URSI - RCRS 2022, IIT (Indore), India, 1 - 4 December 2022

2-D blue Phosphorene/Molybdenum Disulfide (BlueP/MoS_2) Hybrid Structure with Enhanced Sensitivity based on SPR for Chemical Sensing

Mohan Kumar Paswan [(1)], Rikmantra Basu* [(2)],
(1) National Institute of Technology Delhi, 110036, INDIA,
(2) National Institute of Technology Delhi, 110036, INDIA, https://nitdelhi.ac.in/?page_id=13670/?action=profile&id=251

Abstract

SPR (surface Plasmon resonance) based sensors have a significant role in sensing applications in real-time monitoring. Label-free detection and repeatable measurements. Chemical produced in fruits during food adulteration is detrimental to the health; hence, SPR sensors play a vital role in detecting these chemicals. In the present study, two-dimensional (2D) materials-based, such as black phosphorus (B.P.), the optimized structure of the SPR-based chemical sensor with the increased sensitivity and better figure of merit (FOM), have been proposed. The Heterostructure of the Blue P and 2D materials has enhanced the sensitivity. The excellent performances can be achieved by accurate the silver film thickness and the number of interlayers. In this configuration, the Blue Phosphorene/MoS2 Heterostructure with a silver metal layer and the B.P. layer. Simulation of the adapted structure's sensitivity properties using angular interrogation reveals that the sensitivity can be improved highly with the new design.
Moreover, the number of Blue Phosphorene/MoS2 layers for best simulation results is also clarified. The maximum sensitivity of the proposed optimized structure has been found at 458 Degree/RIU for the 5×10^{-3} index variation at the wavelength of 662*nm*. The results from the proposed structure show that the Sensor can enhance the sensitivity of the aqueous solution of the chemicals having the refractive index from 1.33 *RIU* to 1.36 *RIU*.

Keywords: Blue Phosphorene, Surface Plasmon Resonance, Chemical Sensor, Angular interrogation,

1. Introduction

In Prism-based SPR sensor has a metal layer on Prism. Surface Plasmon resonance (SPR) based sensors are essential for chemicals and Bio-chemical sensing; basically, they work on the Resonance phenomenon, in which; surface Plasmon waves (SPWs) are excited at the metal/dielectric interface. The two types of prism-based structures used in SPR sensors used (i) Otto configuration [10] and (ii) Kretschmann configuration [11]. The metal is directly coated onto the top of the coupling prism in the Kretschmann configuration. In contrast, in the Otto configuration, some gap is provided between the coupling prism and the metal layer [12-13]. We used here a Prism-based SPR sensor of Kretschmann configuration. A metal film is evaporated onto the glass block in the Kretschmann configuration. The light illuminates the glass block, and an evanescent wave penetrates through the metal film. The Plasmons are excited at the outer side of the film [1]. Transverse magnetic (T.M.) Polarized monochromatic light is made to an incident on one face of the Prism and reflected light observed from another front. Since the angular interrogation method is used, the angle of incident varies to achieve phase matching and excite the SPW. At the resonance angle, the light gets maximally coupled to the surface Plasmons, and the reflectance shows a corresponding minimum. The position of the reflectance minimum is highly dependent on the R.I. of the sensing medium and changes accordingly [2]. Gold (Au), silver (Ag), copper (Cu), nickel (Ni), and aluminum (Al) metals are commonly used as SPR active metals in plasmonic devices because they exhibit negative absolute permittivity and contain a substantial amount of charge carriers [8-9]. More importantly, BlueP/MoSe2 heterostructure shows significant absorption in visible and U.V. light areas. The heterostructure formation can improve the charge separation of photo-induced electron-hole pairs and broaden the light absorption range. The excellent performances can be achieved by accurate tuning, the gold film's thickness, and the number of B.P. interlayers [3-4].). Mishra et al. [2] have proposed SPR-based sensors with an extensive dynamic refractive index range. They have used the silicon layer over the gold material in the Kretschmann configuration. Zhitao et al. [1] proposed a prism-based structure for biosensing purposes. They enhanced the sensitivity of the Sensor with the help of graphene-covered $Au - MoS_2 - Au$ material layers. They achieved the sensitivity of the optimized structure up to $182^0/RIU$. The 2D materials like black phosphorus and graphene are used to enhance the sensitivity of the SPR-based chemical sensor in the work proposed by Y. Singh and M.K. Paswan [2]; the sensitivity of the proposed Sensor was $218°/RIU$ for the refractive range of 1.33to 1.36*RIU*. A.K. Sharma et al. [4] have submitted a two-dimensional Bluephosphorene/molybdenum disulphide (i.e., BlueP/MoS_2) heterostructure-based SPR sensor for bio-and gas sensing application. The proposed Sensor achieves the

highest sensitivity is 432^0/*RIU* for Heavy water (D_2O) in the proposed design study, a theoretical analysis has been done for the structure as an SPR-based bio/chemical sensor. The complete analysis is done through the FEM (finite element method) based simulations. For this purpose, MATLAB software has been used. We have done this study for the sensitivity enhancement of the diluted chemicals. The sensitivity of the proposed Sensor is analyzed and found to be high compared to the previously published results [1, 2, 4, 5, 6,].

2. Proposed structure

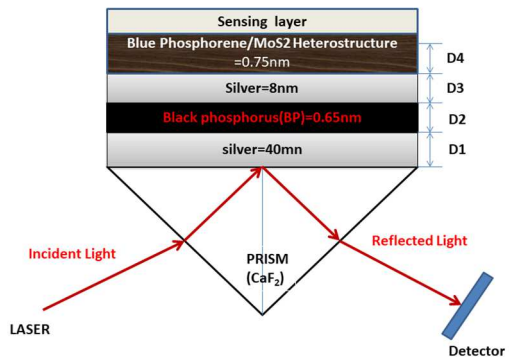

Fig.1: Schematic diagram of a proposed 6-layers SPR sensor configuration Ag/B.P./Ag/ Blue Phosphorene/MoS2 Heterostructure.

A proposed 6-layer novel SPR sensor structure is based on the Kretschmann configuration, shown in Fig.1. Angular interrogation method is taken for the study of this proposed structure. The incident angle (θ) is varied with a monochromatic light beam (p-polarized) due to a change in the refractive index of the media. At one face of the Prism, a T.M. Polarized light from the source at an operating wavelength (λ) = 662 nm was launched. Using suitable photo-detector arrays instruments, the reflected light is collected at the other face.

3. Theory

The prism and gold layer traditionally takes traditionally taken in SPR structure; hence we can achieve that the sensitivity of the Chemical sensor in our structure has enhanced as compared with the previous structures by adding B.P. and BlueP/Mos2 heterostructure layer using Ag as a metal layer. The sensitivity of the chemical Sensor by the analysis can be controlled by the refractive index of the sensing layer. We were sensing layer refractive index range taken at this time from 1.33 to 1.36 for B. P. (M) and BlueP/Mos2 heterostructure (N) layers. Here we investigate the sensitivity for BlueP/Mos2 heterostructure layers and B.P. layer.

4. Equations

Coupling Equation for incident light and S.P.s at the metal-dielectric interface, as shown

$$K_z = K_{sp} = \frac{2\pi}{\lambda} n_p \sin\theta_{SPR} = \text{real}\left(\frac{2\pi}{\lambda}\sqrt{\frac{\varepsilon_m\,\varepsilon_s}{\varepsilon_m+\varepsilon_s}}\right) \quad \textbf{(1).}$$

In above Eq. (1), n_p refers to a refractive index (R.I.) of the substrate medium (glass/prism), and lambda(**λ**) is the light wavelength. ε_m and ε_s are the dielectric constants of the metal layer and the sensing (analyte) layers, respectively. The Above Eq. (1) also signifies the coupling of incident light and S.P.s at the metal-dielectric interface.

Transfer Matrix Method

TMM (transfer matrix method) has been used to calculate the Rp (reflectance) of the Prism, in which an N-Layer matrix method has been used to realize the theoretical study [7]. The characteristics matrix for N-layer structure can be expressed as

$$M = \prod_{k=2}^{N-1} M_k = \begin{bmatrix} M_{11} & M_{12} \\ M_{21} & M_{22} \end{bmatrix} \quad (2)$$

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

Where $d_k = thickness,\ \varepsilon_k = permitivity\ of\ K^{th}$, $n_k = complex\ value\ of\ the\ refractive\ index$

$$\beta_k = \left(\frac{2\pi d_k}{\lambda}\right)\sqrt{\varepsilon_k - n_1^2 sin^2\theta_1}$$

$$q_k = \sqrt{\varepsilon_k - n_1^2 sin^2\theta_1/\varepsilon_k}$$

$$r_p = \frac{H_y^{ref}}{H_y^{inc}} = \frac{(M_{11}+M_{12}q_N)q_1-(M_{21}+M_{22}q_N)}{(M_{11}+M_{12}q_N)q_1+(M_{21}+M_{22}q_N)} \quad (3)$$

And then, the reflectance is calculated on the other side of the Prism as

$$R = |r_p|^2 \quad (4)$$

Where H_y^{inc} and H_y^{ref} are the incident and reflected magnetic fields through the multilayer structure.

5. Results discussion and Tables

5.1 Results discussion

In the proposed novel structure, the chemical Sensor's characteristic has been simulated Addition of BlueP/MoS2 heterostructure, silver metal, and B. P. in the Kretschmann configuration, given the better sensitivity for simply M=1 and N=1. Here M shows the number of B.P. layers, and N

indicates the number of BlueP/MoS2 heterostructure in our proposed structure.

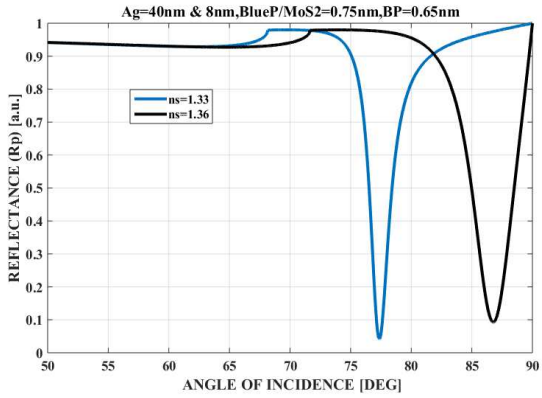

Fig.2. Reflectance as functions of the incident angle at the refractive index change for Ag+ BP+ Ag+ BlueP/MoS_2 heterostructure.

At different refractive indexes of the sensing material, we have simulated and plotted the reflectance of the proposed structure as a function of an incident angle for the improvement of the sensitivity performance

To illustrate the improvement of the sensitivity performance, we plot the reflectance of the structure as a function of the incident angle at the different refractive indexes of sensing materials, as shown in Fig.2. It is clearly found that the reflectance exists a sharp dip at a specific angle range due to the excitation of SPR. This phenomenon indicates that the chemical sensor configuration absorbs the incident light by the exciting SPR. While the refractive index of the sensing layer has small changes due to the molecular interaction, the resonance dip has a small excursion about $\delta\theta = 9.40^0$. Therefore, we can get the enhanced sensitivity 313.33^0/RIU of the structure according to the corresponding calculation expression $S_n = \delta\theta_{SPR}/\delta n_s$.This result, we simulated for refractive index range of 1.33 to 1.36. These results show a reflectance dip for only changing the refractive index range from 1.33 to 1.36 where $\delta n_s = 0.03$ more than 1.36 refractive index reflectance curve not shown significant dip. So, we consider R.I. ranges below 1.37. when increasing the B.P. layer for the same R.I. ranges, it offers very high FWHM. So, we simulated R.I. results ranging from 1.331 to 1.340.

5.1.1. Study Effect of Variation of B.P. and BlueP/MoS_2 heterostructure layers

Fig.3(a) shows the graph of reflectance variation with respect to the incident angle for different numbers of B.P. (M) layers at RI 1.331. We consider single BlueP/MoS2 heterostructure(N=1) layers in the whole simulation. This simulated result shows that when we increase the B.P. layers, reflectance dip increases till M=9 and also getting SPR angle changes. More than M=9 layers of B.P. reflectance dip start decreasing, and FWHM increases. So, in this particular case, we observed that M=9 BP layers give suitable sensitivity parameters

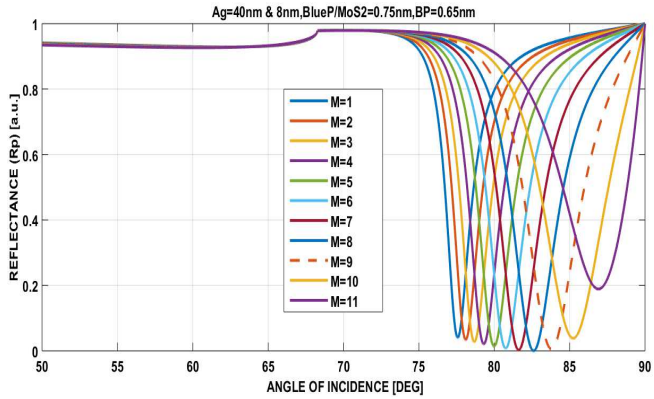

Fig.3 (a). Variation of reflectance concerning the incident angle for R.I. (refractive index) 1.331 with changing black phosphorus (B.P.) layer (M)

Further, we simulated the results for changing the BlueP/MoS_2 heterostructure layers (N) for the constant B.P. layer (M=1).

5.1.2. Study Effect of Variation BlueP/MoS_2 heterostructure layers (N) for constant B.P. layer (M=1).

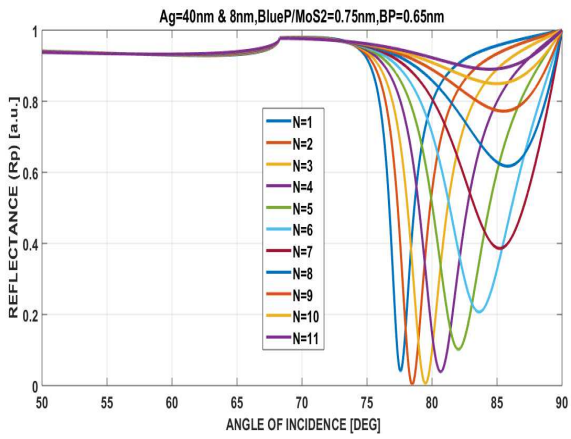

Fig.3(b). variation of reflectance concerning the incident angle for R.I. of 1.331for different BlueP/MoS_2 Heterostructure layers.

Fig.3(b) shows the results for single B.P. (Black phosphorus) layers and changing BlueP/MoS_2 Heterostructure layers; we got enhanced sensitivity when increases the BlueP/MoS2 Heterostructure layer, but after 3 layers, the FWHM value increases drastically. Due to a change in BlueP/MoS_2 Heterostructure layers or increases in the BlueP/MoS_2 Heterostructure layers value, the value of reflectance dip changes and full width at half maximum (FWHM) value increases which lead to the decreased detection accuracy. Detection accuracy is an essential parameter in checking the efficiency of sensors. The detection accuracy (D.A) or detection precision is defined as the inverse of the SPR (surface Plasmon Resonance) curve's angular full width at half maximum (FWHM)

Detection accuracy (D.A) = $\frac{1}{FWHM}$ (5).

So, we have not considered more than three layers of BlueP/MoS2 Heterostructure for our proposed structure. At the same time, when we increase the B.P. layers, it shows good sensitivity up four layers with two layers of BlueP/MoS2 Heterostructure. We observed that N=2 gives some relevant results, but when we used N=1 and increased the B.P. (M) layers, its sensitivity increased to 461^0/RIU for M=9, N=1. So, we consider the single layers of BlueP/MoS_2 heterostructure layers for further investigation. So above graphs shows that we can't blindly change the B.P. layers and BlueP/MoS_2 heterostructure layers as well as R.I. because the proposed structure shows its highest sensitivity at a particular configuration. This study helps to consider B.P. layers materials used more in place of BlueP/MoS2 Heterostructure layers. We simulate the results for different B.P. layers and check the sensitivity.

5.1.3. Study Effect of Variation Refractive index (R.I.) ranges from 1.330 to 1.340 for M=9, N=1

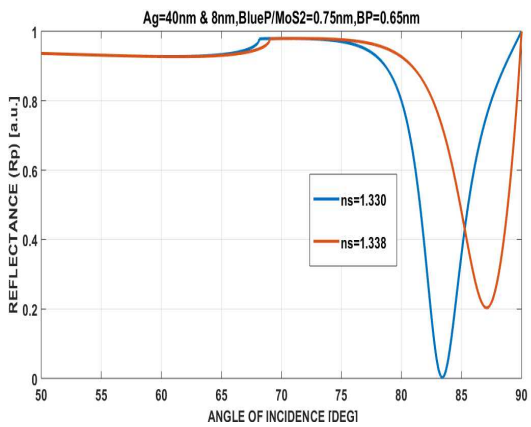

Fig.3(c). Variation of reflectance with respect to the incident angle for R.I. (refractive index) ranges from 1.330 to 1.340 BP (N=9) layers and BlueP/MoS_2 heterostructure (N=1) layer.

Figure 3(c) shows the result of M=9-layers of B.P. and N=1 layer of BlueP/MoS_2 heterostructure Reflectance V/S incident angle curve for the refractive index ranges 1.33 to 1.338 with two sandwich Ag(silver) metal layer. It shows the enhanced sensitivity 461.25^0/RIU at R.I. (refractive index) 1.338. it also indicates a sensitivity of 458^0/RIU for δn_s= 0.005 RI ranges 1.331 to 1.340. we choose M=9 and N=1 Because it shows enhanced sensitivity; when considering other than that configuration, we got high FWHM and somewhere, we got good FWHM but very low sensitivity, so the above configuration for our proposed structure suited well and give good FWHM and enhanced sensitivity.

5.2 Tables

Table I
Sensitivity comparison table with some recent papers works

Reference	Wavelength λ (nm)	n_s ($\Delta n_s \approx 0.005$)	Max. Sensitivity (^{0}/RIU)
Lin et al.[1]	633	1.33	182
Y. Singh et al.[5]	633	1.33	218
Wu et al.[6]	633	1.33	279
A. K. Sharma et al. [4]	662	1.3264	355.525
		1.33	432.15
Proposed scheme	662	1.336($\Delta n_s \approx 0.005$)	458
		1.330 to 1.340($\Delta n_s \approx 0.008$)	461.25

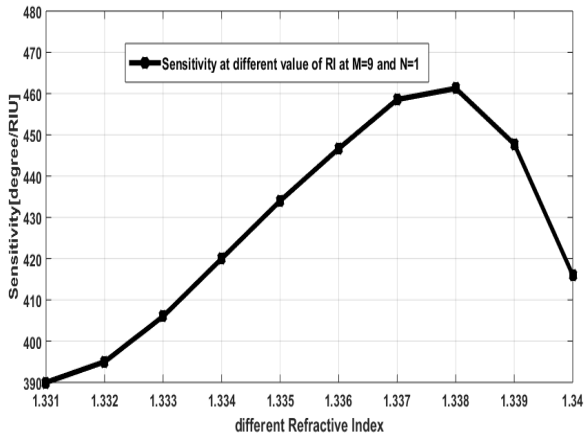

Fig.4 sensitivity increases with RI range 1.331 to 1.340 for M=9 &N=1.

Fig.4 shows the sensitivity v/s refractive index graph for R.I., which ranges from 1.331 to 1.340. figure 4 shows maximum sensitivity of 461.25°/RIU at the R.I. (refractive index) of 1.338. we used various R.I. (Refractive index ranges) and different proposed materials layer combinations. We got the highest sensitivity, 461.25°/RIU for M=9 (B.P. layers), N=1 (BlueP/MoS_2 heterostructure) for the RI ranges 1.331 to 1.340. The above Table I shows the recent discovery in SPR-based sensors with their sensitivity. Our proposed sensors show better sensitivity compared to Table I recent papers on SPR-based Sensors. These proposed sensors can be used in various chemical/bio-chemical/check food quality from adulteration sensing. During the simulation, we found that it is very much useful for hard water D_2O, ice, and blood sensing.

6. Acknowledgements

The DST supported this work -SERB Project under Core Research Grant (CRG) Scheme vide File No CRG/2020/002966. Dr. Rikmantra Basu is thankful to DST-SERB (CRG scheme 2021), India, for supporting the project's work.

7. References

1. Lin, Zhitao, Leyong Jiang, Leiming Wu, Jun Guo, Xiaoyu Dai, Yuanjiang Xiang, and Dianyuan Fan. "Tuning and sensitivity enhancement of surface plasmon resonance biosensor with graphene covered Au-MoS 2-Au Films." *IEEE Photonics Journal* 8, no. 6 (2016): 1-8.

2. Mishra, Akhilesh K., Satyendra K. Mishra, and Rajneesh K. Verma. "An SPR-based sensor with an extremely large dynamic range of refractive index measurements in the visible region." *Journal of Physics D: Applied Physics* 48.43 (2015): 435502.

3. Li, K., Li, L., Xu, N., Peng, X., Zhou, Y., Yuan, Y. Qu, J. (2020). Ultrasensitive Surface Plasmon Resonance Biosensor Using Blue Phosphorus–Graphene Architecture. Sensors, 20(11), 3326. doi:10.3390/s20113326

4. Sharma, Anuj & Pandey, Ankit. (2018). Blue Phosphorene/MoS2 Heterostructure based SPR Sensor with Enhanced Sensitivity. IEEE Photonics Technology Letters. P.P. 1-1. 10.1109/LPT.2018.2803747.

5. Singh, Y., Paswan, M.K. and Raghuwanshi, S.K., 2021. Sensitivity enhancement of SPR sensor with the black phosphorus and graphene with bi-layer of gold for chemical sensing. *Plasmonics*, *16*(5), pp.1781-1790.

6. Wu, Leiming, et al. "Sensitivity enhancement by using few-layer black phosphorus-graphene/TMDCs heterostructure in surface plasmon resonance biochemical sensor." Sensors and Actuators B: Chemical 249 (2017): 542-548.

7. Raghuwanshi, S.K. and Kumar, M., 2018. Highly dispersion tailored property of novel class of multimode surface plasmon resonance biosensor assisted by teflon and metamaterial layers. *IEEE Transactions on Instrumentation and Measurement*, *68*(8), pp.2954-2963.

8. Verma R, Gupta BD, Jha R (2011) Sensitivity enhancement of a surface plasmon resonance-based biomolecules sensor using graphene and silicon layers. Sens Actuators B Chem. 60(1):623–631.

9. Chu P, Chen J, Xiong Z, Yi Z (2020) Controllable frequency conversion in the coupled time-modulated cavities with phase delay. Opt Commun

10. Otto A (1968) Excitation of nonradiative surface plasma waves in silver by the method of frustrated total reflection. Zeitschrift für Physik A Hadrons and nuclei 216(4):398–410

11. Kretschmann E, Raether H (1968) Radiative decay of non radiative surface plasmons excited by light. Zeitschrift für Naturforschung A 23(12):2135–2136

12. Homola J, Yee SS, Gauglitz G (1999) Surface plasmon resonance sensors. Sensors and Actuators B: Chemical 54(1–2):3–15

13. H. Raether (1988) Surface plasmons on smooth surfaces, in Surface plasmons on smooth and rough surfaces and on ratings. Springer, pp. 4–39