Available online at www.sciencedirect.com

ScienceDirect

Procedia Engineering 140 (2016) 134 – 139

Procedia Engineering

www.elsevier.com/locate/procedia

MRS Singapore – ICMAT Symposia Proceedings

8th International Conference on Materials for Advanced Technologies

Sensitivity Enhancement of MoS_2 Nanosheet based Surface Plasmon Resonance Biosensor

Qingling Ouyang[a,b], Shuwen Zeng[a,b], Xuan-Quyen Dinh[a], Philippe Coquet[a,c], Ken-Tye Yong[a,b]*

[a]CINTRA CNRS/NTU/THALES, UMI 3288, Research Techno Plaza, 50 Nanyang Drive, Border X Block, Singapore 637553, Singapore
[b]School of Electrical and Electronic Engineering, Nanyang Technological University, Singapore 639798, Singapore
[c]Institut d'Electronique, de Microélectronique et de Nanotechnologie (IEMN), CNRS UMR 8520 – Université de Lille 1, 59650 Villeneuve d'Ascq, France

---

Abstract

A surface plasmon resonance based biosensor consisting of SF10 prism, silicon layer, gold thin film and MoS_2 enhanced nanosheet is presented. We systematically investigated the SPR reflectivity and resonance angle through the transfer matrix method. Furthermore, with the optimized thickness of gold, silicon and MoS_2, we calculated the change of resonance angle to a fixed refractive index change of sample solutions and the full width at half maximum of the reflectivity curves. The excitaition wavelengths of light sources that we use range from 600nm to 1024nm which covers both visible and near infrared light. In addition, the optimum configuration for MoS_2-enhanced SPR biosensors are monolayer MoS_2 and 7 nm silicon layer coated on 50 nm Au thin film with 633 nm as the excitation wavelength. With these optimized parameters we can efficiently increase the sensitivity by ~10%. Even without the silicon layers, the pure MoS_2 enhanced nanosheet can also improve the sensitivity by ~8%. The performance of MoS_2 enhanced nanosheet is almost 3-fold higher than that of graphene.

Selection and/or peer-review under responsibility of the scientific committee of Symposium 2015 ICMAT

Keywords: Surface plasmon resonance, MoS_2, silicon thin film, prism coupling, optical biosensor

---

* Corresponding author. Tel.: +65 67905444.
E-mail address: ktyong@ntu.edu.sg

Selection and/or peer-review under responsibility of the scientific committee of Symposium 2015 ICMAT
doi:10.1016/j.proeng.2015.08.1114

1. Introduction:

Surface plasmon resonance based biosensors have been studied over the past three decades [1-5], which shown remarkable capability in real-time detection of biomolecule and monitoring of the interaction process in various research fields [6-10]. These prominent performances owe to the SPR sensing mechanism. Specifically, the small refractive index changes of the dielectric sample layer can affect the surface plasmon, which will reduces observable changes in optical characteristics such as resonance angle and polarization. These can be quantitatively expounded by the surface plasmon dispersion equations [11]. Although SPR-based biosensors have been widely applied in the studies of biological and chemical interactions due to its flexibility in various detection circumstances, but the limited sensitivity still become an obstacle for the further developments. To solve the sensitivity issue various enhanced nanosheet has been add into the configuration [9, 12-14], among them graphene is the favorite choice [10, 14]. It has been reported that for the graphene enhanced SPR biosensor, the optical property of graphene can modify the SPR curves and improve the sensitivity by 0.025L (L represented the number of graphene layers) [10, 12], which in some ways can only be regarded as an incremental enhancement. This can be explained by the relatively low optical absorption of graphene, experimental results shown that monolayer graphene can only absorb 2.3% of the incident light [10, 15], and the simulated results also shown each additional graphene layer can absorb another 2.3% of the light [10], which means that optical absorption of graphene decreases with the increasing number of graphene layers. This reduce the graphene layers absorb too low energy to promote the charge transfer between graphene layers and metal films, which directly impacts the intensity of the surface plasmon and hence the sensitivity.

In our work, we focus on other materials with higher optical absorption to replace the graphene enhanced layer. MoS_2 which belongs to the group of TMDCs has been reported to have amazing optical and electrical properties. 2D materials usually show different features with bulk material, MoS_2 is not an exception, it has been reported that the bulk MoS_2 is indirect bandgap (1.2eV) semiconductor while the monolayer MoS_2 is direct bandgap (1.8eV) semiconductor [16], this property has been used to achieve better switch off/on ratio and higher photoresponsivity (7.5×10^{-3} A/W) in the nano-transistor [17, 18]. Besides, there are records that when few-layered MoS_2 applied in MSM photodetectors, it can obtain ultrahigh responsivity reaching to 0.57 A/W, this owns to the high optical absorption (~10%) and photogain of the 2D MoS_2 [18, 19]. Considering the 2D MoS_2 has notable performances in photoelectric devices due to the considerable optical absorption, we propose a new SPR biosensor structure based on MoS_2 and silicon enhanced nanosheet (shown in figure 1). It consists of SF10 prism, gold thin film, silicon and MoS_2 nanolayer as well as dielectric sample layer (resolved in the buffer solution). Here, we applied the well-known Kretschmann configuration [11], The prism is mainly used for concentrating the incident light to the resonant surface. The thin film gold is evaporated and deposited on the lower surface of the prism. The silicon and MoS_2 nanolayer are sequentially stacked under the gold layers, they can attached firmly with the Van der Wals force [12, 14, 17].

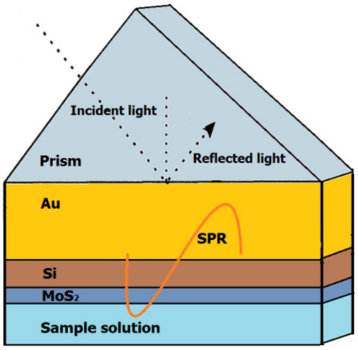

Fig.1. Kretschmann configuration of SPR biosensor based on silicon and MoS_2 enhanced nanosheet.

2. Analysis:

SPR biosensors have been studied in angular and phase measurements [6, 10, 12, 14, 17], in our work we study its angular measurement. Surface plasmon resonance (SPR) is mathematically described by evanescent wave (see Eq. 1), so it can be analysed using diffusion equations (see Eqs. 2). The complex reflection coefficient r_p of the incident light electric field is described by Fresnel's equations, and the reflectivity R_p is defined as square of the absolute-value r_p (see Eqs. 3).

$$E = E_0 \exp(j\omega t - j\vec{k} \cdot \vec{r}) \tag{1}$$

$$r_P = \frac{E_i}{E_r} = |r_P| e^{j\varphi} = \left|\frac{\tan(\alpha-\beta)}{\tan(\alpha+\beta)}\right| e^{j\varphi} \tag{2}$$

$$R_P = |r_P|^2 \tag{3}$$

$$M = \prod_{K=2}^{N-1} M_k$$

Where

$$M_k = \begin{bmatrix} cos\beta_k & \frac{-isin\beta_k}{q_k} \\ -iq_k sin\beta_k & cos\beta_k \end{bmatrix}$$

$$q_k = (\varepsilon_k - n^2 sin^2\theta)^{1/2}$$

$$r_P = \frac{(M_{11}+M_{12}q_N)q_1-(M_{21}+M_{22}q_N)}{(M_{11}+M_{12}q_N)q_1+(M_{21}+M_{22}q_N)} \tag{4}$$

$$S = \Delta\theta_{SPR}/\Delta n \tag{5}$$

For our multi-layered configuration, the transfer matrix method (TMM) can be used, which actually is the repeated application of the Fresnel's equations. See Eqs. 4, M represent the combination of the transfer matrix for the multi-layered SPR structure, k represent the kth layer in the structure, and θ, λ, ε, d represent the incident angle, incident light wavelength, the layer thickness and the dielectric constant respectively. The expression of the total reflectance coefficient (r_p) is presented, after algebraic manipulation we can easily find that the thickness (d) and the dielectric constant (ε) of each layer are the significant parameters to affect the r_p value. Thus, the fundamental step of our analysis is to find out the optimized parameters.

The first layer is SF10 prism, the refractive index is obtained by Eq. 6. For the silicon and gold layers the refractive index is obtained from the Pailk's work [20]. As for the optical constant of 2D MoS_2, we use the latest measurement parameters in Li's work [21]. Here, we test 5 wavelengths of the p-polarization incident light source including 600 nm, 633 nm, 660 nm, 785 nm, 1024 nm which contain visible and near infrared light. The incident angle we set ranges from 35 to 70 degree. In order to select out suitable thickness for each layer, we set different combinations. For gold we change the thickness from 30 nm to 50 nm, for silicon we set 0nm, 5nm and 7nm. While for MoS_2, we increase the number of layers gradually from 0 to 15 (we even go further to 35 in wavelength 785nm and 1024nm). The thickness of monolayer MoS_2 we used is 0.65nm [19, 22, 23].

$$n^2 - 1 = \frac{1.62153902\lambda^2}{\lambda^2-0.0122241457} + \frac{0.256287842\lambda^2}{\lambda^2-0.0595736775} + \frac{1.64447552\lambda^2}{\lambda^2-147.468793} \tag{6}$$

3. Optimization

Firstly, we optimized the number of MoS_2 layers. Using the TMM we can figure out the minimum value of the reflectivity corresponding to the resonance angle (or SPR angle). We studied the relationship between the minimum reflectivity and the increasing number of the MoS_2 layers with variant thickness of gold and silicon. Figure2 (a-c) shown the plot of the minimum R_p versus the number of MoS_2 layers. We can easily find that except the condition of 50nm gold, the minimum R_p is decreasing with the increasing number of MoS_2 layers until reaching to the lowest point of the curve. This strongly proves that adding appropriate thickness of MoS_2 can improve the optical absorption of the multi-layered structure thus enhancing the SPR excitation. The best enhancement effect established at the lowest point of the curve which corresponding to the optimized number of MoS_2 layers. However, if we continue to increase the number of the MoS_2 layers, the minimum R_p value will rise significantly, this is attributed to the thick MoS_2 layer that leads to inevitable energy loss, which overwhelms the enhanced performance.

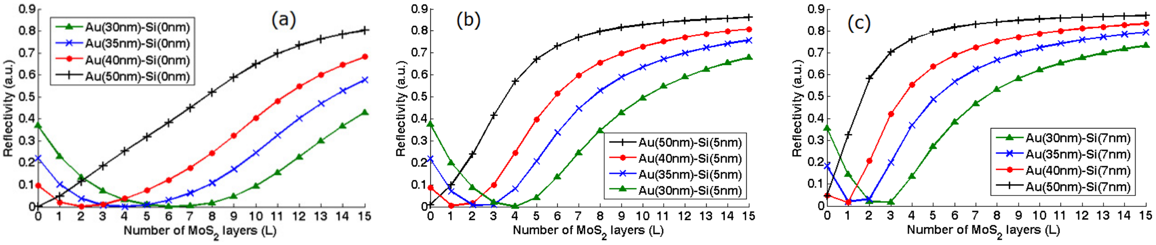

Fig.2. (a) The minimum reflectivity versus the number of MoS_2 layers without silicon (b) The minimum reflectivity versus the number of MoS_2 layers without silicon with 5nm thick silicon (c) The minimum reflectivity versus the number of MoS_2 layers without silicon with 7nm thick silicon.

As shown in Fig. 2 (a-c), it's obviously that with thickness of gold/silicon increasing, less number of MoS_2 layers is needed to achieve the lowest point of the minimum reflectivity. This demonstrates that additional gold and silicon, to some extent, can compensate the enhancement performance of the MoS_2. Then we find out the optimized number of MoS_2 layers for each combination of variant thickness of gold and silicon. Based on optimized thickness of MoS_2, we calculated the changes of resonance angle (or SPR angle) with a fixed refractive index change for 0.005 of the sample layer (see table1). Considering the large change of the resonance angle as well as the low full width at half maximum (FWHM) of the reflectivity curves, we finally select out the optimized parameters where the light source wavelength is set at 633nm, gold thickness is 35nm, silicon thickness is 7nm and monolayer MoS_2. With the optimized parameters, we can obtain a large change of SPR angle reaching to 0.6272 degree for a tiny change of refractive index in sample solutions.

Table 1. Change of the SPR angle with fixed change of refractive index in sample layer and the full width at half maximum of SPR curve at wavelength 633nm.

D_Au(nm)	D_Si(nm)	N_layers	Min_Reflectivity	SPR angle 1(Deg)	SPR angle 2(Deg)	ΔSPR angle(Deg)	FWHM (Deg)
30	0	6	3.89E-04	66.1331	66.5098	0.3767	23.7630
35	0	4	9.50E-05	62.1984	62.5488	0.3504	17.3194
40	0	2	7.48E-05	59.1843	59.4871	0.3028	9.0412
50	0	0	2.40E-03	56.9957	57.2561	0.2604	3.1054
30	5	4	7.63E-04	76.8978	77.3058	0.4080	23.6847
35	5	2	7.32E-03	71.5300	72.0468	0.5168	20.6084
40	5	1	4.54E-03	68.7373	69.2507	0.5134	16.2213

50	5	0	7.98E-03	66.1402	66.6355	0.4953	9.0950
30	7	3	1.80E-02	81.1397	81.3955	0.2558	21.4153
35	7	1	1.95E-02	76.9095	77.5367	0.6272	19.7343
40	7	1	1.56E-02	78.2051	78.8247	0.6196	18.6737

The sensitivity of the biosensor in our work is defined as the radio of the resonance angle changes to the refractive index changes in the sample layer. The Fig.3 (a) shows the plot of the change in refractive index in sample layer versus the change of resonance angle with the optimized parameters.

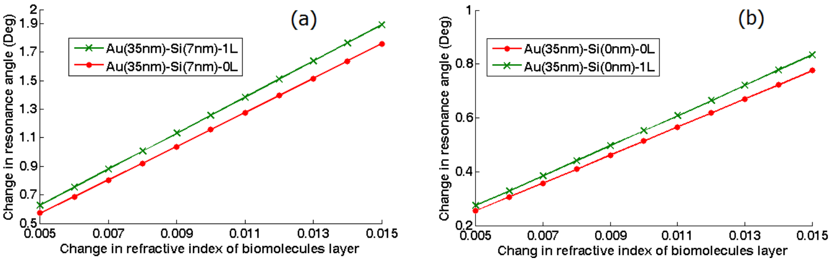

Fig.3. (a) Change in resonance angle versus the change in refractive index of sample layer with optimized thickness of gold and silicon at wavelength 633nm (b) Change in resonance angle versus the change in refractive index of sample layer at the optimized light source wavelength and thickness of gold.

The results shown clearly that the sensitivity of the MoS_2 enhanced SPR configuration (green line in fig. 3a) is ~10% higher compared with non-enhanced one (red line in Fig. 3a). We also studied the plot without silicon layers (see Fig. 3b), it shows that even the pure MoS_2 enhanced SPR structure can still improve the sensitivity by ~8%. These results are better than the famous graphene enhanced SPR structure [10].

4. conclusion

In this work, we proposed a SPR based biosensor with silicon and MoS_2 enhanced nanolayers. In order to investigate the sensitivity of the configuration, we firstly optimized the thickness of MoS_2. Then based on the modified number of MoS_2 layers we calculated the change of the resonance angle to a fixed 0.005 refractive index change of the sample layer through the transfer matrix method. Taking into account the largest change of the resonance angle and the FWHM, we selected out the optimum parameters. The best performance is obtained when the light wavelength is 633nm, the number of MoS_2 layer is 1, and the thickness of gold, silicon is 35nm, and 7nm respectively. Finally, we figured out the sensitivity with the optimized parameters, and our proposed MoS_2 enhanced structure can achieve ~10% higher sensitivity than the non-enhanced one. Through our systematic simulation work on the MoS_2 enhanced SPR configuration, we convince that MoS_2 nanosheet will also have good performance in the further experiment studies.

References

[1] J. Van der Geer, J.A.J. Hanraads, R.A. Lupton, The art of writing a scientific article, J. Sci. Commun. 163 (2000) 51–59.
[1] Homola, J., Present and future of surface plasmon resonance biosensors. Analytical and bioanalytical chemistry, 2003. 377(3): p. 528-539.
[2] Homola, J., S.S. Yee, and G. Gauglitz, Surface plasmon resonance sensors: review. Sensors and Actuators B: Chemical, 1999. 54(1): p. 3-15.
[3] Rich, R.L. and D.G. Myszka, Advances in surface plasmon resonance biosensor analysis. Current opinion in biotechnology, 2000. 11(1): p. 54-61.

[4] Liedberg, B., C. Nylander, and I. Lunström, Surface plasmon resonance for gas detection and biosensing. Sensors and actuators, 1983. 4: p. 299-304.

[5] Homola, J., Surface plasmon resonance based sensors. Vol. 4. 2006: Springer Science & Business Media.

[6] Law, W.-C., et al., Sensitivity improved surface plasmon resonance biosensor for cancer biomarker detection based on plasmonic enhancement. ACS nano, 2011. 5(6): p. 4858-4864.

[7] Zeng, S., et al., Size dependence of Au NP-enhanced surface plasmon resonance based on differential phase measurement. Sensors and Actuators B: Chemical, 2013. 176: p. 1128-1133.

[8] Homola, J., Surface plasmon resonance sensors for detection of chemical and biological species. Chemical reviews, 2008. 108(2): p. 462-493.

[9] Verma, R., B.D. Gupta, and R. Jha, Sensitivity enhancement of a surface plasmon resonance based biomolecules sensor using graphene and silicon layers. Sensors and Actuators B: Chemical, 2011. 160(1): p. 623-631.

[10] Wu, L., et al., Highly sensitive graphene biosensors based on surface plasmon resonance. Optics express, 2010. 18(14): p. 14395-14400.

[11] Schasfoort, R.B. and A.J. Tudos, Handbook of surface plasmon resonance. 2008: Royal Society of Chemistry.

[12] Choi, S.H., Y.L. Kim, and K.M. Byun, Graphene-on-silver substrates for sensitive surface plasmon resonance imaging biosensors. Optics express, 2011. 19(2): p. 458-466.

[13] Caide, X. and S.-F. Sui, Characterization of surface plasmon resonance biosensor. Sensors and Actuators B: Chemical, 2000. 66(1): p. 174-177.

[14] Sreekanth, K.V., et al., Sensitivity enhanced biosensor using graphene-based one-dimensional photonic crystal. Sensors and Actuators B: Chemical, 2013. 182: p. 424-428.

[15] Nair, R., et al., Fine structure constant defines visual transparency of graphene. Science, 2008. 320(5881): p. 1308-1308.

[16] Mak, K.F., et al., Atomically thin MoS_2: a new direct-gap semiconductor. Physical Review Letters, 2010. 105(13): p. 136805.

[17] Zeng, S., et al., Graphene–MoS_2 hybrid nanostructures enhanced surface plasmon resonance biosensors. Sensors and Actuators B: Chemical, 2015. 207: p. 801-810.

[18] Tsai, D.-S., et al., Few-layer MoS_2 with high broadband photogain and fast optical switching for use in harsh environments. Acs Nano, 2013. 7(5): p. 3905-3911.

[19] Lopez-Sanchez, O., et al., Ultrasensitive photodetectors based on monolayer MoS_2. Nature nanotechnology, 2013. 8(7): p. 497-501.

[20] Palik, E.D., Handbook of optical constants of solids. Vol. 3. 1998: Academic press.

[21] Li, Y., et al., Measurement of the optical dielectric function of monolayer transition-metal dichalcogenides: MoS_2, $MoSe_2$, WS_2, and WSe_2. Physical Review B, 2014. 90(20): p. 205422.

[22] Radisavljevic, B., et al., Single-layer MoS2 transistors. Nature nanotechnology, 2011. 6(3): p. 147-150.

[23] Bertolazzi, S., J. Brivio, and A. Kis, Stretching and breaking of ultrathin MoS_2. ACS nano, 2011. 5(12): p. 9703-9709.