Theoretical and Experimental Investigation on SPR Gas Sensor Based on ZnO/Polypyrrole Interface For Ammonia Sensing Applications

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Theoretical and experimental investigation on SPR gas sensor based on ZnO/Polypyrrole interface for ammonia sensing applications

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Abstract

This work includes the exploitation of laboratory-assembled SPR technique for the application of gas sensor at room temperature. The refractive index change at the interface of ZnO/Polypyrrole with adsorption of gases (NO₂ and NH₃) is the basis of SPR gas sensor. The theoretical simulations were done to find out the optimum thickness of ZnO and Polypyrrole composite films for sharp SPR reflectance values. Theoretical SPR curves obtained by changing the value of thickness of Gold nanoparticles film and incident wavelength are also presented in the manuscript. Experimental studies were done to validate the theoretical studies and discussion were done about the interaction of NH₃ gas with prism/Au/ZnO/Polypyrrole system. Here, ZnO/Polypyrrole multilayer structure is the sensing layer to develop highly efficient SPR based NH₃ gas sensor. The outcome of these results validate the significance of SPR technique for application of interaction of surface adsorbed analytes, with the interface of dielectrics and sensing material.

Introduction

Research community has always been putting efforts to develop highly sensitive and efficient gas sensors in order to keep the environment and work places safe from any accidental leakage at domestic and Industrial production.[1, 2]. At present, we have various technologies of gas sensing which include conductometric and optical sensing technologies. Out of which, conductometric sensing technology has various disadvantages like requirement of elevated temperature demanding high power consumption and poor selectivity. Hence, we need to think for the preference of highly efficient and selective gas sensor based on optical sensing technologies [3]. The major advantage of optical gas sensor is due to its ability of operation, which use less power, at room temperature [4]. A lot of optical techniques are available for sensing purposes such as, FTIR [5], UV-Vis photo spectrometry [6], ellipsometry [7] and Surface Plasmon Resonance technique [8]. Out of all the known techniques, optical gas sensors based on SPR have enormous advantages like simple sample preparation, operation at room temperature, lower detection limit, high selectivity and response. The Surface Plasmon Resonance (SPR) technique is one of the oldest techniques for the application in gas sensing and researchers have exploited it for gas sensing applications [9, 10, 11]. But, results were lacking in terms of poor response and complicated and bulky setup. Therefore, the first step to develop a gas sensor for optimization of thickness of sensing layer. The present work is initiated with theoretical simulation for optimization of thickness of ZnO layer and Polypyrrole layer separately. SPR technique is very sensitive technique which can be used for sensing of minute changes near the boundary interface of dielectric with the metal [12]. Thus, the variance in the reflectance values can be related for the indication of a particular gas in the vicinity of the interface showing the change of the refractive index.

Now, the focus in this work presented here is on the detection of highly toxic and dangerous ammonia (NH_3) gas. NH_3 gas is produced from as a waste product from livestock or emanation from industry and automobile. Many efforts are continuing in the aim of detection of NH_3 gas by research community [13, 14]. The present focus of the researchers is to develop an efficient gas sensor to sense very low concentration of NH_3 leaks (≤ 5 ppm) [15]. There are very few reports available on SPR gas sensors focused for the detection of NH_3 gas [16, 17]. But, they all reported poor sensitivity and aim to detect higher concentration of ammonia (> 25 ppm). Maciak et al. have utilised polyaniline sensing layer based SPR spectroscopy technique to monitor ammonia vapours for a lower concentration value of 32 ppm [16]. Dolbec et al. have also detected higher concentration of ammonia using a different sensing layer i.e. Nafion/ WO_3 [17].

This has been previously discussed that gas sensing using SPR technique requires an optimized sensing layer for detection. Hence, choosing a suitable material and its optimization is highly crucial for the development of the sensor. Therefore variation of refractive index in the sensing layer after the exposure of target gas on it, is in direct relation with the detection sensitivity of the analytes interacting with it. For the past few decades, semiconductor metal oxides possess suitable properties for sensing applications i.e. for sensing various toxic gases and among all the explored metal oxides in the application as the sensing material, ZnO is the best choice. ZnO has suitable semiconducting, piezoelectric and pyroelectric properties [18]. Another class of materials which recently has been explored are the conducting polymers due to good electrical and optical properties [19]. Out of all the conducting polymers, Polypyrrole (PPy) is the most famous due to stable nature at elevated temperature and easy sample preparation [20]. PPy thin films were prepared electrochemically for NH_3 sensing in the concentrations of 0.01–1% [21]. Yadav et al. have reported 4-8% of sensing response towards NH_3 gas using chemically synthesized Ppy films [22]. Hence, mostly results show low sensing response at

higher temperature. There is no study available in literature on the development of SPR sensor using ZnO/PPy multilayer structure for NH₃ gas sensing. This may pave the way of the fabrications of an SPR gas sensor for low level detection of ammonia gas having high sensitivity and efficiency.

In this work, we have done optimization of the thicknesses of Au, ZnO & PPy thin films theoretically and experimentally for sharp SPR curve. The change in refractive indexes of the ZnO/Polypyrrole composite multilayer thin film structure deposited at their optimized value of thickness on the of gold were examined using SPR technique with varying concentration of toxic gas like NH₃ gas.

Theoretical simulation details

The behaviour of intensity of reflected light with angle of incidence (angular interrogation mode) can be described by Fresnel's equations where light is reflected from different interfaces (metal/dielectric, prism/metal, dielectric/dielectric interfaces). The theoretical values of reflectance for single layer (prism/metal/air) and double layer (prism/metal/dielectric/air) systems have applied for the determination of the refractive index of gold(metal) and dielectric layer respectively.

One layer system (prism/metal/dielectric (air))

Let n_i ($i = 0, 1, 3$) be the values of refractive index for the any one of the medium(prism/metal/dielectric), and θ_i is corresponding value of incident angle at the prism/metal/air boundary of these media (figure 1.11), here we will use the subscripts as 0 corresponding to the prism, as 1 corresponding to metal and 3 as for the dielectric (air) media. The Fresnel's reflection coefficient for a p-polarized light passing from i^{th} medium to k^{th} medium is given as [23]

$$r_{ik} = \frac{n_k \cos \theta_i - n_i \cos \theta_k}{n_k \cos \theta_i + n_i \cos \theta_k} \quad (1)$$

The z-component of the propagation constant in i^{th} medium is given by [23]

$$k_{zi} = \frac{2\pi}{\lambda} n_i \cos \theta_i = \frac{2\pi \sqrt{\epsilon_i - \epsilon_0} \sin^2 \theta}{\lambda} \quad (2)$$

Since, dielectric constant, $\epsilon = (\text{refractive index}, n)^2$ and using equations (1) and (2), we have,

$$r_{ik} = \left(\frac{k_{zi}}{\epsilon_i} - \frac{k_{zk}}{\epsilon_k} \right) / \left(\frac{k_{zi}}{\epsilon_i} + \frac{k_{zk}}{\epsilon_k} \right) \quad (3)$$

where ' ϵ_i ' and ' ϵ_k ' are the dielectric constants of the i^{th} and k^{th} medium, and ' ϵ_0 ' is the dielectric constant for the prism.

So, the Reflectance for single layer system (prism/metal/dielectric (air)) is given by [23]:

$$R_{013} = \left| \frac{r_{01} r_{13} \exp(2ik_{z1}d_1)}{1 + r_{01} r_{13} \exp(2ik_{z1}d_1)} \right|^2 \quad (4)$$

where, subscripts '0', '1' and '3' refer to prism, metal layer and dielectric(air) media respectively. ' d_1 ' is the thickness of metal thin film. ' r_{ik} ' and ' k_{zi} ' are Fresnel's reflection coefficients and z components of propagation constant as given by equations (3) and (2) respectively. The reflectance is calculated for the single layer system (prism/metal/dielectric (air)) by equation (4) using known values for λ , θ , and ϵ , and value of complex dielectric constants of metal layer may be obtained.

Double layer system (prism-Au-dielectric-air)

For realization of gas (optical)sensors, a suitable sensing layer (dielectric) has to be integrated with metal layer, which should be sensitive to the stimulus under consideration. Also, to probe the property of any unknown material (dielectric), it has to be in the vicinity of metal layer Therefore, study of double layer system consisting of prism/metal/dielectric thin film/dielectric(air) is important. Using the Fresnel's equation for the calculation of the reflectance of this double layer system is as follows [23]:

$$R_{0123} = \left| \frac{r_{01} + r_{123} \exp(2ik_{z1}d_1)}{1 + r_{01} r_{123} \exp(2ik_{z1}d_1)} \right|^2 \quad (5)$$

where

$$r_{123} = \frac{r_{12} + r_{23} \exp(2ik_{z2}d_2)}{1 + r_{12}r_{23} \exp(2ik_{z2}d_2)} \quad (6)$$

and r_{ik} are the Fresnel's reflection coefficients given by equations (1) and (3). Here, subscript '2' refers to the deposited ZnO/Polypyrrole as sensing material and ' d_2 ' is its depth. Considering the dielectric constant of the sensing layer (ϵ_2) as the fitting parameter, the SPR reflectance obtained for prism/metal/dielectric/dielectric(air) system is fitted with equation (5) and the complex dielectric constant of sensing layer is obtained.

Experimental Details: Fabrication of SPR based NH₃ gas sensor

In this work, multilayer structure of the films was prepared. We deposited the gold(Au) thin film of optimized value on the surface of glass prism by thermal evaporation method on the parameters reported in our previous report [24]. After this, ZnO film is coated on Au coated prism. Sol-gel method was utilised to synthesis ZnO nanoparticles and then they were put in thin film form by using spin coating technique [25]. Finally, Polypyrrole(PPy) thin films were coated over this structure. PPy nanoparticles were fabricated by the method of chemical polymerization and their films were prepared by spin coater [25].

We use Kretschmann configuration for the excitation of surface plasmon(SP) on the prism/gold interface by using a BK-7 glass prism ($n_p = 1.517$) and the optimized thickness of Au film with the help of a SPR measurement system. For the measurement of the SPR reflectance, He-Ne laser (p-polarised and of wavelength 633 nm) was used for the irradiation on the prism/Au/ZnO/PPy/air system and the reflected light (which is a function of incident angle) was monitored. Schematic of our SPR gas (optical) sensor, as shown in figure 1, uses a cylindrical cell for the target gas attached to the prism deposited with the gold(Au) and the target gas sensitive material's coating (prism/Au/ ZnO/PPy/air) is placed in contact with this cylindrical gas cell so that the target gas molecules can interact with the deposited gas sensitive material interface (ZnO/PPy). A mechanical rotary pump was used for creating vacuum. Static and dynamic modes measurements were done. The Ammonia (NH₃) target gas of a specific concentration value was inserted into this gas cell with a calibrated needles connected to inlet valve. In the static mode, we insert the ammonia gas inside the gas cylindrical cell for the full angle variation and the SPR reflectance plot was recorded with an optical power meter. The dynamic measurements were done with the system of prism/Au/ ZnO/PPy/air, where we get a minimum value of SPR reflectance (R_{min}). We then record the intensity of the reflected light keeping incident light at a fixed angle (as a function of time) with the help of a CCD camera interfaced to a computer. The change in intensity is measured for the various concentrations of the ammonia gas, when it is introduced into the gas cell and as well as for outgoing of the ammonia gas. We use rotatory pump for the ejection of ammonia gas for the recovery time measurement of our gas sensor system of (prism/Au/WO₃/air), Which then filled with the fresh

clean air for the reference.

Figure 1: Schematic of the Kretschmann configuration based SPR gas sensor

Results and discussion

Theoretical simulation studies

Varying thickness of gold thin film:

SPR reflectance curves by varying the thickness of Au in equation (4) are depicted in figure 2. SPR reflectance sharpest value is observed for 40 nm thickness of Au having minimum FWHM.

Figure 2: Theoretical SPR reflectance Plots the system of prism/Au/air by changing the thickness of Au layer

SPR reflectance plots of the system prism/Au/air, prism/Au/ZnO/air and prism/Au/ZnO/PPy/air:

Schematic of the two and three layer configuration used is shown in figure 3 (a). Theoretical simulation of the SPR reflectance plots by increasing the number of layers is shown in figure 3(b) (i.e. prism/Au/air, prism/Au/ZnO/air and prism/Au/ZnO/PPy/air). The angle of resonance shifts towards higher values by increasing the number of layers from ZnO/air interface to ZnO/PPy/air interface.

Figure 3: (a) Schematic of SPR system used for theoretical simulation, (b) Plots of the SPR reflectance for the system of prism/Au/air, prism/Au/ZnO/air and prism/Au/ZnO/PPy/air

Varying thickness of ZnO:

Figure 4 shows the SPR reflectance plots for the system of prism/Au/ZnO/PPy/air by changing the thickness of ZnO.

Figure 4: Plots of the SPR reflectance for the system of prism/Au/ZnO/PPy/air by changing the thickness of ZnO

The variation of resonance angle, minimum reflectance and FWHM have been presented in figures 5 (a), (b) and (c) respectively. All the parameters increase with increase in thickness of ZnO. SPR reflectance curve having minimum FWHM is chosen for experimental studies. Hence, 100 nm ZnO SPR has minimum FWHM (or absorption losses) is the optimized

Figure 5: Plots of (a) Angle of resonance, (b) minimum reflectance and (c) FWHM with the thickness of ZnO

Varying thickness of Polypyrrole thin film

Figure 6 shows the plots of SPR reflectance of the gas sensing system of prism/Au/ZnO/PPy/air by changing the thickness of PPy.

Figure 6: SPR reflectance plots for the system of prism/Au/ZnO/PPy/air by changing the thickness of PPy

The variation of resonance angle, minimum reflectance and FWHM are presented in figures 7 (a), (b) and (c) respectively. All the parameters increase linearly with the increase in thickness of PPy. SPR reflectance curve having minimum FWHM is chosen for experimental studies. Hence, 150 nm PPy SPR has minimum FWHM (or absorption losses) is the optimized thickness of PPy layer

a

(b)

(c)

Figure 7: Variation of (a) resonance angle, (b) minimum reflectance and (c) FWHM with the thickness of ZnO

Varying incident wavelength

SPR reflectance plots of the optimized system of prism/Au/ZnO/PPy/air with the 100 nm ZnO and 150 nm PPy are shown in figure 8. With increase in the wavelength of the incident light, the resonance angle shifts to lower value. FWHM of the SPR curve for 355 nm incident wavelength is maximum which decreases with increase in wavelength and is found to be minimum for 633 nm wavelength. After 633 nm wavelength, the SPR curves becomes attenuated. The experimentally obtained SPR reflectance curves are shown by dotted lines and theoretically simulated curves by solid line.

Figure 8: SPR plots for the system of prism/Au/ZnO/PPy/air with different incident wavelength

Varying effective refractive index

Theoretical simulations were also done on the system of prism/Au/ZnO/PPy/air by varying the refractive index of the exposed sensing material, which is in contact with the ZnO/PPy interface on exposure to NH_3 gas of different concentration. Refractive index is sequentially

varied and SPR reflectance curves are measured. It is observed from figure 9 (a) that ATR curves shift towards right i.e., resonance angle increases with increase of the effective refractive index of the sensing material. The linear change of the angle of resonance and minimum reflectance with increase in the effective refractive index is shown in figure 9 (b) and (c) respectively. This confirms the possibility of developing a highly sensitive sensor utilising the system of prism/Au/ZnO/PPy/air as a detector for the Ammonia(NH_3) gas with the varying concentration.

(a)

b

(c)

Figure 9: (a) SPR reflectance plots of the system of prism/Au/ZnO/PPy/air for varying effective refractive index, (b) Linear increase of resonance angle and (c) the minimum reflectance with changing effective refractive index

Experimental studies

The data of SPR reflectance obtained for the system of prism/Au/ZnO/PPy/NH₃ when exposed to changing concentration of NH₃ gas (0 to 200 ppm) is plotted in figure 10. A continuous change in θ_{SPR} towards higher values of angles (from 54.9° to 95.3°) is observed with the incremental change of the concentration of NH₃ gas from 1 to 200 ppm (figure 10).

Figure 10: Experimental data obtained for the system of prism/Au/ZnO/PPy/NH₃ SPR reflectance plots upon exposure of NH₃ gas with increasing concentration. The theoretical value is also plotted for comparison.

Figure 11 (a) and (b) depict the exponential increment of the values of θ_{SPR} and R_{min} for our gas sensing system of prism/Au/ZnO/PPy/NH₃ when we vary the concentration of NH₃ gas from 0 to 200 ppm. The observed change of the SPR data is due to the variation of the effective refractive index of ZnO/PPy interface when the ammonia gas is adsorbed at various concentrations. As evident from figure 11 (a) and (b), there is linear increase in θ_{SPR} and R_{min} till 10 ppm concentration of the Ammonia (NH₃) gas. As the concentration of the Ammonia gas increases, the values of θ_{SPR} and R_{min} saturates. This is due to the fact that with the high Ammonia gas concentration, there is no appreciable change in effective refractive index which is reflected in the nonlinear variation of θ_{SPR} and R_{min} . We can also see, for the FWHM of SPR response of sensing system shows the same variation as that of θ_{SPR} and R_{min} (figure 11 (c)), showing that the losses increase continuously until 10 ppm concentration is reached.

Figure 11: Plots of (a) SPR angle of resonance (θ_{SPR}), (b) R_{min} , and (c) FWHM of the SPR sensing system with variation in the concentration of NH_3 gas

The experimental data for the SPR reflectance measured in the presence of NH_3 gas of various concentrations has been fitted theoretically with the help of Fresnel equations as mentioned earlier, and the estimation of the values of n_i and k_i were done. The variation with the effective index of ZnO/PPy interface when the adsorbed NH_3 gas with its increasing concentration is as shown in figure 12 (a) (calibration curve). The refractive index was found to increase linearly till 10 ppm concentration as shown in figure 12(b). The graph is fitted linearly and the value of sensitivity is found from the slope of the calibration curve i.e. 3.15×10^{-3} RIU/ppm.

Figure 12: (a) Variation of effective index of ZnO/PPy interface when the NH₃ gas get adsorbed, with the increase of its concentration and (b) Variation of the refractive index till 10 ppm concentration

When NH₃ gas is present in the bulk media, its adsorption on the ZnO/PPy interface leads to the Surface plasmon propagation distortion and so the losses in the gas sensing system keep on increasing as depicted from plots of the increasing FWHM of the SPR reflectance curves. We find the important fact that to the gas sensing system of prism/Au/ZnO/PPy shows good sensitivity and high linearity over a wide good range (1 to 10 ppm) of NH₃ gas.

Figure 13 (a) depicts the dynamic response for the system of prism/Au/ZnO/PPy upon exposure with the changing concentration of NH₃ gas from 0 to 200 ppm and the incident angle is kept at value of $\theta = 54.9^\circ$. Here we use a CCD for measuring the changes in the reflectance of our gas sensing system. The gas sensing system shows a continuous increase in the sensitivity (change in reflectance) with the change in concentration of NH₃ gas from 1 to 200 ppm kept at the room temperature (figure 13 (a)). The calibration curve of the SPR gas sensor is also plotted as shown in the figure 13 (b). Figure 13 (b) shows that there is a saturation of change in reflectance after 10 ppm concentration. A linear increase in the response i.e., change in reflectance with increase in concentration of NH₃ gas over the range 1 to 10 ppm is shown in figure 13(c). The variation in sensing response (ΔR) is similar to that obtained for $R_{\min}$ and θ_{SPR} with NH₃ gas concentration. The sensitivity of the fabricated SPR sensor prism/Au/SnO₂ is about 0.112 /ppm for NH₃ concentration varying from 1 ppm to 10 ppm (figure 13 (c)). The obtained result represents the development of a sensitive SPR gas sensor for efficient detection of NH₃ gas.

Figure 13: (a) Dynamic response of SPR gas sensor (system of prism/Au/ZnO/PPy), (b) the calibration curve of the SPR gas sensor for the NH_3 gas, and (c) linear increment of reflectance with the increasing concentration of NH_3 gas

Conclusion

A specially designed gas cell has been integrated with the indigenously developed SPR set up for detection of various toxic and harmful gases. SPR system is demonstrated successfully for detection of NH_3 gas using the interface of ZnO and PPy. Surface plasmon resonance gas sensor system of prism/Au/ZnO/PPy, has been developed using optimized thickness of ZnO and PPy obtained by theoretical simulation for the detection of Ammonia (NH_3) gas. The 100 nm thin ZnO film and 150 nm thin PPy film were deposited which exhibits sharpest SPR reflectance curve, and is found useful for the successful detection of NH_3 gas. The SPR gas sensor shows

a fast response (1 s) and good sensitivity (3.15×10^{-3} °/ppm) towards NH₃ gas over wide concentration (1 to 10 ppm). The dynamic response was also observed and the sensitivity was estimated from the calibration curve i.e. 0.112 /ppm. Thus, efficient SPR gas sensors are realized in the present work with enhanced response characteristics.

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Conflicts of Interest/Competing interests

Authors declare no conflict of interest.

Availability of data and material:

The data sets generated during and/or analysed during the current study are available from the corresponding author on reasonable request.

Code Availability: Not applicable

Authors' contributions:

Ajay Pratap Singh Gahlot: Methodology, editing Conceptualization; Ayushi Paliwal: Methodology, Writing- original draft; Avinashi Kapoor: Supervision, Writing-review and editing

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