

Surface Plasmon Resonance-Based Fiber-Optic Metallic Multilayer Biosensors

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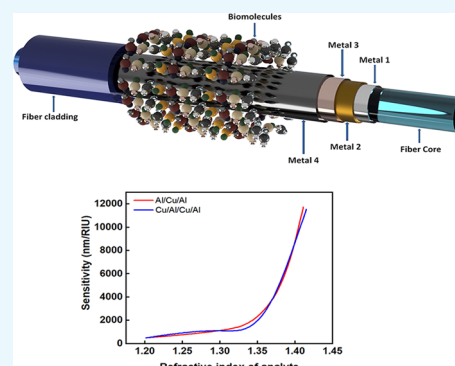


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ABSTRACT: Accurate and quick sensing of various biomolecules relevant to different health conditions is indispensable in modern diagnosis and treatment procedures. Different multilayer metallic surface plasmon resonance (SPR) biosensor configurations comprising Au, Ag, Al, and Cu are analyzed in this work by employing an *N*-layer matrix formalism as applied to the fixed-angle spectral SPR sensing methodology. Stringent standards for sensitivity, detection accuracy, and figure of merit (FOM) of the sensor configurations are set to analyze the relative merits of one configuration over another. It is observed that three- and four-layer configurations using Al and Cu provide the best FOM among all sensors that passed the set standard criteria. The highest FOM (1433.82/RIU) is observed for the four-layer Al/Cu/Al/Cu sensor for an analyte refractive index of 1.408. The sensors are best suited for detecting analytes with a refractive index range of 1.350–1.414.



1. INTRODUCTION

Biomedical instrumentation is fast emerging as an integral part of modern diagnosis and treatment procedures. Proper analysis of body fluids, tissues, and exhaled air can provide clear information on various illnesses and guide early detection of diseases. For instance, biosensing of blood can yield information on hemoglobin content,¹ antibodies,² and blood glucose concentration, among others.^{3,4} Similarly, an analysis of the refractive index of the cornea can give indications of various corneal diseases like cataract and glaucoma.⁵ Exhaled air of human beings contains many volatile organic compounds (VOCs) formed as a result of complex biochemical processes within the human body. Analysis of the VOCs can provide early indications of various diseases and health conditions.^{6–11}

Different types of sensors are available for sensing VOCs. Sensors based on the principle of surface plasmon resonance (SPR) have proved to provide quick and accurate sensing of physical, chemical, and biochemical parameters.^{12–15} Consider a metal placed in contact with a dielectric. Here, p-polarized electromagnetic waves resulting from collective oscillations of the conducting electron cloud will propagate through the interface. This wave is called the surface plasmon wave (SPW). When the propagation constant of the incident photons of a p-polarized light becomes equal to that of the SPW, a portion of the light gets absorbed, resulting in surface plasmon resonance.¹⁶ Even minute changes in the refractive index (RI) of the metal–air interface largely affect the SPR. Adsorption of external materials such as biomaterials and VOCs on the surface of the metal will alter the RI of the interface, and hence the change in the RI of the outer

ambience of the metal can be judged from the change in SPR absorption spectra. To harness the advantages of optical fibers in biosensing applications, we have modeled various fiber-optic SPR sensor configurations. These fiber-optic SPR sensors enable compactness, ease of sensing, flexibility, and reliability for noninvasive and invasive sensing and biosensing.^{17–19} Usually, in fiber-optic sensing probes, a small portion of the cladding is removed, and the conducting layer(s) enabling SPR sensing are coated on this portion. The sensor makes use of the Kretschmann configuration with the spectral SPR method. When white light is launched on one end of this fiber-optic sensor, above the critical angle, the light propagates to the other end by total internal reflection (TIR). During the TIR, a part of the light penetrates into the low-refractive-index thin metal layers as exponentially decaying evanescent waves, which couple with the surface plasmon waves at the metal–dielectric (analyte) interface, at the resonance condition. Hence, a part of the energy of the incident white light is transferred to the surface plasmons at the resonance condition, corresponding to which a dip in the transmitted light is observed. This waveform is the SPR curve.

SPR sensors with a single metallic layer have been modeled, realized, and reported. Usually, Au and Ag are employed as the

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metal since they contain a substantial amount of charge carriers. Furthermore, Au and Ag are found to be suitable for sensing operation in the visible region of the spectrum.²⁰ The quality parameters sensitivity (S), detection accuracy (DA), and figure of merit (FOM) are defined as follows:

$$\text{sensitivity (S)} = \frac{\text{change in resonant wavelength}}{\text{change in refractive index of analyte}} \quad (1)$$

$$\text{detection accuracy (DA)} = \frac{1}{\text{spectral width}} \quad (2)$$

$$\text{FOM} = \text{sensitivity} \times \text{detection accuracy} \quad (3)$$

The sharpness of the SPR curve determines the accuracy of detecting the resonant wavelength. The larger the spectral width, the lower is the accuracy. The detection accuracy facilitates easy interpretation of the accuracy in detecting the resonance wavelength and also the analysis of the relevant graphs.

Even though Au-based sensors offer a massive shift in the resonance wavelength with the change in RI (in other words high sensitivity), the detection accuracy is low. On the other hand, Ag can provide better accuracy due to its narrow spectral width, but the sensitivity is low.¹⁶ Moreover, Ag is chemically not stable, as it oxidizes on exposure to air. Studies also confirmed that Cu and Al could be used for designing SPR-based sensors, although they too oxidize.^{16,21} Studies have shown that although single-layer metallic sensors provide a sensitivity up to a maximum of 3500 nm/RIU, the trade-off between sensitivity and DA indicates that single-layer metallic SPR sensors possess many disadvantages.¹⁶ Specific sensing applications demand sensors having a high figure of merit. Studies on sensors with metallic multilayers have been reported to yield some positive results.^{16,22–25} Sensors with multilayers of different metals combine the features of each metal, and this undoubtedly reflects in parameters like the position and shift of the resonant wavelength as well as the spectral width and depth of the SPR curve. This opens new options for designing fiber-optic biosensors. Thus, in our work, we analyze the pertinent properties of SPR-based fiber-optic biosensors based on a spectral method, employing two, three, and four layers of metals.²⁶ The metals selected are Au, Ag, Al, and Cu. Theoretical modeling is done with Matlab. Unless otherwise specified, all sensor properties are analyzed for an analyte refractive index ($\text{RI}_{\text{analyte}}$) of 1.36, corresponding to ethanol, which is one of the significant VOCs.

Many different types of SPR sensors with different materials as sensing layers have already been proposed. Hybrid nanostructured SPR sensors utilizing 2D materials have attracted attention with advantages for specific sensing applications. They are usually costly and it is very difficult to ensure the accurate and precise thickness of the layers of the sensor with these materials during sensor fabrication and requires highly sophisticated equipment. The proposed sensing probe utilizes only metals, which are comparatively cheaper (except gold). Further, controlled deposition of these metals to achieve a precise thickness of sensing layers can be easily realized with thermal, e-beam evaporation, or sputtering. Thus, these sensors possess the advantages that they are simple to realize and are cost-effective. Metallic multilayer SPR sensors have the main advantage that they combine the features of the constituent metals and can be utilized for a wide range of sensing applications. Many of the configurations in the

proposed metallic multilayer sensors offer sensing features that are comparable to or even higher than that of the reported hybrid nanostructured SPR sensors.

2. THEORETICAL MODELING

In the modeled SPR sensor, the cladding is removed for a length of about 15 mm from a plastic-clad silica (PCS) fiber with a core diameter of 0.6 mm and a numerical aperture of 0.24. With the PCS fiber, the plastic cladding can be removed easily with selective etchants, leaving the silica core surface suitable for further fabrication of subsequent metal layers. The literature also shows that fiber-optic SPR sensors for different applications are modeled and successfully implemented with PCS fibers.^{12,14,16,20} This cladding-removed portion is uniformly covered with thin layers of metals. The proposed sensing probe is illustrated in Figure 1. A beam of collimated

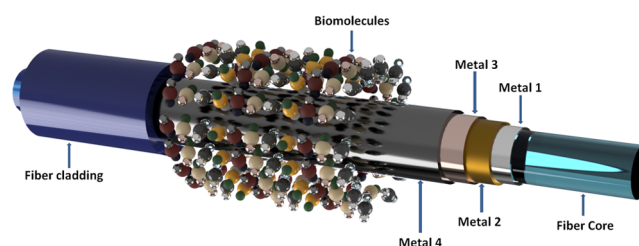


Figure 1. Schematic of the proposed metallic multilayer biosensor probe.

white light falling on one face of the fiber at a suitable angle is transmitted to the other end of the fiber, albeit with a reduced intensity if conditions for SPR absorption are met. Hence, the normalized transmitted intensity recorded at this end of the fiber gives ample information regarding the resonance wavelength (λ_{res}) and the spectral width and depth of the SPR curve. For minute changes in $\text{RI}_{\text{analyte}}$, a good SPR sensor shows a detectable change in λ_{res} . From this data, the sensitivity, DA, and FOM of the sensors are arrived at and compared to identify the optimal sensor configuration, which should aid the device engineer.

The nature and thickness of the metal layers of the sensor and $\text{RI}_{\text{analyte}}$ will affect the shape, spectral width, and depth of the SPR curve. These parameters are critical to accurate sensing. The spectral width, which is very crucial in deciding the accuracy of sensing, is usually calculated corresponding to the full-width at half-maximum (FWHM) of the SPR curve.²⁷ However, this poses a problem (illustrated in Figure 2), which shows three kinds of SPR curves normally encountered in real sensing applications. While curve A is very shallow (which affects the accurate determination of λ_{res} and hence the sensitivity) and broader (which makes DA very low), curve B may be considered ideal. Curve C, on the other hand, is ambiguous because the tail end of the dip is missing, which makes finding the FWHM practically impossible. Hence, in this work, the spectral width is calculated at a height corresponding to 0.1 unit above the tip of the SPR dip.²⁸ Stringent standards are set for the suitability of any sensor configurations in practical sensing applications: (a) only those SPR curves whose spectral width measurement is possible at the height of at least 0.1 unit above the tip of the curve is considered in our work, (b) the sensitivity (which is the ratio of change in λ_{res} corresponding to a unit change of $\text{RI}_{\text{analyte}}$) should be greater than 3000 nm/RIU,^{16,28} (c) the DA of the

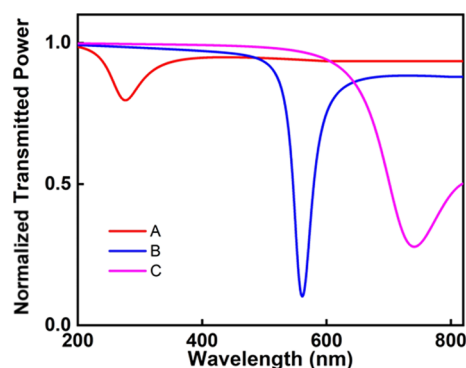


Figure 2. Typical SPR curves. Curve B is an acceptable SPR curve showing a well-defined absorption dip due to surface plasmons. Curve A is very shallow, while curve C shows a wider absorption dip. The curves illustrate the variation in the shape of the SPR curves, depending on parameters such as the thickness and type of the conducting layer(s) and RI_{analyte} .

sensor must be greater than 0.03 nm^{-1} , and (d) it is also set that the λ_{res} be in the visible range of the spectrum between 250 and 700 nm.

The spectral SPR method has been adopted, and hence due consideration of the wavelength dependence of the different materials constituting various layers of the sensing probe is essential. The refractive index dependence of the silica core of the PCS fiber on wavelength is calculated as defined by the Sellmeier relation:²⁹

$$n(\lambda) = \sqrt{1 + \frac{A_1 \lambda^2}{\lambda^2 - B_1^2} + \frac{A_2 \lambda^2}{\lambda^2 - B_2^2} + \frac{A_3 \lambda^2}{\lambda^2 - B_3^2}} \quad (4)$$

where λ is the wavelength in μm and A_1 , A_2 , A_3 , B_1 , B_2 , and B_3 are Sellmeier coefficients with values of $A_1 = 0.6961663$, $A_2 = 0.4079426$, $A_3 = 0.8974794$, $B_1 = 0.0684043$, $B_2 = 0.1162414$, and $B_3 = 9.896161$.

The Drude dispersion model quantifies the wavelength dependence of the dielectric constant of the metals with the relation¹⁶

$$\epsilon_m(\lambda) = \epsilon_{\text{mr}} + i\epsilon_{\text{mi}} = 1 - \frac{\lambda^2 \lambda_c}{\lambda_p^2 (\lambda_c + i\lambda)} \quad (5)$$

where λ_p and λ_c are the plasma and collision wavelengths of the metal, respectively, ϵ_{mr} and ϵ_{mi} are the real and imaginary values of the dielectric constant of the metals, respectively, and ϵ_{∞} the dielectric constant at very high frequencies approaches unity. The values of λ_p and λ_c for Au (Au), Ag (Ag), Cu (Cu), and Al (Al) are furnished in Table 1.^{30,31}

For an SPR-based sensor, the normalized transmitted power through the fiber measured at one end due to a white light source fed at the other end can be expressed as³²

Table 1. Plasma and Collision Wavelength of Metals

metal	λ_p (m)	λ_c (m)
Cu	1.3617×10^{-7}	4.0852×10^{-5}
Ag	1.4541×10^{-7}	1.7614×10^{-5}
Al	1.0657×10^{-7}	2.4511×10^{-5}
Au	1.6826×10^{-7}	8.9342×10^{-6}

$$P_{\text{trans}} = \frac{\int_{\theta_{\text{cr}}}^{\pi/2} R_p^{N_{\text{ref}}(\theta)} \frac{n_1^2 \sin \theta \cos \theta}{(1 - n_1^2 \cos^2 \theta)^2} d\theta}{\int_{\theta_{\text{cr}}}^{\pi/2} \frac{n_1^2 \sin \theta \cos \theta}{(1 - n_1^2 \cos^2 \theta)^2} d\theta} \quad (6)$$

where R_p is the net reflection coefficient of the ray incident at the core metal interface. θ_{cr} denotes the critical angle of the fiber, n_2 is the refractive index of the cladding of the fiber, and $N_{\text{ref}}(\theta)$ is the number of reflections the ray launched at an angle θ undergoes inside the fiber core and is given by $N_{\text{ref}}(\theta) = L/D \tan \theta$, where L is the length of the sensing probe and D is the diameter of the fiber core.

In this work, the sensing probes considered are multilayered structures, and hence an N -layer matrix method³³ has been utilized to determine the value of R_p accurately. Accordingly, the characteristic matrix for an N -layer structure can be expressed as

$$M = \prod_{k=2}^{N-1} M_k = \begin{bmatrix} M_{11} & M_{12} \\ M_{21} & M_{22} \end{bmatrix} = \begin{bmatrix} \cos \beta_k & (-i \sin \beta_k)/q_k \\ -iq_k \sin \beta_k & \cos \beta_k \end{bmatrix} \quad (7)$$

with

$$q_k = \left(\frac{\mu_k}{\epsilon_k} \right)^{1/2} \cos \theta_k = \frac{(\epsilon_k - n_1^2 \sin^2 \theta_1)^{1/2}}{\epsilon_k} \quad (8)$$

and

$$\beta_k = \frac{2\pi}{\lambda} n_k \cos \theta_k (z_k - z_{k-1}) = \frac{2\pi d_k}{\lambda} (\epsilon_k - n_1^2 \sin^2 \theta_1)^{1/2} \quad (9)$$

where ϵ_k , n_k , μ_k , and d_k are the dielectric constant, refractive index, permeability, and thickness of the k th layer, respectively. The reflection coefficient r_p of the incident wave through the N -layered structure is given by

$$r_p = \frac{(M_{11} + M_{12} q_N) q_1 - (M_{21} + M_{22} q_N)}{(M_{11} + M_{12} q_N) q_1 + (M_{21} + M_{22} q_N)} \quad (10)$$

The resonance condition for excitation of the surface plasmon wave is given by¹⁶

$$\frac{2\pi}{\lambda} n_1 \sin \theta = \left[\frac{2\pi}{\lambda} \left(\frac{\epsilon_m n_s^2}{\epsilon_m + n_s^2} \right)^{1/2} \right] \quad (11)$$

where λ , θ , ϵ_m , n_1 , and n_s are the wavelength of the incident light, angle of incidence of the incident light, dielectric constant of the metal layer, refractive index of the fiber core, and refractive index of the sensing layer, respectively.

The different configurations modeled in this work can be classified as single-layer, two-layer, three-layer, and four-layer configurations. In multilayer configurations, the coupling of the electromagnetic field of the incident light with the propagation constant of the surface plasmon waves at the outer metal–insulator (analyte) interface depends strongly on the plasma frequency and damping constant of the outer metal as well as the coupling of the electromagnetic field with the mobile charges of the various metal layers. Hence, in two-, three-, and four-layer configurations, the order of metals and the relative thickness of the layers are important. Therefore, for clarity, the

convention of $A/B/C/D$ is used throughout, wherein A denotes the innermost and D the outermost metal layer. In addition, a quantity called layer fraction given by $LF_A = dA_i / (dA_i + dA_o)$ is defined, where dA_i and dA_o are the thickness of the inner and outer layers of metal A , respectively, for a three- or four-layer configuration involving two layers of metal A .

3. RESULTS AND DISCUSSION

The typical normalized transmitted power obtained as a function of wavelength is shown in Figure 3a. Evidently, for a given configuration, as RI_{analyte} changes, the SPR absorption varies, which allows determination of sensitivity, DA, and FOM of that configuration.

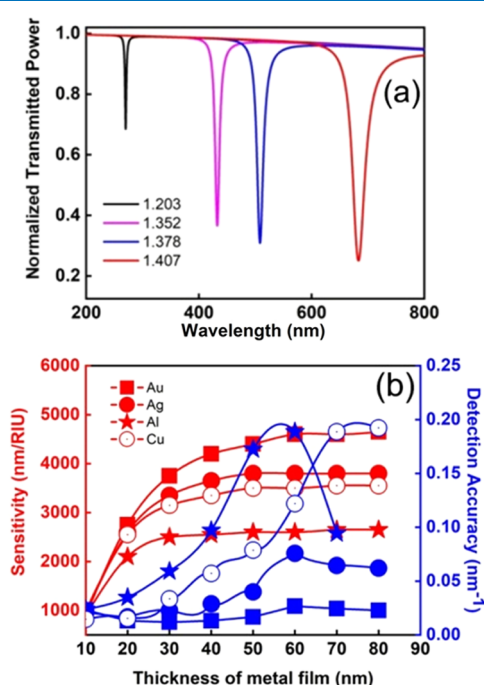


Figure 3. (a) Typical variation of normalized transmitted power as a function of wavelength for a sensor configuration at different values of RI_{analyte} . (b) Sensitivity and DA for sensors with different thicknesses of single metal layers for $RI_{\text{analyte}} = 1.361$.

3.1. Single- and Two-Layer Metallic Sensors. Analysis of the performance of single metal layer SPR sensors shows that as the thickness of the metal layer increases, sensitivity increases and saturates. A thickness of 60 nm is found to yield optimal values for both sensitivity and DA, as plotted in Figure 3b. Furthermore, increasing the thickness beyond 60 nm yields no marked improvement in sensitivity and DA. Hence, the total thickness of the metal layers has been fixed to be 60 nm throughout the study.

Bimetallic combinations of fiber-optic SPR sensors have been found to yield better sensing than those with a single layer of metal.^{16,21,22} All possible configurations such as A/B and B/A were modeled by varying $dA/(dA + dB)$, where dA and dB are the thickness of layers A and B , respectively, keeping $dA + dB = 60$ nm. As an illustration, the sensitivity and detection accuracy as a function of the ratio of inner layer thickness to the total bimetallic thickness for the better-performing configurations (a) Cu/Ag and Ag/Cu and (b) Cu/Al and Al/Cu are plotted in Figure 4a,b, respectively. Although

the sensitivity is observed to be lower than 4000 nm/RIU for all bimetallic configurations, the DA is exceptionally good.

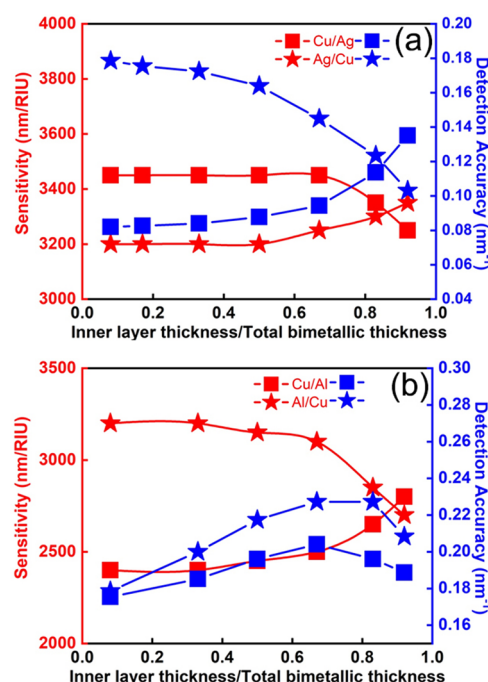


Figure 4. (a) Sensitivity and detection accuracy as a function of the ratio of inner layer thickness to total bimetallic thickness for sensor configurations Cu/Ag and Ag/Cu , and (b) sensitivity and detection accuracy as a function of the ratio of inner layer thickness to total bimetallic thickness for bilayer sensors Cu/Al and Al/Cu .

3.2. Three-Layer Metallic Sensors. The performance of SPR sensors made of three-layer metallic configurations of the type $A/B/A$ is analyzed below. The data obtained for only the better-performing configurations, viz., $\text{Au}/\text{Ag}/\text{Au}$, $\text{Ag}/\text{Au}/\text{Ag}$, $\text{Au}/\text{Cu}/\text{Au}$, $\text{Cu}/\text{Au}/\text{Cu}$, $\text{Cu}/\text{Al}/\text{Cu}$, and $\text{Al}/\text{Cu}/\text{Al}$ are considered and are shown in Figure 5. The impact of the variations in layer thickness in the sensor on its performance on sensitivity and the spectral width is analyzed for different layer fractions (LF_A) and different thicknesses of the middle layer (dB) and is depicted in Figure 5.

A quick perusal of Figure 5 reveals the influence of the choice of metals and their layer fractions on the sensitivity and DA of the sensors. For a fixed dB , with an increase in LF_A , sensitivity is found to decrease for $\text{Au}/\text{Ag}/\text{Au}$ (Figure 5a), whereas it increases for $\text{Ag}/\text{Au}/\text{Ag}$ (Figure 5b). The opposite is true for DA. When the thickness of the middle layer is varied, the sensitivity remains almost constant at lower LF_A values. However, for higher LF_A values, with a decrease in the thickness of the middle layer, the sensitivity is found to increase slightly for $\text{Au}/\text{Ag}/\text{Au}$ and decrease slightly for $\text{Ag}/\text{Au}/\text{Ag}$. For $RI_{\text{analyte}} = 1.361$, $\text{Au}/\text{Ag}/\text{Au}$ yielded a maximum sensitivity of 4500 nm/RIU for LF_A values less than 0.15 irrespective of the thickness of the middle layer, whereas $\text{Ag}/\text{Au}/\text{Ag}$ yielded a maximum sensitivity of 3800 nm/RIU for an LF_A of 0.8 and middle layer thickness of 30 nm. The resonant wavelength was well in the visible range around 570–700 nm in both these sensor configurations. The λ_{res} decreased in $\text{Au}/\text{Ag}/\text{Au}$ and it increased in $\text{Ag}/\text{Au}/\text{Ag}$ with an increase in LF_A for fixed values of middle layer thickness. Similarly, with an increase in middle layer thickness, λ_{res} and spectral width

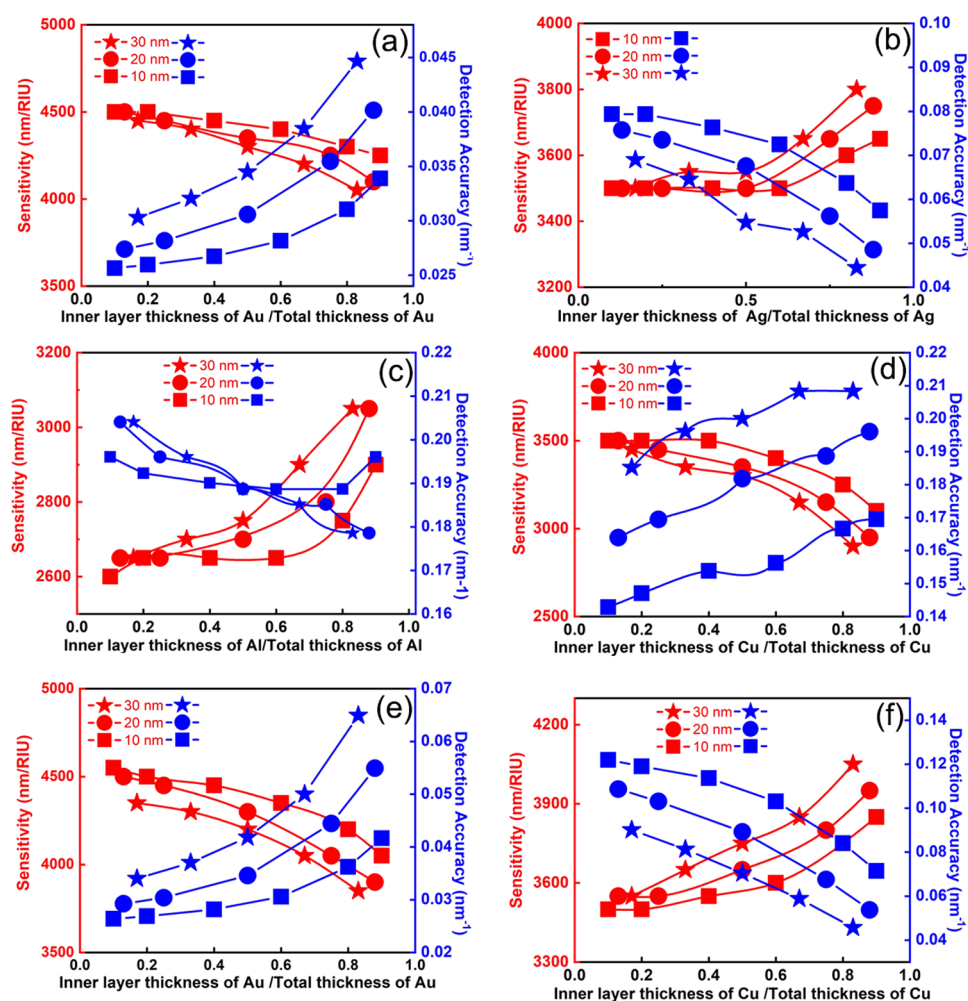


Figure 5. Sensitivity and DA as a function of inner layer fraction for three-layer sensor configurations: (a) Au/Ag/Au, (b) Ag/Au/Ag, (c) Al/Cu/Al, (d) Cu/Al/Cu, (e) Au/Cu/Au, and (f) Cu/Au/Cu. All curves were obtained by keeping the total thickness of metal layers at 60 nm and $RI_{\text{analyte}} = 1.361$.

increased in Au/Ag/Au and decreased in Ag/Au/Ag. For the same values of LF_A and middle layer thickness, the sensitivity, λ_{res} , and DA of Au/Ag/Au were lower compared to those of Ag/Au/Ag.

Figure 5c,d depicts the variations of sensitivity and DA with LF_A and dB for Al/Cu/Al and Cu/Al/Cu, respectively. For fixed values of dB, the sensitivity is found to decrease in Cu/Al/Cu and increase in Al/Cu/Al with the increase in LF_A . An exact opposite trend is observed for DA. Moreover, the sensitivity remained almost constant in both Cu/Al/Cu and Al/Cu/Al for lower LF_A values, irrespective of dB. However, for higher LF_A , the sensitivity is found to increase slightly in Cu/Al/Cu and decrease slightly in Al/Cu/Al with a decrease in dB. The λ_{res} in both the combinations are well in the visible range from about 410 to 560 nm, with Al/Cu/Al having a comparatively lower λ_{res} . Cu/Al/Cu is calculated to have a higher sensitivity of 3500 nm/RIU with a lower LF_A compared to Al/Cu/Al, which offered a maximum sensitivity of 3050 nm/RIU with a higher value of LF_A . The DA remained in an impressive range of 0.140–0.210 nm^{-1} in both the configurations. The Cu/Al/Cu configuration with the middle Al layer of about 10 nm thickness and the Al/Cu/Al with the middle Cu layer of about 30 nm yielded better performance. However, the Al/Cu/Al configuration with dB = 10 nm did not yield acceptable sensitivity for any LF_A .

The variations of sensitivity and spectral width with LF_A and dB for Au/Cu/Au and Cu/Au/Cu, respectively, are depicted in Figure 5e,f. Irrespective of dB, a decrease in sensitivity, spectral width, and λ_{res} for Au/Cu/Au and an increase of the same for Cu/Au/Cu are noticed with an increase in LF_A . However, with a decrease in dB, the sensitivity, spectral width, and λ_{res} are observed to increase in Au/Cu/Au, whereas it decreased in Cu/Au/Cu. The λ_{res} in both the configurations are well in the visible range from about 500 to 700 nm. Au/Cu/Au is found to offer a higher sensitivity with a maximum of 4550 nm/RIU at an $LF_A < 0.2$ and the middle Cu layer thickness of about 10 nm. Similarly, Cu/Au/Cu offered a maximum sensitivity of 4050 nm/RIU for an $LF_A > 0.82$ and middle Au layer thickness of about 30 nm. Apart from the above details, the following results (graphs not shown) are also confirmed with the different three-layer sensor configurations discussed above and are furnished in Table 2.

Furthermore, asymmetric three-layer configurations with different metals on the three layers are also investigated (graphs not shown). All of the combinations yielded a sensitivity greater than 3000 nm/RIU at an RI_{analyte} value of 1.36. The sensitivity and FOM corresponding to an RI_{analyte} value of 1.361 for the different three-layer sensor configurations are furnished in Table S1. Although the combinations of Al/Cu/Au, Al/Ag/Au, Ag/Al/Au, and Ag/Cu/Au yielded

Table 2. Sensing Range and Sensitivity Corresponding to the Maximum Possible Value of RI_{analyte} for the Better-Performing Three-Layer Sensor Configurations

configuration	sensing range	highest sensitivity (nm/RIU)
Au/Ag/Au	1.340–1.374	5400
Ag/Au/Ag	1.342–1.386	6000
Cu/Al/Cu	1.352–1.400	9250
Al/Cu/Al	1.360–1.410	11 750
Au/Cu/Au	1.340–1.380	5800
Cu/Au/Cu	1.344–1.390	6950

the highest sensitivity of 4500 nm/RIU, the low value of detection accuracy resulted in a very low value of FOM. However, the Au/Al/Cu, which offered a sensitivity of 3500 nm/RIU at an RI_{analyte} value of 1.361, is observed to yield the highest FOM value of 461 RIU.

For $RI_{\text{analyte}} = 1.361$, the combination with Au as the inner and outer layers and Ag or Cu as the middle layer offers a higher sensitivity of around 4500 nm/RIU but with a larger spectral width. The Cu/Au/Cu configuration also yields a better sensitivity and sharpness but is chemically less stable.

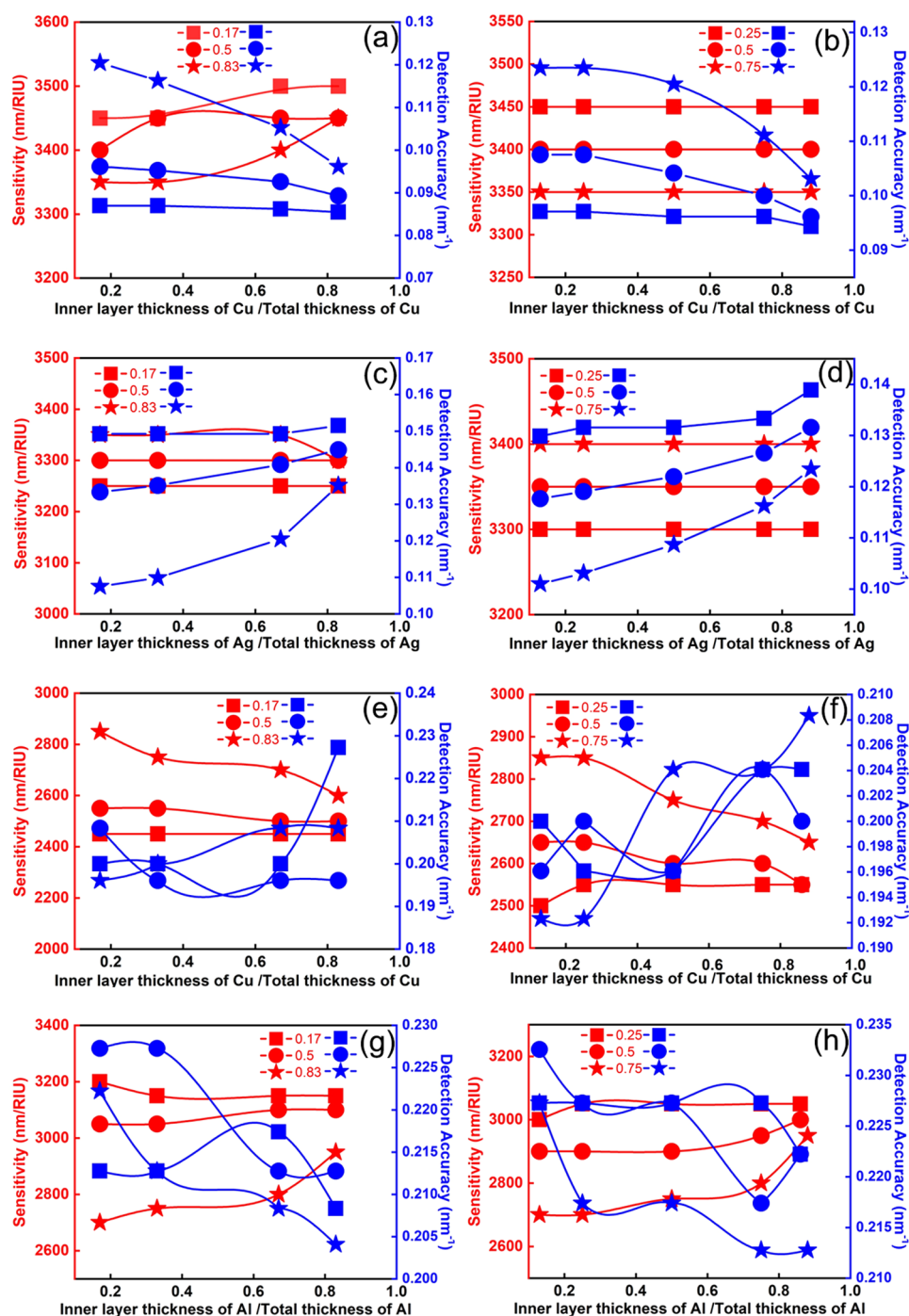


Figure 6. Sensitivity and DA as a function of layer fraction LF_A for the configuration $A/B/A/B$, for different LF_B with $dA/dB = 1$, when (a) A is Cu and B is Ag, (c) A is Ag and B is Cu, (e) A is Cu and B is Al, and (g) A is Al and B is Cu. The corresponding curves when $dA/dB = 2$ are shown in (b), (d), (f), and (h), respectively. All curves were obtained by keeping $dA + dB = 60$ nm and $RI_{\text{analyte}} = 1.361$.

Calculations with a higher RI_{analyte} on Ag/Au/Ag, Cu/Al/Cu, Al/Cu/Al, and Cu/Au/Cu configurations yielded a higher sensitivity than that of the Au/Cu/Au configuration. However, the outer layers of Al, Cu, and Ag are usually chemically more reactive unless kept in inert ambient or vacuum. With its inherent properties, Au is much more resistant to chemical reactions. Hence, the choice among three-layer metallic sensors considered in this work must be made depending on the conditions prevailing for applications.

3.3. Four-Layer Metallic Sensors. The performance of SPR sensors made of four-layer metallic configurations of the type A/B/A/B is analyzed below. The data obtained for only the better-performing configurations, viz., Cu/Ag/Cu/Ag, Ag/Cu/Ag/Cu, Cu/Al/Cu/Al, and Al/Cu/Al/Cu are considered and are shown in Figure 6. Figure 6a depicts the variation of sensitivity and DA with LF_{Cu} for the sensor configuration Cu/Ag/Cu/Ag, for different fixed LF_{Ag} , with a thickness ratio of Cu/Ag = 1:1. The corresponding curves for the thickness ratio of Cu/Ag = 2:1 is shown in Figure 6b. Similarly, Figure 6c,d represents the variation of sensitivity and DA when the order of metals is reversed. For a thickness ratio of 1:1, sensitivity increases slightly with an increase in LF_{Cu} for any fixed LF_{Ag} while it decreases with an increase in LF_{Ag} . However, DA shows the opposite trend; λ_{res} is in the range of 548.3–576 nm. For Ag/Cu/Ag/Cu, with a thickness ratio of 1:1, the sensitivity is again found to increase with the increase in LF_{Cu} but remained almost constant with variation in LF_{Ag} . DA shows a decrease with an increase in LF_{Cu} and a decrease in LF_{Ag} ; λ_{res} ranges from 534 to 561 nm.

For a thickness ratio of Cu/Ag = 2:1, with the configuration Cu/Ag/Cu/Ag, the sensitivity remains constant for varying LF_{Cu} at fixed LF_{Ag} . However, the sensitivity is found to decrease with an increase in LF_{Ag} . λ_{res} varies inversely with LF_{Ag} and directly with an increase in LF_{Cu} and lies in the range 547–571 nm. The spectral width varies between 8.3 and 11.4 nm. In Ag/Cu/Ag/Cu, the sensitivity remains constant for varying LF_{Ag} and fixed LF_{Cu} . However, the sensitivity increases slightly with an increase in LF_{Cu} . λ_{res} decreases with an increase in LF_{Ag} and increases with an increase in LF_{Cu} and is in the range 538–562 nm. The calculated spectral width is about 7–10 nm. For the same values of the total thickness, LF_{Cu} and RI_{analyte} , the Cu/Ag/Cu/Ag structure offers a higher sensitivity than the Ag/Cu/Ag/Cu structure. A maximum sensitivity of 3500 and 3400 nm/RIU is observed with Cu/Ag/Cu/Ag and Ag/Cu/Ag/Cu, for the thickness ratios Cu/Ag = 1:1 and 2:1, respectively.

Figure 6e depicts the variation of sensitivity and DA with LF_{Cu} for the sensor configuration Cu/Al/Cu/Al, for different fixed LF_{Al} , with a thickness ratio of Cu/Al = 1:1. The corresponding curves for the thickness ratio of Cu/Al = 2:1 are shown in Figure 6f. Similarly, Figure 6g,h represents the variation of sensitivity and DA when the order of metals is reversed. For a thickness ratio of 1:1, with Cu/Al/Cu/Al, the sensitivity remains constant for varying LF_{Cu} at a lower LF_{Al} , whereas it decreases slightly with an increase in LF_{Cu} for higher LF_{Al} . Moreover, it is observed that the sensitivity increases with an increase in LF_{Al} . The λ_{res} decreases slightly with an increase in LF_{Cu} and increases with an increase in LF_{Al} and is in the range 404–471 nm. The spectral width is very narrow and ranges from 4 to 5.2 nm. With Al/Cu/Al/Cu, the sensitivity almost remains constant for varying LF_{Al} at fixed LF_{Cu} , except for the high LF_{Cu} , where sensitivity increases with an increase in LF_{Al} . Furthermore, the sensitivity is found to decrease with

an increase in LF_{Cu} . The λ_{res} increases with an increase in LF_{Al} and decreases with an increase in LF_{Cu} . λ_{res} ranges from 454.8 to 530 nm.

With the thickness ratio of 2:1, Cu/Al/Cu/Al exhibits nearly a constant sensitivity for varying LF_{Cu} at lower LF_{Al} , and it shows a slight decrease with an increase in LF_{Cu} for higher LF_{Al} . Furthermore, it shows an increase in sensitivity with an increase in LF_{Al} . The observed spectral width is around 5.5 nm. The λ_{res} varies from 416 to 475 nm. Moreover, λ_{res} is observed to decrease with an increase in LF_{Cu} and increase with an increase in LF_{Al} . For Al/Cu/Al/Cu, upon varying LF_{Al} , the sensitivity remains almost constant for lower LF_{Cu} . However, for higher LF_{Cu} , the sensitivity increases with an increase in LF_{Al} . Moreover, with an increase in LF_{Cu} , the sensitivity is found to decrease. The spectral width is found to be around 4.5 nm. The λ_{res} ranges from 452 to 515 nm. It increases with an increase in LF_{Al} and decreases with an increase in LF_{Cu} . For similar LF, total thickness, and refractive index, Al/Cu/Al/Cu is found to yield a higher sensitivity than Cu/Al/Cu/Al. It is observed that the Cu/Al/Cu/Al configuration does not yield an acceptable sensitivity at $n_s = 1.361$. A maximum sensitivity of 3200 nm/RIU is calculated with Al/Cu/Al/Cu.

For $n_s = 1.361$, the Cu/Au/Cu/Au and Ag/Au/Ag/Au configurations yield a higher sensitivity of 4050 nm/RIU. However, for a higher RI_{analyte} , the Cu/Al/Cu/Al configuration is found to yield a higher sensitivity of 11 550 nm/RIU. Since the outer layer is Al and is highly reactive, this configuration is not perfect for biosensing applications. Similar is the case of sensors with Cu as the outer layer. However, most real applications of SPR sensors involve keeping the probe region in inert ambient or vacuum and introducing the analyte gases and liquids through regulated flow cells. In such controlled environments, the sensors with Al and Cu top layers can be the top choice. Otherwise, the sensors with Au as the outer layer may be considered. Among such sensors, the four-layer configuration of Cu/Au/Cu/Au is the best choice with a sensitivity of 6050 nm/RIU, DA of 51.81 nm^{-1} , and FOM of 336.11/RIU. Moreover, for the same set of parameters, Cu/Ag/Cu/Ag offers a narrow range in resonance wavelength (548–576 nm). The results (graphs not included) as furnished in Table 3 are also confirmed with the different four-layer configurations.

Asymmetric four-layer combinations with different metals were also investigated (graphs not shown). All of the

Table 3. Sensing Range and Sensitivity Corresponding to the Maximum Possible Value of RI_{analyte} for the Better-Performing Four-Layer Sensor Configurations

configuration	sensing range (nm)	maximum sensitivity (nm/RIU)
Au/Ag/Au/Ag	1.35–1.384	5850
Ag/Au/Ag/Au	1.344–1.378	5300
Cu/Al/Cu/Al	1.365–1.414	11 550
Al/Cu/Al/Cu	1.359–1.408	9750
Au/Cu/Au/Cu	1.35–1.392	6750
Cu/Au/Cu/Au	1.344–1.386	6050
Cu/Ag/Cu/Ag	1.354–1.390	6450
Ag/Cu/Ag/Cu	1.354–1.394	7050
Al/Ag/Al/Ag	1.357–1.39	6550
Ag/Al/Ag/Al	1.36–1.405	8200
Au/Al/Au/Al	1.36–1.396	7250
Al/Au/Al/Au	1.353–1.372	4850

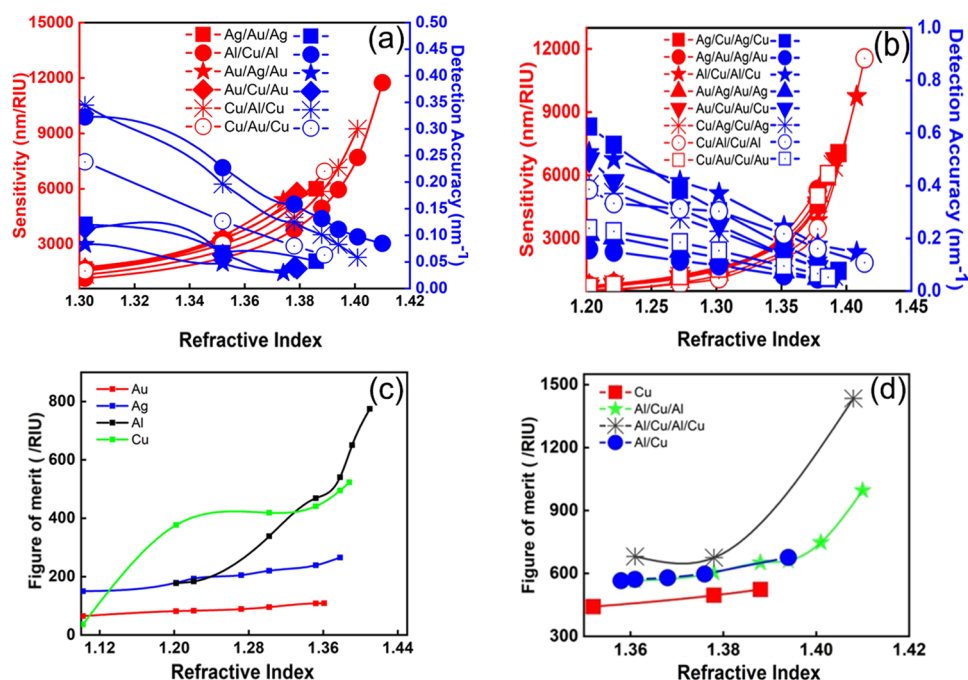


Figure 7. Sensitivity and detection accuracy as a function of RI_{analyte} for the better-performing sensors among (a) three-layer and (b) four-layer configurations. The calculated FOM as a function of RI_{analyte} for (c) single metal layers and (d) best-performing metallic multilayer sensor configurations from this work.

Table 4. Sensitivity, DA, and FOM of the Best-Performing Single and Multilayer Metallic Sensor Configurations from This Work

configuration	metal 1	metal 2	metal 3	metal 4	sensitivity at $RI_{\text{analyte}} = 1.361$ (nm/RIU)	DA (nm^{-1}) at $RI_{\text{analyte}} = 1.361$	FOM at $RI_{\text{analyte}} = 1.361$	highest acceptable sensitivity (nm/RIU), at (RI_{analyte})	DA (nm^{-1}) at maximum possible sensitivity	highest FOM
single-layer	Cu				3500	0.12195	426.83	6750 at (1.388)	0.07751	523.26
two-layer	Al	Cu			3200	0.17857	571.42	6900 at (1.394)	0.09804	676.47
three-layer	Al	Cu	Al		3050	0.18519	564.81	11 750 at (1.410)	0.08475	995.76
four-layer	Al	Cu	Al	Cu	3200	0.21277	680.85	9750 at (1.408)	0.14706	1433.82

combinations except Au/Cu/Ag/Al, Cu/Au/Ag/Al, and Ag/Au/Cu/Al yielded a sensitivity greater than 3000 nm/RIU at an RI_{analyte} value of 1.36. The sensitivity and FOM corresponding to an RI_{analyte} value of 1.36 for the different four-layer sensor configurations are furnished in Table S2. Although the combinations of Al/Cu/Ag/Au and Cu/Al/Ag/Au offered a higher sensitivity of 3900 and 3800 nm/RIU, respectively, the DA was very low. Au/Ag/Al/Cu is observed to have a higher FOM value of 596.15/RIU among the combinations. Another combination of Ag/Au/Al/Cu offered an FOM value of 554.55/RIU.

For any sensor configuration, the sensitivity, DA, and hence FOM vary with RI_{analyte} . Figure 7a,b shows the variations of sensitivity and DA with RI_{analyte} for the better-performing three- and four-layer configurations analyzed in this work. An increase in sensitivity and decrease in DA are observed with an increase in RI_{analyte} for any given configuration. The figures serve as a guideline in choosing a particular configuration for practical applications. In Figure 7c, the variation of FOM with RI_{analyte} is plotted for a single metal layer. For low values of RI_{analyte} , Cu is better suited, while for higher RI_{analyte} , Al is a better choice. Sensors made of Au or Ag show a linear response of FOM with RI_{analyte} . The FOM values of the best sensors in single and multilayer configurations satisfying all of the stringently set criteria are plotted in Figure 7d. Evidently,

the four-layer configuration of Al/Cu/Al/Cu is superior compared to other structures, especially at high RI_{analyte} . Table 4 summarizes the performance details of all of the best configurations in single and multilayer sensors analyzed in the present study.

4. CONCLUSIONS

In our present work, the sensing characteristics of three- and four-layer metallic fiber-optic SPR sensors are analyzed based on their sensitivity, DA, and operating range. It has already been established in previously reported works that single metallic structures suffer from many disadvantages and that bimetallic combinations can rectify these disadvantages to a great extent. The proposed three- and four-layer metallic sensing probes work effectively for RI_{analyte} in the range 1.34–1.414. Maximum sensitivities of 11 750 and 11 550 nm/RIU are observed with Al/Cu/Al and Cu/Al/Cu/Al, respectively. These sensors also have a higher FOM of 995.76/RIU and 1241.94/RIU, respectively. Al/Cu/Al/Cu yielded a maximum sensitivity of 9750 nm/RIU and an FOM of 1433.82/RIU. Considering the unique chemical properties of Au and calculated sensitivities, Au/Cu/Au and Cu/Au/Cu/Au can be generally considered as a good choice for biosensors. However, the choice of the configuration should be made

carefully depending on the nature of the analyte and the sensing surroundings. The present work is based on theoretical modeling, and hence the chance of slight changes in the observed results when a physical model is implemented should not be ignored. The sensing probe is best suited for the biosensing of volatile organic compounds like ethanol and acetone.

■ ASSOCIATED CONTENT

SI Supporting Information

The Supporting Information is available free of charge at <https://pubs.acs.org/doi/10.1021/acsomega.1c01236>.

Sensitivity and FOM corresponding to an RI_{analyte} value of 1.36 for the different three-layer sensor configurations (Table S1) and sensitivity and FOM corresponding to an RI_{analyte} value of 1.36 for the different four-layer sensor configurations (Table S2) (PDF)

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Notes

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