Theoretical study of hazardous carbon-di-oxide gas sensing using MIM structure-based SPR sensing scheme

Akash Srivastava1 | Alka Verma2 | Yogendra Kumar Prajapati1

1Department of Electronics and Communication Engineering, Motilal Nehru National Institute of Technology Allahabad, Prayagraj, Uttar Pradesh, India
2Department of Electronics Engineering, Institute of Engineering and Rural Technology, Allahabad, Uttar Pradesh, India

Correspondence
Yogendra Kumar Prajapati, Department of Electronics and Communication Engineering, Motilal Nehru National Institute of Technology Allahabad, Prayagraj- 211004, Uttar Pradesh, India.
Email: yogendrapra@mnnit.ac.in

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Abstract
This work mainly focussed on the sensing of the environmentally damaging gas carbon dioxide (CO₂) by designing a gas sensor based on a surface plasmon resonance (SPR) principle. The proposed model is based on the metal-insulator-metal (MIM) model which mainly relies on metal thickness, dielectric thickness, and incident light wavelength. A comparative analysis between conventional as well as MIM-based structure is shown in this study and it is observed that by operating at 4400 nm incident light wavelength, the MIM-based structure shows sharp resonance curve, high resolution, minimum FWHM, and extremely high FOM. By using the modified Elden’s formulae, the variation in refractive index is investigated by changing the numerical values of humidity, temperature, pressure, and CO₂ content from the reference value, respectively. For each case, the sensitivity has been estimated. By using the proposed MIM-based structure, FOM value as high as 1273.11RIU⁻¹; at the end of this article, limit of detection (LOD) is calculated by varying the CO₂ gas concentration.

1 | INTRODUCTION

Detection of ecologically harmful gas like carbon dioxide is always essential for environmental monitoring as well as in the automobile industry because it affects the living, directly or indirectly. Essentially, CO₂ exists in nature as an odourless and colourless gas at low concentrations (0.04% of the total atmosphere) [1]. CO₂ causes health concerns, for example, if someone inhales the gas containing concentrations between 2% to 10%, it will cause vomiting, dizziness, depression, and irritation, which also affects the respiratory system resulting in high blood pressure [2]. If CO₂ concentration reaches more than 10%, oxygen deprivation can happen rapidly, that is death [3]. In the current scenario, gas sensing devices are applicable in the private/government organization, buildings, homes, hospitals, laboratories and moreover in tunnels (exhaust emissions) [4]. Fast, distinction detection between different gases, chemical and physical stability are the major needs for an ideal gas sensor. In the commercial market, a number of gas detecting devices are available [5] and dedicated to a variety of applications. A gas sensor works as a transducer, transforming the chemical information of gas like concentration into an analytically useful signal like voltage. Nowadays major part of the research is related to SPR sensors [6,7], centralised towards biochemistry for the detection of liquid analytes commercially. Gas detection through surface plasmon resonance (a kind of plasmonic sensor) was first observed in 1982, eventhough its commercial development is still very limited. Plasmonic sensors are not only limited to gas sensing but also are widely used in various applications such as pressure sensing [8], chronic diseases detection caused by bacteria [9], terahertz absorption [10, 11], pesticides analysis [12], new biomaterials detection like ether, ethyleneglycol, chlorobenzene, and quinoline [13], street light controlling [14], lab on chip application like spectroscopy and sensing application [15] etc. Particular gas molecules absorb IR light at a certain wavelength (also called as characteristic wavelength) [16], which are proportional to the gas concentration. The absorbance of light affects the intensity of light which is measured as a sensing device response. One more point should be noted here that if CO₂ needs to be measured, the system should be designed at a wavelength close to the absorption peak of CO₂. The vibrational absorption peak of CO₂ is located close to 4300 nm [17] that is why simulation is performed to design suitable structures able to
exhibit SPR at this wavelength so that 4400 nm taken as operating light wavelength. Quantum cascade laser is suitable to produce 4400 nm incident light for the proposed structure. Some well cited research papers claimed that the SPR sensor based on metal-insulator-metal (MIM) type structures [18, 19] exhibit appreciable sensitivity and Figure of Merit (FoM). In this article, a detailed theoretical investigation based on MIM type structure consist of two couples of metallic layers, separated by a dielectric poly-methyl-methacrylate (PMMA) [20] layer is given.

In general, SPR based CO$_2$ gas sensor monitors the changes of the air refractive index by measuring the position of the resonance angle dip value comparing its position for normal air samples. The tiny variation in SPR angle is caused due to change in the concentration of the CO$_2$ gas molecules, and the changes in its physical condition from the reference value. Other techniques that are also reported for CO$_2$ gas sensing includes chemiresistive sensor of nickel-doped tin oxide (Ni-SnO$_2$) for sensing CO$_2$ and humidity [21]; another work presents polymer composite-based chemiresistive type carbon dioxide (CO$_2$) gas sensors using different degree of sulfonated poly (ether ether ketone) (SPEEK) incorporated with diethanolamine (DEA)-functionalised multi-wall carbon nanotubes (d-MWCNTs) [22].

In another work, low-temperature hollow nanostructured CeO$_2$-based sensor for CO$_2$ detection was proposed. Here the synthesis of yolk-shell CeO$_2$ nanospheres is carried out via a simple microwave-assisted solvothermal method and their subsequent application as a CO$_2$ sensor under humid conditions [23].

The article is ordered as follows: Section 2 contains the design consideration of the proposed diagram, mathematical and theoretical concept, Section 3 includes discussions regarding refractive index calculation by using modified Edlen’s, formula by changing humidity, temperature, pressure from its reference value, and CO$_2$ content, respectively. Section 4 is dedicated to results and discussion and in the conclusion section, the main outcomes of the article have been highlighted. At the end of this article, it can be observed that the proposed structure performs very well in the form of high FoM, resolution, and sensitivity when compared with conventional SPR prism-based sensors.

### 2 | PROPOSED STRUCTURE AND OVERVIEW OF MATHEMATICAL CONCEPT

This section includes the detailed mathematical analysis of surface plasmon excitation, their types, and design consideration of the proposed model and performance parameters.

#### 2.1 | Excitation of surface plasmons as well as their types

Excitation of surface plasmons can be carried out mainly by three methods (a) prism coupling [24] where plasmon is excited by attenuated total internal reflection method, (b) grating coupling [25] where optical excitation of surface plasmons is based on the diffraction of light on a diffraction grating, (c) Waveguide coupling [26] where surface plasmons can also be excited by modes of a dielectric waveguide.

The most common approach to excitation of surface plasmons is by means of a prism coupler. Otto [27] and Kretschmann with Reather [28] developed prism-coupling configurations for SPR excitation based on concepts involving attenuated total reflectance. In the Otto configuration, the prism and metal surface are separated by a dielectric (usually air). In the Kretschmann configuration (Figure 1a), the metal film is placed between the dielectric and the prism. In order to study SPR in solid-phase media, Otto configuration is a suitable method, but maintaining distance between the metal and total internal reflection (TIR) surface is a very tedious task as it reduces the SPR efficiency, so it is less useful. In Kretschmann configuration, the metal layer is in immediate contact on top of the TIR surface, which makes it an efficient plasmon generator configuration. Current research is based on Kretschmann configuration due to its simplified, user-friendly, metal-dielectric interface. Free electrons of a metal, which can be treated as a high density liquid or plasma, can be excited by applying P polarized electromagnetic waves resulting in plasma oscillation under total internal reflection (TIR) condition [28]. This phenomenon arises an evanescent field [29] which is the strongest at metal-dielectric interface, because resonance
coupling between incident radiation and surface plasmon wave takes place. The most frequently used setup for plasmon excitation is the Kretschman’s configuration where resonance realized by the maximum dip in SPR angle with respect to the reflection intensity. The necessary condition for resonance of surface plasmon is that the propagation constant of evanescent wave must match to surface plasmon which can be matched by fixing the incident angle [27, 28]. This is called as wavevector matching [30] because the incident light wavevector is matched to the surface plasmon wave vector.

\[ k_n \sin \theta_{pr} = \text{Re}\left\{ k_0 \sqrt{\varepsilon_m \varepsilon_s / (\varepsilon_m + \varepsilon_s)} \right\} \]  

(1)

where \( \varepsilon_m \) and \( \varepsilon_s \) are the dielectric constants of the metal and the sensing layer, respectively, and \( k_0 = 2\pi/\lambda_0 \) is the wavenumber of the incident light in free space, \( n_{prism} \) is refractive index of dielectric material (prism). The prism is a key element for the angle interrogation-based SPR sensor which increases the wavevector of incident light to match the wavevector of the surface plasmon. In general, it contributes in to match the wavevector of surface plasmon wave with wavevector of incident light. In order to get excellent performance parameter and maximum electromagnetic wave absorption, prism selection must be carried out carefully. As a dielectric substrate, prism CaF\(_2\) has been opted due to its low refractive index and, as a result, it proves to be a good supplementary material for high sensitivity. Eq.1 shows the relation between surface plasmons wavelength and incident wavelength and wavevector matching condition. For surface-plasmons, excitation energy and momentum conservation is very essential. The relation between wavevector and angular frequency in propagating x direction [30] is given by –

\[ k_x = \frac{\omega}{c} \sqrt{\frac{\varepsilon_1 \varepsilon_2}{\varepsilon_1 + \varepsilon_2}} \]  

(2)

Reflection and transmission of the proposed multi-layered structure or the reflectivity of P polarized light can be calculated by transfer matrix method [31–33]. The tangential field between the boundaries is related by-

\[ \begin{bmatrix} A_1 \\ B_1 \end{bmatrix} = M_2 M_3 M_4 \ldots \ldots M_{N-1} \begin{bmatrix} A_{N-1} \\ B_{N-1} \end{bmatrix} = M \begin{bmatrix} A_{N-1} \\ B_{N-1} \end{bmatrix} \]  

(3)

where \( A_1 \) and \( B_1 \) are the tangential components of the electric and magnetic field, respectively, at the boundary of the first layer. \( A_{N-1} \) and \( B_{N-1} \) are the tangential components of electric and magnetic field respectively at the boundary of the \( N^{th} \) layer. \( M \) is the characteristic transfer matrix of \( N \)-Layered structure, given by-

\[ M = \prod_{K=2}^{N-1} M_K = \begin{bmatrix} M_{11} & M_{12} \\ M_{21} & M_{22} \end{bmatrix} \]  

(4)

with,

\[ M_K = \begin{bmatrix} \cos \beta_k & -\sin \beta_k \\ -iq_k \sin \beta_k & \cos \beta_k \end{bmatrix} \]  

(5)

In Eq. 5 \( q_k \) and \( \beta_k \) are defined as-

\[ q_k = \left( \frac{\mu_k}{\varepsilon_k} \right)^{\frac{1}{2}} \]  

and

\[ \beta_k = \frac{2\pi}{\lambda} n_k \cos \theta_k (d_k) \]

After mathematical calculation, the total reflection coefficient (r) as well as reflectivity (R) [34] obtained by-

\[ R = |r|^2 = \frac{(M_{11} + M_{12}q_N)q_1 - (M_{21} + M_{22}q_N)(M_{11} + M_{12}q_N)q_1 + (M_{21} + M_{22}q_N)}{(M_{11} + M_{12}q_N)q_1 + (M_{21} + M_{22}q_N)} \]  

(6)

Interestingly, only materials (Ag, Au, Cu, Al, etc) having complex refractive index are capable of exhibiting surface plasmons. According to Eq.(1), \( \theta_{spr} \) increases with the increase of \( \varepsilon_s \), which is related to the physical conditions of the sensing gas, like temperature, concentration, pressure, humidity, etc. The SPR curve relies on dip position, peak depth of angle, width of the curve. The maximum dip in the curve refers to the minimum intensity and maximum reflection, and minimum width of the curve is responsible for maximum resolution and highest signal to noise ratio (SNR) [35]. The shift in the SPR angle dip can be done by changing the refractive index of sensing medium, measured by using the proposed sensor.

### 2.2 Design consideration and performance parameters

The proposed sensor resembles nearly guided-wave SPR (NGWSPR) [36] which contains a nano-thick dielectric layer between the metal films and sensing medium, and shows appreciable enhancement in sensitivity as well as in FoM when compared with conventional SPR sensor. The schematic structure arrangement shown in Figure 1.

Table 1 includes major design parameters like refractive index and the thickness of the layer for the proposed sensor. In this article, the bimetal stack of gold (Au) over silver (Ag) has been taken because gold has more advantage in terms of stability and it prevents Ag from getting oxidised and sulphurised, while Ag contributes to the sharpness of resonances curve. The term sensitivity(S) [31–34] characterises the minimal measurable variation of refractive index which is defined as-
and pressure can be calculated as hanging the temperature, pressure, humidity, etc. of the gas.

Medium’s density affects the refractive index of gases along molecule or atom, respectively. It is also referred that the particular gas by utilising polarisability of the accordant gas significant role in estimating the refractive index (n) of a gas. For the past years, the Lorentz-Lorenz equation [37] plays a significant role in estimating the refractive index (n) of a particular gas by utilising polarisability of the accordant gas molecule or atom, respectively. It is also referred that the medium’s density affects the refractive index of gases along incident light wavelength. Gas density is modulated by changing the temperature, pressure, humidity, etc. of the gas. The absolute refractive index of a gas in terms of temperature and pressure can be calculated as:

$$n = \sqrt{1 + \frac{Na\pi4\alpha}{R_gT}}$$  \hspace{1cm} (9)$$

where Na is Avagadro's constant, \(\alpha\) polarisability of gas, \(R_g\) is gas constant, \(p\) pressure, and T temperature. As this article is focused on CO\(_2\), by using eq. (4), the value of the refractive index of CO\(_2\) gas can be obtained. 1.0004 (by applying Na = 6.02 × 10\(^{23}\) mol\(^{-1}\), \(\alpha\) = 2.507, \(R_g\) = 188.92 J/Kg–K, \(p\) = 100,000 Pa, \(T = 25^\circ\text{C}\) in Eq.4).

Table 1

| Materials Used | Refractive Index for \(\lambda = 4400\ \text{nm}\) | Refractive Index for \(\lambda = 633\ \text{nm}\) |
|----------------|----------------------------------|----------------------------------|
| (n)            | (k) | Thickness (nm) | (n) | (k) | Thickness (nm) |
| Prism (CaF\(_2\)) | 1.4061 | -- | 1.43 | -- |
| Metal (Ag) layer | 2.5606 | 28.585 | 2 | 0.056206 | 4.2776 | 2 |
| Metal (Au) layer | 2.8620 | 27.805 | 3 | 0.18344 | 3.4332 | 20 |
| Polymer PMMA | 1.4805 | 10 | 1.4888 | -- | 15 |
| Sensing layer (n\(_s\)) | 1.0004 + \(\Delta n\) | -- | 1.0004 + \(\Delta n\) | -- |

Thus full width half maximum (FWHM) must be as least as possible for high FoM and high detection accuracy (DA).

\((\text{DA} = 1/\text{FWHM})\) of SPR sensor.

3 | REFRACTIVE INDEX CALCULATION

This section includes the mathematical formulae required to estimate the refractive index of the gas under consideration in its natural form as well as by changing the physical parameters from their natural values. This section also includes the mathematical equations required to calculate dielectric medium and metal.

3.1 | Calculation of CO\(_2\) gas refractive index under various condition

For the past years, the Lorentz-Lorenz equation [37] plays a significant role in estimating the refractive index (n) of a particular gas by utilising polarisability of the accordant gas molecule or atom, respectively. It is also referred that the medium’s density affects the refractive index of gases along incident light wavelength. Gas density is modulated by changing the temperature, pressure, humidity, etc. of the gas. The absolute refractive index of a gas in terms of temperature and pressure can be calculated as:

$$n = \sqrt{1 + \frac{Na\pi4\alpha}{R_gT}}$$  \hspace{1cm} (9)$$

Similarly, the change in temperature and pressure from reference conditions also affected the refractive index. For this case, the dispersion relation given in Eq.12.
\[(n - 1)_{\text{pp}} = \frac{(n - 1)_{\text{p}} (p/P_d)}{93214.60 \times \left\{ 1 + 10^{-8} \times (0.5953 - 0.009876 \times t/ {^\circ} \text{C}) \times p/P_d \right\}} \] 

\[1 + 0.0036610 \times t/ {^\circ} \text{C} \]  

(12)

when dry air is partly replaced by water vapour with partial pressure f, the refractive index of gas is also affected. If \(n_{pp} \) is the refractive index of moisturised air (total pressure p, temperature t, and CO\(_2\) content \(x_t\), \(n_{pp} \) may be calculated using modified Edlen's formulae from Eq. 13.

\[n_{pp} - n_p = -\frac{f}{P_d} \cdot \left\{ 3.8020 - 0.0384 \times \left( \sigma / \mu m^{-1} \right)^2 \right\} \cdot 10^{-10} \]  

(13)

3.2 Refractive index calculation of dielectric medium and metal

In this article, for the proposed sensing device structure, PMMA material has been taken as an insulating layer. In photonics techniques, PMMA is frequently used organic materials because it is easy to fabricate and has several advantages. It provides the preparation of functional materials for optical and photonic applications. The refractive index of PMMA [20] and prism CaF\(_2\) [44] can be calculated by using the following dispersion formulae given in equation (14) and (15), respectively.

\[n_{\text{PMMA}} = \sqrt{1 + \frac{0.99654 \lambda^2}{\lambda^2 - 0.00787} + \frac{0.18964 \lambda^2}{\lambda^2 - 0.02191} + \frac{0.00411 \lambda^2}{\lambda^2 - 3.85727}} \]  

(14)

where \(n_{\text{PMMA}} \) is the refractive index of polymer PMMA and \(\lambda\) is incident light wavelength.

\[n_{\text{CaF}_2} = \sqrt{1 + \frac{0.5675888 \lambda^2}{\lambda^2 - 0.050263605} + \frac{0.4710914 \lambda^2}{\lambda^2 - 0.1003909} + \frac{3.8484723 \lambda^2}{\lambda^2 - 34.649040} \]  

(15)

where \(n_{\text{CaF}_2} \) is refractive index of prism CaF\(_2\), \(\lambda\) is the incident light wavelength. Silver and gold are taken as metal layers in this study; the refractive index of these two metals can be calculated directly from the Lorentz–Drude Model [45].

4 RESULTS AND DISCUSSION

The major issue with conventional SPR sensors is its limited resolution or more easily broad SPR curve. \(Q\) In MIM arrangement, two inner metal insulator interfaces exist, and both of the interfaces have their own SPP modes, when these two independent modes couple each other, they are responsible to produce symmetric(S-SPP) as well as anti-symmetric (AS-SPP) modes [46], provided that the insulator layer must be thick enough. This overall phenomenon is responsible to exhibit a sharp resonance curve. A comparative analysis between the proposed MIM-based sensor and conventional sensor is shown in Figure 2 in terms of SPR angle width. It is concluded that the proposed MIM-based SPR sensing device produces a sharp and high-resolution SPR angle, which results in much improved FoM value in comparison with the conventional structure.

4.1 Thickness optimization and incident light wavelength

First, modified Edlen’s formula is used and the value of the refractive index of CO\(_2\) gas is computed at ideal reference conditions \((t = 20{^\circ}\text{C}, \text{air pressure} = 100,000 \text{ Pa}, \text{vapour pressure} = 23,331.41 \text{ Pa or 17.5 torr, concentration 0.04%})\). Next, by changing the CO\(_2\) gas concentration, the performance parameter analysis has been carried out for the proposed structure. It is observed that the sensing device shows the least value of FWHM as 0.45 deg, Detection Accuracy (DA) 2.2deg\(^{-1}\), and maximum value of FoM 1273.11RIU\(^{-1}\) when operated with a fixed value of 4400 nm incident light wavelength. Table 2 contains detailed investigation data to optimise the metal as well as dielectric layer thickness. It is found that for 3 nm of Au, 2 nm of Ag, and 10 nm of dielectric layer thickness, minimum reflectance (Rmin = 0.00129) is obtained along with the highest sensitivity of 59.64\(^{\circ}\)/RIU (refer to Figure 3).

However, when sensing structure works in the visible region [32–34] (633 nm incident light wavelength) the relative sensitivity obtained as 68.52\(^{\circ}\)/RIU, which is greater than the previous case. Sensitivity enhancement is directly related to the metal nature having a complex refractive index. Both the real part and the imaginary part of the metal refractive index is
responsible for the transparency features of the metal layer and they become larger when increasing the wavelength. The real part is responsible for metal reflecting nature, so the higher value of the real part makes the metal more reflective from the initial prism/metal interface [47]. Similarly, the imaginary part governs the absorption property of metal, therefore, increasing the imaginary part makes it more absorptive and as a result, the evanescent field experiences more attenuation when it propagates through the whole system. When the refractive index of the metal changes from the visible region to the IR region real and imaginary part value get major enhancement (refer to Table 1). Thus, the amplitude of the fields at the analyte interface is significantly attenuated, and consequently, the sensitivity of the structure decreases. Even though the sensitivity of the proposed device is not up to the mark, the value of FoM in the visible region is 13.86 RIU$^{-1}$ is very less in comparison with the value obtained by the proposed sensing device.

### Table 2

| Gold (Au) | Silver (Ag) | Dielectric layer (nm) | $R_{\text{min}}$ | SPR Angle (deg) at CO$_2$ Concentration = 0.04% | SPR Angle (deg) at CO$_2$ Concentration = 100% | $\Delta\theta_{\text{SPR}}$ | Sensitivity $(^\circ/\text{RIU})$ |
|----------|-------------|-----------------------|------------------|-----------------------------------------------|-----------------------------------------------|--------------------------|-------------------------------|
| 1        | 0           | 2                     | 0.21594          | 41.33318                                      | 41.57955                                     | 0.24637                  | 48.30                         |
| 1.5      | 0.5         | 4                     | 0.15146          | 46.87941                                      | 47.21172                                     | 0.33231                  | 65.15                         |
| 2        | 1           | 6                     | 0.08127          | 46.06581                                      | 46.38093                                     | 0.31512                  | 61.78                         |
| 2.5      | 1.5         | 8                     | 0.00881          | 45.78506                                      | 46.08873                                     | 0.30367                  | 59.54                         |
| 3        | 2           | 10                    | 0.00129          | 45.63528                                      | 45.95694                                     | 0.30366                  | 59.54                         |
| 3.5      | 2.5         | 12                    | 0.04197          | 45.57879                                      | 45.88246                                     | 0.30367                  | 59.54                         |
| 4        | 3           | 14                    | 0.09001          | 45.53869                                      | 45.83662                                     | 0.29793                  | 58.41                         |
| 4.5      | 3.5         | 16                    | 0.14837          | 45.51004                                      | 45.80798                                     | 0.29794                  | 58.41                         |
| 5        | 4           | 18                    | 0.21225          | 45.49285                                      | 45.79079                                     | 0.29794                  | 58.41                         |
| 5.5      | 4.5         | 20                    | 0.28172          | 45.48139                                      | 45.77933                                     | 0.29794                  | 58.41                         |
| 6        | 5           | 22                    | 0.3471           | 45.46093                                      | 45.76787                                     | 0.29794                  | 58.41                         |

**Figure 3** Optimization of dielectric layer thickness to get minimum reflectance with the highest sensitivity. The sensitivity is carried out by the shift in SPR angle as well as a change in the refractive index between CO$_2$ concentrations 0.04% to 100%.

**Figure 4** Theoretical computation of SPR angle to get least minimum reflectance ($R_{\text{min}}$), FWHM and maximum FoM in visible and IR region

In Figure 4 a comparative analysis of SPR angle has been shown, the blue colour graph is for SPR angle when the operating wavelength is 633 nm and the black colour line graph is dedicated to SPR curve when operating wavelength is of 4400 nm. It’s observed in Figure 4 that when the device operates in the IR region with a least value of FWHM, a sharp SPR curve with high resolution is observed. As stated above, the tunability of SPR sensor depends strongly on the shape of the nanostructure and the type of the metal used in structure. moreover, by using different other methods other than those used in this paper. The performance parameters improved significantly, such as addition of grating on top of metal layer, using long range SPR(LRSPR) technique in Krestchman configuration where the dielectric buffer layer is introduced between metal and prism, by applying single or multilayers of 2D materials like graphene [48], black phosphorus [49], MoS$_2$ [32-33], MXene [31] etc. heterostructures of 2D/TMD [32,33,50] materials or by applying different kinds of perovskite [34] and sulfosalts [24] etc.
4.2 Effect of prism refractive index on the proposed structure’s sensitivity

The prism refractive index has an important role in the sensitivity determination of the SPR sensor based on TIR configuration. Sensitivity increases by decreasing the prism refractive index [51] and sensitivity enhancement which is attributed to the large penetration depth obtained in the case of small prism refractive index [52]. The sensitivity versus prism refractive index was calculated when the metal layer thickness is optimised under the resonance condition (Rmin <0.01), where Rmin is the dip level at resonance. Figure 5 clearly demonstrates the correlation between the sensitivity enhancements by lowering the refractive index of the prism. The case demonstrated in Figure 5 relates to fixed operation wavelength (λ = 4400 nm) while sensitivity calculated in the case when angle shift observed between CO₂ (Concentration) 0.04% to 100%.

A comparative study between different prisms was carried out and it is concluded that the CaF₂ prism shows highest sensitivity.

4.3 Analysis of SPR angle and sensitivity by changing reference values

(a) CO₂ gas Concentration variation

In the upcoming addition, increasing the resonance angle by increasing CO₂ gas concentration (reflection spectrum of the sensor for different CO₂ concentrations) is shown in Figure 6 (a), (b). It appears in the figure that the SPR angle increases in a linear fashion by changing the gas concentration. The SPR angle at each 10% linear increment in gas concentration is calculated by following the estimation of the refractive index using Eq. (10) and (11).

Table (3) refers to give the detailed analysis of SPR angle and shift in angle, respectively. According to the data given in Table 3 it is observed that the resonance angle changes with

![Figure 5](image-url) Enhancement in Sensitivity versus prism refractive index for the proposed MIM-based SPR gas sensor

![Figure 6](image-url) (a) SPR angle estimation and shift in SPR angle by varying CO₂ gas concentration from 0.04% to 100% (refer Table 3 for data analysis), (b) Reflectance as a function of the incident light angle before and after variation of analyte refractive index in case of gas concentration variation (variation order is 10%)

| CO₂ gas Concentration (%) | SPR Angle | Shift in SPR Angle |
|---------------------------|-----------|--------------------|
| 0.04                      | 45.65328  | --                 |
| 10                        | 45.67047  | 0.01719            |
| 20                        | 45.704849 | 0.051569           |
| 30                        | 45.73349  | 0.08021            |
| 40                        | 45.76214  | 0.10886            |
| 50                        | 45.80225  | 0.14897            |
| 60                        | 45.83089  | 0.17761            |
| 70                        | 45.85954  | 0.20626            |
| 80                        | 45.89392  | 0.24064            |
| 90                        | 45.92257  | 0.26929            |
| 100                       | 45.95604  | 0.30366            |
variation in refractive index which takes place when there is a change in CO$_2$ gas concentration from 0.04% to 100%. In the present work, the variation of angular shift $\Delta \theta$ is linear and not saturated at a concentration above 50%.

(b) Variation in air pressure

As mentioned earlier through Eq. (12), the deviation of temperature and pressure from its reference conditions is responsible for the change in refractive index of gas under consideration.

As a reference condition, the value of temperature $t = 20^\circ$C, pressure $p = 100,000$ Pa (1 bar) and CO$_2$ gas concentration 0.04% of the total atmosphere is taken. In Fig. (7), the shift in SPR angle is shown by increasing the air pressure from 1 to 1.2 bar (pressure variation 0.01 bar) whereas other reference conditions remain unchanged. It is shown in Figure 7 that the SPR angle increases at each air pressure increment. Investigated data is given in Table 4 in detail. The sensitivity in this case will be calculated as 66.16°/RIU, note that SPR angle shift from $\theta_{SPR} = 45.95694$ to $\theta_{SPR} = 59.20946$ ($\Delta \theta = 13.25$) and change in refractive index is $\Delta n = 0.2003$.

(c) Temperature variation

After investigating the effect of air pressure on SPR angle, the effect of temperature enhancement on SPR angle is observed. In this case, the temperature has been changed from 0°C (273.15 K) to 50°C (323.15 K) by keeping other parameters like pressure, concentration etc. unchanged to its reference condition. From Figure 8 and analytical data given in Table 5 it is observed that SPR angle decrease linearly by varying temperature. If the SPR angle is focussed for the proposed sensor, it is observed that by varying the temperature from 20°C (293.15 K) to 50°C (323.15 K) SPR angle decreases from 45.65(°deg) to 40.39(°deg). Sensitivity in this case calculated as 56.43°/RIU at $\Delta \theta = 5.25$ and $\Delta n = 0.0932$.

(d) Humidity effect

As mentioned in the above sections, when dry air gets moisturised with partial pressure (lets $f$), the refractive index of gas also affected. If $n_{spf}$ is the refractive index of water vapour contained air then under total pressure $p$ and for

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**Table 4** SPR angle at each 0.01 bar variation in air pressure, a relevant shift in the SPR angle

| Pressure(bar) | SPR Angle | Shift in SPR Angle |
|--------------|-----------|--------------------|
| 1            | 45.95694  | --                 |
| 1.01         | 46.24342  | 0.28648            |
| 1.02         | 46.84503  | 0.88809            |
| 1.03         | 47.45256  | 1.49542            |
| 1.04         | 48.07689  | 2.11995            |
| 1.05         | 48.69568  | 2.73874            |
| 1.06         | 49.32594  | 3.369              |
| 1.07         | 49.96765  | 4.01071            |
| 1.08         | 50.61509  | 4.65815            |
| 1.09         | 51.26826  | 5.31132            |
| 1.1          | 51.93862  | 5.98168            |
| 1.11         | 52.61471  | 6.65777            |
| 1.12         | 53.30799  | 7.35105            |
| 1.13         | 54.007    | 8.05006            |
| 1.14         | 54.71747  | 8.76053            |
| 1.15         | 55.44513  | 9.48819            |
| 1.16         | 56.17851  | 10.22157           |
| 1.17         | 56.8546   | 10.97666           |
| 1.18         | 57.63955  | 11.68261           |
| 1.19         | 58.49326  | 12.53632           |
| 1.2          | 59.20946  | 13.25252           |
TABLE 5 Effect of temperature variation from its reference value on SPR angle

| Temperature(K) | SPR angle(deg) | Shift in SPR Angle |
|----------------|----------------|--------------------|
| 293.15         | 45.65328       | -4.53209           |
| 298.15         | 44.66779       | -5.51758           |
| 303.15         | 43.72814       | -6.45723           |
| 308.15         | 42.84005       | -7.34532           |
| 313.15         | 41.98635       | -8.19902           |
| 318.15         | 41.17275       | -9.01262           |
| 323.15         | 40.39352       | -9.79185           |

TABLE 6 Effect of humidity from its reference value on SPR angle

| T (°C) | f (Vapour Pressure of Water) | f(Vapour Pressure of Water)Pа | SPR Angle | Shift in SPR Angle |
|--------|-----------------------------|-----------------------------|-----------|-------------------|
| 20     | 17.5                        | 2333.141                    | 45.65328  | --                |
| 21     | 18.7                        | 2493.128                    | 45.45274  | -0.20054          |
| 22     | 19.8                        | 2639.783                    | 45.25221  | -0.40107          |
| 23     | 21.1                        | 2813.102                    | 45.05167  | -0.60161          |
| 24     | 22.4                        | 2986.421                    | 44.8626   | -0.79068          |
| 25     | 23.8                        | 3173.072                    | 44.66779  | -0.98549          |
| 26     | 25.2                        | 3359.724                    | 44.47871  | -1.17457          |
| 27     | 26.7                        | 3559.707                    | 44.28964  | -1.36364          |
| 28     | 28.4                        | 3786.355                    | 44.09483  | -1.55845          |
| 29     | 30                          | 3999.67                     | 43.91149  | -1.74179          |
| 30     | 31.8                        | 4239.651                    | 43.72814  | -1.92514          |

temperature t and CO₂ content x, n_ref can be calculated using modified Edlen's formulae using Eq. (13). The value of f changes according to temperature T. In Table 6, the variation in the value of vapour pressure of water ( f) concerning temperature is given and relative change in SPR angle is also calculated. In this case, the temperature increases from 20°C to 30°C and relative change in water vapour pressure in Torr and Pascal also given in Table 6. It is observed that the SPR angle decreases by varying T and relevant water vapour pressure f. The vapour pressure of water at temperature 20°C is 17.5 torr or 2333.141 Pa, the increment is taken from this reference value. On focussing the SPR angle for the proposed sensor, it is observed that by changing the temperature from 20°C(293.15 K) to 30°C(323.15 K) vapour pressure also increases and this makes an effect on SPR angle. From Figure 9 and Table 6 it is concluded that the SPR angle decreases from 45.65328(deg) to 43.72814 (deg) and shift in SPR angle reported in a decreasing order. Sensitivity, in this case, will be 58.30°/RIU at Δθ = 1.93 and Δt = 0.0331 (change in refractive index concerning humidity is calculated by using Eq.13)

4.4 | Limit of detection estimation (LOD)

The limit of detection with variation in CO₂ concentration variation (in parts per million or shortly ppm) shown in Figure 10. Limit of detection (LOD), is a key term that indicates the smallest CO₂ gas concentration that can be measured under the Angular interrogation method (AIM) which can be calculated by using Eqn. (16) [53–55].

\[
\text{LOD(ppm)} = \frac{\Delta C_{\text{CO}_2}}{\Delta \theta} \times 0.001
\]

Here, the change in Δθ corresponding to a small change in CO₂ gas concentration is taken into consideration and 0.001 is the smallest angular shift that can be detected. The proposed work in this article is theoretical, but from previously published research work about the experimental realization of metals such as Au, Ag, and insulating PMMA layer, it is expected that
the proposed sensor can be fabricated for experimental work. From the best of the authors’ knowledge, this work is new in its current form because of the effect on SPR angle and sensitivity utilising the variations in humidity, temperature, pressure, and CO₂ content (concentration) which are studied from their reference value analysis for the first time on a single platform.

5 | CONCLUSION

In this study, a theoretical concept of a gas sensor for carbon dioxide detection based on surface plasmon resonance has been described. The shift in the position of the resonance dip of the reflected spectrum due to the modulation of the incident light angle and the variation of the refractive index can be monitored. The performance of the proposed SPR-based gas sensor has been numerically simulated and analysed by following the prism/bimetal/insulator/bimetal or generally the Metal Insulator Metal (MIM)-based structure. It is observed that the sensing device shows high sensitivity and almost four times better FoM than a conventional SPR sensor. The proposed design of the investigated sensor is capable and very sensitive for measuring a low and a wide range of CO₂ concentrations. By using the modified Eden’s formulae, the refractive index has been investigated by changing the values of humidity, temperature, pressure, and CO₂ content, respectively, and the corresponding change in SPR angle and sensitivity for each case is calculated in a step by step manner.

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ORCID

Yogendra Kumar Prajapati 🔹 https://orcid.org/0000-0002-6752-5667

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