Research Article

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High Performance Bimetallic(Cu-Co) Surface Plasmon Resonance Sensor using Hybrid Configuration of 2D Materials

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ABSTRACT

The performance of prism-based surface plasmon resonance sensor utilizing kretschmann configuration composed of thin metallic (Cu–Co) film coated with 2D material such as BP/Graphene layer is investigated theoretically based on angular interrogation method. It is observed that optimizing the thickness of bimetallic (Cu–Co) and BP/Graphene layers, the sensitivity of the sensor improved greatly and still can maintain its minimum reflectivity and line width of the SPR reflectivity curve. We also observed that addition of BP/ Graphene over the bimetallic layer, its further enhanced the sensitivity. Numerical results shows that sensitivity as high as 504deg/RIU is achieved for the well optimized bimetallic configuration consist of 45nm of Cu and 10nm of Co thickness for the analyte refractive indices ranging from 1.330 - 1.335.

Keywords: Surface Plasmon Resonance; Graphene; Sensitivity; Copper; Cobalt.

1. INTRODUCTION

Surface plasmon resonance (SPR), a subset of surface plasmons (SPs), exhibits a wide range of unique optical features, including varying resonant frequencies in host media with varying refractive indices.Numerous practical applications in biosensors to detect and identify chemical, environment and biological substances have been discovered, owing to SPR's distinctive optical properties (Roli*et al.*2011; Rikta*et al.*2021).Otto's and Kretschmann configurations are the two types of configurations used to excite SPR waves. Otto's configuration maintains an air gap between the prism and the metal layer, whereas in a Kretschmann configuration, the metal layer is directly coated on the prism. As it is difficult to maintain air gap in Otto's configuration usually the kretschmann configuration are considered as simple and most effective method (Homola*et al.*,1999; Lee *et al.* 2015; Cai*et al.*2008; Gwon and Lee, 2010; Flanagan and Pantell, 1984; Nylander*et al.*1982; Huang *et al.*2010). SPR sensor performance has significantly improved with the use of bimetallic layer combinations (Maharana*et al.*2013; Sharma *et al.*2017).The most common bimetallic combinations for SPR excitation are Au-Ag. Thus, it takes advantage of gold's large shift in resonance dip matching to changes in refractive index of the sensing medium, which improves the sensor's sensitivity, and silver's short FWHM, which gives the sensor an good signal to noise ratio(SNR) (Zynio*et al.*2022; Wu and Ho, 2002; Ong *et al.* 2007). Several researchers have demonstrated the benefits of using bimetallic arrangements, but Au and Ag have been found to have poor adhesion with prisms, therefore thin coatings of (Cr), Teflon, and InP have been employed to improve adherence, sensitivity, and SNR (Yuan *et al.*2006; Ghorbanpour*et al.*2013; Chen *et al.*2011; Tran *et al.*2017). Rouf et al was Design of a new bimetallic SPR sensor and reported that utilization of thin InP layer with the coupling Ag-Au films enhances the sensitivity from 65°/RIU to 70°/RIU (Hasan*et al.*2018). Yuan et al analyzed Sensitivity–stability of a surface plasmon resonance sensor with double-metal-layer (gold-silver) configuration which utilizes stability of the gold and sensitivity of the silver and reported the obtained FWHM of the reflectivity curve for the bimetallic-layer configuration is 4.8 times narrower than the conventional configuration and its stability is better than that of the silver film configuration as well (Yuan *et al.*2006). Copper (Cu) is the most common conductive material after silver and is substantially cheaper than Au and Ag. Since Cu oxidizes much easily, it has not receive much attention as a plasmonic material. Recently Singh et al. suggested that the oxidization problem of Cu can be avoided by suitable oxide coatings (Mitsushio*et al.*2006; West *et al.*2010). Sharma *et al.* (2017) suggested that utilizing a thin layer of Pt over copper can enhance the sensitivity of the SPR sensor apart from preventing the cu being oxidized (Singh *et al.*2013).Rifat et al. suggested that graphene coating over Cu protects the Cu being oxidized and improved durability of the sensor, and its plasmonic performance is more stable (Rifat*et al.*2016). Cobalt being attractive is a material which is notable for its alluring applications in information capacity, optoelectronics and media communications. Cobalt particles are fascinating a direct result of their non straight, magneto-optical and attractive (Ordal*et al.*1985; Gilliot*et al.*2006).Recently Sarika Shukla et al. theoretically studied SPR based fiber optics sensor with Cobalt and Nickel layers. They suggested the utilization of magnetic materials such as Co and Ni in place of noble materials such as Gold and Silver not for only curtails the cost of SPR sensor but greatly improved its sensitivity .The sensitivity increases linearly with increase in refractive index of sensing medium for all thicknesses of Co and Ni layers. SPR sensor with Co layer possesses higher sensitivity than that of Ni layer(Shukla *et al.*2016).When working in an aqueous environment, selecting an appropriate bimetallic structure protects the plasmonic layer from oxidation and other chemical processes. Our Proposed work Cu-Co bimetallic layers were used for the enhancing the sensitivity of the SPR biosensor.Recently, Black Phosphorus (BP) is identified as one the of potential 2D material which gains rapid attention due to its widely tunable and direct bad gap, remarkable electrical and optical properties and higher carrier mobility (Maheswari*et al.*2021). The BP also provides attractive physical, chemical and mechanical anisotropic properties which makes it a suitable candidate for high performance potential and chemical applications(Nannan*et al.*2016). To improve the sensitivity of the biosensor lies in the utilization of bimolecular recognizing element [BRE] such as graphene over the metal layer. The large surface area and rich π configuration structure with superior optical properties makes graphene as suitable candidature for bimolecular adsorption and hence graphene growth on metallic surface greatly improves SPR biosensor sensitivity (Maharana*et al.*2012; Benaziez*et al.*2018). HailinXu reported enhancing the SPR and preventing the oxidation and graphene optical sensor is 3.4 times more sensitive than the Al-based sensor without the graphene layers (Hailin*et al.*2016).

In this paper we suggested a sensing configuration with enhanced sensitivityconsisting of 2D materials and bimetallic layers of Cu-Co. Cobalt have magneto optical propertyand it prevent copper from oxidation and effect of thickness of cobalt have been studied. Also the 2D material such as graphene/BP are employed to enhance the lightabsorption capacity of the sensor, which is much beneficial to get higher sensitivity and reduced FWHM. The reflectance curve, resonance angle and the corresponding sensitivity are analyzed theoretically using Fresnel equation and transfer matrix method. Results showthat such a hybrid configuration with well optimized thickness of bimetallic layer of (Co) overCu and the proper utilization of 2D materials such as BP/graphene can increases the sensitivity much higher than the conventional sensor.

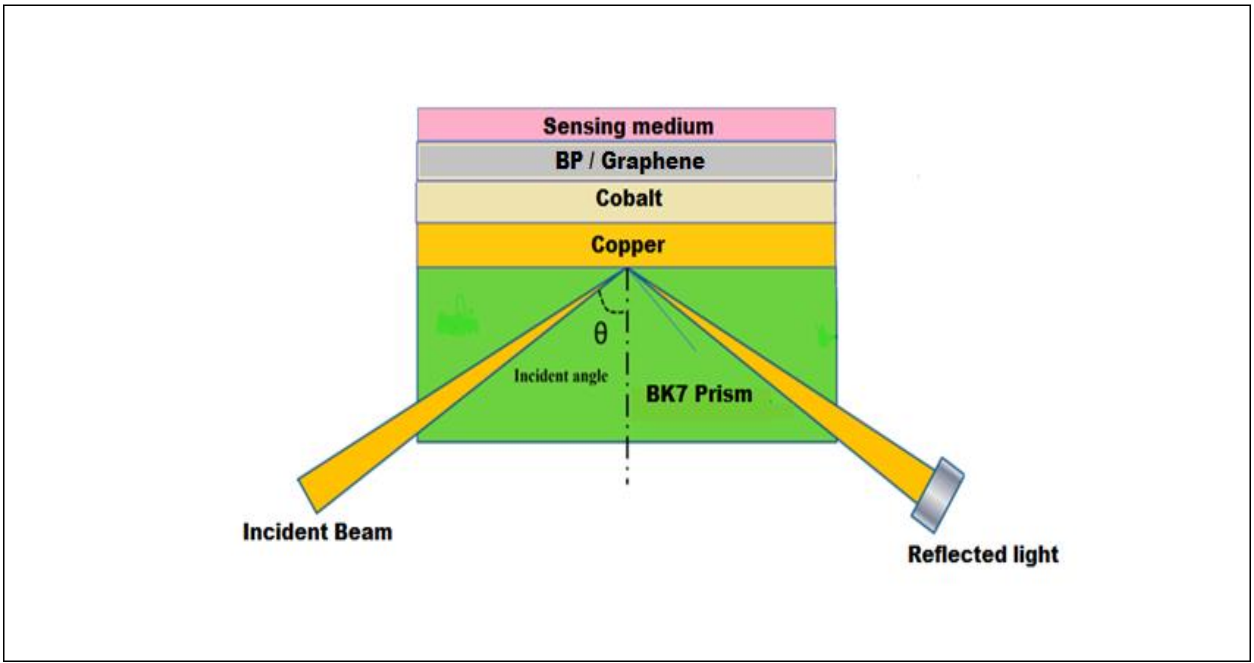


Fig. 1: Schematic diagram of a proposed Cu-Co-graphene/BP based SPR biosensor theoretical setup.

2. DESIGN CONSIDERATION AND THEORETICAL MODEL

The proposed configuration consisting of four different layers with the operating wavelength of 633nm based on the kretschmann configuration. The refractive index of BK7 prism is 1.515, the choice of BK7 prism is because of its lower refractive index compared with other, also it is acting as amplifier for enhancing sensitivity and other factors (Maheswari*et al.*2021).

The refractive indexes of the Cu and Co layers are calculated by the Drude formula (Shukla *et al.*2016; Vibisha*et al.*2020).

$$\varepsilon_{2,3}(\lambda)=\varepsilon_r+i\varepsilon_r=1-\frac{\lambda^2\lambda_c}{\lambda_p^2(\lambda_c+i\lambda)} \quad \text{................} \quad (1)$$

Where, λp is plasma wavelengths and λc defines the collision wavelengths of given materials, the optical constant values of Cu and Co are given below,

Table 1. Plasma and Collision wavelength values of Cu & Co

Metals	λp	λc
Copper(Cu)	$1.3617\times10^{-7}m$	$4.0853\times10^{-5}m$
Cobalt(Co)	$3.1215\times10^{-7}m$	$3.3578\times10^{-5}m$

The change in reflectance (R) of the proposed configuration is analyzed using transfer matrix method. The tangential field of the first boundary is $Z=Z_1=0$, tangential field of the final boundary $Z=Z_{N-1}$ as follows (Shukla *et al.*,2016),

$$\begin{bmatrix} U_1 \\ V_1 \end{bmatrix}=M\begin{bmatrix} U_{N-1} \\ V_{N-1} \end{bmatrix} \quad \text{......................} \quad (2)$$

Where, U_1, and V_1 are the tangential components of magnetic and electric fields of the first layer.

U_{N-1} and V_{N-1} are the tangential components of magnetic and electric fields of the N^{th} layer.

M is the characteristic matrix method for the proposed structure it is calculated by the following equation,

$$M=\prod_{k=2}^{N}M_k=\begin{pmatrix} M_{11} & M_{12} \\ M_{21} & M_{22} \end{pmatrix} \quad \text{....................} \quad (3)$$

$$M_k=\begin{pmatrix} \cos\beta_k & -i\sin\beta_k/q_k \\ -iq_k\sin\beta_k & \cos\beta_k \end{pmatrix} \quad \text{..................} \quad (4)$$

Here β_k and q_k are

$$q_{k=}(\varepsilon_k-n_1^2\sin^2\theta_1)^{1/2}/\varepsilon_k$$

$$\beta_k=(2\pi d_k/\lambda)(\varepsilon_k-n_1^2\sin^2\theta_1)^{1/2}$$

Where θ_1 and λ are the incident angle and incident light wavelength, d_k and $\varepsilon_k$are the thickness and dielectric constant of the k^{th} layer.

The r_p is total reflection coefficient of the p-polarized light,

$$r_p=\frac{(M_{11}+M_{12}\chi_N)\chi_1-(M_{21}+M_{22}\chi_N)}{(M_{11}+M_{12}\chi_N)\chi_1+(M_{21}+M_{22}\chi_N)} \quad \text{........} \quad (5)$$

Finally, the reflectivity of the given multilayer configuration is expressed by

$$R_p=\left|r_p\right|^2$$

The sensitivity of the SPR sensor is calculated by the below equation (Maheswari*et al.*2021),

$$S=\frac{\delta\theta_{res}}{\delta n_c} \quad \text{................} \quad (6)$$

Where,

S defines as a ratio of change in the refractive index and shift in resonance angel. δn_c Change in the refractive index of the sensing medium and $\delta\theta_{res}$ Changes in the resonance angle.

Detection Accuracy is defined

$$DA=\frac{\delta\theta_{res}}{\delta\theta_{0.5}} \quad \text{...................} \quad (7)$$

Where,

$\delta\theta_{res}$ is shift in resonance angle.

$\delta\theta_{0.5}$ is full width at half maximum (FWHM) of the reflectance curve.

Signal to Noise Ratio (SNR) is defined as,

$$SNR=\frac{S}{\delta\theta_{0.5}} \quad \text{...............} \quad (8)$$

Where

S defines the sensitivity.

$\delta\theta_{0.5}$ is FWHM of the reflectance curve.

3. RESULT AND DISCUSSIONS

We have numerically simulated and analyzed the behavior ofour proposed system using Fresnel transfer matrix method at the wavelength of 633nm. Fig. 2(a&b) shows the variation of minimum reflectance and sensitivity with respect to the change in thickness of copper. In the first phase of optimization the variation of R_{min} as a function of thickness of Cu varying from 30nm to 55nm for the thickness of Co as 0nm, 2nm, 4nm, 6nm,8nm and 10nm is calculated. Here, Co exhibits large value of real part of its dielectric constant at all wavelengths. Hence, Co enhances the shift between resonance angle for a given change of refractive index of sensing medium(Shukla *et al.*2016). It is noted from the fig. 2(a), initially high R_{min} values are obtained for all the thickness of Co layers considered when the thickness of Cu is as low as 30nm. However it is found to approach zero respectively at 45nm,50nm and 55nmof Cu for the corresponding thickness of Co as 10nm, 8nm, 6nm,4nm and 2nm respectively.Fig. 2(b) shows that the sensitivity increases with increasing the thickness of Co from 0nm to 10nm. Here the maximum sensitivity and R_{min} occurred in the thickness of copper as 45nm with 10nm of Co respectively. The maximum sensitivity value is 263deg/RIU. The optimum sensitivity and minimal reflectance (R_{min}) can be achieved by optimizing double metal layer thicknesses. R_{min}'s minimum value reveals the reflectance curve's dip point as well as the maximum coupling of incident light to the SPW(Vibisha*et al.*2020). Table 1 shows the R_{min} and sensitivity values of optimized thickness of bimetal layers.

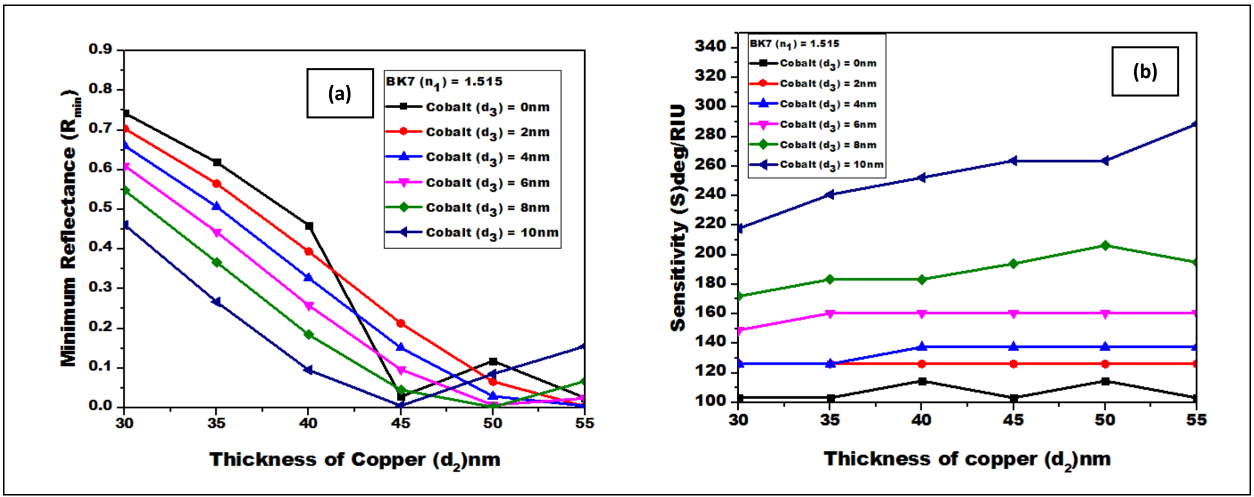


Fig. 2(a &b):Shows the variation of minimum reflectance and sensitivity as afunction of change in thickness of Cu layer thickness with fixed thickness of the Co layer as0nm, 2nm, 4nm,6nm,8nm and 10nm.

Table 2. R_{min} and sensitivity value for different thickness of bimetallic layers(Cu-Co).

S.No.	Thickness of Copper (nm)	Thicknessof Cobalt (nm)	R_{min}	Sensitivity (deg/RIU)
1	55	2	0.0034	126
2	55	4	0.0045	137
3	50	6	0.0068	165
4	50	8	0.0016	206
5	45	10	0.0051	263

Table 3. Comparison among proposed biosensor with other existing biosensor.

S. No.	Configuration	Sensitivity (deg/RIU)	Reference
1.	Prism/Few layer BP film/graphene/PBS solution	125	(Sarika Pal *et al.*2018)
2.	Prism/Chromium/Au/BP/2Dmaterial	187	(Bahar and Barvestani, 2018)
3.	Prism/Ag/BP/Graphene	217	(Wu *et al.*2017)
4.	Prism/Cu/Ni/BP/Mxene	305	(Rajeev *et al.*2021)
5.	Prism/Ag/BP/Pt/graphene	412	(Maheswari*et al.*2021)
6.	Prism/Cu/Ni/Ws_2	426	(Vibisha*et al.*2020)
7.	Prism/Cu/Co/Graphene	286	Proposed work
8.	Prism/Cu/Co/BP	504	Proposed work

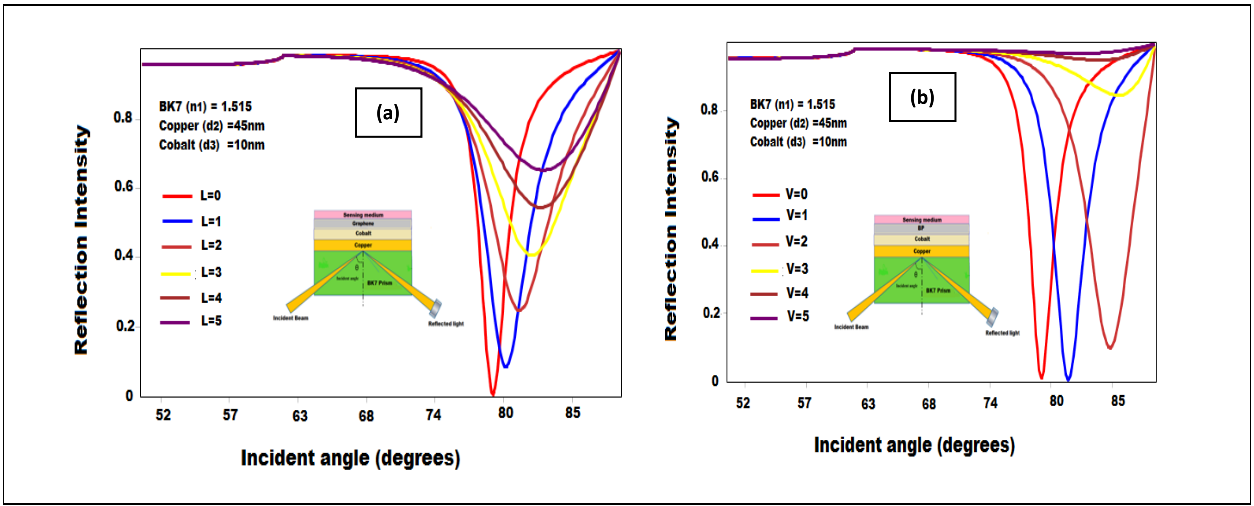
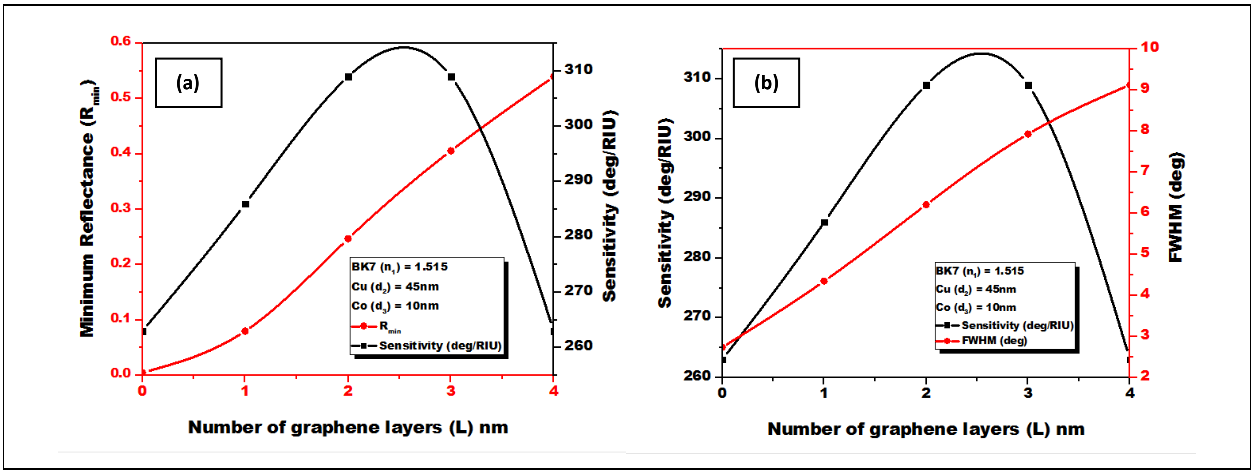


Fig. 3 (a & b): Reflection intensity at resonance angle with varying number of graphene/BP layers.



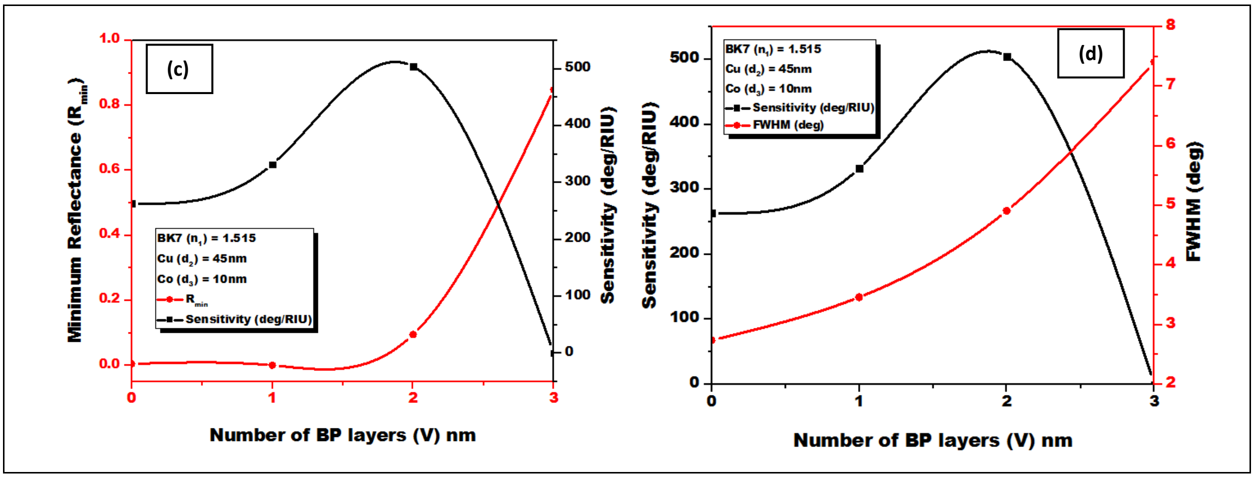


Fig. 4 (a, b, c & d): Minimum reflectance (R_{min}), Sensitivity and FWHM as a functions of number of grapheme (L) / BP Layers(V).

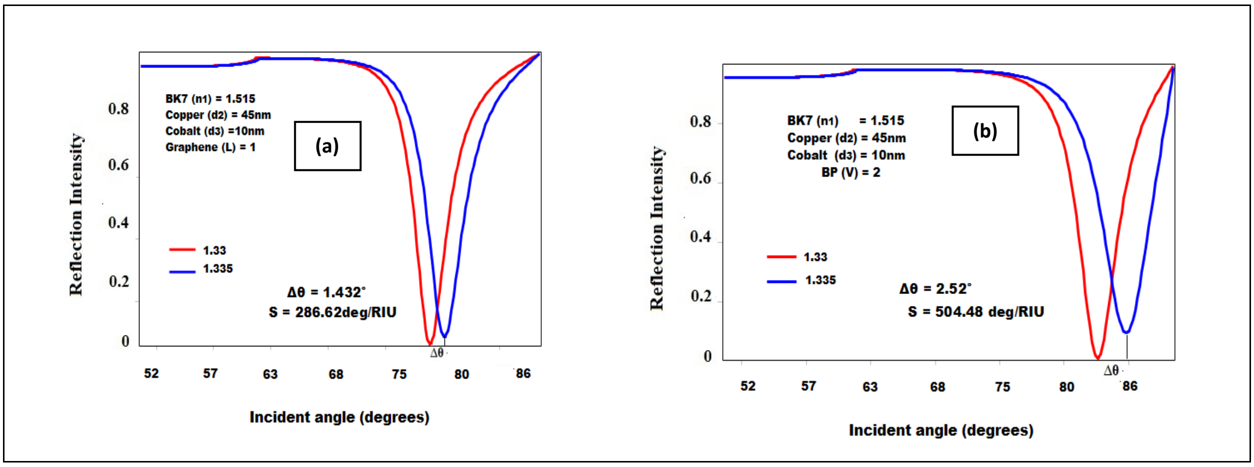


Fig. 5 (a & b): Change in reflection intensity with respect to incidence angle at wavelength of 633nm for the mono and bi-layers of graphene and BP.

Form the above table 1 reveals that first four combination of bimetallic layers of Cu-Co the sensitivity values are lower than last combination of bimetallic layer i.e., the sensitivity value is 263deg/RIU. Hence for this all the above combination of bimetallic layers though R_{min} is close to zero, the sensitivity obtained is very low and hence we rule out first four combination for further optimization. In order to functionalizing the metal layers with biomolecular recognizing elements for better biocompatibility, enriched functional group and high physiological stability. Here, we propose the utilization of coating of 2D materials(graphene/BP) over Co. These 2D materials act as a protective layer apart from increasing efficiency of the light absorption(Zhao *et al.*2018).

In order to further improve the sensitivity of the proposed biosensor we optimize the number of graphene and BP layer and are shown inFig.3 (a&b). Fig. 3(a) shows the increasing the number of layers of graphene layer shifts the reflectance dip to larger incident angle which implies that the sensitivity of the biosensor can be enhanced by manipulating the number of graphene layer. We also noted that similar trend is also observed with the increase of BP layer as shown in Fig. 3(b). From fig.3 (a&b) we conclude that that the SPR curve broadens and shallows with the addition of graphene layers due to the SPs' being dampened by the high extinction coefficient of graphene. Because BP has a lower extinction coefficient than graphene, the SPR curve for BP just becomes wider as the number of layers increases rather than shallower. In addition, when the number of graphene or BP layers increases, the reflectivity broadens and swallows more light due to a shift in the surface Plasmon's' (SPs') wave vector, which satisfies the resonance condition at resonance angle (Sarika*et al.*2017).

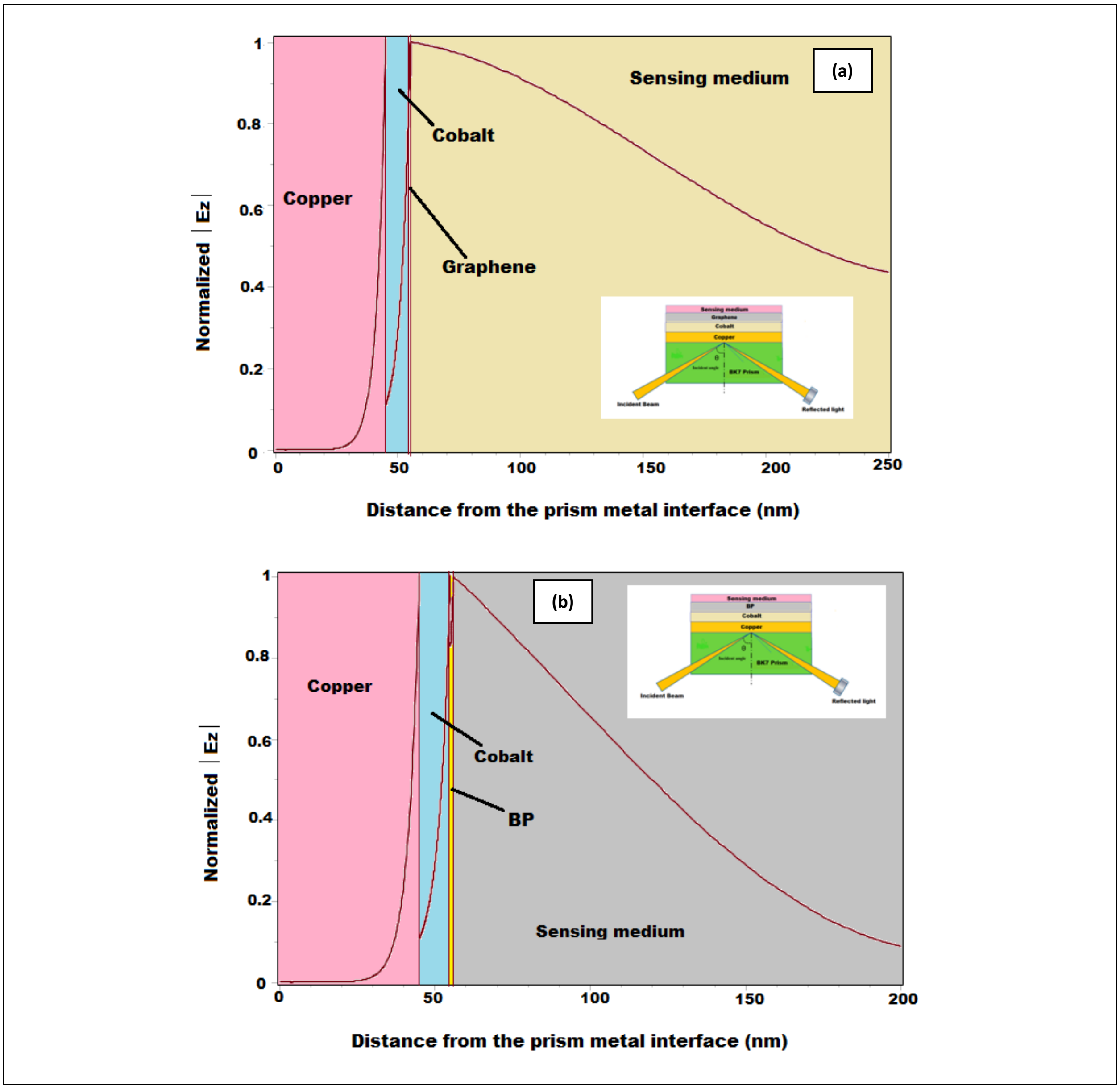


Fig. 6 (a&b): Normalized electric field distribution of SP wave in the proposed SPR sensor as a function of distance from the prism metal interface.

Next phase, Fig.4(a &b) shows that R_{min}, sensitivity and FWHM as a function of number of graphene layers. It is clear that, obtained results shows the R_{min}, sensitivity and FWHM is increasing from 0.0051 to 0.54, 263°/RIU to 263deg/RIU and 2.74 to 9.13deg while increasing the refractive index of the sensing medium from 1.330 to 1.335. It is noted that the maximum sensitivity and FWHM values are 286°/RIU and 4.35deg respectively. The similar manner number of BP layers are analyzed. Fig. 4(c&d) shows that R_{min}, sensitivity and FWHM as a function of number of BP layers. From the results, R_{min}, sensitivity and FWHM is increasing from 0.0051 to 0.849, 263deg/RIU to 504deg/RIU and 2.74 to 7.41deg respectively.

We have also examined the change in resonance angle and sensitivity of the proposed sensor corresponding to the change in the refractive index of the sensing medium in the range of 1.33 to 1.335. The plot of resonance angle versus refractive index of the sensing medium obtained by keeping the other parameters constant are shown in Fig.5 (a & b).It is observed that the reflectance curve obtained for 45nm thickness of Cu and 10nm thickness of Co with monolayer of graphene and bilayer of BP separately. It is observed from the figure, the shift in the resonance curve corresponding to the change in the RI of the sensing medium from 1.330 to 1.335 improved very much as (Δθ=1.432° and 2.52°) and the corresponding enhanced sensitivity is calculated as

(286deg/RIU and 504deg/RIU). Moreover the FWHM of the resonance curve is still found to be (4.35° and 4.91°) which is much smaller than the conventional sensor (Minghong *et al*. 2017). The DA and SNR are calculated as (0.32/deg and 0.52/deg) and (65.74/RIU and 102.54/RIU) respectively.The sensitivity obtained for the proposed sensor is found to be much higher than all the recently reported SPR sensor schemes and are compared in Table 3.

Next phase of investigation, the behavior of transverse electric field intensity for the proposed work is analyzed.Fig.6 (a & b), shows the normalized electric field distribution of SP wave in the proposed SPR sensor. As the reflection intensity approaches to minimum, the intensity of electric field approaches its maximum value. The maximum excitation of SP occurs at the moment when the field is at its maximum intensity, resulting in the minimum intensity of reflected light. It is noted from the Fig.6 (a&b) that the field is increased at the Cu-Co bimetallic layer interface which is due to the magneto optical property of cobalt and the plasmonic effect occurs to this interface. Furthermore, graphene and BP layers are deposited separately on the Cu-Co bimetallic thin filmwhich enhances the field which represents the excitation of surface plasmons(SPs) at the Cu-Co-graphene/BP interface. The field intensity decreases in the interface of graphene/BP-sensing medium interface and falls continuously in the sensing medium which represents that increasing the depth of evanescent field in the sensing medium, interaction between biomolecules and evanescent field is increased which results maximize the sensitivity. From our proposed work, interaction of evanescent field with biomolecules, sensitivity is maximum for BP compare than graphene.

4. CONCLUSION

In this present work, high sensitivity SPR sensor is proposed based on kretschmann configuration. The system consists of BP, graphene and Cu-Co bimetallic thin film. We systematically analyzed the optimized thicknesses of bimetallic layer of Cu-Co and 2D materials at the wavelength of 633nm. The Utilization of magnetic material like Co in place of noble metals curbs the cost of SPR sensor. The results shows that monolayer of graphene and bilayer of BP are coated over Cu-Co bimetallic layer, the maximum sensitivity and FWHM values are 286deg/RIU, 4.35deg and 504deg/RIU, 4.915deg respectively. Hence, it is believed that the present sensor can be used for better sensing of biomolecules, DNA detection and environmental applications.

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CONFLICTS OF INTEREST

The authors declare that there is no conflict of interest.

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