

Full Research Paper

## Development of a Surface Plasmon Resonance n-dodecane Vapor Sensor

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Received: 7 June 2007 / Accepted: 17 September / Published: 21 September 2007

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**Abstract:** Using a high density polyethylene thin film over gold layer, a Surface Plasmon Resonance sensor for detecting n-dodecane vapor is developed. Preliminary results will be presented, showing that samples in the range of a few hundred ppm(V) of n-dodecane vapor in butane gas can be sensed. Also, studying the response as a function of time, it is demonstrated that the sensing process is quickly reversible.

**Keywords:** Gas sensors, SPR sensors, Sensing films, Polyethylene thin films, ultra-thin films, Chemical sensors.

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### 1. Introduction

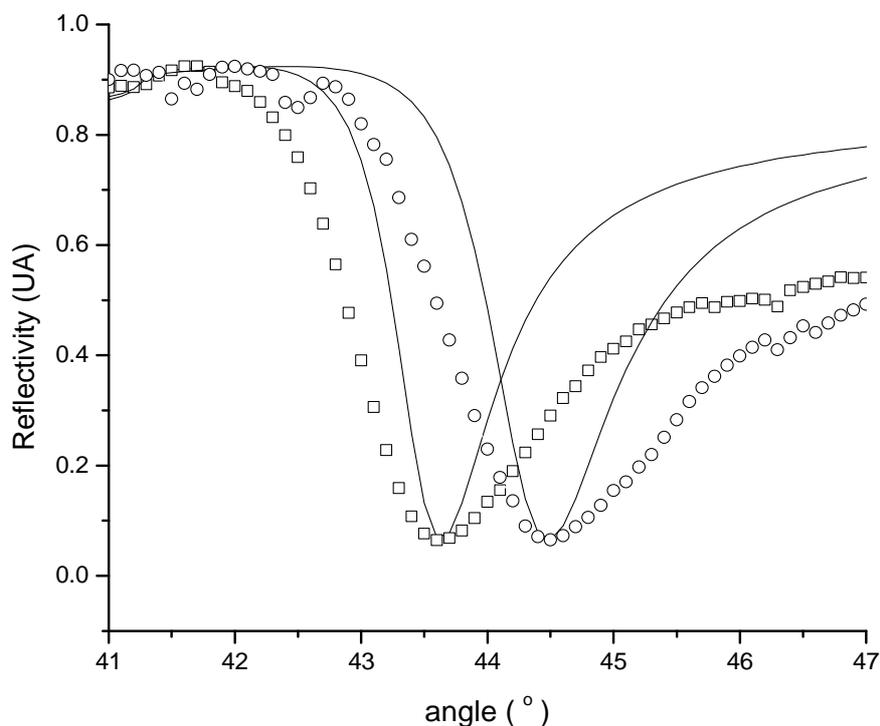
Despite it being well demonstrated that Surface Plasmon Resonance (SPR) sensors are highly sensitive to small changes of the Refractive Index with resolutions up to  $10^{-5}$  RUI [1-3], common in the design of SPR-based biosensors [4-6], there has been little work in gas and chemical vapor detection in the last five years [3, 7-15]. In SPR sensors, the principal task is the development of the sensing layer over the metal film (gold or silver). Inorganic and organic thin films are commonly tested as the interacting layer with the gas specimen to be detected. For example, recently E. Maciak et. al.[7] reported inorganic  $WO_3$  thin films as active layers for  $NH_3$  vapor detection. Also, organic thin films like SAM's of cavitands have shown selectivity to aromatic vapors [8]. Polymeric thin films, for

example N-methylaniline, present response to gaseous HCl [11]. LB organic ultra thin calyx[4]pyrrole films are also used as sensing layers for organic vapors under the SPR technique [13]. With the aim improving the sensitivity and selectivity of the SPR sensors, thin films of hybrid systems [12, 15] of organic and inorganic materials and composites [9] are tested. For example, TiO<sub>2</sub> thin films in an organic passivating shell [12] have shown to be more selective to alcohol vapors than usual TiO<sub>2</sub> films.

In the same context, it is well demonstrated that organic polyethylene thin films present selectivity to petroleum hydrocarbon vapors under the QCM sensing procedure as reported by Sugimoto et. al. [16]. The question arising now is: are we capable of sensing the same petroleum hydrocarbon vapors using polyethylene thin films and Surface Plasmon Resonance as the transduction method. The answer is yes and as an example, the sensitivity of very thin polyethylene films to n-dodecane vapor using Surface Plasmon Resonance as the sensing technique is shown.

## 2. Results and Discussion

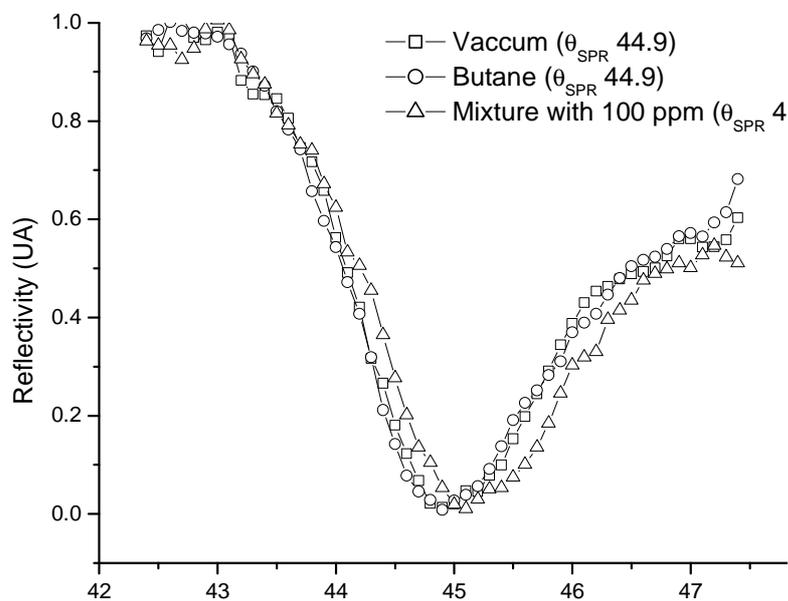
Figure 1 shows the SPR spectra of the polyethylene thin films deposited on gold films before exposure to the gas sample. From the theoretical fitting of the SPR reflectivity to the experimental data, as done in Ref. [17], it was found that the dielectric function of the gold film for a 632.8 nm wavelength of the incident light was  $\epsilon_{Au} = -12.32 + 1.5i$  and the thickness of the thin polyethylene film was 7.1 nm [17].



**Figure 1.** SPR spectra for a gold film of 52.4 nm measured thickness (squares), and after deposition of a 7.1 nm polyethylene film (circles). Lines correspond to the theoretical model (See Ref. [17]).

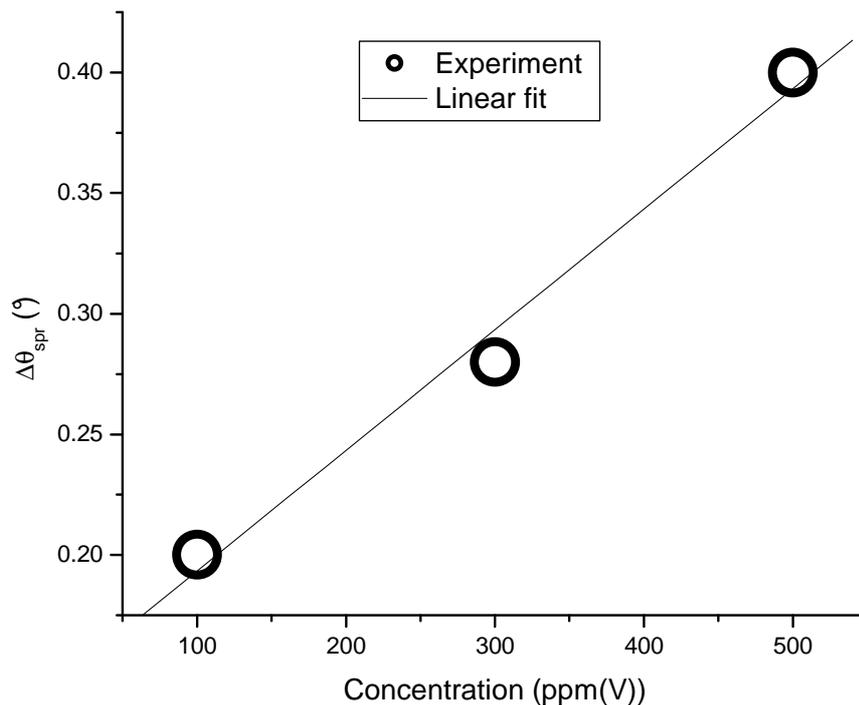
### 2.1. Sensitivity of the sensor

Figure 2 shows the SPR response for 100 ppm(V) of n-dodecane in butane gas. Squares in the plot correspond to when a vacuum of the order of 52 cmHg was achieved in the gas cell. Circles correspond to when the butane gas valve was turned on, increasing the pressure in the gas cell to approximately atmospheric pressure. After that, another previous vacuum of 52 cmHg was made in the cell for removing the butane gas. Triangles plot when the valve of the mixture n-dodecane in butane gas was turned up to restore atmospheric pressure. A shift can be observed in the SPR angle of the sample with respect to butane gas on the order of 0.2 degrees with a systematic error of  $\pm 0.1$  degrees. The systematic error was principally associated with the resolution of the rotation stage of 0.1 degrees when the data were taken.



**Figure 2.** SPR spectra showing the response of the sensing element to 100 ppm(V) of n-dodecane in butane gas (triangles).

Figure 3 shows the sensitivity of the sensor. In the range of 100-500 ppm(V), an approximately linear relationship between the SPR angle shift and the concentration of the n-dodecane vapor can be observed. Because the precision rotation stage used gives more resolution (of the order of 0.002 degrees), it should easily measure SPR spectra every 0.01 degrees and therefore concentrations lower than 100 ppm(V) should be studied.

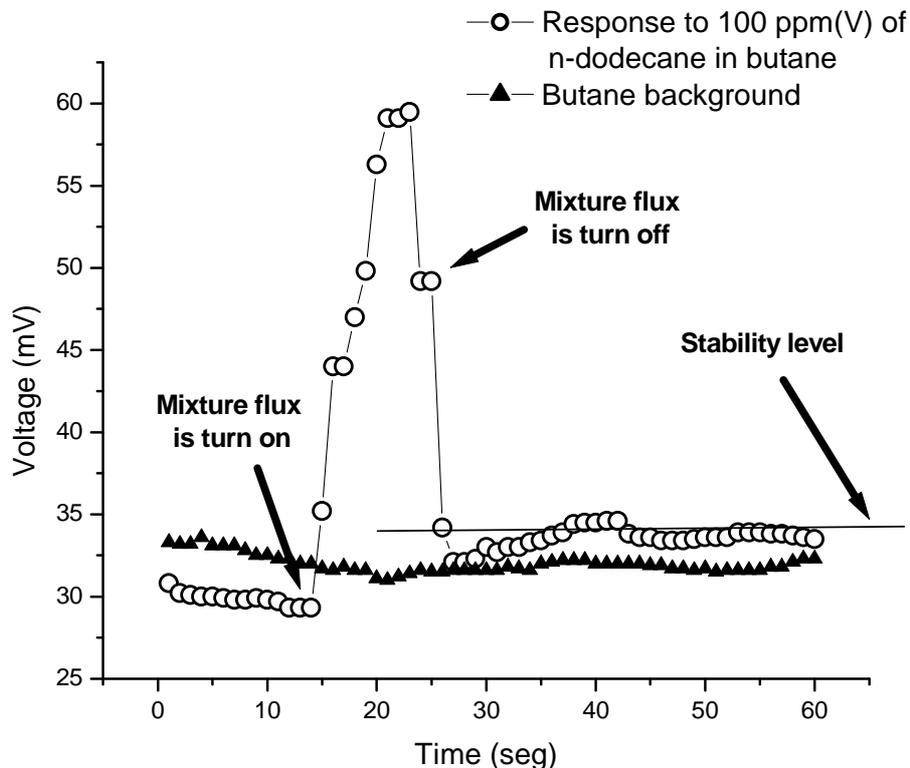


**Figure 3.** Sensor response measured by means of the SPR angle shift versus concentration. An approximately linear relationship can be observed.

## 2.2. Response as a function of time

Figure 4 shows the sensor response as a function of time. Each second, reflectivity data were taken at a fixed angle close to the SPR angle ( $44.9^\circ$ ). The black triangles plotted correspond to when, after taking the mechanical vacuum (52 cmHg), the valve of the butane gas was turned on. The circles plotted correspond to when the vapor sample of 100 ppm (V) n-dodecane in the butane mixture was turned on after a previous mechanical vacuum. An appreciable small change in the reflectivity of the butane response can be seen in comparison to the response of the n-dodecane mixture in butane. Such behavior confirms the selectivity of the polyethylene layer to n-dodecane vapor as was shown by Sugimoto et. al. [16]. Briefly, the SPR response of the polyethylene thin film to the n-dodecane vapor can be described as follows. When the gas mixture sample valve was turned on, a rapid increase of the reflectivity took place as is shown by the peak in the circles plotted in Fig. 4. After about 10 seconds, when the pressure in the cell was constant and equal to the atmospheric pressure, the same valve was turned off. After the sample valve was turned off, a decrease in the quantity of the molecules striking the polyethylene surface layer took place. Therefore, the response continued decreasing but the signal recovered and stabilized after about 10 seconds because the rate of molecules striking the surface also stabilized. From Fig. 4, it should also be said that the response time of the sensor was fast. It is important to mention that after 1 minute of the experiment, vacuum in the gas cell was recovered almost immediately to the initial response of about 30 mV (not shown in Fig. 4). The last result means

that the SPR sensor had a fast reversibility but more experiments should be done to demonstrate such a statement.



**Figure 4.** Response as a function of time of the sensing polyethylene layer. The selectivity to n-dodecane vapor can be observed to present a fast response.

### 3. Experimental Section

#### 3.1 Preparation of the sensing element

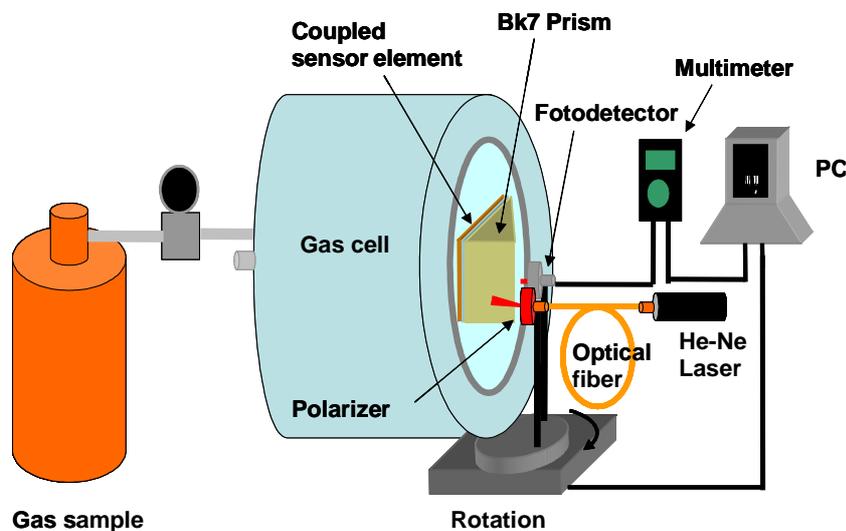
As was detailed in Ref. [17], gold films of 52.4 nm thicknesses were coated on 7059 glass corning substrates by the thermal evaporation method. The commercial monitor *MASTEK Inc.*, which uses a crystal resonator as a sensor, was used to measure the thickness of the gold films. After that, the reflectivity SPR spectrum for their optical characterization was obtained. Soon after, transparent polyethylene ultra-thin films of different thicknesses were deposited over the gold thin films by means of the RF sputtering method. The completed structural and optical characterizations of the polyethylene thin films on gold were reported in Ref. [17]. In this work, the same developed polyethylene thin films were applied as vapor sensing layers [17].

#### 3.2 Detection gas experimental configuration

In Figure 5, the gas detection experimental set up is shown. A gas cell (see Fig. 5) with a special window for coupling the SPR sensing element was designed. Design and detailed dimensions of the cell are reported in a manuscript which was submitted to the Mexican Patent Office (IMPI, in Spanish)

[18]. The cell was developed in order to avoid leaking and guaranteed the thermodynamic stability of the gas sample. The SPR measurements were obtained using a Newport Inc. controlled high precision compact rotation stage with a resolution of 0.002 degrees and a silicon detector for capturing the reflected light (see also Ref. [17]).

SPR measurements of the sensing element polyethylene\_film/gold\_film were carried out at vacuum and in the presence of the gas sample at ambient conditions. SPR spectra was first obtained in a vacuum on the order of 52 cmHg from mechanical pumping. After that, the gas sample (butane gas or mixture) was injected into the gas cell to achieve atmospheric pressure and SPR spectra were obtained.



**Figure 5.** Experimental set up for the SPR sensor.

### 3.3 Preparation of the gas samples

At the High Pressure Thermodynamic Laboratory of the Mexican Institute of Petroleum (IMP, in Spanish), a gas sample was prepared using an in house method reported in Ref. [19]. The sample was conformed by a mixture of n-dodecane (molar fraction 0.00017) with butane gas (molar fraction 0.99983) and stored in a cylindrical gas sample container of 0.244 m<sup>3</sup> of volume (see Fig. 1). The volume was used in order to guarantee the stability of the vapor phase of n-dodecane at atmospheric pressure and temperature (80.8 kPa and 273 °K). In the mixture preparation method of Ref [19], the n-dodecane liquid was introduced in a little cell of 30 cm<sup>3</sup> of volume. After that, the n-dodecane and the butane gas were injected towards an expansion system consisting of two bullets of about 3 liters in volume, both connected to the gas sample container and a gas chromatograph, respectively. During the sample injection, the entire system was heated using heating tape in order to obtain a homogenous mixture.

#### 4. Conclusions

A Surface Plasmon Resonance sensor for detecting n-dodecane vapor was developed. It was shown that an approximately linear relationship existed between the SPR angle shift and the concentration in the range of 100-500 ppm(V) of n-dodecane in butane gas. Studying the response as a function of time at a fixed angle close to the SPR angle indicated at first glance that the sensing process was quickly reversible.

#### Acknowledgements

This work was partially supported by CGPI-IPN project number 20061992 from Instituto Politécnico Nacional, México. The authors want to acknowledge Professor Orlando Zelaya Angel from the Departamento de Física del CINVESTAV-IPN, México, for support in his facilities.

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