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Black Phosphorus Based Surface Plasmon Resonance Sensor for Detection of Formalin

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Abstract

The proposed design introduces improved sensitivity with a four-layer Design and investigates its performance as a Refractive Index sensor for formalin concentration detection using KSPR. The design consists of a **CaF_2 prism/Ag/BP/Analyte** where silver (Ag=57nm) is metal over the CaF_2 prism and black Phosphorus (BP=0.65nm) between the metal and analyte layer. The sensing layer containing the Analyte is placed on top of the BP layer. Kretschmann configuration with CaF_2 prism is employed to excite SPR, and results analysis used the Transfer matrix method (TMM). Analysis of the design used a visible wavelength, i.e., λ =662nm. Sellmer equation and Lorentz-Drude Model were used to calculate the CaF_2 prism and silver Metal refractive index, respectively. Also, study the effect of the variation in the metal layer's thickness and the combined effect of the Metal and BP layers. The proposed Design with Silver (Ag) and BP layer shows a sensitivity of **538°**/RIU for analysing RI changes 1.331 to 1.336 (Δns =0.005).

Keywords: Refractive index Unit (RIU), Surface Plasmon, Refractive index sensor, black phosphorus, Angular interrogation.

I. Introduction

Health is a significant global concern, with food adulteration being a major factor in health degradation. This issue has garnered considerable attention from food safety authorities due to its detrimental health effects. Surface Plasmon Resonance (SPR) is a modern, label-free detection technology capable of real-time analyte detection, offering a promising solution to this problem. This research focuses on enhancing the performance of sensors for detecting formalin, a 30%–50% aqueous solution of formaldehyde. Formalin is commonly used as a preservative in foods such as seafood and frozen meat to prevent decomposition and extend shelf life. However, consuming formalin in significant amounts can lead to severe toxic effects on the body, including life-threatening diseases such as cancer. This study aims to improve formalin detection to mitigate these health risks[1].

The researchers proposed different designs to improve sensor performance. Recently, 2-D materials have attracted attention due to their unique electrical and optical properties [2]. 2D materials are atomically thin-layered structures and exhibit phenomenal biochemical-sensing properties. It has excellent carrier mobility, a high surface-to-volume ratio, and biocompatibility. It also shows better fluorescence quenching ability and broad light absorption and is extremely robust and flexible. Researchers have been utilizing 2-D materials like MXene, TMDCs [3], graphene, molybdenum disulfide (MoS_2), tungsten disulfide (WS2), and black phosphorous (BP) in improving the performance parameters of the sensor. Recently, BP attracted more attention in 2D materials due to its structure and properties like Higher carrier mobility (1000 cm^2/V. s) than MoS_2, an adjustable bandgap varying from 0.2 to 3eV and excellent optical properties. This leads to a wide range of Sensing applications. Sensitivity tunned by layer thickness optimization across the light spectrum for detecting various analytes [4]. As far as its fabrication is concerned, there are various techniques of 2D materials fabrication [5]. Bilayers of BP show a 35% enhanced sensitivity compared to conventional gaseous sensors, which increases by 73% by adding a single layer of MoS_2 [6].

It was found that the BP layered structure can enhance the sensitivity of the gas sensor because the BP has a high absorption coefficient at a wavelength of 633 nm. The RI of the maximum gases lies between 1.0 and 1.1 RIU. So, the main advantage of the proposed structure is to enhance the sensing of the gaseous analyte with the help of SPR active material Gold and 2-D material BP. The sensitivity of the proposed optimized structure was enhanced by ~80.5% from the conventional sensor, and it again improved up to ~102.39% with the addition of extra BP layers between the gold layers [7].

We theoretically analyse our proposed SPR-based Refractive index sensor for formalin detection containing Black Phosphorus with a silver metal layer. The analysis is based on finite element method (FEM) relying on MATLAB simulation. Our analysis reveals that higher detection accuracy for the system may be achieved by using an optimized number of layers of BP. Which has enhanced sensitivity comparable to recent SPR-based sensors.

II. An Overview of the Proposed Design

The design consists of a four-layer structure, including the prism and analyte layer, as shown in Fig. 1; the Kretschmann configuration is employed for the excitation of surface plasmon resonance. Angular interrogation was used for the analysis of the Design, a TM polarized monochromatic light source was used for the incident on the Design and the other side photodetector was used to revive the reflected light.

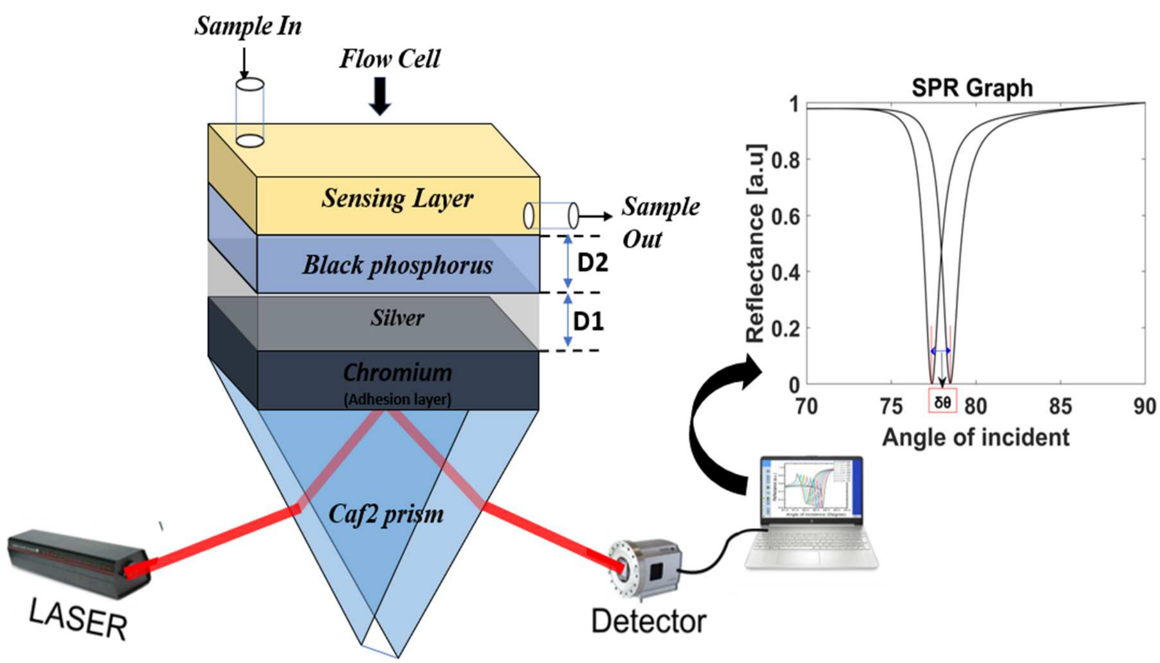

Figure 1: Schematic of the five-layer (Ag/BP//BlueP/MoS2) proposed SPR sensor design.

The angle of incident light changes with respect to the analyte Refractive index. A light source with an operational wavelength of = 662nm is used on one face of the prism, and the other face of the prism uses a photodetector array connected to the computer display unit to Observe the reflected light.

The Photodetector arrays are coupled to detect the reflected light and display units. D1 stands for the metal's thickness, as seen in Fig. 1. The other layers, shown in Fig. 1, are black phosphorous (D2), where the symbols within parentheses denote the respective thickness. On top of the structure is the sensing layer through which the sample flows in and out. The thicknesses of the layers are listed in Table I in Section II:

The design parameters of the 4-layer sensor at a wavelength of 662 nm are shown in Table I, along with the layer thicknesses and refractive indexes. The thickness of the Ag is considered to be 57 nm. The thickness of the BP has been estimated to be D2 = M x 0.65 nm, where M is the number of layers. The wavelength of excitation light is chosen to be 662 nm. Other parameters of the proposed sensor structure are shown in Table I.

Table I

Design specifications for the proposed Design

Material	RI at the wavelength (λ = 662nm)	Thickness (nm)	reference
CaF2	1.432860	--	[8]
Ag	0.04944+i*4.5027	57	[9]
BP	3.8337+i*0.01521	0.65x M	[10]
Analyte	1.331 to 1.36	--	

The RI corresponds to the different concentrations of formalin in Table II [4]. The change in the reflectance angle shift from reference to any selected formalin contraction will be impacted by this change in RI as an input to the suggested structure.

Table II

RI of formalin at various concentrations [4]

Concentration(nM)	Refractive Index
0(PBS Solution)	1.34
10	1.3422
100	1.3442
500	1.3453
1000	1.3464
1100	1.3475
1200	1.3486
1500	1.3492

III. Results and Discussion

In this study of KSPR sensors, the results demonstrated a significant enhancement in sensitivity due to the 2D materials. In order to get the best results, optimizations are carried out, which results in the creation of a sensor that is improved to current ones. Here, optimization was performed for the material used, and the thickness of each material was tuned. This study shows the best results for the optimized Ag and BP thickness in the proposed Design.

The initial step is to use modified Kretschmann configuration-based SPR setups as a sensing tool. As shown in Fig. 1, all layers are arranged along the z-axis, with a P-polarized light at a wavelength of 662 nm. For the Interrogation of the design, the angle interrogation method was for investigating the resonance dip, and the rotational stage was utilised to change the angle of incidence. When the Phase matching condition meets, a resonance dip occurs at an incident's angle, called the SPR angle or resonance angle. The resonance angle of the reflectance dip changes by variations in the sensing medium's refractive index, which ranges between 1.331 and 1.36. Any SPR sensor must be developed with the goal of maximizing surface plasmon penetration into the detecting medium and obtaining R_{min} close to zero. The angle-dependent reflectivity of the two typical SPR structures (prism/Ag/Analyte, prism/Ag/BP/ Analyte) that have been injected with an analyte for RI modification (Δn_s = 0.005).

A. Optimization of Ag (prism/Ag/Analyte) Design

Variation in Reflectance curve for Design (prism/Ag/Analyte) with Variation in Ag(silver) Thickness shown in Fig.2. Ag thickness varying 40nm to 59nm at a fixed refractive index of 1.331; the Ag thickness is optimized in the initial stages of the Simulation to get R_{min} close to zero.

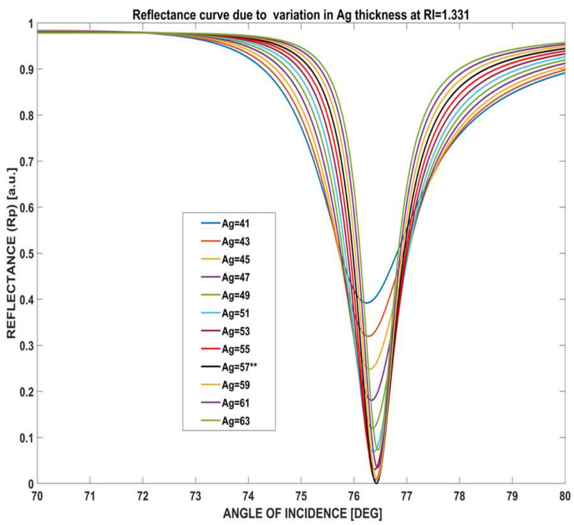

Figure. 2. Variation of the SPR curve with different thicknesses of Ag Layers Thickness.

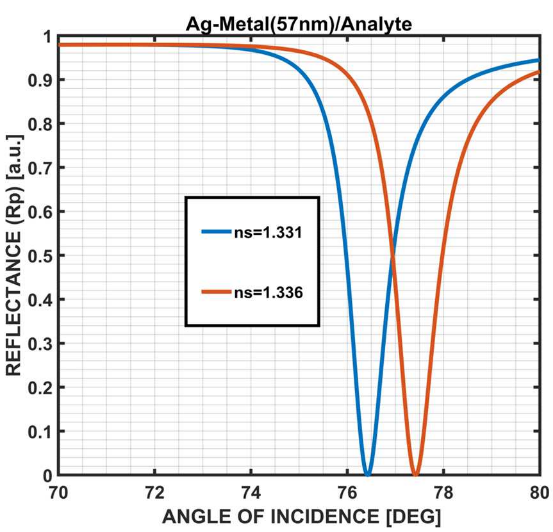

Figure 3. Reflectance curve for SPR (prism/Ag/s.m) design with a 1.33 and 1.34 refractive indices sample.

Further study Ag=57nm thickness layer Design for the different analyte RI to showcase the SPR curve and Sensitivity for the analyte variation ($\Delta n_s = 0.005$). The KSPR for the structure (prism/Ag/Analyte) with a thickness (57 nm) occurs at angles θ_{SPR}=76.42° and θ_{SPR} =77.42° for n_s = 1.331 RIU. and n_s = 1.336 RIU, respectively, as shown in Fig.3.

The R_{min} and FWHM are Zero and 0.97° respectively at $n_s = 1.331$. In addition, the R_{min} and FWHM are Zero and 1.04° respectively at $n_s = 1.336$. variation in refractive index 1.331 to 1.336 shows a slight increase in FWHM. The design shows the $\Delta\theta_{spr} = 1°$ for the $\Delta n_s = 0.005$, Sensitivity (S) = 200°/RIU. Increasing the sensing medium's RI for different thick Ag layers also increases the real component of the SP wave's wave vector (KSPW), increasing the resonance angle [11].

B. Optimization of prism/Ag/BP Design

The SPR sensor uses black Phosphorus (BP) in the proposed design prism/Ag/BP. For best sensitivity achievement, optimization is required.

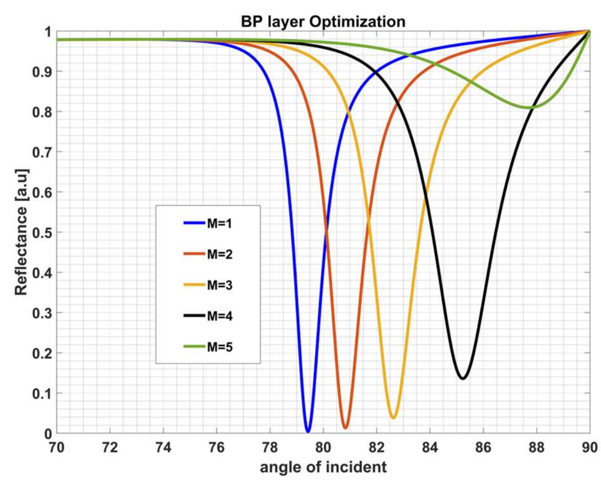

Figure. 4. The SPR curve for the variation in no. of BP layer (M=1 to M=5) at n_s=1.34.

The proposed SPR sensor prism/Ag/BP/Analyte Design optimization used Ag=57nm thickness and BP=0.65nm*M, where M is no. of BP layers for the RI 1.34. Fig.4 demonstrates that as the number of black phosphorus (BP) layers increases from M=1 to M=5, the reflectance curve's Full Width at Half Maximum (FWHM) also increases, indicating improved resolution. For an analyte with a refractive index of 1.34, the sensor performs optimally with 4 BP layers, offering the best combination of FWHM and minimum reflectance. This suggests that while more BP layers generally enhance sensitivity and resolution, optimal performance is achieved by fine-tuning the number of BP layers to match the specific refractive index of the analyte and other design parameters. This is limited to some specific value of RI changes only. Above optimization base RI, we took 1.34, which is RI of 0 (PBS solution) concentration of Formalin

The study demonstrates that enhancing an SPR sensor's design by using a 57 nm thick silver (Ag) layer and increasing the black phosphorus (BP) layers up to 5 significantly improves its sensitivity. This prediction is based on the FWHM and QF for an RI difference of 0.005 (RI ranges from 1.331 to 1.336). This design is highly effective for applications requiring precise and sensitive detection, such as formalin detection, thereby offering substantial potential for advancements in food safety and health diagnostics.

Table III. The performance parameters of optimized SPR sensor design.

Optimized structure	n_s	θ_{spr}	FWHM (°)	S (° /RIU)	DA	QF [RIU]$^{-1}$
Prism/Ag(57 nm)/BP(M=5)/Analyte	1.331	84.03	2.41	-	0.414	
	1.336	86.72	2.50	538	0.400	215.20
	Δn_s=0.005	$\Delta\theta$ = 2.69				

C. Detection of different concentrations of formalin

Finally, an optimised BP-based sensor design directly linked to a sensing medium is used to monitor and detect the concentration of formalin, as shown in Fig.5. So, the above graph shows the Reflectance curve for the increasing concentration of the formalin.

Here, the formalin concentration taken 0(PBS concentration)nM, 10nM, 100nM, 500nM, 1000nM, 1100nM, 1200nM and 1500nM for each value of the concentration reflectance graph is shown. For 0 concentration of formalin shows that sharp curve, and when the formalin concentration reflectance curve, sharpness decreases, and at the same time, the Angle shift or angle difference increases, which leads to increased sensitivity of the Design.

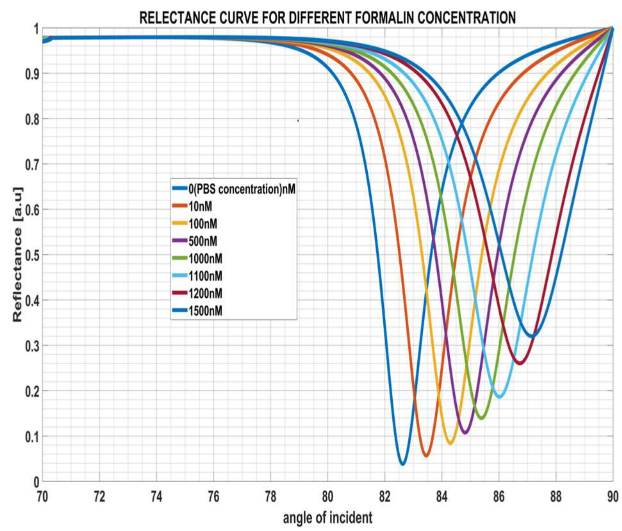

Fig. 5. Reflection intensity at various incident angles for different concentrations of formalin

IV. Conclusion

Based on optimization, we can conclude that when we increase the BP thickness, then the sensitivity at specific thicknesses, like 5 times of M with Ag 57nm, is increased, but at the same time, the FWHM is distorted. This calculation for the range of RI is 1.331 to 1.336. Further optimization of the design shows that when the Thickness Increases, the sensing range Decreases. This means that when the RI ranges start at 1.34, then more than that again, optimization is required to find the perfect Design. For formalin detection, the range of RI is 1.34 to 1.3492 for different concentrations of formalin, so up to 3 layers of BP along with 57nm Ag layers provide a balanced sensitivity with good FWHM and QA. The optimized design with a 57 nm Ag layer and 5 BP layers exhibits a sensitivity of 538°/RIU, a quality factor of 215.2 [RIU]$^{-1}$, an FWHM of 2.50, and a detection accuracy (DA) of 0.40 at a refractive index change (Δn_s) of 0.005. Our findings demonstrate that increasing the number of black phosphorus layers enhances the sensor's sensitivity for refractive indices ranging from 1.33 to 1.36.

Acknowledgements

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V. Reference

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