Design and Simulation of Graphene/2D Interlayer Surface Plasmon Resonance Biosensor Based on Ellipsometry Method

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ABSTRACT— Two-dimensional nanomaterials have attracted increasing attention for enhancing surface plasmon resonance (SPR) biosensors application. In this work, we use the graphene layer to improve the sensitivity of the SPR biosensors based on the conventional Kretschmann configuration. We employ Tungsten disulfide (WS_2) and Molybdenum disulfide (MoS_2) Two-dimensional materials as an interlayer to enhance the sensitivity of Au/Graphene biosensor in angle interrogation method. The transfer matrix method (TMM) is used to analyze the characteristics of the device. Results show that using WS_2 in Au/Graphene structure increases sensitivity by about 12.64%, which is higher than MoS_2. Combining graphene based SPR and ellipsometry as a highly sensitive, label-free, real-time, and versatile method can be used to measure a very small concentration of biomolecules, which leads to 170-fold enhancement compared to angle interrogation method and improves the detection accuracy and quality factor.

KEYWORDS: Ellipsometry, Graphene, Surface plasmon resonance, Transition metal dichalcogenides (TMD).

I. INTRODUCTION

Surface plasmon resonance (SPR) based biosensors have attracted great attention due to their high sensitivity, reliability, label-free, and ability for real-time detection [1]. Since the propagation constant of surface plasmon waves is larger than the light's propagation constant in vacuum, different methods are used to couple these two waves [2]. One of the most common methods is to use a prism with a refractive index higher than one, which was demonstrated by Kretschmann [3]. In this method, a transverse magnetic (TM)-polarized light passing through the prism at a certain angle and after total reflection, creates an evanescent wave at the interface between the metal and the prism. This evanescent wave penetrates the metal with the propagation constant $k_x=n_p(2\pi/\lambda)\sin\theta$, where, n_p, λ, and θ are the refractive index of the prism, wavelength, and angle of the incident light, respectively [4]. The excitation of the surface plasmons results in a resonant dip in the angular/wavelength spectrum of the reflected light with a fixed excitation light angle/wavelength.

The most widely used metal in plasmonic sensors is gold (Au) because it has a strong resonant response, chemical stability, and low loss [5]. Sensitivity enhancement and improving efficiency always are challenges in SPR based biosensors. Due to poor interaction between biomolecules with conventional Kretschmann SPR chip, the graphene layer was introduced as a biomolecular recognition element (BRE) [6]. Graphene, a two-dimensional (2D)-material with a honeycomb structure, has a high aspect ratio, π-π stacking interaction with biomolecules, and unusual optical properties [7]. So it provides a highly sensitive sensor and improves the efficiency of conventional prism/Au chip. Furthermore, due to effective charge transfer in Au/Graphene interface, electric field enhancement is generated [8]. Physical adsorption of the biomolecules on the graphene surface leads to changes in the refractive index near the sensor surface and consequently induces specific alternations in the propagation constant and SPR characteristics [1], [4].

Also, 2D transition metal dichalcogenides (TMD) were proposed as interlayers to enhance the sensitivity of biosensors [9]. The large surface area and hydrophobic nature are special features of TMDs which makes them potential material to develop biosensing interfaces. Moreover, the TMD layers have been employed to inhibit the oxidation of metallic layers such as aluminum in SPR sensors. Y. Xu, *et al.* demonstrated that the Molybdenum disulfide (MoS_2)-based SPR sensor possesses higher sensitivity and detection accuracy than graphene-based SPR sensors [10]. Due to the effective charge transfer, hybrid structures of TMD/Graphene lead to larger electric field enhancement at the sensing surface, so there will be higher sensitivity to analytes. However, the phase measurement of these structures has not been investigated in detail yet.

In this work, highly sensitive surface plasmon resonance enhanced ellipsometry, a novel method for sensitivity enhancement, has been used to probe the phase response of graphene based Kretschmann SPR structures. Then, the calculated sensitivity of these structures in the angle interrogation method has been compared to ellipsometry results.

II. THEORY

Figure 1 shows an SPR sensor that is based on the Kretschmann configuration. In the interlayer portion, Tungsten disulfide (WS_2) and MoS_2 are used. The reflectance (R) of the structure shown in Fig. 2 can be calculated for TM polarized light with the N-Layer model [1], [2]. For TM polarized light, the reflectance is shown by R as a function of matrix elements [6],

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

where

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

in which

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

$$\beta_k = d_k \left(\frac{2\pi}{\lambda_0} \right) \left(\varepsilon_k - n_1^2 \sin^2\theta \right)^{1/2}, \quad (4)$$

$$q_k = \frac{\left(\varepsilon_k - n_1^2 \sin^2\theta \right)^{1/2}}{\varepsilon_k}, \quad (5)$$

where, λ_0 is the wavelength of incident TM-polarized light, which is considered 633 nm, θ is the incident angle, n_k and d_k are the refractive index (RI), and the thickness of the kth layer, respectively, with k=2 to N-1[6]. The first layer is BK7 (n=1.5151) prism or SF10 (n=1.7231) prism. The Nth is the analyte defined as n_w=1.33 (water medium) and changes to n_{bio}=1.332 as a biomolecule and immobilizer. The RI of Au is calculated with the Drude-Lorentz model, which is 0.1378+i3.6196 at 633 nm. The thickness of monolayer graphene, MoS_2, and WS_2 is 0.34 nm, 0.65 nm, and 0.8 nm, respectively. Moreover, their corresponding refractive indices at 633 nm are 3+i1.1487, 5.0805+i1.1723, and 4.8937+i0.3123, respectively [6], [11]. The reflectance is related to change in RI of sensing medium, and dip in reflectance shows resonance angle (Fig. 2). As the RI of the sensing medium increases with Δn, the dip in reflectance shifts to a higher value that can be considered as $\Delta\theta$. To analyze sensor performance, sensitivity, detection accuracy (DA), and quality factor (QF) are the main parameters and should be as high as possible. Sensitivity is defined by $S = \frac{\Delta\theta}{\Delta n}$ [6].

Detection accuracy is defined as the ratio of the shift in resonance angle $(\Delta\theta_{SPR})$ to FWHM [12]:

$$DA = \frac{\Delta\theta_{SPR}}{FWHM}, \tag{6}$$

In these biosensors, the quality factor is defined as the ratio of sensitivity to FWHM (RIU^{-1}) [12]:

$$QF = \frac{S}{FWHM}, \tag{7}$$

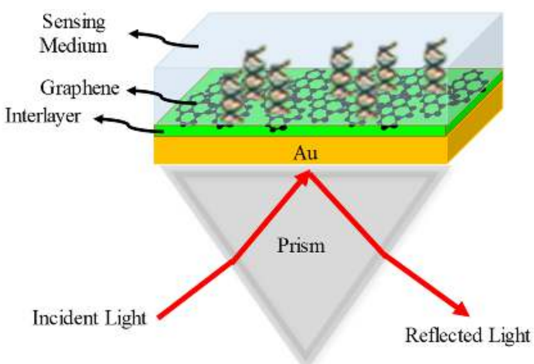

Fig. 1. The schematic of the proposed five-layer SPR structure.

Ellipsometry, a non-destructive and non-contact method, measures the polarization changes of a light passing through or reflected from a surface. In this technique, two highly-sensitive quantities of Ψ and Δ are calculated. Ψ and Δ are the amplitude ratio and the phase difference between p-polarized and s-polarized light reflected from the sample surface, respectively. They are obtained as follows [13]:

$$\tan\psi = |r_p| / |r_s| \rightarrow \psi = \tan^{-1}\left[\frac{\sqrt{R_p}}{\sqrt{R_s}}\right], \tag{8}$$

where $r_{s,p}$ is the Fresnel reflection coefficient. Using the Kramers-Kronig relation, we have [13]:

$$\mathrm{Ln}\left[r_{s,p}(\omega)\right] = Ln\left[\sqrt{R_{s,p}(\omega)}\right] + i\theta(\omega), \tag{9}$$

$$\theta_{s,p}(\omega) = -\frac{2\omega}{\pi}\Phi\int_0^{\infty}\frac{\mathrm{Ln}\left[\sqrt{R_{s,p}(\omega')}\right]}{\omega'^2-\omega^2}d\omega' + \theta_0, \tag{10}$$

therefore, Δ is calculated as:

$$\Delta = \theta_p(\omega) - \theta_s(\omega) = -\frac{2\omega}{\pi}\Phi\int_0^{\infty}\left[\frac{\mathrm{Ln}\left[\sqrt{\frac{R_p(\omega')}{R_s(\omega')}}\right]}{\omega'^2-\omega^2}\right]d\omega', \tag{11}$$

For ellipsometry measurement, we use the same approach proposed in [13].

III. Results and Discussion

The graphene layer absorbs biomolecules because of its carbon rings. This property of graphene leads to larger refractive index changes at the interface between graphene and the sensing environment. Also, the presence of graphene on the surface of Au causes a change in surface plasmon propagation constant and thus increases the sensitivity to refractive index variation. The performance of SPR based biosensors is related to the sensitivity to refractive index changes and absorption efficiency of biomolecules on BRE which will be enhanced by the Graphene layer.

Figure 2(a) shows reflectance results for single layer graphene (SLG), bilayer graphene (Bi-G), trilayer graphene (Tri-G) and Fig. 2(b) shows WS_2/SLG and MoS_2/SLG structures in water (W) and biomolecule (Bio) medium on the BK7/Au substrate. Adding biomolecule to sensing medium leads to a slight change in the resonance angle of the SPR curve. This variation ($\Delta\theta_{SPR}$) in the dip of reflectance determines structure sensitivity, which means higher $\Delta\theta_{SPR}$ leads to higher sensitivity. The results of the obtained curves shown in Figs 2(a) and 2(b) are listed in Tables 1 and 2, which give us information about different structures used in this work. From Table 1, BK7/Au/WS_2/SLG has the best sensitivity in angle interrogation (156°/RIU), better than

BK7/Au/MoS_2/SLG (152°/RIU). Therefore, employing MoS_2 and WS_2 as an interlayer enhances the sensitivity, which has two main reasons. Firstly, the additional layer leads to an increase in the slope of θ-n_d dispersion, so by the change in RI of sensing medium, $\Delta\theta$ takes higher value as compared to the case of without interlayer. Secondly, effective charge transfers in Au/WS_2 or MoS_2/Graphene, lead to larger electric field enhancement, which results in higher sensitivity to sensing medium. In addition, the sensitivity in the cases with WS_2 interlayers is enhanced more as compared with those with MoS_2, due to the aforementioned reasons and its physical characteristics like refractive index.

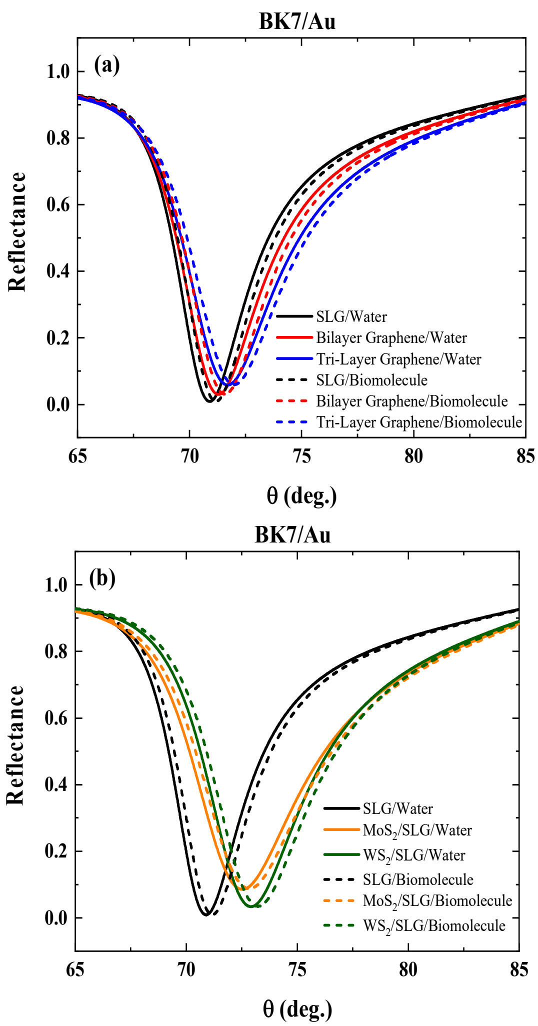

Fig. 2. SPR reflectance curves for (a) SLG, bilayer graphene, trilayer graphene, and (b) WS_2/SLG and MoS_2/SLG structures in water and biomolecules medium on the BK7/Au substrate.

Table 1. Simulation results for BK7/Au substrate, angle interrogation.

Structure	θ_{SPR} (W) (°)	θ_{SPR} (Bio) (°)	$\Delta\theta_{SPR}$ (°)	S (°/RIU)
SLG	70.890	71.175	0.272	138.5
Bi-G	71.288	71.571	0.283	141.5
Tri-G	71.697	71.986	0.289	144.5
WS_2/SLG	72.917	73.229	0.312	156
MoS_2/SLG	72.529	72.833	0.304	152

Table 2. Simulation results for BK7/Au substrate, detection accuracy, and quality factor.

Structure	FWHM (W) (°)	FWHM (Bio) (°)	DA	QF (RIU^{-1})
SLG	4.303	4.371	0.064	32.187
Bi-G	4.826	4.874	0.059	29.320
Tri-G	5.264	5.310	0.055	27.451
WS_2/SLG	5.450	5.478	0.057	28.620
MoS_2/SLG	5.778	5.799	0.053	26.307

Table 2 shows a decline in detection accuracy and quality factor by employing an additional layer to SLG. This is due to additional optical absorption induced by adding graphene, WS_2, and MoS_2 layers.

Figure 3 shows the reflectance of TM and TE light, Ψ, and Δ for BK7/Au/SLG. As can be seen in Fig. 3, in the resonance angle, that is the dip in reflectance and Ψ, there is a linear and abrupt change in phase (Δ). This provides a very high sensitive measurement that can be used to monitor very slight changes in the sensing medium. Fig. 4 shows the phase response of different layers of graphene, WS_2/SLG, and MoS_2/SLG in water and biomolecules medium on BK7/Au substrate. The results of Fig. 4 are listed in Table 3, which shows that phase response of all structures provides much higher sensitivity to measure a small change in sensing medium and Au/SLG structure has the best sensitivity. In the Au/SLG structure, the ellipsometry technique provides the phase sensitivity enhancement of more than 170 fold compared to angle interrogation. So, without adding any layer, high sensitive approach with a simple Au/Graphene SPR structure can be achieved by using the ellipsometry technique.

Using Ψ, we can define detection accuracy and quality factor in ellipsometry measurement. From Fig. 3, it appears that ellipsometry gives better DA and QF due to its narrower Ψ spectrum. Results in Table 3 show that there is 24% to 60% increase in both detection accuracy and quality factor by using ellipsometry.

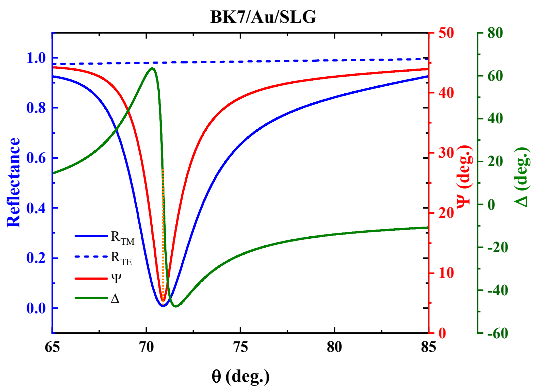

Fig. 3. Reflectance of TM (solid blue line) and TE (blue dashed line) light, Ψ (red), and Δ (olive) for BK7/Au/SLG. Orange vertical line shows that in resonance angle abrupt change in phase occurs.

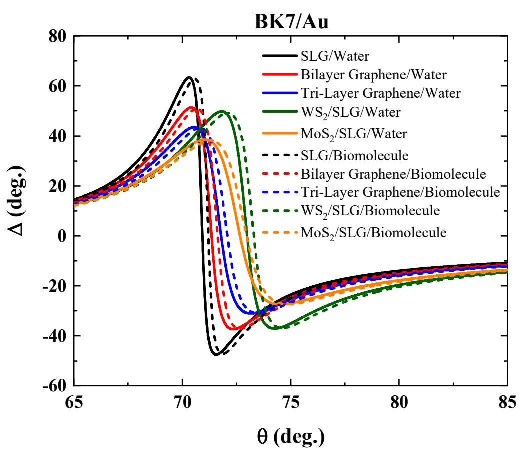

Fig. 4. Ellipsometry results for different structures.

So, by using ellipsometry not only much higher phase sensitivity is yielded but it also provides better resolution and quality factor, as a consequence overall performance of the SPR biosensor is improved.

Table 3. Ellipsometry results for BK7/Au substrate, detection accuracy, and quality factor with Ψ parameter

Structure	Δ (°)	FWHM (W) (°)	DA	QF (RIU^{-1})
SLG	47.158	2.675	0.103	51.776
Bi-G	27.736	3.192	0.089	44.330
Tri-G	17.835	3.765	0.077	38.380
WS_2/SLG	24.248	3.879	0.080	40.217
MoS_2/SLG	12.362	4.602	0.066	33.029

Tables 4, 5, and 6 show the results of using SF10 prism instead of BK7, which has a lower sensitivity in angle interrogation. Ellipsometry results show that SF10 prism provides slightly lower phase sensitivity in graphene based structures. Although by adding TMD nanomaterials, SF10 based SPR sensors show better phase response compared to BK7 based SPR chip. This is due to a slightly sharper phase change which is caused by adding these layers. On the other hand, the detection accuracy and quality factor of BK7 based structures are better than SF10 based structures. In other words, by adding WS_2 and MoS_2, due to the physical characteristics of these materials, the slope of the Δ and the range of the phase changes decrease at the resonance angle for both BK7 and SF10 based structures. Consequently, the phase change by adding biomolecule decreases.

Table 4 Simulation results for SF10/Au substrate, angle interrogation

Structure	θ_{SPR} (W) (°)	θ_{SPR} (Bio) (°)	$\Delta\theta_{SPR}$ (°)	S (°/RIU)
SLG	59.397	56.545	0.148	74
Bi-G	56.614	56.765	0.151	75.5
Tri-G	56.840	56.993	0.153	76.5
WS_2/SLG	57.501	57.659	0.158	79
MoS_2/SLG	57.303	57.459	0.156	78

Table 5 Simulation results for SF10/Au substrate, detection accuracy, and quality factor.

Structure	FWHM (W) (°)	FWHM (Bio) (°)	DA	QF (RIU^{-1})
SLG	2.269	2.282	0.065	32.613
Bi-G	2.798	2.815	0.054	29.986
Tri-G	3.091	3.109	0.050	24.749
WS_2/SLG	3.230	3.248	0.049	24.458
MoS_2/SLG	3.535	3.554	0.044	22.065

Table 6 Ellipsometry results for SF10/Au substrate, detection accuracy, and quality factor with Ψ parameter

Structure	Δ (°)	FWHM (W) (°)	DA	QF (RIU^{-1})
SLG	47.105	1.564	0.095	47.310
Bi-G	27.100	1.864	0.082	40.899
Tri-G	17.804	2.153	0.071	35.532
WS_2/SLG	25.600	2.172	0.073	36.372
MoS_2/SLG	12.589	2.592	0.060	30.093

However, this kind of decrease in the slope of the Δ is slightly lower in SF10 based structures. Therefore, by adding TMD materials, the calculated phase change is slightly larger in

SF10 based structures as compared to BK7 structures.

IV. Conclusion

Two dimensional transition metal dichalcogenides (TMD) materials like Tungsten disulfide (WS_2) and MoS_2 have been used as an interlayer to enhance Au/Graphene sensitivity. BK7/Au/WS_2/SLG (single layer graphene) chip shows the most sensitivity in angle interrogation with an enhancement of about 12.64% compared to BK7/Au/SLG. In angle interrogation, using BK7 prism leads to higher sensitivity compared to SF10 prism, but using TMD materials as an interlayer, SF10 based structures have shown better sensitivity in phase measurement. Ellipsometry results show BK7/Au/SLG has the best phase response. Using the ellipsometry technique as a non-destructive, high sensitive measurement not only provides phase sensitivity enhancement more than 170 fold compares to the angle interrogation, but it also improves the detection accuracy and quality factor of SPR biosensors.

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References

[1] E. Wijaya, C. Lenaerts, S. Maricot, J. Hastanin, S. Habraken, J.-P. Vilcot, R. Boukherroub, and S. Szunerits "Surface plasmon resonance-based biosensors: From the development of different SPR structures to novel surface functionalization strategies," Current Opinion in Solid State and Materials Science, Vol. 15, pp. 208-224, 2011.

[2] M.S. Alexander, *Plasmonics: Fundamentals and Applications,* Springer Science & Business Media, 2007.

[3] E. Kretschmann and H. Raether, "Radiative decay of non-radiative surface plasmons excited by light," Z. Naturforsch. A, Vol.23 pp. 2135-2136, 1968.

[4] H. Raether, *Surface plasmons on smooth and rough surfaces and on gratings,* Springer, Berlin, Heidelberg, 1988.

[5] E. Hutter and J.H. Fendler, "Exploitation of localized surface plasmon resonance," Adv. Mater. Vol.16, pp. 1685-1706, 2004.

[6] 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.

[7] S. Szunerits, N. Maalouli, E. Wijaya, J.P. Vilcot, and R. Boukherroub, "Recent advances in the development of graphene-based surface plasmon resonance (SPR) interfaces," Anal. Bioanal. Chem, Vol. 405, pp. 1435-1443, 2013.

[8] S. Zeng, D. Baillargeat, H.-P. Ho, and K.-T. Yong, "Nanomaterials enhanced surface plasmon resonance for biological and chemical sensing applications," Chem. Soc. Rev. Vol. 43, pp. 3426-3452, 2014.

[9] M.S. Rahman, M.S. Anower, M.R. Hasan, M. B. Hossain, and M.I. Haque, "Design and numerical analysis of highly sensitive Au-MoS_2-graphene based hybrid surface plasmon resonance biosensor," Opt. Commun. Vol. 396, pp. 36-43, 2017.

[10] YI. Xu, L. Wu, and L. Kee, "MoS_2-based highly sensitive near-infrared surface plasmon resonance refractive index sensor," IEEE J. Sel. Top. Quantum Electron. Vol. 25, pp. 1-7, 2018.

[11] C. Hsu, R. Frisenda, R. Schmidt, A. Arora, S. M. d. Vasconcellos, R. Bratschitsch, H.S.J.V.D. Zant, and A. Castellanos-Gomez "Thickness-dependent refractive index of 1L, 2L, and 3L MoS_2, $MoSe_2$, WS_2, and WSe_2," Adv. Opt. Mater. Vol. 7, pp. 1900239 (1-6), 2019.

[12] J. Maurya, Y. Prajapati, V. Singh, and J. Saini, "Sensitivity enhancement of surface plasmon resonance sensor based on graphene–MoS2 hybrid structure with TiO 2–SiO 2 composite layer," Appl. Phys. A, Vol.121, pp. 525-533, 2015.

[13] F. Sohrabi and S.M. Hamidi, "Optical detection of brain activity using plasmonic ellipsometry technique," Sens. Actuator B-Chem.Vol. 251, pp. 153-163, 2017.

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