using MATLAB. The results showed that by adding a graphene layer on silver surface in a SPR biosensor the sensitivity enhanced as compared to that of conventional sensor. This is due to a better adsorption efficiency of graphene and greater change in refractive index of water near the sensor surface after biomolecule adsorption. The model suggested that the total sensitivity increases with the number of graphene layers used.

REFERENCES

[1] Garaj S., Hubbard W., Reina A., Kong J., Branton D. and Golovchenko J.A. 2010. 'Graphene as a subnanometre trans-electrode membrane', Nature, Vol. 467, No. 7312, pp. 190-U173.

[2] Anker J.N., Hall W.P., Lyandres O., Shah N.C., Zhao J. and Van Duyne R.P. 2008. "Biosensing with plasmonic nanosensors', Nature Materials, Vol. 7, No. 6, pp. 442-453.

[3] Homola J. 2008. 'Surface plasmon resonance sensors for detection of chemical and biological species', Chemical Reviews, Vol. 108, No. 2, pp. 462-493.

[4] Maier S.A. and Atwater H.A. 2005. 'Plasmonics: Localization and guiding of electromagnetic energy in metal/dielectric structures', Journal of Applied Physics, Vol. 98, No. 1.

[5] Homola J. 2003. "Present and future of surface plasmon resonance biosensors', Analytical and Bioanalytical Chemistry, Vol. 377, No. 3, pp. 528-539.

[6] Piliarik M., Sipova H., Kvasnicka P., Galler N., Krenn J.R. and Homola J. 2012. 'High-resolution biosensor based on localized surface plasmons', Optics Express, Vol. 20, No. 1, pp. 672-680.

[7] Blanchard-Dionne, A.P., Guyot L., Patskovsky S., Gordon R. and Meunier M. 2011. 'Intensity based surface plasmon resonance sensor using a nanohole rectangular array', Optics Express, Vol. 19, No. 16, pp. 15041-15046.

[8] Jia S., Wu Y.M., Wang X.H. and Wang N. 2014. "A Subwavelength Focusing Structure Composite of Nanoscale Metallic Slits Array With Patterned Dielectric Substrate', IEEE Photonics Journal, Vol. 6, No. 1.

[9] Grigorenko A.N., Polini M. and Novoselov K.S. 2012. 'Graphene plasmonics', Nat Photon, Vol. 6, No. 11, pp. 749-758.

[10] Kravets V.G., Nair R.R., Blake P., Ponomarenko L.A., Riaz I., Jalil R., Anisimova S., Grigorenko A.N., Novoselov K.S. and Geim A.K. 2011. 'Optics of Flat Carbon - Spectroscopic Ellipsometry of Graphene Flakes', Nato Sec Sci B Phys, pp. 3-9.

[11] Bruna M. and Borini S. 2009. 'Optical constants of graphene layers in the visible range', Applied Physics Letters, Vol. 94, No. 3.

[12] Szunerits S., Maalouli N., Wijaya E., Vilcot J.P. and Boukherroub R. 2013. 'Recent advances in the development of graphene-based surface plasmon resonance (SPR) interfaces', Analytical and Bioanalytical Chemistry, Vol. 405, No. 5, pp. 1435-1443.

[13] Tang Z.W., Wu H., Cort J.R., Buchko G.W., Zhang Y.Y., Shao Y.Y., Aksay I.A., Liu J. and Lin Y.H. 2010. 'Constraint of DNA on Functionalized Graphene Improves its Biostability and Specificity', Small, Vol. 6, No. 11, pp. 1205-1209.

[14] Song B., Li D., Qi W., Elstner M., Fan C. and Fang H. 2010. "Graphene on Au(111): A Highly Conductive Material with Excellent Adsorption Properties for High-Resolution Bio/Nanodetection and Identification', Chemphyschem, Vol. 11, No. 3, pp. 585-589.

[15] Kiraly B., Iski E.V., Mannix A.J., Fisher B.L., Hersam M.C. and Guisinger N.P. 2013. 'Solid-source growth and atomic-scale characterization of graphene on Ag(111)', Nat Commun, Vol. 4.

[16] Yamamoto M. 2002. 'Surface plasmon resonance (SPR) theory: tutorial', Review of Polarography, 48, (209).

[17] Wu L., Chu H.S., Koh W.S. and Li E.P. 2010. 'Highly sensitive graphene biosensors based on surface plasmon resonance', Optics Express, Vol. 18, No. 14, pp. 14395-14400.

[18] Choi S.H., Kim Y.L. and Byun K.M. 2011. 'Graphene-on-silver substrates for sensitive surface plasmon resonance imaging biosensors', Optics Express, Vol. 19, No. 2, pp. 458-466.