33rd Annual International Conference of the IEEE EMBS
Boston, Massachusetts USA, August 30 - September 3, 2011

Comparison of Performance Parameters for Conventional and Localized Surface Plasmon Resonance Graphene Biosensors

Md. Saiful Islam, Abbas Z. Kouzani, Xiujuan J. Dai, Wojtek P. Michalski and Hamid Gholamhosseini

Abstract—**This paper investigates the enhancement of the sensitivity and adsorption efficiency of a localized surface plasmon resonance (LSPR) biosensor that includes a layer of graphene sheet on top of the gold layer. For this purpose, biomolecular interactions of biotin-streptavidin with the graphene layer on the gold thin film are monitored. The performance of the LSPR graphene biosensor is theoretically and numerically assessed in terms of sensitivity and adsorption efficiency under varying conditions, including the thickness of biomolecule layer, number of graphene layers and operating wavelength. Enhanced sensitivity and improved adsorption efficiency are obtained for the LSPR graphene biosensor in comparison with its conventional counterpart. It is found that the LSPR graphene biosensor has better sensitivity with lower operating wavelength and larger number of graphene layers.**

I. Introduction

THE position shift of plasmon dip in the localized surface plasmon resonance (LSPR) approach can be monitored in terms of incidence angle or wavelength (angular integration or wavelength integration). However, the angle integration scheme is the extensively used method because of its low angular resolution. Several LSPR platforms have been designed and implemented including attenuated total reflection, optical waveguide, optical fiber and intensity measurement [1-3]. These platforms are capable of recognizing biological events on their sensing surfaces.

The LSPR technique enables improved device integration. The optical signal is detected using a conventional biosensor configuration where a thin metal film is coated on one side of the prism [4]. The metallic thin film is typically chosen as gold, copper, silver and aluminum [5] to support the propagation of surface plasmon polariton waves (SPP) at visible light wavelength. Gold is usually opted for most the LSPR applications as it offers better sensitivity, good resistance to oxidation and corrosion in different environment. However, the detection accuracy is poor in gold as compared to other metallic configuration. The sensitivity of conventional LSPR biosensor can be further boosted by using graphene where a graphene sheet is coated on top of the gold thin film. This improved sensitivity is due to the stronger adsorption of biomolecules on graphene and the optical property of graphene. For a fixed operating wavelength, as the sensitivity increases meaning that the incidence angle to meet the resonance condition increases thereby reducing the sharpness of the plasmon dip. Although its signal to noise ratio (SNR) is weaker than that of the conventional SPR, graphene biosensor shows good promise for the adsorption efficiency and hence the sensitivity. In earlier technology used to enhance the sensitivity, complex arrangements including the integration of metal nanoparticles and nanoholes and colloidal gold nanoparticles in aqueous solution is required [6-8]. However, in this study, we employ a graphene layer on top of the gold layer to significantly boost the sensitivity.

Although the LSPR biosensors have been comprehensively studied [9-11], a few recent articles have reported on the LSPR graphene biosensors. Wu et al. [12] have recently demonstrated that a graphene-on-gold LSPR biosensor had better sensitivity than its conventional counterparts but its SNR was substantially reduced. Choi et al. [13] have described a numerical investigation for graphene-on-silver SPR biosensor with sensitivity greater than the conventional gold-film-based biosensor. It was demonstrated that the sharp dip SPR curve of silver together with a graphene layer on top of silver resulted in enhanced sensitivity. However, there were a number of issues that were not addressed in the study [13]. For example, the sensitivity was not measured. Recently, Islam et al. [14] have studied a LSPR graphene biosensor the effect of different prism configuration was studied. However, the influence of operating wavelength was not addressed.

In this paper, a LSPR graphene biosensor is proposed where the graphene is introduced on top of gold layer (Fig. 1). The focus is on sensitivity, adsorption and efficiency. A set of simulations is carried out to investigate the improvement of these parameters in respect to the number of graphene layers and effect of the operating wavelength on the sensor's performance.

II. Theory and Detection Principle

Above a certain incident critical angle, no light is refracted across the interface. While the light is totally reflected back to the medium of higher refractive index, the electromagnetic field component pierces several nanometers distance into a lower refractive index producing an

Manuscript received April 15, 2011.

M. S. Islam is with the School of Engineering, Deakin University, Geelong, Victoria 3217, Australia (e-mail: msi@deakin.edu.au).

A. Z. Kouzani is with the School of Engineering, Deakin University, Geelong, Victoria 3217, Australia (phone: 61-3-52272818; fax: 61-3-52272167; e-mail: kouzani@deakin.edu.au).

X. J. Dai is with the Institute for Technology Research and Innovation, Deakin University, Geelong, Victoria 3217, Australia (e-mail: jane.dai@deakin.edu.au).

W. P. Michalski is with the Australian Animal Health Laboratory, CSIRO Livestock Industries, Geelong, Victoria 3220, Australia (e-mail: Wojtek.Michalski@csiro.au).

H. Gholamhosseini is with the School of Engineering, Auckland University of Technology, Private Bag 92006, Auckland 1142, New Zealand (e-mail: hamid.gholamhosseini@aut.ac.nz).

exponentially extenuating evanescent wave. When the interface between the media is coated with a thin layer of material (e.g., gold) and the light is monochromatic and p-polarized, the intensity of the reflected wave starts to reduce. This produces a sharp dip at a certain incidence angle. Since the strength, decay characteristic and distribution of evanescent filed are much affected by the operating wavelength, polarization and that of the material characteristics including refractive index of dielectric layer, refractive index of prism, metal film and film thickness, the SPR signal becomes very sensitive to changes at the vicinity of the surface. In our investigation, a prism is placed against a metal thin film in the Kretschmann configuration [15] (Fig. 1). To detect the presence of any biomolecules, the surface of metal layer is coated with the target probe. When any of SPR conditions is met, a dip in reflectivity of the light occurs in the reflectivity curve. Then, the interaction between the captured target and probe molecules modifies the resonance conditions which shifts the plasmon dip.

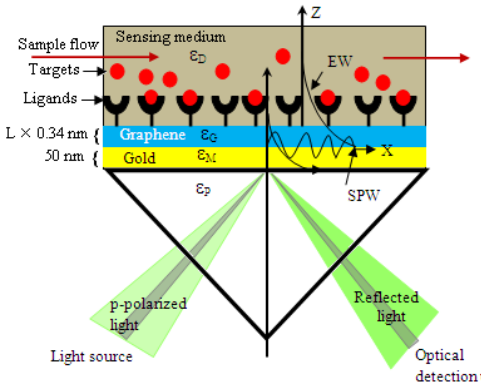

Figure 1. Schematic representation of basic Kretschmann configuration of prism coupling to show the LSPR in graphene biosensor.

The classical LSPR coupling condition can be obtained from the Maxwell's theory. Applying the appropriate boundary conditions, the Maxwell's equation reveals that the wave vector of surface plasmon is:

$$K_{sp} = \frac{\omega}{c}\sqrt{\frac{\varepsilon_M \varepsilon_D}{\varepsilon_D + \varepsilon_M}} \quad (1)$$

where K_{sp} is the wave vector of the propagation constant of surface plasmon and c is the speed of light. ε_M and ε_D are the dielectric constant of metal and dielectric layer respectively.

The wave vector of the propagation constant of evanescent wave at prism-air interface with a dielectric constant of prism ε_p, is given by the following equation:

$$K_{ev} = \frac{\omega}{c}\sqrt{\varepsilon_p}\,\sin\theta \quad (2)$$

In order to get the plasmon resonance with photons, the energy and momentum should be preserved. To achieve this, the wave vector of the propagation constant of the evanescent wave K_{ev} has to be exactly matched with that of the surface plasmon K_{sp} of similar frequency and state of polarization. The resonance condition for a variable incidence angle is therefore expressed as:

$$K_{sp} = K_{ev} = \frac{\omega}{c}\sqrt{\frac{\varepsilon_M \varepsilon_D}{\varepsilon_D + \varepsilon_M}} = \frac{\omega}{c}\sqrt{\varepsilon_p}\,\sin\theta_{res} \quad (3)$$

And,

$$\theta_{res} = sin^{-1}\left(\frac{1}{\sqrt{\varepsilon_p}}\sqrt{\frac{\varepsilon_M \varepsilon_D}{\varepsilon_D + \varepsilon_M}}\right) \quad (4)$$

Under this condition, the optical energy of the incident laser beam is converted to that of a SP wave. Thus, the resonance occurs based on the certain value of dielectric constant, incidence angle, incidence wavelength and hence, the angle required for the resonance (variable incidence angle), θ_{res} depends on the dielectric constant ε_D when ε_M and ε_p are maintained constant. However, for a variable wavelength LSPR biosensor, the resonance occurs at a fixed incidence angle where the resonance wavelength λ_{res} is related to ε_D when ε_M and ε_p are maintained fixed. The sensitivity and adsorption efficiency, which are crucial parameters for determining the performance of any biosensor can be defined for this LSPR graphene biosensor in terms of overall sensitivity S^L as [16]:

$$S^L = \frac{\Delta P^L}{\Delta M} = \frac{\Delta P^L}{\Delta n}.\frac{\Delta n}{\Delta M} = S^L_{RI}\,.E \quad (5)$$

where P is the sensor output which can be incidence angle (for variable incidence angle LSPR graphene biosensor) or wavelength (for variable wavelength LSPR graphene biosensor), Δn is the amount of refractive index altered by the biomolecular binding, and M refers to moles for biomolecules. $S_{RI}{}^L$ represents the sensitivity to refractive index change whereas E represents the adsorption efficiency of the target biomolecules. This adsorption efficiency defines how many biomolecules in the sample analyte takes part to alter the refractive index. The sensitivity to the refractive index change for a variable incidence angle is defined as:

$$S^L_{\theta n} = \frac{\Delta\theta_{res}}{\Delta n_D}\ (\text{deg/RIU}) \quad (5)$$

where,

$$\Delta\theta_{res} = \theta_{res}\langle antigen\rangle - \theta_{res}\langle antibody\rangle \quad (6)$$

and,

$$\Delta n_D = n_D\langle antibody\rangle - n_D\langle antigen\rangle \quad (7)$$

Similarly, the sensitivity to refractive index change for a variable wavelength can be found as:

$$S^L_{\lambda n} = \frac{\Delta\lambda_{res}}{\Delta n_D}\ \ (\text{nm/RIU}) \quad (8)$$

III. Numerical Simulations

A simulation was carried out for calculating the Fresnel coefficients of the LSPR graphene biosensor. To excite the surface plasmon for matching with the evanescent wave, the laser beam is coupled with a prism (fused silica glass prism). A gold thin film was used to cover the base. Later on, the gold was also coated with a graphene layer. Finally, the outer surface of graphene layer is immobilized with the sensing medium (biotin-streptavidin). Light from a laser

beam of 632.8 nm with various incidence angles is launched into the prism to find out the optimum coupling condition. The reflected beam was directed to an optical detection system producing the SPR curve. The refractive index profile and other properties of the examined materials were included in the simulation to analyze the performance parameters. This simulation was verified using the WINSPALL SPR simulator by Knoll group at Max-Planck-Institute (Mainz, Germany) [17]. The simulator calculates the Fresnel coefficients of the layer system with recursion formalism. We have shown in Fig. 2 that the sensitivity of the graphene-on-gold LSPR biosensor increases almost linearly with the number of graphene layers deposited on top of the gold thin film. In another simulation, it is found that the resonance reflectivity and the change in resonance reflectivity are affected by the graphene layers (Fig. 3).

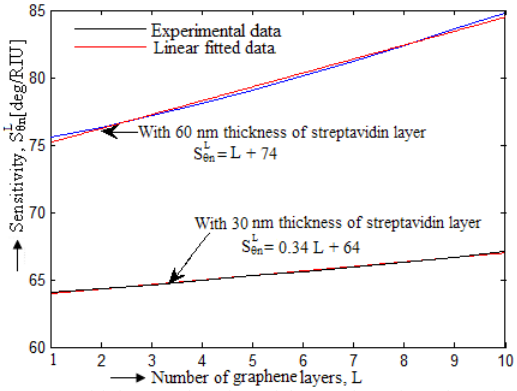

Figure 2. Sensitivity as a function of the number of graphene layers.

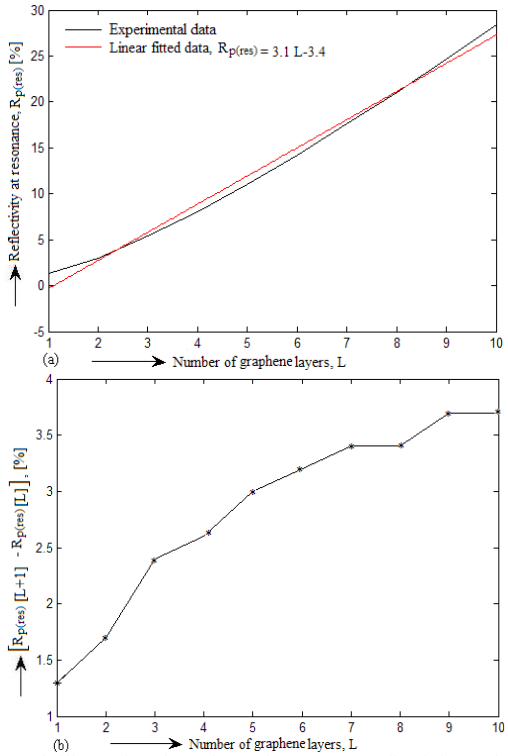

Figure 3. Graph illustrating the values of resonance reflectivity and change in resonance reflectivity for different numbers of graphene layers: (a) resonance reflectivity and (b) change in resonance reflectivity.

IV. Results and Discussions

The sensitivity of biosensors depends on a number of factors (e.g., coated materials, and target probe), but in the context of this study, the sensitivity improvement was the result of introducing a biomolecular recognition element onto the coated material, prism configuration, proper interface with prism, proper selection of the thin film, and also the proper selection of operating wavelength. As summarized in Fig. 4, the introduction of the graphene layer onto the gold thin film improved the shift of plasmon dip in the optical spectrum.

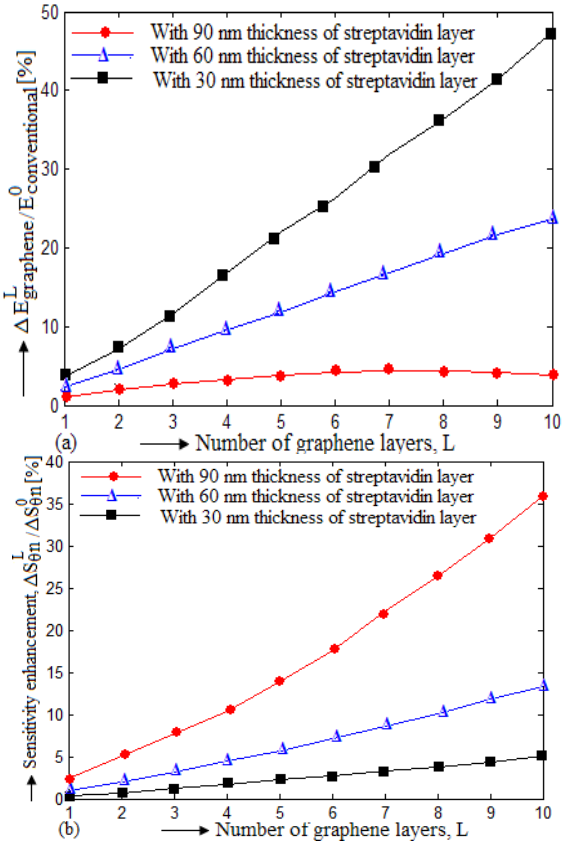

Figure 4. Performance comparison of the LSPR conventional and grapheme biosensors: (a) adsorption efficiency enhancement $\Delta E^L{}_{graphene}/E^0{}_{conventional}$ and (b) sensitivity enhancement $\Delta S^L{}_{\theta n}/S^0{}_{\theta n}$.

A. LSPR Conventional and Graphene Biosensor

The LPSR graphene biosensor is attractive because of its stable adsorption of biomolecules. In contrast, adsorption of biomolecules occurs poorly in gold surface in the conventional LSPR biosensors. Functionalization of graphene layer on top of gold thin film enables greater refractive index change near the sensing layer interface. Furthermore, the presence of graphene layer on gold surface alters the propagation constant of SPP, which ensures the modification of the sensitivity to refractive index change. Thereby, increasing the adsorption efficiency due to the graphene layer coated on the gold thin film enhances the sensitivity. Fig. 4 shows that the graphene biosensor significantly enhances both adsorption efficiency and sensitivity as compared to the conventional LSPR biosensor.

B. *Effect of Operating Wavelength on the Performance*

The effect of the operating wavelength on the design parameters of the LSPR graphene biosensor is studied and produced a match with the mathematical theory. An agreement was achieved between the theoretical developed formula and our numerical simulation. On the other hand, the shift of resonance angle decreased with higher wavelengths. However, the effective refractive index decreased under the same conditions which could compensate for the reduction of shift of resonance angle in order to keep the sensitivity stable (5). Furthermore, we have mathematically established a relationship between these $\Delta\theta_{res}$ with the wavelength (Fig. 5). The nature of these two parameters in terms of the operating wavelength can be best described by the following two equations:

$$\Delta\theta_{res} = e^{-0.0041\lambda + 5.601} \quad (9)$$

where λ is the operating wavelength. As can be seen from Fig. 5, $\Delta\theta_{res}$ decrease with the wavelength. Whereas, a higher values of $\Delta\theta_{res}$ is desired for obtaining improved sensitivity.

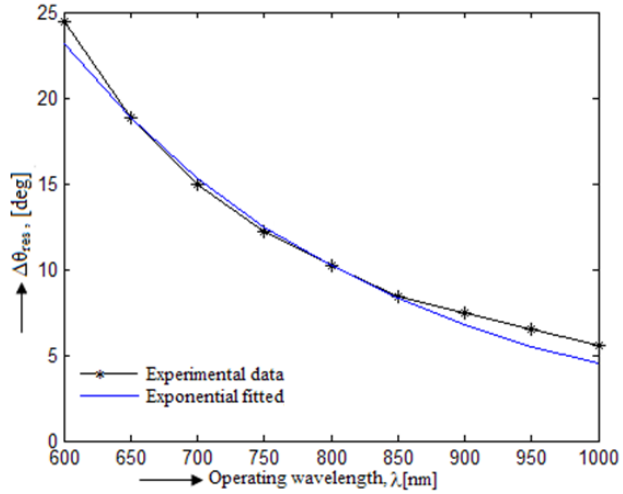

Figure 5. Numerical predictions and exponential fitted values of $\Delta\theta_{res}$ as a function of the operating wavelength. Waveguide structure: Fused silica glass prism, gold thin film (50 nm), graphene sheet (2nm) and streptavidin (60nm).

V. CONCLUSIONS

This paper presented the design of a LSPR graphene biosensor with a theoretically developed framework for the analysis of the biosensor. The streptavidin was used as a target biomolecule to interact with the graphene layer coated on the gold surface. It was demonstrated that the resonance condition is significantly affected by the introduction of the graphene layer. Additionally, the resonance condition is also greatly enhanced by the operating wavelength. An exponential relation is numerically established between the plasmon shift and the operating wavelength. As gold provides better resonance shift in conjunction with stable operation, it was chosen for the further investigation. Apart from its good performance, its greatest advantage is its tunable operation.

REFERENCES

[1] J. Dostalek, J. Ctyroky, J. Homola, E. Brynda, M. Skalsky, P. Nekvindova, J. Spirkova, J. Skvor, and J. Schrofel, "Surface plasmon resonance biosensor based on integrated optical waveguide," *Sensors and Actuators B: Chemical*, vol. 76, pp. 8-12, 2001.

[2] M. Keita, H. Yoichiro, and K. Kotaro, "Optical fiber affinity biosensor based on localized surface plasmon resonance," *Applied Physics Letters*, 2004.

[3] M. Kanso, S. Cuenot, and G. Louarn, "Sensitivity of optical fiber sensor based on surface plasmon resonance: modeling and experiments," *Plasmonics*, vol. 3, pp. 49-57, 2008.

[4] E. Kretschmann and H. Raether, "Radiative decay of non radiative surface plasmons excited by light(Surface plasma waves excitation by light and decay into photons applied to nonradiative modes)," *ZEITSCHRIFT FUER NATURFORSCHUNG, TEIL A*, vol. 23, pp. 2135, 1968.

[5] M. S. Islam, A. Z. Kouzani, X. J. Dai, and W. P. Michalski, "Investigation of the effects of design parameters on sensitivity of surface plasmon resonance biosensors," *Biomedical Signal Processing and Control*, vol. 6, pp. 147-156, 2010.

[6] J. Zhao, X. Zhang, C. Yonzon, A. Haes, and R. Van Duyne, "Localized surface plasmon resonance biosensors," *Nanomedicine*, vol. 1, pp. 219-228, 2006.

[7] M. Stewart, C. Anderton, L. Thompson, J. Maria, S. Gray, J. Rogers, and R. Nuzzo, "Nanostructured plasmonic sensors," *Chem. Rev*, vol. 108, pp. 494-521, 2008.

[8] P. Englebienne, A. Van Hoonacker, and M. Verhas, "Surface plasmon resonance: principles, methods and applications in biomedical sciences," *Spectroscopy*, vol. 17, pp. 255-273, 2003.

[9] B. Patel, "Excitation of Surface Plasmons in Thin Metal Films of Gold, Silver and Aluminium." [Online]. Available: http://ucl-4c00-spr-bpatel.tripod.com/.

[10] M. Manesse, V. Stambouli, R. Boukherroub, and S. Szunerits, "Electrochemical impedance spectroscopy and surface plasmon resonance studies of DNA hybridization on gold/SiO x interfaces," *The Analyst*, vol. 133, pp. 1097-1103, 2008.

[11] A. Sharma, R. Jha, and B. Gupta, "Fiber-optic sensors based on surface plasmon resonance: a comprehensive review," *IEEE Sensors Journal*, vol. 7, pp. 1118-1129, 2007.

[12] L. Wu, H. S. Chu, W. S. Koh, and E. P. Li, "Highly sensitive graphene biosensors based on surface plasmon resonance," *Opt. Express*, vol. 18, pp. 14395-14400, 2010.

[13] S. H. Choi, Y. L. Kim, and K. M. Byun, "Graphene-on-silver substrates for sensitive surface plasmon resonance imaging biosensors," *Opt. Express*, vol. 19, pp. 458-466, 2011.

[14] M. S. Islam and A. Z. Kouzani, "Variable Incidence Angle Localized Surface Plasmon Resonance Graphene Biosensor," 2011 IEEE/ICME International Conference on Complex Medical Engineering (ICME 2011), Harbin, Heilongjiang, China, 2011 (Accepted on 11 Februaty 2011), 2011.

[15] E. Kretschmann, "Die Bestimmung optischer Konstanten von Metallen durch Anregung von Oberflächenplasmaschwingungen," *Zeitschrift für Physik A Hadrons and Nuclei*, vol. 241, pp. 313-324, 1971.

[16] J. Homola, "Present and future of surface plasmon resonance biosensors," *Analytical and Bioanalytical Chemistry*, vol. 377, pp. 528-539, 2003.

[17] W. Knoll, "Interfaces and thin films as seen by bound electromagnetic waves," *Annual Review of Physical Chemistry*, vol. 49, pp. 569-638, 1998.