Zinc sulfide, silicon dioxide, and black phosphorus based ultra-sensitive surface plasmon biosensor

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Abstract
The optical biosensor is the emerging research area in the field of bio-photonics. The black phosphorus zinc sulfide-based hybrid configuration is suitable for implementing and analyzing ultrasensitive biosensors. Ag/Zinc sulfide/silicon dioxide/black phosphorus-based biosensor has been implemented in the proposed work using the modified Kretschmann configuration. The sensitivity improvement of the designed SPR sensor is analyzed in the different arrangements of the layers. The thickness of the layers of all the materials has been optimized. The thickness of the Ag metal layer is optimized and taken as 45 nm. The sensitivity and quality factor measured here is as high as 664.6°/RIU and 200 at 1.37 refractive index with the P-polarized light source of 633 nm wavelength. The proposed biosensor confirms tremendous sensitivity, detection accuracy, and quality factor growth compared with the traditional SPR sensors. Zinc sulfide has multiple applications in the sensing fields, like sensors based on UV rays, lasers, and gas.

Keywords Surface plasmon resonance · Zinc sulfide · SiO2 · Sensor

1 Introduction
The surface plasmon resonance is a condition that exists when a P polarized wave is an incident on the interface of a metal and dielectric material through a coupling prism. Some part of incident light penetrates into the metal layer, generally known as an evanescent wave, causing excitation of the free electrons, which finally produces surface plasmon
polaritons (SPPs) (Liao et al. 2021). The matching of the wave vector and evanescent wave vector intensity gives resonance. The whole mechanism is based on the attenuation total reflection (ATR). The electrons on the metal surface absorb the incident wave, decreasing the reflected light (Yang et al. 2019). The refractive index (RI) of metal generally varied in accordance with the incident angle (Roether et al. 2019; Pal 2020). Surface plasmon resonance is gaining more popularity due to unique features like greater sensitivity, real-time response during monitoring, high detection accuracy, fast response, etc. (Kim et al. 2019). These sensors have a wide area of applications in the development of vaccines, drugs, doping, food safety testing, various diseases detection, gene treatments, and some other areas (Jena et al. 2019; Qin et al. 2018).

The conventional sensors are implemented using the Otto or Kretschmann configuration, with coupling metal and sensing layers. The metals such as silver (Ag) (Rahman et al. 2020), gold (Au) (Dai et al. 2018), aluminum (Al), and copper (Cu) (Karki et al. 2022) (Mishra and Mishra 2016) are primarily used in SPR design. The sensitivity obtained using the conventional configuration of the biosensor (i.e., prism, metal, and sensing layer) is generally low. So, to improve the sensitivity to an extent, modification in the conventional configuration is required. Mishra and Mishra (2016) proposed an SPR sensor for deoxyribose nucleic acid (DNA) hybridization using Ag and graphene layer with silver nitride (Si$_3$N$_4$) achieved a maximum sensitivity of $212.2^\circ$/RIU with figure of merit (FOM) and detection accuracy (DA) as 138.24 RIU$^{-1}$ and 9.124, respectively. Singh and Raghuwanshi (2019) theoretically investigated a gas detection SPR sensor design using Au layer (bimetallic) and two BP layers, found the sensitivity as 245.5$^\circ$/RIU at the operating wavelength 633 nm. Pal and Jha (2021) proposed SPR sensor design with the help of two silver metal layers and barium titanate (BaTiO$_3$) layer and achieved $280^\circ$/RIU sensitivity. Maharana et al. (2014) theoretically analyzed an SPR sensor design using Otto configuration with graphene film as the basic recognition element (BRE). The sensitivity of the proposed work was enhanced by 10.71% at 700 nm and by 5% at 1000 nm. Verma et al. (2015) attained high sensitivity of SPR biosensor using an air gap as high as 2.35 times of basic graphene-based sensor in the absence of airgap. Chen and Lin (2019) designed an SPR based bio gas-sensor with MgF$_2$ as a coupling prism. The rhodium (Rh) and a silver (Ag) metal used as bimetallic layers found sensitivity as high as 220$^\circ$/RIU. Bijalwan et al. give an SPR sensor design with graphene (2D-material) nanolayers and metal layers of Au, Al sensitivity of 160$^\circ$/RIU is calculated and with other combination of WSe$_2$ with Au and Al(bi-metal films) sensitivity of 163$^\circ$/RIU was obtained (Bijalwan 2020). Karki et al. demonstrated a SPR bio-sensor with dual metal layers of Nickel and Ag between them a franckeite layer is inserted. The highest sensitivity of 352$^\circ$/RIU is achieved (Karki et al. 2021). These researches clearly signify that after addition of 2D materials in the conventional SPR sensor structure the sensitivity tremendously increases. Singh et al. (2021) investigated simulation-based study for designing a SPR based bio-sensor. The performance parameters like sensitivity as high as 218$^\circ$/RIU, FWHM as 8.34 and quality factor as 26.13 has been achieved. Zhao et al. (2019b) proposed a heterogeneous structure (Au/Bi$_2$Te$_3$/BP/Cytop) based SPR biosensor. They improved the sensitivity about 29% over the traditional (Au/ Bi$_2$Te$_3$) biosensor. Srivastava and Jha designed a SPR bio-sensor structure giving sensitivity rise up to 73% (using Ag as metal and MoS$_2$ as BRE) than the conventional one (Srivastava and Jha 2018).
performance parameters like sensitivity, the figure of merit (FoM), detection accuracy (DA) change is limited using Ag alone in the SPR designs can be improved by using 2D material. In sensing applications, the commonly used 2D materials are graphene (Mohanty et al. 2016), black phosphorus, and transition metal dichalcogenides (TMDCs). The basic recognition element (BRE) used in the proposed work is Black phosphorus (BP). Since 2014, with honeycomb lattice structure BP gaining popularity in SPR sensor designing. The optoelectronic and mechanical features such as high surface to volume ratio (SVR) (Singh et al. 2021), higher biomolecular adsorption energy than graphene, and molybdenum disulfide (MoS$_2$) (Cho et al. 2016), high mobility, low extinction constant (Mao et al. 2016), direct bandgap. Toward target, analytes are more sensitive. Its sensing capability is approximately twenty times of other 2D materials like MOS$_2$ (Su et al. 2020) due to its greater molar response factor. Although BP oxidizes quickly, adding other material results in low oxidation as molecular binding is effective inside the sensing layer.

The other material we are using in our work is zinc sulfide (ZnS). It is a compound semiconductor with exclusive optical properties like a broad energy band gap of 3.72 eV and 3.77 eV and excellent chemical, thermal stability. Its popular applications are in the sensing field, including lasers, gas, light sensors (Wang et al. 2012). With the entry of ZnS in photonics, optoelectronics significantly grew over the years and gained popularity (Heydarian et al. 2019). Another optimized layer in which we include our proposed design is silicon dioxide (SiO$_2$). Its inclusion in our design is due to its unique properties like higher surface area (700 and 500 m$^2$/g), good chemical and thermal stability, larger bio compatibility, and non-toxic makes it useful for adsorption, in bio sensing catalysis (Karki et al. 2021; Zhao et al. 2019a; Ud et al. 2018).

Section 2 explains the constructional part of our design and various mathematical expressions used to model the SPR sensor. Section 3 gives the results and discussions for the proposed sensor. Section 4 consists of the conclusion of the proposed work.

## 2 Designing and modeling of sensor

### 2.1 Prism and metal layer refractive indices

The proposed design based on modified Kretschmann configuration consists of a coupling prism (BK$_7$ type) with layers of Ag metal, ZnS, BP, and sensing medium (analyte) to produce required surface plasmons (SPs), as shown in Fig. 1. These SPs get generated when a P-polarized wave (TM mode) is incident on the coupling prism, generating an evanescent wave along the interface section of prism and metal and penetrates the structure. At resonance angle ($\theta_{\text{res}}$) the SPs generates at the next interface of metal (Ag) and ZnS. It is used as a fundamental recognition element with some exclusive optical properties of black phosphorus (2D material). The refractive index of the sensing medium changes as BP adsorbs biomolecules on its surface.

The refractive index $\mu_{BK7}$ expressed by the numerical formula (Zeng et al. 2015):

$$\mu_{BK7}^2(\lambda) = \frac{1.03961212\lambda^2}{\lambda^2 - 0.00600069867} + \frac{0.231792344\lambda^2}{\lambda^2 - 0.0200179144} + \frac{1.01046945\lambda^2}{\lambda^2 - 103.560653} + 1$$

(1.1)
Here $\lambda$ is the wavelength of incident light. The He–Ne source is used, and the wavelength is 633 nm.

The metallic layer’s refractive index calculation is given by Drude-Lorentz model (Gupta and Sharma 2004):

$$
\mu_m = 1 - \frac{\lambda^2 \lambda_c}{\lambda_p^2 (\lambda_c + i\lambda)}
$$

where $\lambda_c$ and $\lambda_p$ is the collision and plasma wavelengths, having values $1.7614 \times 10^{-5}$ m and $1.4541 \times 10^{-7}$ m respectively for Ag (metal) layer. The other layers which we are using in our proposed SPR sensor design, ZnS, have a refractive index of $2.35521 + i 0.00523$ (Mei and Menon 2020), SiO$_2$ has $1.4570$, and of BP layer is $3.531 - i 0.04087$ (Singh and Raghuvanshi 2019). The refractive index for sensing layer is computed numerically as:

$$
\mu_s = 1.33 + \delta \mu
$$

Here $\delta \mu = \text{change in sensing media refractive index}.$

### 2.2 Modeling theory

The performance analysis of the SPR biosensor is done by employing a reliable Transfer matrix method (TMM) and Fresnel equations. The TMM used here does not include any approximation. The multilayers used here have a thickness and dielectric dimension of $d_i$ and $\epsilon_k$, respectively.

The different thicknesses of layers mounted on prism are, for Ag, ZnS, SiO$_2$ and BP layer as 45 nm, 0.8 nm, 50 nm, and 0.34 nm, respectively. The matrix formation for tangent component for starting and ending boundary given by Lili et al. (2019):

$$
\begin{pmatrix}
P \\
Q
\end{pmatrix}
= T
\begin{pmatrix}
P_{n-1} \\
Q_{n-1}
\end{pmatrix}
$$

Fig. 1 Constructional view of ZnS and SiO$_2$ based SPR sensor
Here, at the first boundary, P and Q are electric, and magnetic field components are $P_{n-1}$ and $Q_{n-1}$ are electric and magnetic field components at the last boundary. T indicates characteristics transfer matrix, its value given by Maharana and Jha (2012):

$$T = \prod_{k=2}^{n-1} T_r$$

$$T_r = \begin{bmatrix} T_{11} & T_{12} \\ T_{21} & T_{22} \end{bmatrix} = \begin{bmatrix} \cos \beta_r & -i \sin \beta_r/q_r \\ -i q_r \sin \beta_r & \cos \beta_r \end{bmatrix}$$ (1.5)

Here, $T_r = rth$ layer matrix.

Here $\beta_r$, $q_r$ are the optical admittance and phase factor respectively given by,

$$\beta_r = d_r Y_0 \sqrt{(\epsilon_r - n^2 \sin^2 \theta)}$$ (1.6)

and phase factor, $q_r = \sqrt{(\epsilon_r - n^2 \sin^2 \theta)}/\epsilon_r$ (1.7)

Here, $\theta$ = incidence angle, and $Y_0$ = free space wave number.

The mathematical expression for the reflection coefficient $r_p$ is given by Mueller et al. (2010):

$$r_p = \left| \frac{(C_{11} + C_{12}q_n)q_p - (C_{21} + C_{22}q_n)}{(C_{11} + C_{12}q_n)q_p + (C_{21} + C_{22}q_n)} \right|^2 = R_p^{1/2}$$ (1.8)

Here, $R_p$ = reflectivity of input polarized radiation.

The tabulation chart characterizing different SPR parameters is summarized in Table 1. The characteristic parameters that define the SPR biosensor reliability are Sensitivity (S), which defines the ratio of SPR angle change with the RI change. The second is the Figure of merit (FOM)/ quality factor which gives information about the quality of the bio-sensor. The third one is detection accuracy, which gives information about the sensor’s accuracy, and lastly, the Full width half maximum (FWHM) talks about resonance curve width at 50% reflectivity.

### 3 Results and discussions

The prism coupler having greater RI gives sharp resonance curves compared to lower values coupler prism. But the BK7 prism with lower RI for SPR sensor gives better sensitivity (Yue et al. 2019). The coming Fig. 4 gives an idea about the outcomes of inserting Zinc sulfide and Black phosphorus films over the conventional biosensor with RI at 1.33 and 1.335. A silicon dioxide (SiO$_2$) layer is also taken with a constant

### Table 1  SPR characterization defined by parameters

| Parameters                        | Formulas                                      | Unit                |
|----------------------------------|-----------------------------------------------|---------------------|
| Sensitivity (S)                  | $S = \delta \theta_s/\delta \theta$          | Deg(RIU)$^{-1}$     |
| Figure of merit (F.O.M)/ Quality factor (QF) | $F = S * DA$                                  | RIU$^{-1}$          |
| Detection accuracy (D.A.)        | $DA=(\text{FWHM})^{-1}$,                      | Deg$^{-1}$          |
| Full-width half maximum (F.W.H.M) | FWHM=$\theta_b - \theta_a$,                   | Deg                 |
thickness of 50 nm after optimization in the proposed work. Figure 2a shows the plot for reflectivity with different incidence angles from (55° to 90°) for conventional SPR sensor \((Z = 0, B = 0)\) with basic Kretschmann configuration in figure giving sensitivity, \(S = 103.6°/\text{RIU}\), and change in incidence angle, \(\Delta\theta = 0.518\). The sensitivity and reflectivity are the basic sensors analysis parameters which can be varied by placing layers (2D materials) between prism and sensing layer. So, after adding the ZnS layer \((Z = 1, B = 0)\) over the Ag metal layer, and SiO₂ layer also added in the sensor configuration, get sensitivity as \(S = 102.6°/\text{RIU}\) and \(\Delta\theta = 0.513\), reducing reflectivity (shown in Fig. 2b). The third case, with a single BP layer \((Z = 0, B = 1)\) along with SiO₂ layer and no ZnS layer between metal and sensing layer, is shown with Fig. 2c, the parameter, sensitivity, comes out to be \(S = 103°/\text{RIU}\) with \(\Delta\theta = 0.515\).

At last, Fig. 2d gives the impact of single ZnS and single BP layer \((Z = 1, B = 0)\) on the conventional sensor, increasing sensitivity values up to 107°/RIU and lowering the reflectivity value of reflectivity. This happens due to the absorption of the incident light at the BP and sensing layer because surface plasmons are generated. With the continuation to this, the next set of figures shown by Fig. 3 gives an idea about the layer’s

![Diagram]

Fig. 2  a–d Representing impact of incidence angle on reflectivity at RI=1.33 and 1.335
combinations (ZnS and BP) impact on the performance of SPR sensor at variable RI varying from (1.33 to 1.36) with the change of 0.005.

Figure 3 shows sensitivity alteration with sensing media RI (varies from 1.33 to 1.36). For different zinc sulfide (Z) and black phosphorus (B) layers, the minimum sensitivity and maximum sensitivity are given in Table 2.

The analysis made here clearly concludes that with modifications on the conventional sensor (Z = B = 0), the sensitivity increases by inserting zinc sulfide and black phosphorus layers. The sensitivity value is maximum for the case of Z = 1 and B = 1, i.e., S = 129.2°/RIU at RI = 1.36.

The sensitivity and reflectivity values are being calculated with Z = 0, B = 0 as 118°/RIU (maximum), and 0.05676 (minimum) for RI = 1.36, shown in Fig. 4a. Further, by adding a single layer of black phosphorus (BP = 1) without any zinc sulfide (Z = 0) layer (Fig. 4b), the sensitivity and reflectivity come out to be 121.2°/RIU (maximum) and 0.05558 (minimum) respectively at RI = 1.36. The following case is shown by Fig. 4c, giving maximum sensitivity as 126°/RIU and minimum reflectivity at RI = 1.36 for single zinc sulfide and no black phosphorus layer (i.e., Z = 1, B = 0). Figure 3d gives the best values at RI = 1.36, maximum sensitivity as 129.2°/RIU, and minimum reflectivity at 0.04501 for one zinc sulfide and one black phosphorus layer (i.e., Z = B = 1).

Figure 5a shows the variation in sensitivity (S) and detection accuracy (DA) for combination layers for different zinc sulfide (Z) and black phosphorus (B). The interchange of both parameters is visible from the multilayer plot in Fig. 5a. The sensitivity and DA of the sensor should be high for the better performance of the sensor. The DA is low here, and it needs to be improved. The other two performance parameters, Full width half maximum (FWHM) and quality factor (QF) alteration with the same combination of layers (Z/B), as

| Z/B layer case | Minimum sensitivity (deg/RIU) | Maximum sensitivity (in deg/RIU) |
|----------------|-------------------------------|----------------------------------|
| Z = 0, B = 0   | 103.4                         | 118                              |
| Z = 0, B = 1   | 102.6                         | 121.2                            |
| Z = 1, B = 0   | 103                           | 126                              |
| Z = 1, B = 1   | 107                           | 129.2                            |
Fig. 4 Reflectivity and Incidence angle curve for a $Z = 0, B = 0$, RI varies  

(b) $Z = 0, B = 1$, RI varies  

(c) $Z = 1, B = 0$, RI varies  

(d) $Z = 1, B = 1$, RI varies

Fig. 5 a Detection accuracy and sensitivity plot with combinations of layers (for Z and B). b FWHM and QF plot with combinations of layers (for Z and B)
shown in Fig. 5b. The parameter FWHM should be low so that the resonance angle can be computed precisely. The high value of the quality factor is desirable.

The subsequent results for which Fig. 6 is drawn show the sensitivity range for different refractive indices varying from 1.33 to 1.36. The sensitivity varies from 277.8°/RIU to 664.6°/RIU. For RI 1.36, the SPR sensor shows maximum sensitivity.

Figure 7 shows a plot for reflectivity alteration with incidence angle variation in zinc sulfide and black phosphorus layers, respectively. The optimum thickness value taken for our SPR design is 45 nm for the silver (Ag) layer; for Silicon dioxide (SiO$_2$), it is 50 nm. In Fig. 7a gives the analysis for performing parameters after changing the zinc sulfide layer (Z = variable) with constant black phosphorus layer set as $B = 1$. The sensitivity comes to about 664.6°/RIU.

The significance of the statements also boosts up by seeing the increase in reflectivity and SPR curve broadness. With the following Fig. 7b, using single-layer zinc sulfide and variable black phosphorus layer (i.e., $Z = 1$, $B = variable$), we got the maximum sensitivity for our proposed SPR sensor design as high as 266°/RIU. The resonance

![Fig. 6 Sensitivity versus RI (sensing layer) plot](image)

![Fig. 7 a, b Graphs showing the impact of layer variation on sensor’s performance](image)
curve’s shift and reflectivity’s decrement are seen as we increase the black phosphorus layer.

The distribution of the electric field enhancement with respect to the distance, which is orthogonal to the prism interface for different numbers of black phosphorus layers, is shown in Fig. 8.

Figure 8a, b shows the X-component of the electric field and Y-component of the electric field at the RI = 1.33 of the sensing layer. The electric field distribution inside the sensor is shown in Fig. 9. The electric field intensity is high at the metal and zinc sulfide interface, and intercity decreases at zinc sulfide and SiO₂. It indicated that field intercity is more when light absorption is more significant. Further electric field intercity increases at the black phosphorus and sensing layer interface. It shows that greater absorption of light to have significant SPW excitation. A proposed electric field plot has been designed for a single layer of ZnS and BP.

A tabular comparative analysis of this work with earlier literature is being compared here with the help of fundamental parameters with operating wavelength and design configuration of Table 3.

4 Conclusion

We proposed a new SPR optical biosensor in this study with high sensitivity. The suggested biosensor’s configuration includes a ZnS layer to improve sensitivity and protect the nano-composite layer from oxidation. Furthermore, our findings demonstrate that using black phosphorus as a biological diagnosis component can be helpful for sensing. We examined
how different prisms affected the sensitivity of this proposed SPR optical biosensor. The results reveal that when the refractive index of the prism increases, the sensitivity of the suggested SPR biosensor diminishes. As a result, we chose BK7 as the coupling prism in our biosensor design. Our calculations also suggest that the proposed biosensor with the maximum sensitivity requires a SiO₂ layer with a thickness of 50 nm that contains a silver metal layer with a thickness of 45 nm. Finally, we demonstrated that the best-proposed biosensor has six layers of ZnS on both surfaces of the nanocomposite layer, with a maximum sensitivity of 664.6°/RIU.

### Table 3  Comparative analysis of our proposed work with existed researches

| References               | Configuration                       | Sensitivity (Deg/RIU) | FWHM (Deg) | DA | QF |
|--------------------------|-------------------------------------|-----------------------|------------|----|----|
| This work                | BK₇/Ag/ZnS/SiO₂/BP                  | 664.6                 | 3.323      | 0.3009 | 200 |
| Mishra and Mishra (2016) | MgF₂/Rh/Ag/Si/graphene             | 220                   | 10.204     | 0.0980 | 21.56 |
| Kushwaha et al. (2018)   | SF₁₀/ZnO/Au/MoS₂/graphene          | 101.58                | 6.723      | 0.1487 | 15.11 |
| Wu et al. (2017)         | BK₇/Ag/BP/WSe₂                     | 279                   | –          | –    | –   |
| Lin et al. (2016)        | BK₇/Au/MoS₂/Au/graphene            | 182                   | 9.475      | –    | 19.21 |
| Dai et al. (2019)        | BK₇/Ag/Tin selenide (SnSe)         | 178                   | –          | –    | –   |
| Vasimalla et al. (2020)  | SF₁₀/Ag/BP/graphene/affinity/PBS   | 91.54                 | –          | 3.61  | 54.81 |
| Zhao et al. (2019b)      | BK₇/Au/Bi₂Te₃/BP/Cytop             | 175                   | –          | –    | –   |
| Singh et al. (2021)      | BK₇/Au/BP/Au/graphene              | 218                   | 8.34       | –    | 26.13 |

**Author contributions** BK formulated the problem statement, giving the theoretical background and mathematical modeling for the SPR biosensor. He also helped in drafting and finalizing the manuscript. YT provided the theoretical background to biosensing and the importance of Optical Biosensing. He also helped in finalizing the design of the proposed sensor. AU worked towards the complete manuscript, formatting, and finalizing the manuscript. AP provided statistical analysis for the results. He provided the theoretical background to SPR biosensors. He also helped in formatting the manuscript.

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**Declarations**

**Conflict of interest** The author declares no conflict of interest.

**Consent to participate** I am willing to participate in the work presented in this manuscript.

**Consent for publication** The author has given their consent to publish this work.

**Ethical approval** Not applicable. The work presented in this manuscript is mathematical modeling only for the proposed biosensor. No experiment was performed on the human body and living organism/animal. So, ethical approval from an ethical committee is not required.
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