Application of the total internal reflection phenomenon as a gas sensing technique using evaporated SnO_2 thin films

L. Martínez Pérez[a,b], V. Altuzar[c], N. Muñoz Aguirre[c], V. Garibay-Febles[c], M. Lozada-Cassou[c], M. Aguilar-Frutis[a], and O. Zelaya-Angel[d]

[a]*Centro de Investigación en Ciencia Aplicada y Tecnología Avanzada del Instituto Politécnico Nacional, Legaria 694, Col. Irrigación, C. P. 11500 México D.F., México*

[b]*Unidad Profesional Interdisciplinaria en Ingeniería y Tecnologías Avanzadas del Instituto Politécnico Nacional, Av. IPN No. 2580, Col. Barrio La Laguna Ticomán, C.P. 07340, México D.F., México*

[c]*Progrma de Ingenería Molecular, Instituto Mexicano del Petróleo, Apartado Postal 14-805, Eje Central Lázaro Cárdenas no. 152, Col. San Bartolo Atepehuacan, CP 07730 México D.F., México.*

[d]*Centro de Investigación y de Estudios Avanzados del Instituto Politécnico Nacional, Apartado Postal 14-740, Av. IPN 2508, Col. San Pedro Zacatenco, C.P. 07000 México D.F., México,*

e-mail: buhomartin@yahoo.com, valtuzar@imp.mx, nmag804@avantel.net, vgaribay@imp.mx, lozada@imp.mx, maguilar@cicata.ipn.mx ozelaya@fis.cinvestav.mx.

Recibido el 23 de enero de 2004; aceptado el 19 de abril de 2004

In this work it is shown that the Total Internal Reflection (TIR) phenomenon can be exploited for gas detection. Total internal reflectance measurements for evaporated SnO_2 thin films on quartz substrates are measured at ambient conditions. Changes in the reflectance measurements are measured when CO_2 or N_2 gas flows on the surface of the SnO_2 films. The observed shift in the measured reflectance is defined as the signal of the sensor. Preliminary results show that the maximum response takes place at incident angles close to the critical angle of the quartz-air system.

Keywords: Total Internal Reflection; Optical gas sensors; Tin dioxide thin films; anisotropic materials; and CO_2 detection.

En este trabajo se demuestra como puede ser utilizado el fenómeno de Reflexión Interna Total para la detección de gases. En condiciones ambientales normales se midieron espectros de reflexión interna total de películas de SnO_2 evaporadas sobre substratos de cuarzo. Se midieron cambios en los espectros de reflectancia cuando las películas de SnO_2 se expusieron a flujos de gas de CO_2 o N_2. En base a los cambios observados en la reflectancia se define la señal del sensor. Resultados preliminares muestran que la respuesta máxima se obtiene para ángulos de incidencia en la vecindad del ángulo crítico del sistema cuarzo-aire.

Descriptores: Reflexión interna total; sensores ópticos de gas; películas delgadas de bióxido de estaño; materiales anisotrópicos; detección de CO_2.

PACS: 42.15.Eq; 42.25.Gy; 42.25.Ja.

1. Introduction

Tin-dioxide films are widely used in sensors for gas detection due to the change in the conductivity properties of such media upon adsorption of the sensed gas. The traditional sensing methods are based on monitoring the change in the electrical resistance of the sensing film as a response to the adsorption of the gas, and can only be used at high temperatures [1,2]. Measurements in situ and under ambient conditions are the major disadvantages of these devices. In order to overcome these shortcomings, an alternative transduction method is studied in the present work.

Optical methods are among the most potential approaches for sensor transduction [3]. In recent years, a great deal of research has been carried out on optical gas-sensing properties of doped and undoped SnO_2 films, using light transmission techniques to define the response of the sensor [4]. Under both techniques, electrical and optical, gas adsorption changes the measured physical properties of the SnO_2 films, but optical transduction depends especially upon changes in the dielectric constant and therefore in the refractive index.

It is well known that in order to determine the optical properties of isotropic and anisotropic thin films, techniques such as ellipsometry is widely used [5]. But for anisotropic films, the ellipsometry technique is only used in particular cases when orientation of the optical axes are known, and the method is rather too elaborate for sensing applications. In recent years, new reflectometric methods have been proposed [6]. Furthermore, theoretical and experimental research for reflection and transmission of monochromatic light in anisotropic films has advanced in the course of recent years [6-9]. Deviations in reflectance and transmittance spectra, when an anisotropic change takes place, are measured for anisotropic films, and it has been shown that these

deviations principally depend on the degree of change in anisotropy, surface roughness, and film thickness (see for example Refs. 6 and 7). Thus, small changes in the anisotropy of the SnO_2 films after absorption of the gas molecules could occur and therefore influence on reflectance measurements. This work presents experimental observations of changes in the reflectance measurements using the method of total internal reflectance and describes how this effect can be utilized to detect CO_2 and N_2 gas fluxes.

2. Samples and Procedures

Polycrystalline SnO_2 thin films were evaporated on cleaned quartz substrate in an electron-beam evaporator system. A pressure of the order of 8×10^{-6} Torr was sufficient to produce a film of SnO_2. A crystal thickness monitor was used to control the thickness of the evaporated films with a precision of 0.1 nm. The quartz substrate was carefully cleaned in solvent steps of microcleaning solutions [10], distilled water, acetone, ethanol, and isopropanol. For each solvent, except water, the substrate was immersed in the cleanser and set in an ultrasonic bath for 10 minutes. The slides were then "glued" using an optical matching gel (index of refraction equal to that of quartz) to the base of a plano-convex cylindrical lens, which was mounted onto a motorized rotation stage having an angular resolution of 0.1 degrees. The experimental setup is shown in Fig. 1.

A p-polarized He-Ne laser beam (λ=632.8 nm) was focused onto the slide at incidence angles, in the range of [10°–60°] degrees, from the normal to the surfaces of the film as it is shown in Fig. 2. Subsequently, measurements of the reflected light intensity were made from the photodiode voltage output reading which were sent to a computer for processing.

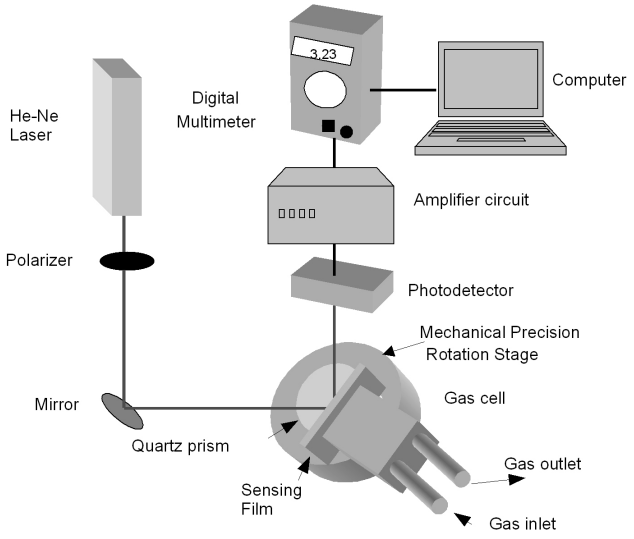

FIGURE 1. Experimental Setup.

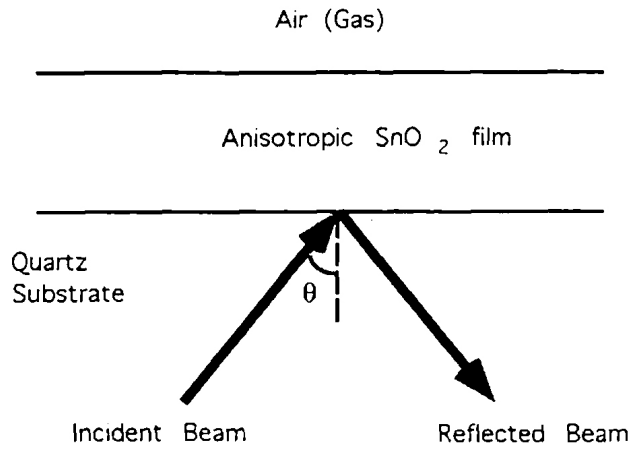

FIGURE 2. The studied thin film configuration.

Prior to flow any gas over the surface of the slide, the reflectivity spectrum was taken. The gas flux was turned on from a gas container to a small gas chamber attached to the SnO_2 film surface and exhausted simultaneously, getting a constant flux. The flux was controlled by means of a GILMONT 23631 precision flowmeter. The amplifier circuit shown in Fig. 1 was only used to get the response as a function of time at a fixed angle. It is important to mention that in any experiment, vacuum in the small chamber (see Fig. 1) was not made. That means this technique is a non-vacuum technique.

3. Response definition

Tin-dioxide presents a weak optical anisotropy. Its dielectric constant in the direction parallel to its optical axis is equal to $\varepsilon_{||} = 4.175$, and in the direction perpendicular to its optical axis is equal to $\varepsilon_{\perp} = 3.785$ [11]. On the other hand, for deposited crystalline thin film materials, there are two principal mechanisms by which anisotropy can be changed. One of these is related to the surface roughness of the film because anisotropy is related to the orientation of the microcrystals [7]. The other mechanism is the gas adsorption by the surfaces of the film, although the correlation of the sensing mechanism and the microstructure of the sensing material has not been clearly established yet [12]. For example, under ambient conditions, M. Egashira [13] showed that when oxygen molecules are adsorbed onto SnO_2 surface, oxygen atoms capture electrons from the conduction band of SnO_2, and oxygen molecules are left as ions until they are desorbed at higher temperatures. Then under ambient conditions, both mechanisms could contribute to the change of the SnO_2 film anisotropy and therefore the shape in the reflectance spectrum.

In Fig. 3, the experimental reflectance measurements for a quartz slide, a SnO_2 film of 25.2 nm thickness and a SnO_2 film of 32.3 nm thickness deposited over a quartz substrate are shown. The experimental error was about $\pm$ 3% in the reflectance values. From Fig. 3 it can be observed

the change in the intensity of the reflection spectrum of the quartz-SnO_2 system with respect to the quartz-air system. A similar behavior of anisotropic films has already been reported in Refs. 6 and 7. Also, because the average refraction index of SnO_2 is of the order of 1.94 as reported in Ref. 14 and the refractive index of quartz is 1.45674, larger than the refractive index of air (≈ 1), TIR still takes place. The experimental critical angle θ_c obtained from Fig. 3 is equal to 44 with an error of $\pm$ 0.5 degree because the reflectance measurements were made at intervals of 0.5 degrees in the vicinity of the critical angle. This value differs slightly with 43.35 ± 0.001 corresponding to the ideal theoretical value for the Quartz-Air system, which was calculated using the Law of Snell [16].

As mentioned above, if a SnO_2 film adsorbs a quantity of gas and this process changes its reflectance spectrum; then we can define the response to the gas as the difference in reflectance as follow:

$$\text{Response} = R_{gas} - R_{air}, \tag{1}$$

where R_{air} is the reflectance under ambient conditions, and R_{gas} is the reflectance at same conditions when a constant gas flux is maintained in the gas flow cell (See Fig. 1).

As a hypothesis, based on the reports in Refs. 6 and 7, we think that an additional change in the anisotropy of the SnO_2 thin films occurs when these ones adsorb a quantity of gas. But, additional detailed studies are necessary for proving such hypothesis.

4. Results and discussion

In Fig. 4, reflectance measurements for a 25.2 nm SnO_2 film, before and after applying a constant 15 mL/min CO_2 gas flux and a constant 15 mL/min N_2 gas flux, are shown. In this Figure, triangle symbols correspond to the reflectance spectrum when 15 mL/min CO_2 gas is flowing in the small chamber. After the CO_2 gas flow was turn off, a 15 mL/min N_2 gas flow was turn on, the reflectance spectrum is denoted by the circles. Square symbols correspond to the reflectance spectrum in an atmosphere of air. The response of this film, as defined by Eq. (1), is shown in Fig. 5. From this figure, we can observe a maximum response taking place at $43 \pm 0.5^\circ$ for CO_2 gas flux, close to the critical angel θ_c. For the case of the N_2 gas flux, a maximum response at the same angle is achieved. In general, a higher response for N_2 flux is observed as compared to that of CO_2 flux. This could be attributed to the molecular diameter of N_2 being smaller than that of CO_2 (0.319 nm for CO_2, 0.315 nm for N_2 [15]). In other words, the non-occupied smaller "holes" of the SnO_2 surface will be occupied by N_2 molecules which implies a decreasing of the SnO_2surface roughness and therefore an increasing on the reflection intensity.

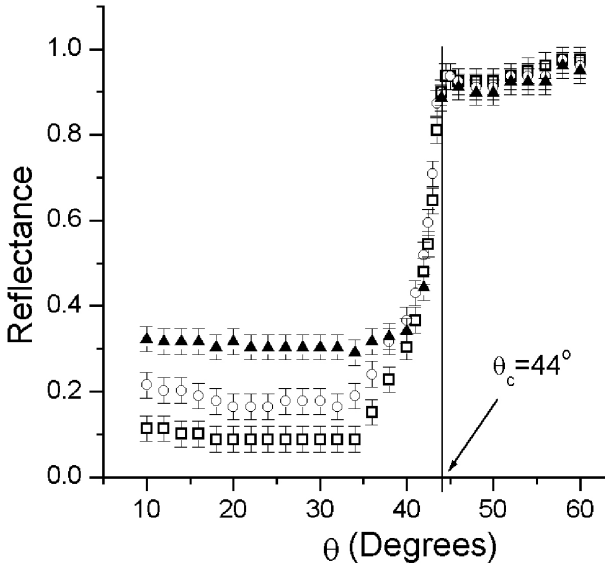

FIGURE 3. Reflectance measurements for three systems. Square symbols are for quartz-air system, circles are for quartz-SnO_2 (25.2 nm)-air and triangles are for quartz-SnO_2 (32.3 nm)-air.

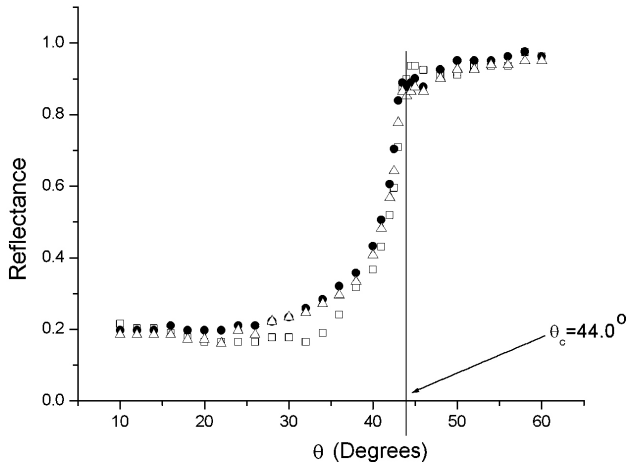

FIGURE 4. Reflectance measurements for a 25.5 nm thick SnO_2 film, when 15 mL/min CO_2 gas is flowing (triangles), and whereafter a 15 mL/min N_2 gas flow was maintained (circles). Square symbols represent the reflection spectrum in air.

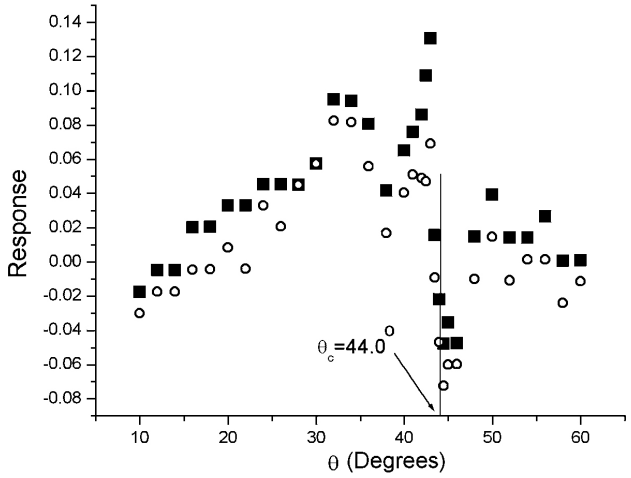

FIGURE 5. Sensor response obtained from Fig. 4 for the 25.5 nm thick SnO_2 film. Circles correspond to CO_2 response and squares to N_2 response.

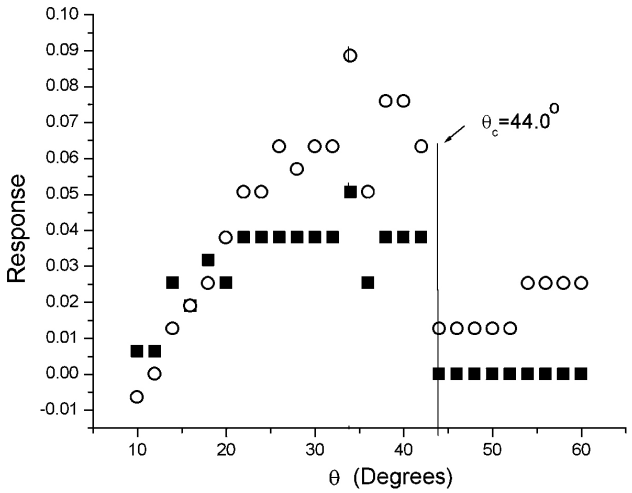

FIGURE 6. Response to different constant fluxes of CO_2 for the 32.3 nm thick SnO_2 film. Squares correspond to a 10 mL/min and circles to a 20 mL/min.

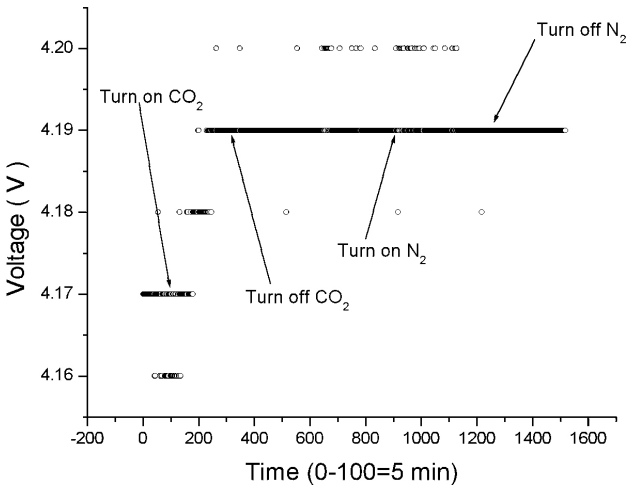

FIGURE 7. Response in real time for an unexposed SnO_2 film of 33.8 nm thickness.

In Fig. 6, we show the response of a 32.3 nm SnO_2 film to different CO_2 gas fluxes. Squares correspond to a 10 mL/min and circles to a 20 mL/min. No differences were got as can be observed. This could be attributed to the saturation of the gas absorption on the films which means the process is irreversible.

Under TIR method, we can also study the response of the gas sensor in real time. Unfortunately, adsorption processes of this type are irreversible and we need to use unexposed samples for each running. Immediately after deposition, a 33.8 nm thickness SnO_2 film was positioned in the experimental setup to study the reflectance intensity versus time at a fixed angle. The measurements were made at $\theta = 43°$. For results interpolated from Fig. 6, we expect an increment on the response of about a 5% for a CO_2 flux of 15 mL/min. Converted to D.C. voltage, this increase corresponds to an order of 3 mV. Electronic noise and the precision of the ordinary multimeter used are of the same order, therefore it was not possible to detect that change. In order to detect such changes in the signal an amplifier circuit of about 10 times was used. So, the new amplified change in the signal should equal to the order of 0.03 V in magnitude. The measurements are shown in Fig. 7. We can observe the fast response when CO_2 flux is turned on. When the N_2 flux is turned on, CO_2 molecules had not been desorbed and the change in the signal is weak.

5. Conclusion

A new gas detection method based on the use of SnO_2 thin films operating under ambient conditions and using reflectance phenomenon has been demonstrated experimentally. Measurable responses to CO_2 and N_2 constant gas fluxes were obtained. It was established that the maximum response takes place at incident angles close to the critical angle of an ordinary quartz-air system. Close to the critical angle the response of the sensor in time is good. The method can be improved using more sensible meters, and can be used to detect other kind of gases depending on the type of the sensing film material.

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