

## Surface Plasmon – Cobalt Phthalocyanine Sensor for NO<sub>2</sub> gas

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*Surface plasmon resonance (SPR) based sensors using Ag thin films have been successfully applied for detection of nitrogen dioxide (NO<sub>2</sub>) gas. The SPR sensors have Cobalt Phthalocyanine (Co-Pc) as active add layer. Surface plasmon was generated via a prism coupler in Kretschmann configuration. It is found that the sensitivity of SPR sensor is 0.14 ppm in ambient environment at NTP. The simple structure of the SPR sensor makes it superior to liquid chemical sensors for the detection of NO<sub>2</sub>.*

### 1. Introduction and Theoretical background:

The ability to detect the toxic gas NO<sub>2</sub> in a wide range of environments has become progressively important over the last decade as a result of increased toxic gas production in the chemical industry[1]. In this paper, we have employed surface plasmon resonance (SPR) technique as an optical method for the detection of NO<sub>2</sub> gas. This method differs from chemical techniques used for detection of NO<sub>2</sub> involved in a complex system of liquid membrane electrode based on ion-selective electrode [2]. Phthalocyanine are  $\pi$ -conjugated macro cyclic legends whose electron-donor properties lead to surface charge transfer interactions with adsorbed electron acceptor gases such as NO<sub>2</sub> [3]. In our technique, an add layer of thickness 300nm of Cobalt-Phthalocyanine trapped in PVC matrix was deposited on the Ag thin film. This constitute the active membrane to interact with NO<sub>2</sub> gas. In this arrangement, an additional wave vector that is proportional to the thickness of the add layer,  $d_s$  is given by [4]:

$$K_T = i \left( \frac{2\pi d_s}{\lambda} \right) \left( \frac{\omega}{c} \right) \left( \frac{\epsilon_m}{\epsilon_m + 1} \right)^2 \frac{1}{(\epsilon_m)^{1/2} (\epsilon_m - 1)} \left( \epsilon_1 + \frac{\epsilon_m}{\epsilon_1} - \epsilon_m - 1 \right) \quad (1)$$

where  $\epsilon_1$  is the dielectric constant of the add layer and  $\lambda$  is the wavelength of light in vacuum. Also, the reflectivity  $R$  in these four media sensor (glass/Ag film/Q<sub>c</sub> film/NO<sub>2</sub>) can be approximately expressed as [4].

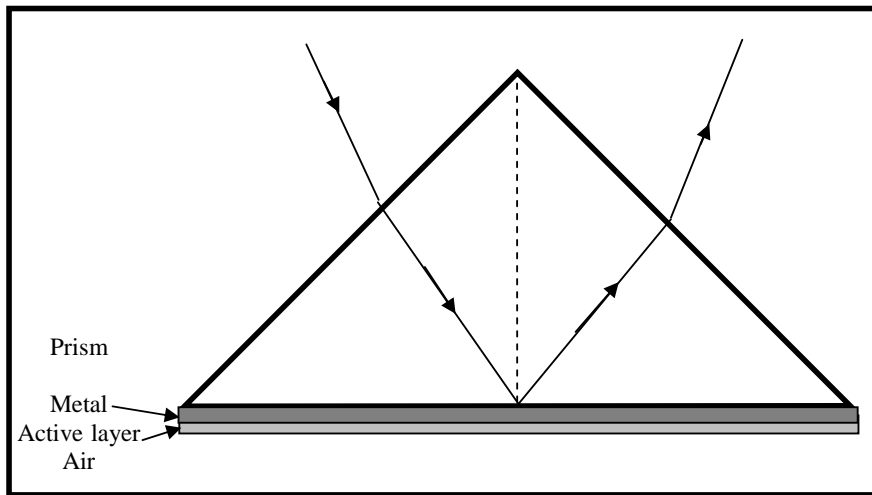
$$R = 1 - \frac{4(\Gamma_i + \Gamma_T)\Gamma_r}{(K_{//} - K_{SP})^2 + (\Gamma_i + \Gamma_T + \Gamma_r)^2} \quad (2)$$

where  $K_{//}$  is the parallel component of the incident wave vector through the prism,  $K_{SP}$  is the surface plasmon wave vector in Ag filme,  $\Gamma_i$  is the intrinsic damping,  $\Gamma_r$  is the radiation damping through the prism and  $\Gamma_T = \text{Im}(K_T)$  the transmission damping due to the add layer. A primary task for spectroscopic analysis is generally to prove the occurrence of the sensing interaction, and in particular to show the selectivity of the sensor to the designated gas. Infra Red (IR) spectroscopy plays a fundamental role in this task, since the IR spectrum can be considered as a finger print of the compound. Furthermore, Raman spectroscopy offers complimentary information about the bonds of the compound, and gives further useful identification of the material. Since different selection rules apply to each spectroscopy. These two-spectroscopy methods give the most definitive characterization of the compound, and we have used both to provide the strong evidence insuring the interaction of Co-Pc with NO<sub>2</sub> gas.

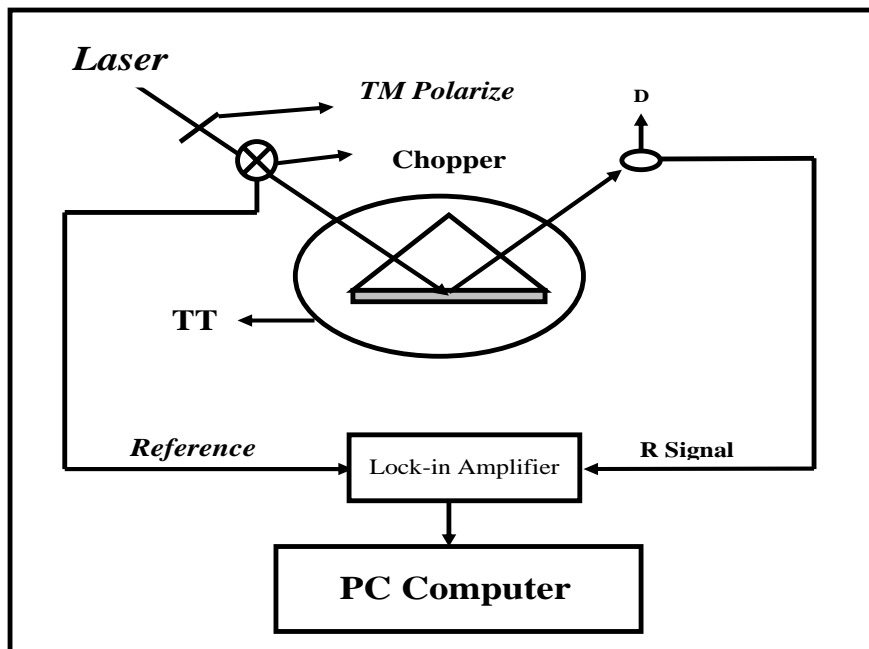
## 2. Experiments

### 2.1. Surface Plasmon Resonance (SPR) Measurements

The angular Attenuated Total Reflection ATR spectroscopy was employed using the Kretschmann configuration (Fig.1) [5]. The metal Ag at the base of the glass prism is placed at the center of a ( $\theta-2\theta$ ) turntable. The reflected intensities were detected by a photodiode mounted on the  $2\theta$  arm of the diffractometer. The ( $\theta-2\theta$ ) turntable has an angular resolution of  $0.005^\circ$  and the absolute error in the angle of incidence is less than  $0.01^\circ$ . The ATR intensities were measured by synchronized heterodyning techniques using optical chopper and lock-in amplifier whose output is connected to PC. The TM-polarized radiation was incident from He-Ne laser of wavelength  $6328 \text{ \AA}$  and Ar<sup>+</sup>- laser of wavelength  $4579 \text{ \AA}$  on the prism (Fig.2).



**Fig.(1):** A schematic of Kretschmann configurations for the generation of surface plasmon at a metal/air interface. The sensing add layer deposited on the metal film is also shown.



**Fig.(2):** A schematic of experimental set up.

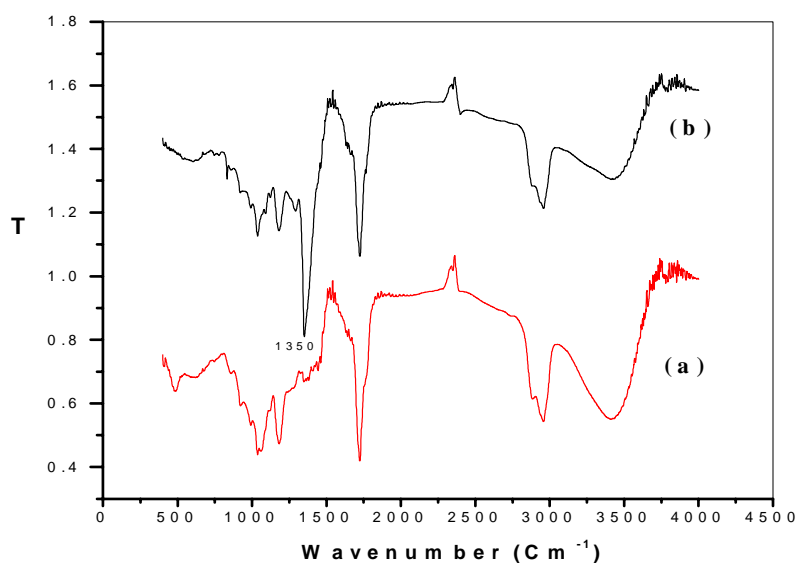
## 2.2. Active Layer Preparation

The active add layer deposited on the metal film was prepared by having polyvinyl chloride (PVC) dissolved in dioctyl phthalate (DOP) then the Co-Pc was added. The actual weights used were 66.51 mg of PVC, 138.67 mg of DOP and 2.91 mg of Co-Pc. A sufficient amount of tetrahydrofuran (THF) was added and mixed to obtain a solution that became actually transparent after a short time. An amount of ( $5.24 \times 10^{-4}$  ml) of this solution was dropped onto the Ag thin film and the THF was allowed to evaporate at room temperature leaving a membrane of Co-Pc trapped in PVC matrix of nearly 300 nm thickness (calculated by weight) that constituted the active membrane to interact with  $\text{NO}_2$ .

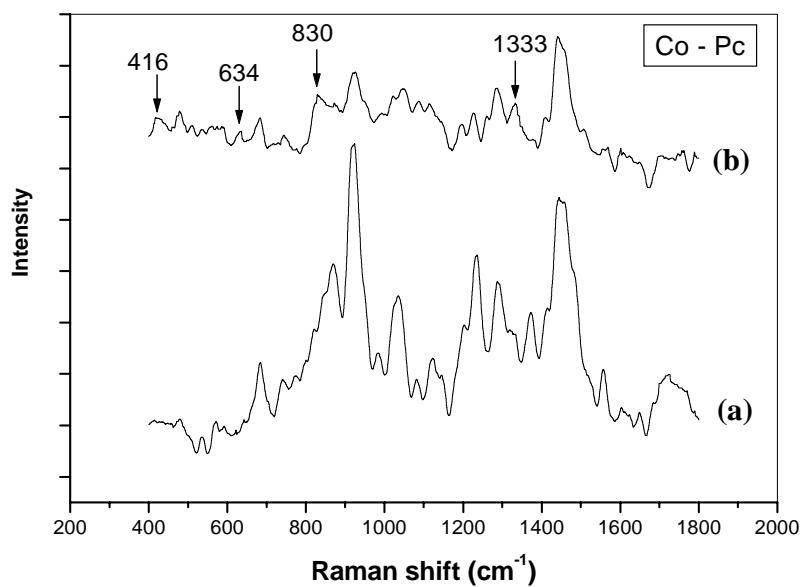
## 3. Results and Discussions:

### 3.1. Selectivity

The FTIR spectrum for Co-Pc add layer prepared in the same manner as the one deposited on Ag film, was carried out using JASCO spectrometer. The spectrum is shown in Fig.(3) for the bare Co-Pc add layer, together with that after exposure to  $\text{NO}_2$  gas for a period of 5 sec. The strong IR line at  $1350 \text{ cm}^{-1}$  corresponds to the  $\text{NO}_2$  gas. This line corresponds to  $\nu_a(\text{NO}_2)$ , "the asymmetric stretching normal mode  $\nu_a$  ( $B_2$ )" [6]. The Raman spectrum for the same layer taken before and after exposure is also shown in Fig.(4). There are four Raman lines characteristic of  $\text{NO}_2$ . These observed Raman lines are at  $1332 \text{ cm}^{-1}$  which corresponds to the  $\nu_s$  ( $\text{NO}_2$ ), the symmetric stretching normal mode of  $\nu_1$  ( $A_1$ ), the line at  $827 \text{ cm}^{-1}$  corresponds to scissoring normal mode,  $\delta_s$  ( $\text{ONO}$ ), the line at  $637 \text{ cm}^{-1}$  corresponds to the normal symmetric wagging mode  $\rho_w$  ( $\text{NO}_2$ ), and the line at  $416 \text{ cm}^{-1}$  corresponds to the symmetric (Co-N) normal mode  $\nu_2$  ( $A_1$ ). These normal modes of vibrations both the antisymmetric (IR) and symmetric (Raman) scattering indicate surface absorption of  $\text{NO}_2$  molecule to the Co-site of the planer Co-Pc molecule. These assignments of the molecules were done following ref. [7].



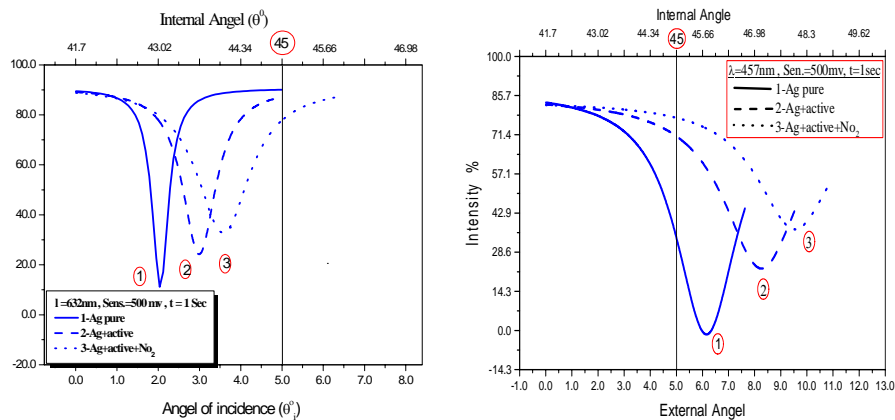
**Fig.(3):** The transmission FTIR for (a) The sensing material plasticized (Co-Pc), (b) the sensing material after exposure to NO<sub>2</sub>, the characteristic absorption line for axial absorption of NO<sub>2</sub> at 1350cm<sup>-1</sup> is indicated.



**Fig.(4):** Raman spectra for: (a) the sensing plasticized Co-Pc, (b) the sensing material after exposure to NO<sub>2</sub>, the characteristic Raman lines for axial absorption of NO<sub>2</sub> are indicated. (See text).

### 3.2. Shifts Of SPR Due To NO<sub>2</sub>

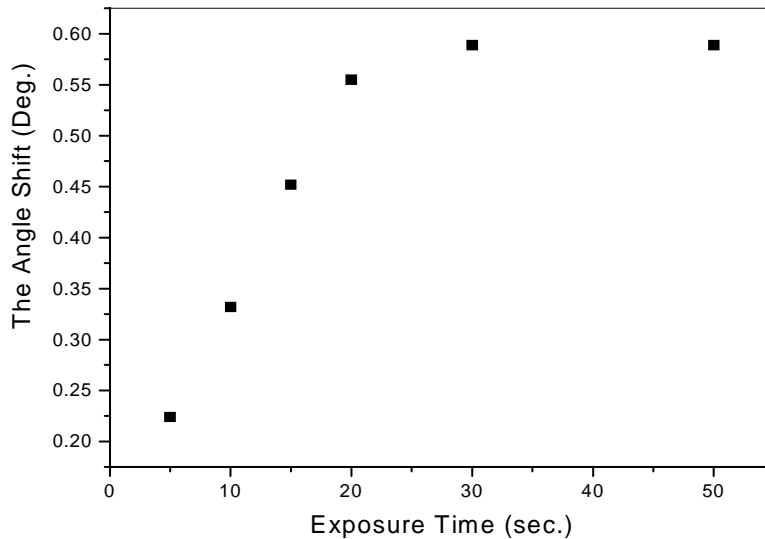
Figures (5-a and 5-b) show the SPR minima of the Co-Pc based sensor measured at an incident wavelength  $\lambda=6328$  and  $4579$  Å, respectively. The curve No.(1) in the two figures represents the reflection minimum of the thin Ag film evaporated on a glass substrate. The curve No.(2) indicates the result for the add layer of Co-Pc film while the curve No.(3) represents the signal after the exposure of the film to NO<sub>2</sub> gas. For the wavelength  $\lambda = 6328$  Å the coupling angle  $\theta_{ATR}$  of SP for the bare Ag thin film is  $43.05^\circ$  and the complex wave vector  $K_{sp} = (1.0233 + i 0.0030) \times 10^5 \text{ cm}^{-1}$ . The calculated dielectric constant of this film is  $\epsilon_m = -17.05 + i 1.62$  and the reflectance minimum is nearly 78% while the resonance half-width is  $\Delta\theta_{ATR} = 2.76 \times 10^{-3}$  rad. After adding Co-Pc onto the Ag film the coupling angle  $\theta_{ATR}$  is shifted towards a larger value ( $43.67^\circ$ ) indicating an increase of the real part of ( $K_{SP}$ ). Using the Eqn.(1), the real part of the dielectric constant of Co-Pc is calculated and equal 12.341. Also, the observed minimum of the SP decreases to 66 % due to the load of the membrane. The resonance half-width  $\Delta\theta_{ATR}$  increases to  $5.05 \times 10^{-3}$  rad. The exposure of the film to NO<sub>2</sub> gas causes a further shift to a higher resonance angle  $44.06^\circ$ , indicating a further increase of the Re ( $K_{SP}$ ) to  $1.04258 \times 10^5 \text{ cm}^{-1}$ . The calculated value of the real part of the dielectric constant of Co-Pc after exposure to NO<sub>2</sub> is 12.51. The SP dip decreases to 57% and the resonance half-width  $\Delta\theta_{ATR}$  increase to  $8.98 \times 10^{-3}$  rad. These changes in the coupling angle and the amplitude of the dip is due to the NO<sub>2</sub> axial adsorption to the metal in Co-Pc as shown in the section (3.1) , as will as to the change of coordination number of Co-Pc. Changing the incident wavelength to  $4579$  Å the same behavior could be observed for the three cases , the bare Ag , bare Ag + Co-Pc and bare Ag + Co-Pc after exposure to NO<sub>2</sub> gas as shown in Fig. 5(b) [8].



**Fig.(5):** Surface Plasmon Resonance (SPR) Spectra (a) for wavelength  $\lambda_1 = 6328$  Å (b) for wavelength  $\lambda_1 = 4579$  Å (1), (2) and (3) indicate the results for Ag film, Co-Pc film and after exposure to NO<sub>2</sub>.

### 3.3. Sensitivity

The values of the dielectric constant for the active material Co-Pc before and after different exposure time (0-50 s) to  $\text{NO}_2$  are calculated by using Eqn.(1) and are given in Table (1). The shifts in coupling angles with varying exposure time are shown in Fig.(6). It is observed that after 30 s of exposure, there are almost no shifts in the coupling angle, indicating no further change to the compound. This may indicate that there is a saturation of the active layer and that all the axial legends are formed. We have used these data together with kinetic theory of gas to calculate the sensitivity of Co-Pc add layer that is determined as 0.07 ppm. It should be mentioned that no such shifts in the coupling angle were observed when other gasses ( $\text{CO}_2$  or  $\text{H}_2\text{O}$ ) were used. Therefore, one may conclude that Co-Pc add active layer can act as a sensor, and is selective to  $\text{NO}_2$  ligand molecules. This SP sensor has the advantages of being easily constructed of low cost components, e.g. an LED or semiconductor laser with a small glass prism. Furthermore the making of a disposable substrate (glass slide) coated with add layer over a thin Ag film can easily be substitute for the non-regeneration of the sensor. Such substrate could be divided into a large number of spots that have the same area of the laser beam ( $\approx 2 \text{ mm}^2$ ) which can then be used sequentially. It should also be mentioned, that the data obtained by the ATR technique, enables one to determine the optical constants for the special chemical compounds as PVC+DOP+ Co-Pc in a form of membrane as well as the change of the dielectric constant of this membrane after exposure to  $\text{NO}_2$  gas.



**Fig.(6):** The shift in the angle of coupling ( $\theta_{\text{ATR}}$ ) for the active layer versus the time of exposure to  $\text{NO}_2$

**Table (1):** The dielectric constants for Ag film and the active layer before and after exposure for different time:

Time of exposure for NO <sub>2</sub> (s)	$\theta_{SP}^{\circ}$ ±0.005	$\frac{1}{2}\Delta\theta_{SP}$ (Rad) ±0.005	K' (cm <sup>-1</sup> ) x10 <sup>5</sup> ±11.13	K''(cm <sup>-1</sup> ) x10 <sup>5</sup> ±56.7	$\epsilon'$ ±0..303	$\epsilon''$ ±0.06
no exposure (Ag)	<b>43.047</b>	2.74x10 <sup>-3</sup>	1.02339	0.00302	-17.046	1.616
no exposure (Active)	<b>43.669</b>	5.55x10 <sup>-3</sup>	1.035247	0.00602	12.341	
<b>5</b>	<b>43.812</b>	6.81x10 <sup>-3</sup>	1.037932	0.00737	12.405	
<b>10</b>	<b>43.897</b>	6.88x10 <sup>-3</sup>	1.039538	0.00743	12.443	
<b>15</b>	<b>43.968</b>	7.25x10 <sup>-3</sup>	1.040883	0.00782	12.474	
<b>20</b>	<b>44.028</b>	7.32x10 <sup>-3</sup>	1.042001	0.00789	15.501	
<b>30</b>	<b>44.059</b>	8.98x10 <sup>-3</sup>	1.042579	0.00968	12.511	
<b>50</b>	<b>44.059</b>	8.98x10 <sup>-3</sup>	1.042578	0.00968	12.511	

In conclusion, we have succeeded in the construction of a simple surface plasmon sensor for the detection of traces of NO<sub>2</sub> by using SPR technique, that is easier, inexpensive and more sensitive than the traditional chemical techniques.

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