

Article

Numerical Investigation on High-Performance Cu-Based Surface Plasmon Resonance Sensor for Biosensing Application

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Abstract: This numerical research presents a simple hybrid structure comprised of TiO₂-Cu-BaTiO₃ for a modified Kretschmann configuration that exhibits high sensitivity and high resolution for biosensing applications through an angular interrogation method. Recently, copper (Cu) emerged as an exceptional choice as a plasmonic metal for developing surface plasmon sensors (SPR) with high resolution as it yields finer, thinner SPR curves than Ag and Au. As copper is prone to oxidation, especially in ambient conditions, the proposed structure involves the utilization of barium titanate (BaTiO₃) film as a protection layer that not only preserves Cu film from oxidizing but enhances the performance of the sensor to a great extent. Numerical results also show that the utilization of a thin adhesive layer of titanium dioxide (TiO₂) between the prism base and Cu film not only induces strong interaction between them but also enhances the performance of the sensor. Such a configuration, upon suitable optimization of the thickness of each layer, is found to enhance sensitivity as high as 552°/RIU with a figure of merit (FOM) of 136.97 RIU^{−1}. This suggested biosensor design with enhanced sensitivity is expected to enable long-term detection with greater accuracy and sensitivity even when using Cu as a plasmonic metal.

Keywords: surface plasmon resonance; biosensor; sensitivity; titanium oxide; copper; barium titanate



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1. Introduction

The SPR sensor is found to be prominent among the various current sensing approaches owing to its reliability, rapid analysis, high sensitivity, accurate detection, and label-free detection method for chemical and biological analytes [1–3]. This makes it possible to use the SPR sensor for various purposes, including environmental monitoring, pressure sensing [4], temperature sensing [5], medical diagnosis [6], DNA hybridization detection, discovering drugs [7], spotting molecules, glucose monitoring [8], formalin detected in the food preservatives [9], etc. The SPR method has the virtue of being able to identify even minute variations in the refractive index (RI) of the sensing medium [10]. The attenuated total reflection (ATR) phenomenon is supported by the angular interrogation method, and SPR sensors frequently prefer the angular method because of its simplicity and high resolution [11]. In general, plasmonic materials, including silver (Ag) and gold (Au), have been utilized in SPR sensors. As gold is invulnerable to degradation and corrosion, it is recommended as a superior plasmonic material for the SPR sensor. The drawbacks of Au are that it has low biomolecule adhesion capabilities and provides wider reflectance curves [12,13]. Ag is considered a potential substitute metal since it is less expensive and

produces a finer SPR spectrum than Au, but it oxidizes easily [9,14]. A lot of recent research favored copper as a plasmonic metal as it benefits higher electrical conductivity, it has the ability to generate narrow SPR peaks, and it is a cost-effective approach when compared to gold and silver [15–17]. The Cu inter-band transition exhibits strong optical absorption properties and is quite similar to Au [18]. Due to its unique aspects, Cu is an ideal choice to use in SPR sensors. Nevertheless, because Cu is an easily and quickly oxidizing metal, using it directly as an individual metal layer will result in dense, fragile oxide layers [19]. Recently, several approaches, including bimetal (such as Cu-Ni) [20], coating metal oxide protection layers (like SiO₂, Fe₂O₃, BaTiO₃, ZnO, MoO₃) [16,19,21–23], or 2D materials [24] are suggested to overcome the oxidation of copper. It is noted that well-optimized suitable protection layers not only inhibit oxidation but greatly improve the performance of the SPR sensors.

Recently, Mumtaz et al. proposed a fiber-based SPR sensor in which magnetron sputtered is used to coat iron oxide (Fe₂O₃) on Ag to protect the Ag layer from oxidation. This inclusion of iron oxide increases the effective absorption coefficient, which in turn improves the SPR sensor's sensitivity [25]. Additionally, Fe₂O₃ is a great prospect for future endeavors in SPR sensor developments since they are environmentally friendly, abundant, air-stable, highly corrosion-resistant, non-toxic, and affordable [26]. Zhang et al. designed a biomolecule detection SPR sensor using Fe₂O₃, which enhances the electric field and evanescent field depth at the Fe₂O₃/sensing medium interface because Fe₂O₃ has a high refractive index value, resulting in highly sensitive performance [27]. Not long ago, Ahmed and Wang et al. reported that the SPR biosensor using Fe₂O₃ layer over Au and Cu thin film provided the best sensing performance due to its good adsorbent property and its low extinction coefficient [19,28]. Lately, Augustine et al. reported the superior biocompatibility of molybdenum trioxide (MoO₃) suitable for the detection of breast cancer [29]. Zakaria et al. developed an SPR sensor with MoO₃ coated on top of Ag and Cu metal, which shows an increase in sensitivity as well as provides protection against oxidation of plasmonic metals [30]. Pandey et al. suggested an approach to increasing the sensitivity of an SPR sensor by sandwiching MoO₃ between Ag and MXene [31]. The solid phase deposition of MoO₃ film on Cu substrate is also reported [32]. Recently, the biocompatibility of the BaTiO₃ made it a suitable candidature for SPR sensors. Apart from being inexpensive, it possesses a wide range of preparation methods accessible for the nanoparticles' in-house synthesis [33–35]. Ihlefeld et al. presented the synthesis and properties of BaTiO₃ solid solution thin films deposited via a chemical solution approach on Cu substrates [36]. Recently, several SPR sensor structures utilizing BaTiO₃ for improved performances have been reported both theoretically and experimentally [37–42].

Recent studies show that the use of an adhesive layer on the prism solves the issue of deteriorating sensitivity and improves plasmonic activity to collect incident light effectively [43]. For adhesive layers, recent SPR biosensor research focused on using high-RI metal oxide layers such as TiO₂ and ZnO [44]. Recently, several studies reported an improvement in the performance of the SPR sensor that utilized TiO₂ as an adhesive layer at the prism/metal interface [45–51].

In this numerical work, a modified Kretschmann configuration is proposed in which the advantages of Cu as a plasmonic metal and the benefits of TiO₂ as an adhesive layer are utilized. Here, the superiority of three different oxide layers (BaTiO₃, Fe₂O₃, and MoO₃) on improving the sensor performance is analyzed in detail on the basis of numerical results. The layer thickness of each film coating is well optimized with the aim of achieving enhanced sensitivity, reduced full width at half maximum (FWHM) of the SPR spectrum, and achieving minimum reflectance to ensure high sensitivity as well as high FOM.

2. Theoretical Model

2.1. Structure Description

A schematic representation of the modified Kretschmann configuration utilizing a five-layer configuration (BK7 prism, TiO₂, Cu, oxide layer, and sensing layer) for biosensing

application is shown in Figure 1. The RI of the first layer (BK7 prism) is 1.5151 [52]. The RI of the second layer (TiO₂) is 2.5837 [48]. The third layer (Cu) is coated on the TiO₂ layer.

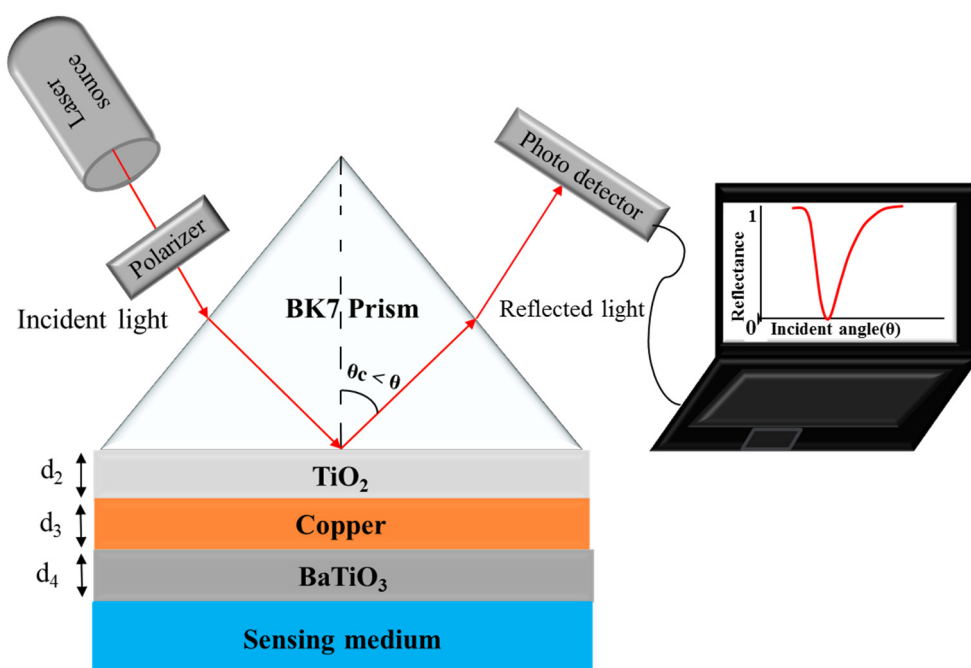


Figure 1. Diagrammatic representation for the hybrid structure of BK7-TiO₂-copper-BaTiO₃-based SPR biosensor.

The dielectric constant of metal (Cu) is obtained using the Drude model and is given by Equation (1)

$$\varepsilon_m(\lambda) = \varepsilon_{mr} + \varepsilon_{mi} = 1 - \frac{\lambda^2 \lambda_c}{\lambda_p^2 (\lambda_c + i\lambda)}, \quad (1)$$

where ε_{mr} and ε_{mi} represent the metal layer dielectric constant real part and imaginary part, respectively. For Cu: plasma wavelength (λ_p) = 0.13617×10^{-6} m and collision wavelength (λ_c) = 40.852×10^{-6} m [16]. The fourth layer (oxide layer) used to inhibit the oxidation of Cu metal and its RI is given in Table 1.

Table 1. Refractive index of the oxide layers at $\lambda = 633$ nm.

Oxide Layer	Refractive Index	Ref.
BaTiO ₃	2.4043	[53]
Fe ₂ O ₃	2.918 + 0.029i	[28]
MoO ₃	1.8233 + 0.00204i	[31]

The fifth layer is the sensing zone, whose RI is assumed to change in the range of $n_s = 1.33$ to $n_s = 1.33 + \delta n$, where δn denotes the change in RI of the sensing medium due to the adsorption of biomolecules. The range of change in refractive index (δn) for biomolecular adsorption is typically on the order of 0.005. This means that even tiny amounts of biomolecules binding to the sensor's surface can lead to detectable shifts in the SPR signal. The specific range of change in RI depends on factors like the size and mass of the biomolecules, the density of the immobilized ligands, and the interactions between the molecules themselves. Here, we assumed the adsorption of biomolecules occurred on the surface of the metal oxide layer, and the refractive index of the sensing medium changed from 1.33 to 1.335 [54].

2.2. Reflectance

The reflectance of incident light (p-polarized) is calculated for this multi-layer structure using the transfer matrix method [55]. The tangential fields at the first boundary $Z = Z_1 = 0$ and the tangential fields at the last boundary $Z = Z_{N-1}$ are related by

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

where U_1 and V_1 are the tangential components of electric and magnetic fields, respectively, at the first layer boundary. U_{N-1} and V_{N-1} are the corresponding fields at the N th layer boundary. M refers to the characteristic matrix of the N -layer model and is given by

$$M = \prod_{k=2}^{N-1} M_k = \begin{bmatrix} M_{11} & M_{12} \\ M_{21} & M_{22} \end{bmatrix} \quad (3)$$

with

$$M_k = \begin{bmatrix} \cos \beta_k & \frac{-i \sin \beta_k}{q_k} \\ -iq_k \sin \beta_k & \cos \beta_k \end{bmatrix} \quad (4)$$

The phase factor (q_k) and optical admittance (β_k) of the k th layer are expressed by

$$q_k = \left(\frac{\mu_k}{\epsilon_k} \right)^{\frac{1}{2}} \cos \theta_k = \frac{(\epsilon_k - n_1^2 \sin^2 \theta_1)^{\frac{1}{2}}}{\epsilon_k} \beta_k = \frac{2\pi}{\lambda} n_k \cos \theta_k (z_k - z_{k-1}) = \frac{2\pi d_k}{\lambda} (\epsilon_k - n_1^2 \sin^2 \theta_1)^{\frac{1}{2}}$$

Here, θ_1 , n_1 , and λ denote the incident angle, RI of the prism, and wavelength of the incident light (633 nm), whereas μ_k , ϵ_k , and d_k represent the permeability, dielectric constant, and thickness of the k th layer, respectively.

Reflectance (R_p) and reflection coefficient (r_p) of incident light are given as

$$R_p = |r_p|^2 \quad (5)$$

$$r_p = \frac{(M_{11} + M_{12}q_N)q_1 - (M_{21} + M_{22}q_N)}{(M_{11} + M_{12}q_N)q_1 + (M_{21} + M_{22}q_N)} \quad (6)$$

2.3. Performance Parameters

2.3.1. Sensitivity (S_n)

Sensitivity is defined as the ratio between the resonance angle switching ($\delta\theta$) and the sensing layer's RI variation (δn_s). It is given as below [13]:

$$S_n = \frac{\delta\theta}{\delta n_s} (\text{deg}/\text{RIU}) \quad (7)$$

Even if the RI of the sensing layer is just slightly changed, the best SPR sensor will offer the largest changes in resonance angle.

2.3.2. Detection Accuracy (DA) or Signal-to-Noise Ratio (SNR)

The detection accuracy is inversely related to the FWHM (curve width at 50% reflectance) of the reflectance curve [13].

$$DA = \frac{1}{FWHM} (\text{deg}^{-1}) \quad (8)$$

The exact spot of the resonance angle can be identified if the reflectance spectrum is narrow (i.e., smaller FWHM), which leads to improved detection accuracy.

2.3.3. Figure of Merit (FOM) or Quality Factor (Q)

A figure of merit is an important criterion used to demonstrate sensitivity and *FWHM* impact on the sensor's performance [43].

$$FOM = \frac{S_n}{FWHM} (RIU^{-1}) \quad (9)$$

2.3.4. Electric Field Intensity Enhancement Factor (EFIEF)

The extent to which the field has been efficiently focused along the BaTiO₃-analyte interface is shown by the electric field intensity enhancement factor [56,57]. For p-polarized light, the EFIEF is the ratio of the square of the electric field (*E*) or magnetic field (*H*) at the oxide layer/analyte interface to the square of the field *E* or *H* at the prism/TiO₂ interface. EFIEF is expressed by the

$$\left| \frac{E\left(\frac{N}{N-1}\right)}{E\left(\frac{1}{2}\right)} \right|^2 = \frac{\varepsilon_1}{\varepsilon_N} \left| \frac{H\left(\frac{N}{N-1}\right)}{H\left(\frac{1}{2}\right)} \right|^2 = \frac{\varepsilon_1}{\varepsilon_N} |t|^2 \quad (10)$$

where *t* is indicated as the transmission coefficient and ε_1 and ε_N are denoted as the dielectric constants of the first layer and the *N*th layer, respectively.

3. Results and Discussion

The Fresnel formula and the transfer matrix method are implemented to properly assess all functional parameters. A proper covering layer strategy is required to avoid a Cu-based SPR sensor showing degraded performance due to the oxidation effect of Cu. Here, we suggested to use three different oxide coatings, namely BaTiO₃, Fe₂O₃, and MoO₃, over Cu to inhibit its oxidation effect [30,38,40], and the proposed model also includes a thin layer of TiO₂ as an adhesive that strongly binds Cu on the prism base [45,47–50]. The thickness of every layer is well optimized, which leads to achieve high sensitivity, the lowest minimum reflectance (*R*_{min}), and the thinnest *FWHM* of the resonance curve [58]. Here, we meticulously examined the role that each layer plays in the proposed configuration.

Initially, we investigated the effect of BaTiO₃ on copper and found out its optimized thickness to achieve the best sensing performance. Figure 2a shows the change in sensing parameters (sensitivity, *R*_{min}, and *FWHM*) corresponding to the change in the Cu layer thickness in the range of 20 nm to 60 nm for 5 nm BaTiO₃ protection coating on the copper layer. It is observed that the *FWHM* and *R*_{min} values of the SPR dip decrease as the Cu layer thickness increases, whereas the sensitivity is observed to increase from 120°/RIU to 132°/RIU. It is also noted that the sensor performance is better for the 55 nm thickness of the copper layer as the resonance curve *R*_{min} value is closer to zero (0.013), with sensitivity around 132°/RIU, and the *FWHM* as small as 0.72°. Further examining the same configuration using a 10 nm thickness of BaTiO₃ cover over the Cu layer, 55 nm thickness of Cu again shows maximum sensitivity (178°/RIU) with *R*_{min} as 0.009 at 1.33RI and 0.0081 at 1.335RI, and the *FWHM* value as 1.23°. It is also observed that further increasing the thickness of BaTiO₃ to 15 nm, the 45 nm Cu layer shows an *R*_{min} value close to zero and exhibits high sensitivity of about 486°/RIU with the *FWHM* of the resonance curve increased to 4.27°. From the above three cases, it is observed that 15 nm BaTiO₃ coated on a 45 nm Cu layer provides excellent sensing capability and hence it is considered for further optimization.

In the next phase of optimization, the impact of utilizing TiO₂ adhesive film between the BK7 prism and the Cu layer is analyzed. Figure 3 shows the same as Figure 2 but for sandwiching a 5 nm thickness of TiO₂ as an adhesive layer between the prism and Cu film. Here, it is observed that the maximum sensitivity achieved for 5 nm and 10 nm of BaTiO₃ cover layers are 132°/RIU and 180°/RIU, corresponding to the thickness of the Cu layer as 55 nm for both cases. Though the sensitivity remains almost the same as in the previous cases without the TiO₂ adhesive layer (Figure 2a,b), the FOM for these cases are improved

to 191.3 RIU^{-1} and 156.5 RIU^{-1} due to a reduction in the FWHM of the resonance spectrum, as shown in Table 2. Figure 3c shows that upon utilizing a 15 nm thickness of BaTiO_3 , the maximum sensitivity around $552^\circ/\text{RIU}$ with FOM around 136.97 RIU^{-1} is achieved for a 45 nm thickness of Cu. This is because the TiO_2 layer induces a significant SPR effect when joined with metal as it assists in enhancing surface plasmons (SPs) at the metal/prism interface and hence improves sensitivity and reduces SP damping (FWHM) [59].

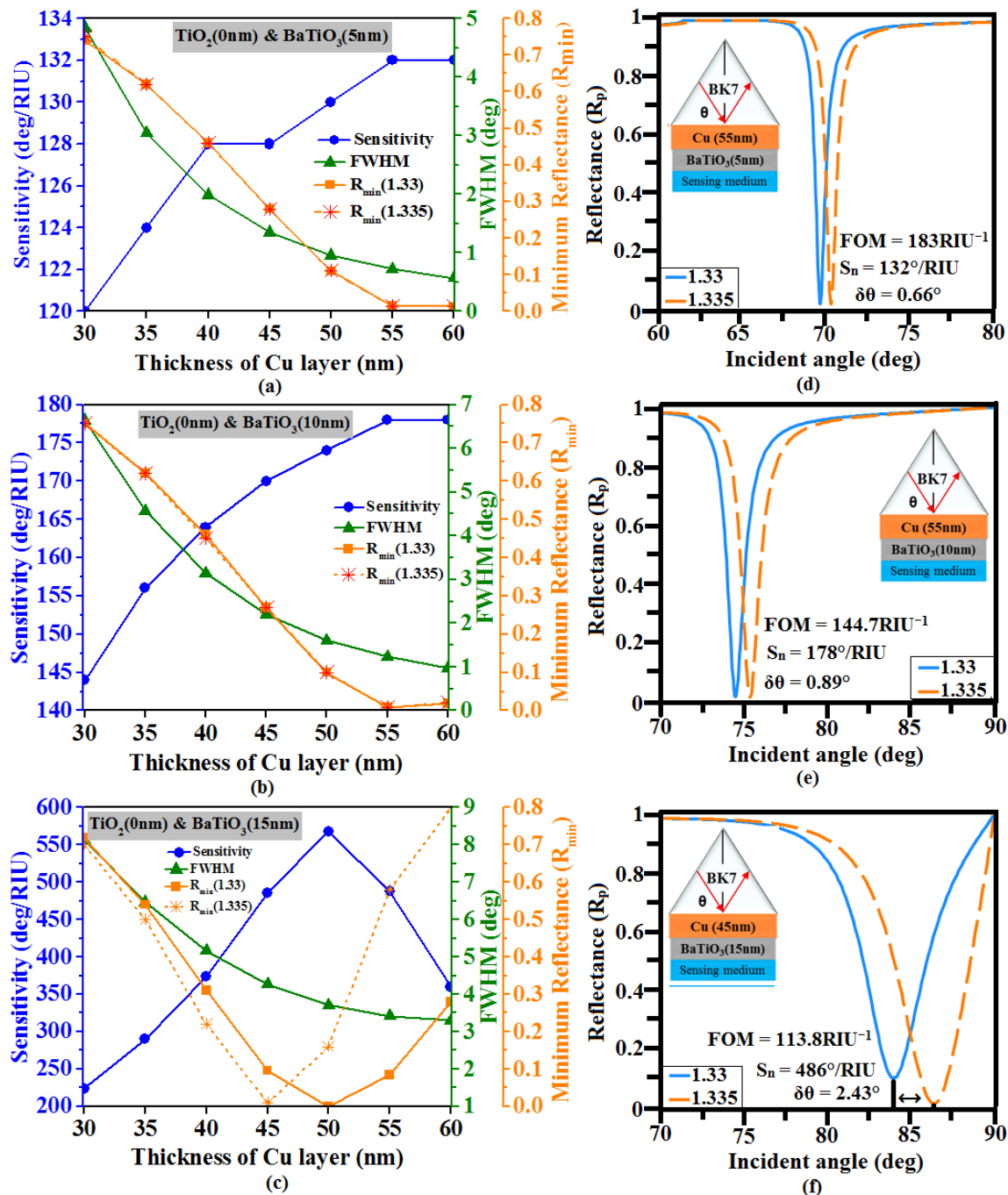


Figure 2. Variation of the sensitivity, minimum reflectance ($R_{\min}$), and FWHM vs. thickness of Cu layer (30 nm to 60 nm) for the thickness of BaTiO_3 layers (a) 5 nm, (b) 10 nm, and (c) 15 nm. Optimized structure SPR curve: (d) Cu (55 nm)- BaTiO_3 (5 nm), (e) Cu (55 nm)- BaTiO_3 (10 nm), and (f) Cu (45 nm)- BaTiO_3 (15 nm).

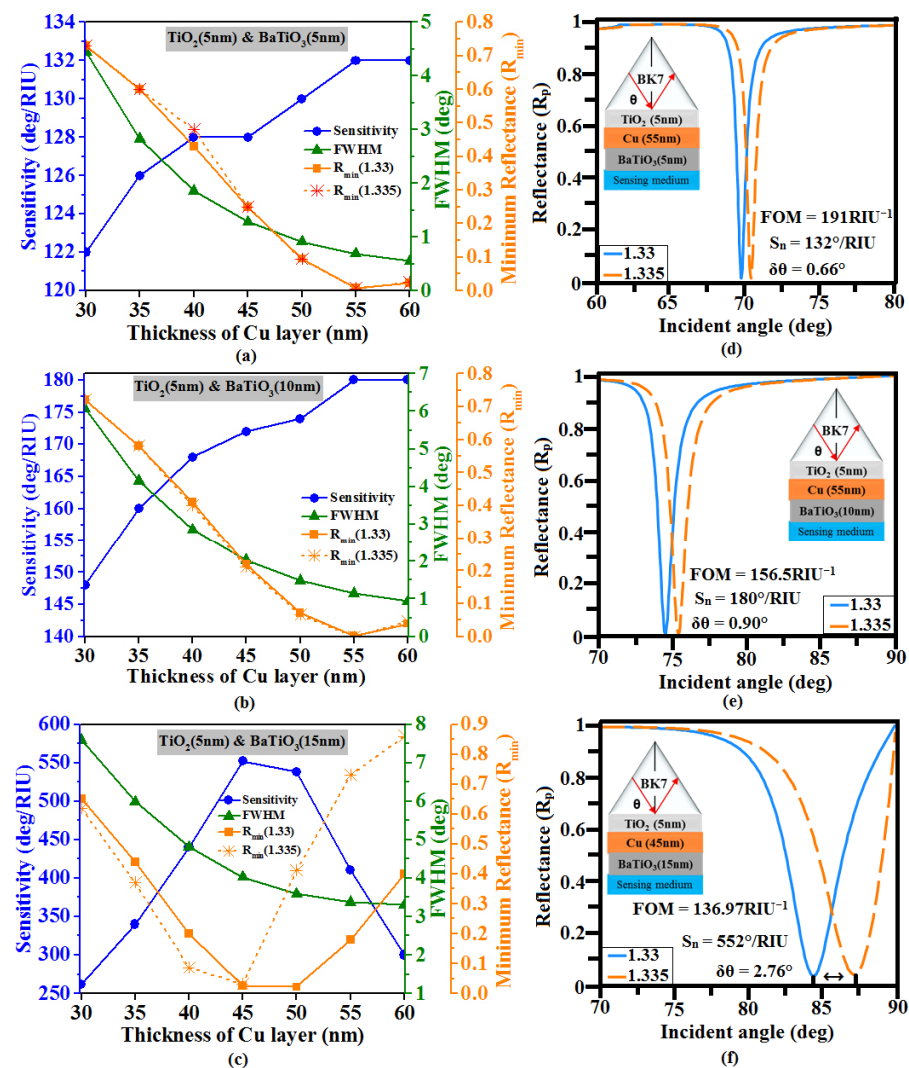


Figure 3. Variation of the sensitivity, minimum reflectance (R_{min}), and FWHM vs. thickness of Cu layer (30 nm to 60 nm) for the thickness of BaTiO₃ layers (a) 5 nm, (b) 10 nm, and (c) 15 nm. Optimized structure SPR curve: (d) TiO₂ (5 nm)-Cu (55 nm)-BaTiO₃ (5 nm), (e) TiO₂ (5 nm)-Cu (55 nm)-BaTiO₃ (10 nm), and (f) TiO₂ (5 nm)-Cu (45 nm)-BaTiO₃ (15 nm).

In the following phase, we examined the sensor performance for Fe₂O₃ protection layer situated over Cu layer. From Figure 4, we found that R_{min} close to zero are obtained at 55 nm, 50 nm, and 45 nm thickness of Cu corresponding to 5 nm, 10 nm, and 11 nm Fe₂O₃ layer.

Table 2. The oxide layers attain the best results (R_{min} , FWHM, sensitivity, and FOM) at the optimized thickness of Cu layer.

Thickness of Oxide Layers (nm)	Thickness of TiO ₂ (nm)	Thickness of Cu (nm)	R_{min} at n_s		FWHM (deg) at n_s		$\delta\theta_{SPR}$ (deg) at $\delta n_s = 0.005$	S_n (°/RIU)	FOM (RIU ⁻¹)
			1.33	1.335	1.33	1.335			
BaTiO ₃ (5 nm)	0	55	0.014	0.013	0.72	0.75	0.66	132	183
BaTiO ₃ (10 nm)	0	55	0.0097	0.0081	1.23	1.29	0.89	178	144.7
BaTiO ₃ (15 nm)	0	45	0.096	0.0095	4.27	4.65	2.43	486	113.8
BaTiO ₃ (5 nm)	5	55	0.0067	0.0061	0.69	0.71	0.66	132	191.30
BaTiO ₃ (10 nm)	5	55	0.0013	0.00053	1.15	1.21	0.90	180	156.5
BaTiO ₃ (15 nm)	5	45	0.026	0.031	4.03	4.49	2.76	552	136.97
Fe ₂ O ₃ (5 nm)	5	55	0.0062	0.0072	0.96	1.003	0.71	142	147.9
Fe ₂ O ₃ (10 nm)	5	50	0.017	0.034	3.28	3.6	1.41	282	85.97
Fe ₂ O ₃ (11 nm)	5	45	0.0043	0.049	5.2	5.78	2.03	406	78.07
MoO ₃ (5 nm)	5	55	0.0046	0.0042	0.58	0.6	0.59	118	203.4
MoO ₃ (10 nm)	5	55	0.0014	0.001	0.75	0.77	0.65	130	173.3
MoO ₃ (27 nm)	5	45	0.013	0.0022	3.68	4.18	1.93	386	104.89

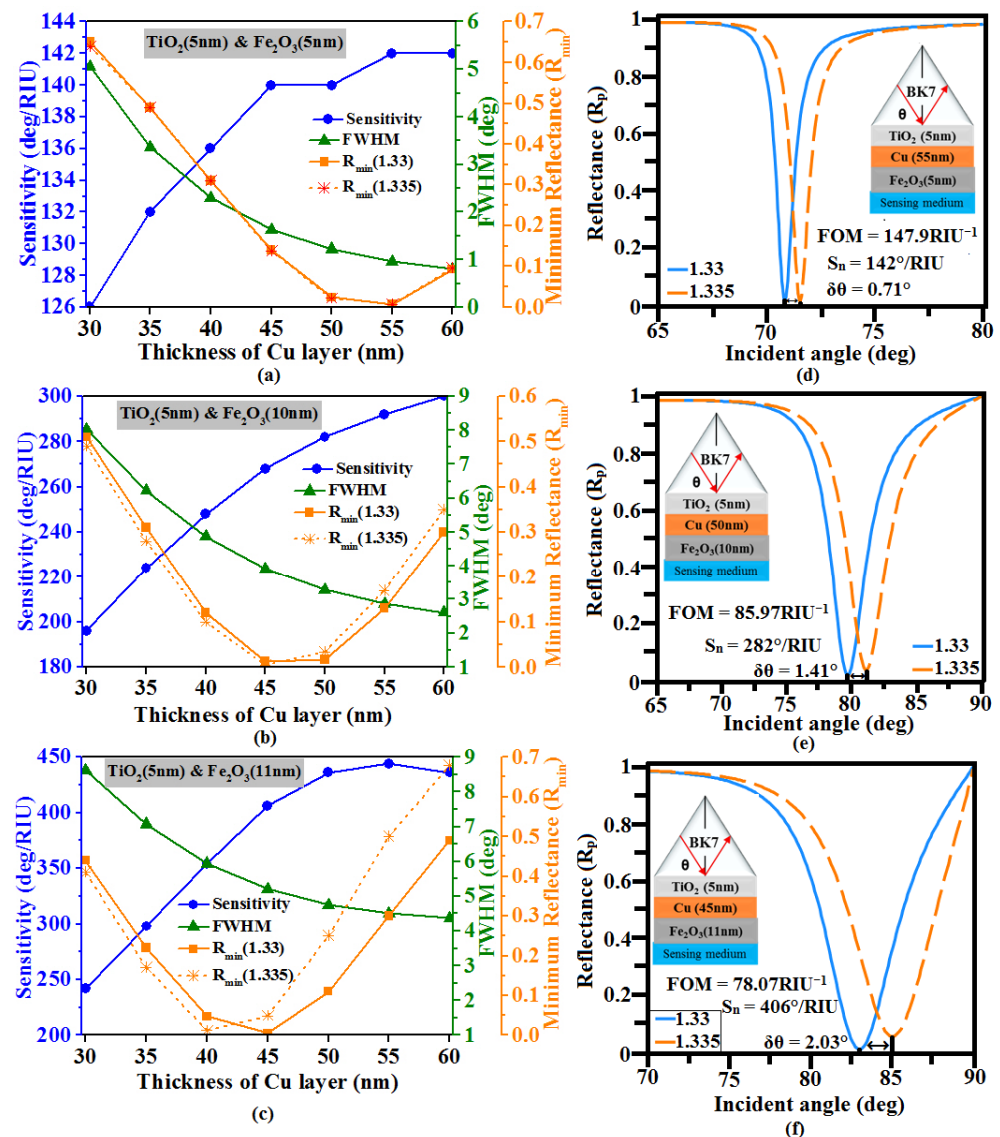


Figure 4. Variation of the sensitivity, minimum reflectance (R_{min}), and FWHM vs. thickness of Cu layer (30 nm to 60 nm) for the thickness of Fe₂O₃ layers (a) 5 nm, (b) 10 nm, and (c) 11 nm. Optimized structure SPR curve: (d) TiO₂ (5 nm)-Cu (55 nm)-Fe₂O₃ (5 nm), (e) TiO₂ (5 nm)-Cu (50 nm)-Fe₂O₃ (10 nm), and (f) TiO₂ (5 nm)-Cu (45 nm)-Fe₂O₃ (11 nm).

The calculated sensitivities are $142^\circ/\text{RIU}$, $282^\circ/\text{RIU}$, $406^\circ/\text{RIU}$ with FOM as 147.9 RIU^{-1} , 85.97 RIU^{-1} , and 78.07 RIU^{-1} , respectively. Moreover, we also analyzed the effect of the MoO₃ cover layer on Cu film.

Figure 5 shows that for the MoO₃ layer with thicknesses 5 nm, 10 nm, and 27 nm, the R_{min} values reach values close to zero corresponding to thicknesses of Cu film as 55 nm, 50 nm, and 45 nm, respectively. For these cases, the sensitivity obtained is $118^\circ/\text{RIU}$, $130^\circ/\text{RIU}$, and $386^\circ/\text{RIU}$ with the corresponding FOM calculated as 203.4 RIU^{-1} , 173.3 RIU^{-1} , and 104.89 RIU^{-1} , respectively. In the above three cases, the BaTiO₃ layer achieves maximum sensitivity as it possesses a large real part of the dielectric constant with no imagery part. So, it is the most suitable covering layer when compared to other oxide layers for the proposed sensor. Thus, we optimize that the 45 nm Cu sandwiched between 5 nm TiO₂ and 15 nm BaTiO₃ outer cover is a better configuration that achieves sensitivity and FOM as high as $552^\circ/\text{RIU}$ and 136.97 RIU^{-1} , respectively, and the effects of each oxide layer (BaTiO₃, Fe₂O₃, and MoO₃) is also compared in Table 2.

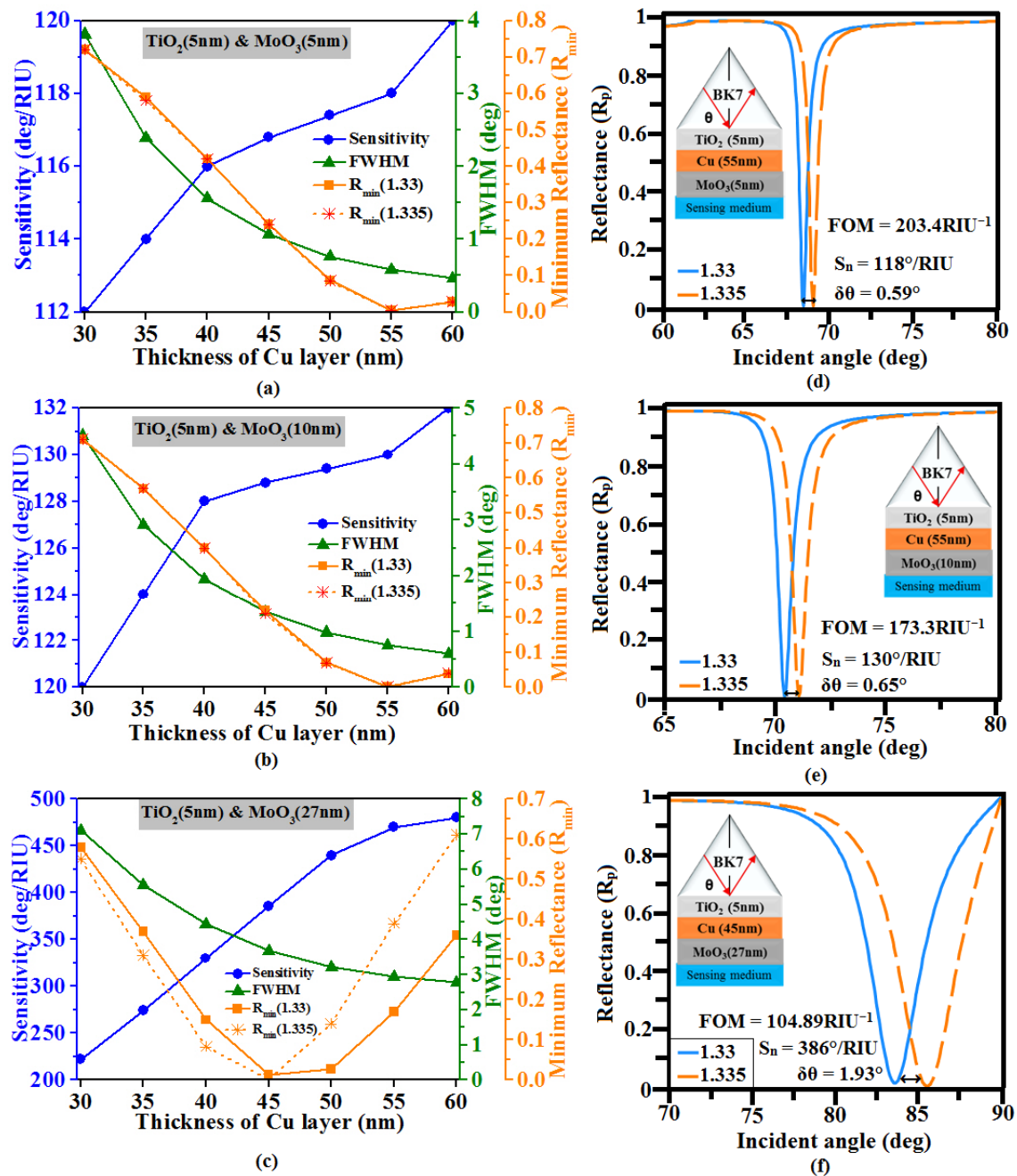


Figure 5. Variation of the sensitivity, minimum reflectance ($R_{\min}$), and FWHM vs. thickness of Cu layer (30 nm to 60 nm) for the thickness of MoO₃ layers (a) 5 nm, (b) 10 nm, and (c) 27 nm. Optimized structure SPR curve: (d) TiO₂ (5 nm)-Cu (55 nm)-MoO₃ (5 nm), (e) TiO₂ (5 nm)-Cu (55 nm)-MoO₃ (10 nm), and (f) TiO₂ (5 nm)-Cu (45 nm)-MoO₃ (27 nm).

The thickness of the oxide layer plays a critical role in the suggested sensor; thus, we carried out an extensive study to ensure the best possible value, as illustrated in Figure 6. It is noticed that the reflectance spectrum moves to a greater incidence angle as the thickness of the outer layer (BaTiO₃, MoO₃, and Fe₂O₃) increases. It is also noted that for 15 nm of BaTiO₃, 27 nm of MoO₃, and 11 nm of Fe₂O₃, the $R_{\min}$ obtained is almost zero, and such condition is much favored for maximum conversion of incident light energy into surface plasmons. Further increasing of thickness above the previously prescribed values for all three cover layers $R_{\min}$ values increases because the rate of light utilization reduces as the oxide layer thickness increases.

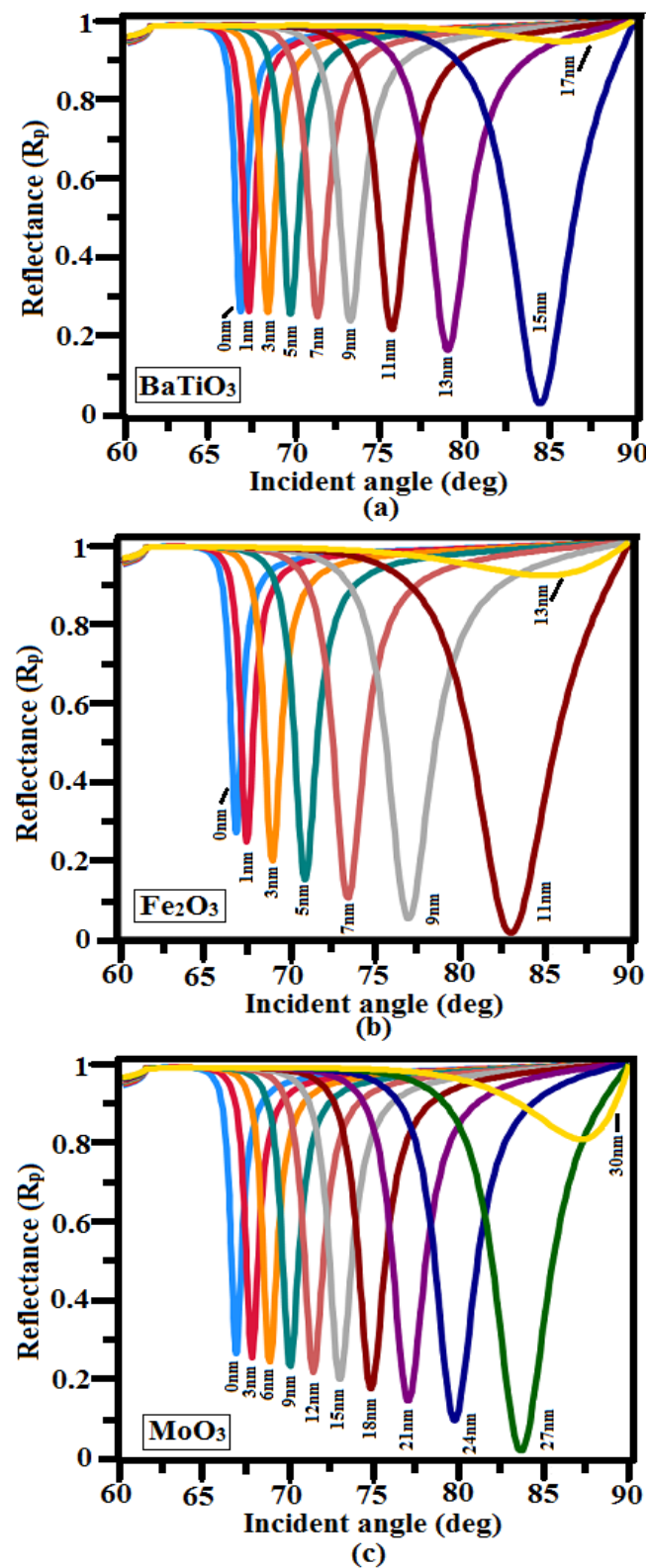


Figure 6. Reflectance vs. the incident angle for the different thicknesses of oxide layers: (a) BaTiO₃, (b) Fe₂O₃, and (c) MoO₃ with TiO₂ = 5 nm and Cu = 45 nm at $n_s = 1.33$.

The performance of the SPR biosensor is also determined by field distribution at the interface of the metal/dielectric interface. The interaction between the evanescent field and the biomolecule in the sensing medium is crucial. There is more biomolecular

interaction when the field dispersion is improved [56,57]. Figure 7 shows that the EFIEF decreases when the sensing medium RI changes from $n_s = 1.33$ to $n_s = 1.335$. This is because biomolecules strongly bind to the detection surface of the biosensor. The electric field distributions of the optimized configuration of the structure $\text{TiO}_2\text{-Cu-BaTiO}_3$ is shown in Figure 8. It is noted that the electric field intensity at the interface of Cu-BaTiO_3 is increasing and reaches its peak at the interface of BaTiO_3 and the sensing medium. In this proposed structure, the numerical value of the probing field is much more intense in the sensing medium, which leads to a stronger excitation of SP waves, resulting in enhanced sensitivity. Comparing this proposed structure to prior published similar sensors structures, the sensing output is much higher and is compared with others in Table 3.

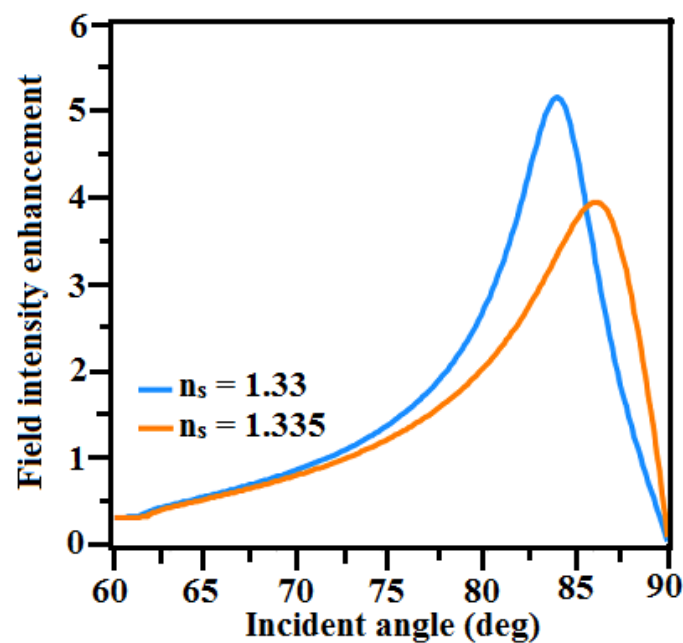


Figure 7. Incidence angle vs. electric field intensity enhancement factor at $n_s = 1.33$ and $n_s = 1.335$ for the proposed $\text{TiO}_2\text{-Cu-BaTiO}_3$ optimized configuration.

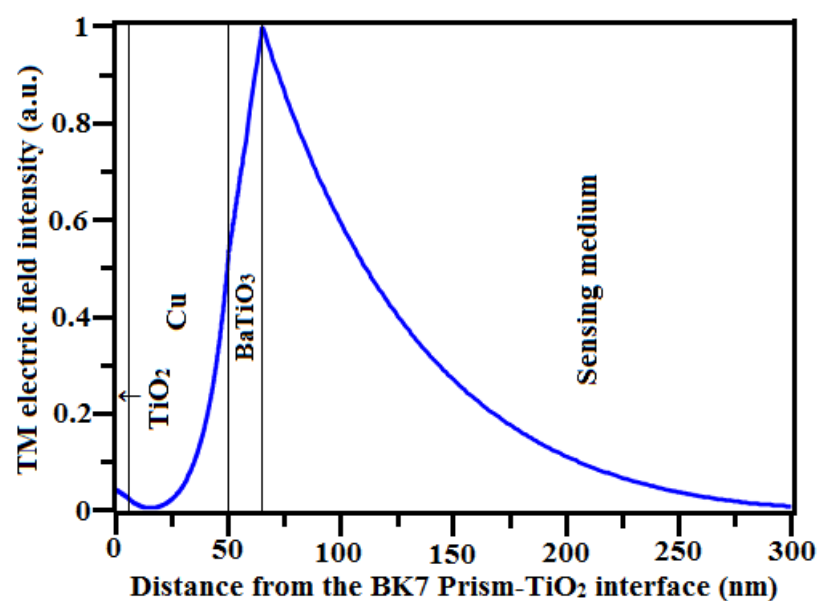


Figure 8. The electric field intensity distributions of the optimized $\text{TiO}_2\text{-Cu-BaTiO}_3$ -based structure for $n_s = 1.33$.

Table 3. The comparison of the proposed structure to the similar type of former reported SPR sensor structure.

Ref.	λ (nm)	Configuration	Sensitivity ($^{\circ}$ /RIU)	FOM (RIU $^{-1}$)	DA (deg $^{-1}$)
[60]	600	SF11-Cu-WSe $_2$	92	-	-
[59]	633	CaF $_2$ -TiO $_2$ -Au-PtSe $_2$	218	53.32	0.2466
[49]	633	BK7-TiO $_2$ -Au-Mxene-Antimonene	224.26	19.05	0.0849
[61]	633	BK7-Cu-Ni-BP-Ti $_3$ C $_2$ T $_x$	304.47	57.85	0.19
[41]	633	FK51A-Ag-BaTiO $_3$ -BlueP/MoS $_2$	347.82	60.52	0.174
[62]	632.8	BK7-Cr-Ag-BaTiO $_3$ -Go	372	88.11	-
[19]	633	CaF $_2$ -Cu-Fe $_2$ O $_3$ -Antimonene	398	-	-
[18]	633	BK7-Cu-Ni-BP-Antimonene	446	93.10	0.2
proposed	633	BK7-TiO $_2$ -Cu-MoO $_3$	386	104.89	0.2717
proposed	633	BK7-TiO $_2$ -Cu-Fe $_2$ O $_3$	406	78.07	0.1923
proposed	633	BK7-TiO $_2$ -Cu-BaTiO $_3$	552	136.97	0.2481

4. Conclusions

This numerical work demonstrates a highly sensitive SPR biosensor with a hybrid configuration made of layers of TiO $_2$, Cu, and BaTiO $_3$ /Fe $_2$ O $_3$ /MoO $_3$. The thickness of the suggested layers (TiO $_2$, Cu, and BaTiO $_3$ /Fe $_2$ O $_3$ /MoO $_3$) is carefully tuned to achieve distinctly higher sensitivity as well as FOM. Here, the utilization of the adhesion layer of TiO $_2$ enhances light trapping capability, which, in turn, also enhances the sensitivity of the suggested sensor. This proposed structure, when using BaTiO $_3$ as a covering layer, attains high sensitivity (552 $^{\circ}$ /RIU) as well as high FOM (136.97 RIU $^{-1}$) when compared to Fe $_2$ O $_3$ (406 $^{\circ}$ /RIU and 78.07 RIU $^{-1}$) and MoO $_3$ (386 $^{\circ}$ /RIU and 104.89 RIU $^{-1}$) for the optimized thickness of 45 nm Cu sandwiched between 5 nm TiO $_2$ and 15 nm BaTiO $_3$ outer cover. The proposed structure is expected to enable long-term detection with greater accuracy and sensitivity even when using Cu as a plasmonic metal. This study offers a novel possibility for the development of a more accurate and highly sensitive biosensor for biological sensing uses.

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References

- Gupta, V.K.; Choudhary, K.; Kumar, S. 2D Materials-based Plasmonic Sensors for Health Monitoring Systems—A Review. *IEEE Sens. J.* **2023**, *23*, 11324–11335. [CrossRef]
- Maharana, P.K.; Jha, R.; Padhy, P. On the electric field enhancement and performance of SPR gas sensor based on graphene for visible and near infrared. *Sens. Actuators B* **2015**, *207*, 117–122. [CrossRef]
- Xu, H.; Wu, L.; Dai, X.; Gao, Y.; Xiang, Y. An ultra-high sensitivity surface plasmon resonance sensor based on graphene-aluminum-graphene sandwich-like structure. *J. Appl. Phys.* **2016**, *120*, 053101. [CrossRef]
- Yu, X.; Yuan, Y.; Xiao, B.; Li, Z.; Qu, J.; Song, J. Flexible Plasmonic pressure sensor based on layered Two-Dimensional heterostructures. *J. Lightwave Technol.* **2018**, *36*, 5678–5684. [CrossRef]
- Mollah, M.A.; Islam, S.M.R.; Yousufali, M.; Abdulrazak, L.F.; Hossain, M.B.; Amir, I.S. Plasmonic temperature sensor using D-shaped photonic crystal fiber. *Results Phys.* **2020**, *16*, 102966. [CrossRef]

6. Yüpapin, P.; Trabelsi, Y.; Vigneswaran, D.; Taya, S.A.; Daher, M.G.; Colak, I. Ultra-high-sensitive sensor based on surface plasmon resonance structure having Si and graphene layers for the detection of chikungunya virus. *Plasmonics* **2022**, *17*, 1315–1321. [\[CrossRef\]](#)
7. Tong, J.; Jiang, L.; Chen, H.; Wang, Y.; Yon, K.T.; Forsberg, E.; He, S. Graphene–bimetal plasmonic platform for ultra-sensitive biosensing. *Opt. Commun.* **2018**, *410*, 817–823. [\[CrossRef\]](#)
8. Hasib, M.H.H.; Nur, J.N.; Shushama, K.N.; Rahaman, I.; Rana, M.M.; Mahfuz, M.A. Enhancement of sensitivity for surface plasmon resonance biosensor with higher detection accuracy and quality Factor. In Proceedings of the 1st International Conference on Advances in Science, Engineering and Robotics Technology (ICASERT) IEEE, Dhaka, Bangladesh, 3–5 May 2019.
9. Karki, B.; Ramya, K.C.; Devi, R.S.S.; Srivastava, V.; Pal, A. Titanium dioxide, black phosphorus and bimetallic layer-based surface plasmon biosensor for formalin detection: Numerical analysis. *Opt. Quant. Electron.* **2022**, *54*, 451. [\[CrossRef\]](#)
10. Suvarnapaet, P.; Pechprasarn, S. Graphene-based materials for biosensors: A review. *Sensors* **2017**, *17*, 2161. [\[CrossRef\]](#)
11. Kretschmann, E.; Raether, H. Notizen: Radiative decay of non radiative surface plasmons excited by light. *Z. Naturf. A* **1968**, *23*, 2135–2136. [\[CrossRef\]](#)
12. Raj, S.; Alotaibi, M.F.; Al-Hadeethi, Y.; Lohia, P.; Singh, S.; Dwivedi, D.K.; Umar, A.; Alzayed, H.M.; Algadi, H.; Baskoutas, S. Numerical study to enhance the sensitivity of a surface plasmon resonance sensor with BlueP/WS₂-covered Al₂O₃-Nickel Nanofilms. *Nanomaterials* **2022**, *12*, 2205.
13. Maharana, P.K.; Jha, R. Chalcogenide prism and graphene multilayer based surface plasmon resonance affinity biosensor for high performance. *Sens. Actuators B Chem.* **2012**, *169*, 161–166. [\[CrossRef\]](#)
14. Choi, S.H.; Kim, Y.L.; Byun, K.M. Graphene-on-silver substrates for sensitive surface plasmon resonance imaging biosensors. *Opt. Express* **2011**, *19*, 458–466. [\[CrossRef\]](#)
15. Saada, Y.; Selmib, M.; Gazzaha, M.H.; Bajahzard, A.; Belmabrouk, H. Performance enhancement of a copper-based optical fiber SPR sensor by the addition of an oxide layer. *Optik* **2019**, *190*, 1–9. [\[CrossRef\]](#)
16. Singh, S.; Mishra, S.K.; Gupta, B.D. Sensitivity enhancement of a surface plasmon resonance based fiber optic refractive index sensor utilizing an additional layer of oxides. *Sens. Actuators A Phys.* **2013**, *193*, 136–140. [\[CrossRef\]](#)
17. Ahmed, S.; Kabir, S. Copper-Germanium-Graphene based highly sensitive plasmonic biosensor for protein detection. In Proceedings of the IEEE International Conference on Computer, Communication, Chemical, Material and Electronic Engineering (IC4ME2), Rajshahi, Bangladesh, 8–9 February 2018.
18. Singh, M.K.; Pal, S.; Verma, A.; Mishra, V.; Prajapati, Y.K. Sensitivity enhancement using anisotropic black phosphorus and antimonene in bi-metal layer-based surface plasmon resonance biosensor. *Superlattices Microstruct.* **2021**, *156*, 106969. [\[CrossRef\]](#)
19. Wang, S.; Liu, N.; Cheng, Q.; Pang, B.; Lv, J. Surface plasmon resonance on the Antimonene–Fe₂O₃–Copper layer for optical attenuated total reflection spectroscopic application. *Plasmonics* **2021**, *16*, 559–566. [\[CrossRef\]](#)
20. Verma, V.K.; Pal, S.; Rizal, C.; Prajapati, Y.K. Tunable and sensitive detection of cortisol using Anisotropic Phosphorene with a surface plasmon resonance technique: Numerical investigation. *Magnetochemistry* **2022**, *8*, 31. [\[CrossRef\]](#)
21. Ishtiaq, K.M.; Imam, S.A.; Khosru, Q.M. BaTiO₃–Blue Phosphorus/WS₂ hybrid structure-based surface plasmon resonance biosensor with enhanced sensor performance for rapid bacterial detection. *Results Eng.* **2022**, *16*, 100698. [\[CrossRef\]](#)
22. Tabassum, R.; Mishra, S.K.; Gupta, B.D. Surface plasmon resonance-based fiber optic hydrogen sulphide gas sensor utilizing Cu–ZnO thin films. *Phys. Chem. Chem. Phys.* **2013**, *15*, 11868–11874. [\[CrossRef\]](#)
23. Nguyen, T.T.; Sau, N.V.; Ngo, Q.M.; Eppe, G.; Tran, N.Q.; Anh, N.T.P. Enhanced sensitivity and detection of Near-Infrared refractive index sensor with plasmonic multilayers. *Sensors* **2021**, *21*, 7056. [\[CrossRef\]](#) [\[PubMed\]](#)
24. Toloue, H.; Centeno, A. Numerical analysis on DNA-sensor based on copper-graphene surface plasmon resonance. In Proceedings of the 2015 International Conference on Smart Sensors and Application (ICSSA), Kuala Lumpur, Malaysia, 26–28 May 2015.
25. Mumtaz, F.; Roman, M.; Zhang, B.; Abbas, L.G.; Ashraf, M.A.; Fiaz, M.A.; Dai, Y.; Huang, J. A simple optical fiber SPR sensor with ultra-high sensitivity for dual-parameter measurement. *IEEE Photonics J.* **2022**, *14*, 6852907. [\[CrossRef\]](#)
26. Polat, K. Thin film photocatalyst made from Fe₂O₃/2D Graphene/Cu working in the visible region of the solar spectrum. *Solid State Commun.* **2020**, *319*, 11393. [\[CrossRef\]](#)
27. Zhang, K.-K.; Wang, Y.-Y.; Wang, Q.; Wang, H.-Y.; Qian, Y.-Z.; Zhang, D.-Y.; Xue, Y.-Y.; Li, S.; Zhang, L. Sensitive monitoring of refractive index by surface plasmon resonance (SPR) with a gold α -iron (III) oxide thin film. *Instrum. Sci. Technol.* **2023**, *51*, 558–573. [\[CrossRef\]](#)
28. Ahmed, A.M.; Shaban, M. Highly sensitive Au–Fe₂O₃–Au and Fe₂O₃–Au–Fe₂O₃ biosensors utilizing strong surface plasmon resonance. *Appl. Phys. B* **2020**, *126*, 57. [\[CrossRef\]](#)
29. Augustine, S.; Joshi, A.G.; Yadav, B.K.; Mehta, A.; Kumar, P.; RenuGOPalakrishnan, V.; Malhotra, B.D. An emerging nanostructured molybdenum trioxide-based biocompatible sensor platform for breast cancer biomarker detection. *MRS Commun.* **2018**, *8*, 668–679. [\[CrossRef\]](#)
30. Zakaria, R.; Mahbub, M.; Lim, C.S. Studies of surface plasmon resonance effect on different metallic layers of silver (Ag) and copper (Cu) with molybdenum trioxide (MoO₃) for formaldehyde sensor. *Results Opt.* **2023**, *11*, 100374. [\[CrossRef\]](#)
31. Pandey, A.K.; Hashemi, M. Plasmonic sensor based on molybdenum trioxide-MXene heterojunction for refractive index sensing. *Arab. J. Sci. Eng.* **2022**, *47*, 829–834. [\[CrossRef\]](#)

32. Macis, S.; Aramo, C.; Bonavolontà, C.; Cibin, G.; D'Elia, A.; Davoli, I.; Lucia, M.D.; Lucci, M.; Lupi, S.; Miliucci, M.; et al. MoO₃ films grown on polycrystalline Cu: Morphological, structural, and electronic properties. *J. Vac. Sci. Technol. A* **2019**, *37*, 021513. [\[CrossRef\]](#)
33. Hsieh, C.-L.; Grange, R.; Pu, Y.; Psaltis, D. Bioconjugation of barium titanate nanocrystals with immunoglobulin G antibody for second harmonic radiation imaging probes. *Biomaterials* **2010**, *31*, 2272–2277. [\[CrossRef\]](#)
34. Gläsel, H.-J.; Hartmann, E.; Hirsch, D.; Böttcher, R.; Klimm, C.; Michel, D.; Semmelhack, H.-C.; Hormes, J.; Rumpf, H. Preparation of barium titanate ultrafine powders from a monomeric metallo-organic precursor by combined solid-state polymerisation and pyrolysis. *J. Mater. Sci.* **1999**, *34*, 2319–2323. [\[CrossRef\]](#)
35. O'Brien, S.; Brus, L.; Murray, C.B. Synthesis of monodisperse nanoparticles of barium titanate: Toward a generalized strategy of oxide nanoparticle synthesis. *J. Am. Chem. Soc.* **2001**, *123*, 12085–12086. [\[CrossRef\]](#) [\[PubMed\]](#)
36. Ihlefeld, J.F.; Borland, W.; Maria, J.-P. Synthesis and properties of barium titanate thin films on copper substrates. *MRS Online Proc. Libr.* **2005**, *902*, 203. [\[CrossRef\]](#)
37. Srivastava, A.; Das, R.; Prajapati, Y.K. Effect of perovskite material on performance of surface plasmon resonance biosensor. *IET Optoelectron.* **2020**, *14*, 256–265. [\[CrossRef\]](#)
38. Fouad, S.; Sabri, N.; Jamal, Z.A.Z.; Poopalan, P. Enhanced sensitivity of surface plasmon resonance sensor based on bilayers of silver-barium titanate. *J. Nano-Electron. Phys.* **2016**, *8*, 04085. [\[CrossRef\]](#)
39. Pal, A.; Jha, A. A theoretical analysis on sensitivity improvement of an SPR refractive index sensor with graphene and barium titanate nanosheets. *Optik* **2021**, *231*, 166378. [\[CrossRef\]](#)
40. Mudgal, N.; Choure, K.K.; Saharia, A.; Agarwal, A.; Falaswal, M.K.; Sahu, S.; Singh, S.V.; Singh, G. Comparative assessment of fiber SPR sensor for sensitivity enhancement using BaTiO₃ layer. *Optoelectron. Adv. Mater. Rapid Commun.* **2022**, *16*, 114–120.
41. Setareh, M.; Kaatuzian, H. Sensitivity enhancement of a surface plasmon resonance sensor using blue phosphorene/MoS₂ hetero-structure and barium titanate. *Superlattices Microstruct.* **2021**, *153*, 106867. [\[CrossRef\]](#)
42. Sun, P.; Wang, M.; Liu, L.; Jiao, L.; Du, W.; Xia, F.; Liu, M.; Kong, W.; Dong, L.; Yun, M. Sensitivity enhancement of surface plasmon resonance biosensor based on graphene and barium titanate layers. *Appl. Surf. Sci.* **2019**, *475*, 342–347. [\[CrossRef\]](#)
43. Singh, S.; Sharma, A.K.; Lohia, P.; Dwivedi, D.K. Theoretical analysis of sensitivity enhancement of surface plasmon resonance biosensor with zinc oxide and blue phosphorus/MoS₂ heterostructure. *Optik* **2021**, *244*, 167618. [\[CrossRef\]](#)
44. Kumar, A.; Yadav, A.K.; Kushwah, A.S.; Srivastava, S.K. A comparative study among WS₂, MoS₂ and graphene based surface plasmon resonance (SPR) sensor. *Sens. Actuators Rep.* **2020**, *2*, 100015. [\[CrossRef\]](#)
45. El-Gohary, S.H.; Choi, M.; Kim, Y.L.; Byun, K.M. Dispersion curve engineering of TiO₂/silver hybrid substrates for enhanced surface plasmon resonance detection. *Sensors* **2016**, *16*, 1442. [\[CrossRef\]](#) [\[PubMed\]](#)
46. Hossain, M.B.; Tasnim, T.; Abdulrazak, L.F.; Rana, M.M.; Islam, M.R. A Numerical approach to design the kretschmann configuration based refractive Index graphene-MoS₂ hybrid layers with TiO₂-SiO₂ nano for formalin detection. *Photonic Sens.* **2020**, *10*, 134–146. [\[CrossRef\]](#)
47. Singh, S.; Prajapati, Y.K. TiO₂/gold-graphene hybrid solid core SPR based PCF RI sensor for sensitivity enhancement. *Optik* **2020**, *224*, 165525. [\[CrossRef\]](#)
48. Moznuzzaman, M.; Khan, I.; Islam, M.R. Nano-layered surface plasmon resonance-based highly sensitive biosensor for virus detection: A theoretical approach to detect SARS-CoV-2. *AIP Adv.* **2021**, *11*, 065023. [\[CrossRef\]](#)
49. Raikwar, S.; Srivastava, D.K.; Saini, J.P.; Prajapati, Y.K. 2D- Antimonene based surface plasmon resonance sensor for improvement of sensitivity. *Appl. Phys. A* **2021**, *127*, 92. [\[CrossRef\]](#)
50. Mostufa, S.; Akib, T.B.A.; Rana, M.M.; Islam, M.R. Highly sensitive TiO₂/Au/Graphene layer-based surface plasmon resonance biosensor for cancer detection. *Biosensors* **2022**, *12*, 603. [\[CrossRef\]](#)
51. Hajjaji, A.; Labidi, A.; Gaidi, M.; Ben-Rabha, M.; Smirani, R.; Bejaoui, A.; Bessais, B.; El Khakani, M.A. Structural, Optical and sensing properties of Cr-doped TiO₂ thin films. *Sens. Lett.* **2011**, *9*, 1697–1703. [\[CrossRef\]](#)
52. Wu, L.; Guo, J.; Wang, Q.; Lu, S.; Dai, X.; Xiang, Y.; Fan, D. Sensitivity enhancement by using few-layer black phosphorus-graphene/TMDCs heterostructure in surface plasmon resonance biochemical sensor. *Sens. Actuators B. Chem.* **2019**, *249*, 542–548. [\[CrossRef\]](#)
53. Fouad, S.; Sabri, N.; Jamal, Z.A.Z.; Poopalan, P. Surface plasmon resonance sensor sensitivity enhancement using gold-dielectric material. *Int. J. Nanoelectron. Mater.* **2017**, *10*, 149–158. [\[CrossRef\]](#)
54. Vahed, H.; Nadri, C. Ultra-sensitive surface plasmon resonance biosensor based on MoS₂-graphene hybrid nanostructure with silver metal layer. *Opt. Quant. Electron.* **2019**, *51*, 20. [\[CrossRef\]](#)
55. Yamamoto, M. Surface plasmon resonance (SPR) theory: Tutorial. *Rev. Polarogr.* **2002**, *48*, 209–237. [\[CrossRef\]](#)
56. Kushwaha, A.S.; Kumar, A.; Kumar, R.; Srivastava, S.K. A study of surface plasmon resonance (SPR) based biosensor with improved sensitivity. *Photonics Nanostructures Fundam. Appl.* **2018**, *31*, 99–106. [\[CrossRef\]](#)
57. Mohanty, G.; Akhtar, J.; Sahoo, B.K. Effect of Semiconductor on Sensitivity of a Graphene-Based Surface Plasmon Resonance Biosensor. *Plasmonics* **2015**, *11*, 189–196. [\[CrossRef\]](#)
58. Ouyang, Q.; Zeng, S.; Jiang, L.; Hong, L.; Xu, G.; Dinh, X.-Q.; Qian, J.; He, S.; Qu, J.; Coquet, P.; et al. Sensitivity enhancement of transition metal Dichalcogenides/Silicon nanostructure-based surface plasmon resonance biosensor. *Sci. Rep.* **2016**, *6*, 28190. [\[CrossRef\]](#)

59. Tiwari, R.; Singh, S.; Lohia, P.; Dwivedi, D.K. Sensitivity enhancement of platinum diselenide based SPR sensor using titanium dioxide as adhesion layer. In *Advances in VLSI, Communication, and Signal Processing*; Dhawan, A., Mishra, R.A., Arya, K.V., Zamarréño, C.R., Eds.; Lecture Notes in Electrical Engineering; Springer: Singapore, 2022; Volume 911, pp. 249–255.
60. Lin, Z.; Chen, S.; Lin, C. Sensitivity improvement of a surface plasmon resonance sensor based on two-dimensional materials hybrid structure in visible region: A theoretical study. *Sensors* **2020**, *20*, 2445. [[CrossRef](#)] [[PubMed](#)]
61. Kumar, R.; Pal, S.; Pal, N.; Mishra, V.; Prajapati, Y.K. High-performance bimetallic surface plasmon resonance biochemical sensor using a black phosphorus–MXene hybrid structure. *Appl. Phys. A* **2021**, *127*, 1–12. [[CrossRef](#)]
62. Islam, M.A.; Paul, A.K.; Hossain, B.; Sarkar, A.K.; Rahman, M.M.; Sayem, A.S.M.; Simorangkir, R.B.V.B.; Shobug, M.A.; Buckley, J.L.; Chakrabarti, K.; et al. Design and analysis of GO coated high sensitive tunable SPR sensor for OATR spectroscopic biosensing applications. *IEEE Access* **2022**, *10*, 103496–103508. [[CrossRef](#)]

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