Enhancing chemiresistor-type NO gas-sensing properties using ethanol-treated lead phthalocyanine thin films

Kuo-Chuan Ho a, b, *, Chun-Ming Chen a, Jung-Yu Liao a

a Department of Chemical Engineering, National Taiwan University, Taipei 10617, Taiwan
b Institute of Polymer Science and Engineering, National Taiwan University, Taipei 10627, Taiwan

Received 13 July 2004; received in revised form 30 November 2004; accepted 20 December 2004

Available online 9 February 2005

Abstract

The gas-sensing properties of ethanol-treated lead phthalocyanine (PbPc) thin films, to be used in a chemiresistor-type nitric oxide (NO) gas sensor, are presented. The gas-sensing properties, including current transient, sensitivity, and response time, were studied. It was found in this study that the PbPc thin films post-treated with an ethanol (EtOH) vapor responded faster to NO gas both in adsorption and desorption processes, comparing to those PbPc thin films without any post-treatment. The sensitivity was also enhanced with the post-treatment. A nonlinear diffusion–adsorption model, proposed in the literature for gas-sensing with a semiconductor thin film, has been used to fit our experimental data. The results obtained from the fitting revealed that the EtOH-treated PbPc thin films possess a larger effective diffusion coefficient and a faster response time. For 100-nm PbPc thin films, the power indexes (sensitivity) for both untreated and treated films are 0.38 and 0.65, respectively. Moreover, the model also gives other physical parameters for both untreated and EtOH-treated PbPc films.

© 2005 Elsevier B.V. All rights reserved.

Keywords: Lead phthalocyanine; Nitric oxide sensor; Nonlinear diffusion; Solvent treatment

1. Introduction

The metal phthalocyanine (MPc), formed by substitution of H atoms in the center of phthalocyanine ring with transition metals, is a chemically and thermally stable semiconductor. Many applications have been identified, which include electrochromic device (ECD) [1,2], CD-R recording medium, solar cell [3], and gas sensing [4–24]. The p-type semiconducting lead phthalocyanine (PbPc) was reported to be sensitive to many gases, such as NO2 [4–15], NH3 [6], Cl2 [15–17], I2 [17], O2 [18], and H2 [19]. Other p-type MPcs, such as CuPc and NiPc, were reported to be sensitive to both NO2 [6,7,10,21–23] and NO [24]. In the chemiresistor-type sensor system, the conductivity increases when a p-type semiconductor was exposed in an oxidizing gas (good electron acceptor) such as NO and NO2, because of the lack of electrons in a hole-carrying matrix.

Among the literature, few were mentioned about the use of MPc films for sensing NO gas, which depletes the ozone layer in the atmosphere and normally coexists with NO2 gas formed in high-temperature and -pressure furnace, with optimized preparation conditions such as morphology and post-treatment. Liu et al. [20] reported that the post-annealing temperature changes surface morphology and sensing response of a nickel phthalocyanine (NiPc) film. This implies that post-treatment can be a very effective tuning technique to obtain a stable and reproducible sensing characteristic. Furthermore, an unsteady-state response versus time relationship is also proposed by considering a reversible adsorption/desorption process between NiPc and NO gas molecule [20]. Besides understanding the transient behavior during sensing process, the relationship between the response current and the concentration of NO (calibration curve)
is another key step to understand the PbPc–NO sensing system, which has been hardly mentioned. Therefore, the effect of post-treatment (solvent-treatment) on a PbPc thin film and the proposed mechanism based on a nonlinear diffusion–adsorption model for sensing NO gas will be discussed.

2. Experimental

The lead phthalocyanine (PbPc) purchased (from Aldrich, 80%) is further purified by vacuum sublimation process at 500 °C for three times. Then purified PbPc powder is thermally evaporated under 2.4 × 10⁻³ N/m² vacuum onto Al₂O₃ substrates where an interdigitated gold electrode (Fig. 1) with 0.2-mm electrode spacing is screen-printed using gold paste and heated at 930 °C for 120 min. Film thickness (100, 200, and 300 nm) and evaporation rate (0.5 nm/s) are monitored and controlled by a quartz crystal oscillator installed inside the vacuum chamber. The Al₂O₃ substrate temperature is 25 °C during the evaporation process. The deposited PbPc thin film is placed in a sealed solvent vapor environment reaching equilibrium at room temperature for 24 h. The selected solvents are ethanol, water, acetone, acetonitrile, isopropanol, and n-hexane. The conductance response of the film, which varies with different concentrations of NO gas tuned by mixing 500 ppm NO with ultrapure N₂ gas stream from tank (SanFu Gas Co., 99.9995%) through a flow meter, is obtained by applying a 10-V DC across both terminals of the electrodes, as shown in Fig. 1. The current responses are recorded by a potentiostat (Keithley 236). The sensing film that faces against the gas inlet at a flow rate of 200 ml/min is placed in the sensing chamber. Detailed experimental setup can be found in the previous work [24,25]. The XRD analysis is obtained by a diffractometer (MAC Science, M03XHF). The SEM pictures are taken by a scanning electron microscope (Hitachi S-800 and S-4000).

3. Nonlinear diffusion/adsorption theory

The general diffusion equation involving adsorption which is relatively rapid compared with diffusion process can be expressed as [26]

\[ \frac{\partial C}{\partial t} = D \frac{\partial^2 C}{\partial x^2} - \frac{\partial N}{\partial t} \]  

(1)

where \( C \) is the concentration of gas which is a function of position \( x \) and time \( t \), \( D \) the diffusivity of gas molecule inside a solid thin film, and \( N \) the concentration of the adsorbed species. Under such a condition, the local equilibrium can be assumed to exist between the free and the adsorbed molecules. The scheme of sensing film is illustrated in Fig. 2, in which the length and the thickness of the film are denoted by \( l \) and \( x₀ \), respectively. The following two sensing cases are discussed separately:

(i) Linear case (in lower concentration sensing)

In the case of low concentration sensing, the adsorption is proportional to the free concentration, or

\[ N = kC \]  

(2)

Eq. (1) can be further simplified by substituting Eq. (2) as

\[ \frac{\partial C}{\partial t} = D_e \frac{\partial^2 C}{\partial x^2} \]  

(3)

where \( D_e \) is the effective diffusivity and is defined by

\[ D_e = D + k \]

The initial and boundary conditions are

\[ t = 0, \quad 0 \leq x \leq x₀, \quad C(x, 0) = 0 \]  

(4)

\[ t > 0, \quad x = x₀, \quad C(x₀, t) = C₀ \]  

(5)

\[ x = 0, \quad \frac{\partial C}{\partial x} = 0 \]  

(6)

The exact solution to Eqs. (3)–(6) can be found [26] as

\[ C(x, t) = C₀ \frac{4C₀}{\pi} \sum_{k=0}^{\infty} \frac{(-1)^k}{(2n + 1)} \exp \left[ -D(2n + 1)^2 \pi^2 \frac{t}{4x₀^2} \right] \cos \left( \frac{(2n + 1)\pi x}{2x₀} \right) \]  

(7)

(ii) Nonlinear case (in higher concentration sensing)
When operating in a higher concentration environment, the gas adsorption follows the Freundlich isotherm model

\[ N = kC^\gamma \]  \tag{8} 

where \( \gamma \) is a characteristic constant or the so-called power index (sensitivity) of the system, which accounts for the relationship between the adsorption coverage and the gas concentration. For a higher concentration case, the adsorption of gas depends weakly on the gas concentration, thus the \( \gamma \) value is usually less than unity. The larger the \( \gamma \) is, the stronger the adsorption dependence is on the gas concentration during the adsorption process. For films with a larger \( \gamma \) value, films are more sensitive in response to the variation of gas concentration. Substituting Eq. (8) into Eq. (1) and assuming that \( \frac{\partial C}{\partial x} \ll \frac{\partial N}{\partial x} \) (i.e., \( k \gg 1 \)), Eq. (1) can be rewritten as

\[ \frac{\partial N}{\partial t} = \frac{\partial}{\partial x} \left[ D_k^{-1/\gamma} N^{(1-\gamma)/\gamma} \frac{\partial N}{\partial x} \right] \]  \tag{9} 

or

\[ \frac{\partial N}{\partial t} = D_k^{-1/\gamma} \frac{\partial^2 N^{1/\gamma}}{\partial x^2} \]  \tag{10} 

The effective diffusivity \( (D_e) \) can be expressed as

\[ D_e = \frac{D_k}{\gamma} \frac{N^{(1-\gamma)/\gamma}}{N_0} \]  \tag{11} 

which is a function of \( N \) and \( \gamma \). If \( \gamma < 1 \), \( D_e \) increases as the adsorbed concentration \( N \) increases. When \( \gamma > 1 \), \( D_e \) decreases as the adsorbed concentration \( N \) increases. Eq. (10) can be further simplified as

\[ \frac{\partial S}{\partial t} = \frac{\partial^2 S^{1/\gamma}}{\partial x^2} \]  \tag{12} 

The associated initial and boundary conditions are

\[ T = 0, \quad 0 \leq X \leq 1, \quad S(X, 0) = 0 \]  \tag{13} 

\[ T > 0, \quad X = 0, \quad \frac{\partial S}{\partial x} = 0 \]  \tag{14} 

\[ X = 0, \quad \frac{\partial S}{\partial x} = 0 \]  \tag{15} 

where the dimensionless groups \( S, T \), and \( X \) are defined as

\[ S = \frac{N}{N_0} \]  \tag{16} 

\[ T = \frac{t}{\tau} \]  \tag{17} 

\[ X = \frac{x}{x_0} \]  \tag{18} 

and

\[ \tau = \frac{k x_0^2}{D} \]  \tag{19} 

or

\[ \tau = \frac{N_0 x_0^2}{D} \frac{1}{C_0} \]  \tag{20} 

where \( N_0 \) is the maximum adsorbed concentration and is normally called trap concentration. Numerical solution for Eqs. (12)–(15) has been proposed \([27]\) by considering the nonlinear diffusion model.

The nonlinear Freundlich isotherm in Eq. (8) is adapted as a general case for a p-type PbPc thin film which undergoes a rapid adsorption and generates holes that increase the conductivity

\[ \text{NO} + \text{PbPc} \rightarrow \text{[NO}^+\text{PbPc]}^+ \] 

\[ = \text{[NO}^+\text{PbPc]}^+ + \text{hole} \]  \tag{21} 

Assuming the conductivity is proportional to the adsorbed amount \( (N) \) or the coverage \( (\theta) \) as

\[ \sigma \propto N \propto \theta \propto kC^\gamma \]  \tag{22} 

the conductivity \( (\sigma = \Omega^{-1} \text{cm}^{-1}) \) of p-type semiconductor is

\[ \sigma = \mu q n \]  \tag{23} 

where \( \mu \) is the hole mobility \((\text{cm}^2/\text{V s})\), \( q \) the charge of a single hole \((\text{e})\), and \( n \) the carrier density \((\text{no./cm}^3)\). Therefore, the drift current density

\[ J = \sigma E = \mu q n E \]  \tag{24} 

The current response is then written by using Eq. (22) and applying the surface integration to the closed electrode surface

\[ \Delta I = k \mu q \int_0^1 \left( C(x, y, z, t) \right)^2 E(x, y, t) \, dx \]  \tag{25} 

Eq. (25) can be simplified further by considering a one-dimensional diffusion and that \( dx \approx dx \) if the dimension in \( y \)-direction \( (l) \) the length of the film shown in Fig. 2) is kept constant

\[ \Delta I = 9 k \mu q \int_0^1 \left( C(x, t) \right)^2 E(x) \, dx \]  \tag{26} 

where constant 9 in Eq. (26) represents nine cross-sectional planes in the design of an interdigitated gold electrode, as shown in Fig. 1. The electric field distribution shown in Eq. (26) is further simplified by Gardner \([28]\)

\[ E(x, t) \approx E(x) = \frac{V}{\pi \left( (x - x_0)^2 + w^2 \right)}^{1/2} \]  \tag{27} 

where \( V \) is the applied potential and \( w \) the distance between two electrodes.

For gas sensing in a higher concentration range, a nonlinear diffusion \( (\gamma \neq 1) \) arises. Substituting Eq. (27) into
Eq. (26) gives
\[ \Delta I = 9k \mu q l V \pi \int_{x_0}^{x} \left( C(x, t) \frac{\gamma}{w} \right) \left( (x - x_0)^2 + \frac{w^2}{4} \right)^{-1/2} dx \]  
(28)

or
\[ \Delta I = 9k \mu q l V \pi N_0 \int_{x_0}^{x} S(x, t) \left( (x - x_0)^2 + \frac{w^2}{4} \right)^{-1/2} dx \]  
(29)

where the profile of \( S(x, t) \) is numerically obtained by solving Eqs. (12)–(15). Since \( x_0 \ll w \), the maximum current response (\( \Delta I_{\text{max}} \)) can be obtained by letting \( t \to \infty \), or
\[ \Delta I_{\text{max}} \approx 18k \mu q l V \pi w C_0 x_0 \]  
(30)

As for sensing in a lower concentration range, \( \gamma \) reaches unity. By substituting Eq. (7) into Eq. (28), the current response can be simplified as
\[ \Delta I = 9k \mu q l V \pi \int_{x_0}^{x} \left( C_0 - 4C_0 \sum_{n=0}^{\infty} \frac{(-1)^n}{(2n+1)} \left( \frac{2n+1}{2x_0} \right) \right) \cos \left( \frac{2(n+1)\pi x}{2x_0} \right) \left( (x - x_0)^2 + \frac{w^2}{4} \right)^{-1/2} dx \]  
(31)

According to the result derived in Eq. (30), the characteristic power index (\( \gamma \)) for the NO–PbPc system can be obtained by plotting log(\( \Delta I_{\text{max}} \)) against log(\( C_0 \)).

4. Results and discussions

4.1. Operating temperature

It is well known that the conductivity of a semiconductor is affected by the surrounding temperature. Generally, the increase in temperature leads to a higher conductivity, because the increase in thermal motion enhances the movement of the carriers within the semiconductor. On the other hand, the increase in temperature retards the gas adsorption, which brings more holes when adsorption occurs. Because of the two competing factors, an optimum temperature will be reached. The result for a 100-nm PbPc thin film exposed to 100-ppm NO for 25 min at different temperatures is shown in Fig. 3. The optimum temperature is 170 °C, at which the maximum current response is obtained. For the rest of the experiments, the temperature is thus fixed at 170 °C.

![Fig. 3. The maximum current response of a PbPc film exposed to 100 ppm NO at different temperatures for 25 min. Film thickness: 100 nm, evaporation rate: 0.5 nm/s, substrate temperature: 25 °C, flow rate: 200 ml/min.](image)

4.2. Calibration curve for an untreated film

Typical sensing curve for a 300-nm untreated, freshly made PbPc thin film exposed to various NO concentrations is shown in Fig. 4. The response time for the adsorption is faster than that of the desorption process. The steady-state current values for a 300-nm PbPc thin film together with those of 200 and 100 nm PbPc thin films obtained under various NO exposures are replotted against the bulk NO concentration (\( C_0 \)) in Fig. 5. The slope in the full log plot is the value of \( \gamma \) mentioned in Eq. (30). It can be found that the slopes for all three film thicknesses (100, 200, and 300 nm), as summarized in Table 1, are roughly the same. It is noted that as the film becomes thicker, the response current is larger as well. This is because a thicker film possesses larger cross-sectional area which is perpendicular to the direction of the electric current.

![Fig. 4. The current responses of a PbPc film exposed to different NO concentrations. Film thickness: 300 nm, evaporation rate: 0.5 nm/s, substrate temperature: 25 °C, operating temperature: 170 °C, flow rate: 200 ml/min.](image)
Thus, a larger current is expected according to the following equation when films are applied at the same potential (10 V DC):

$$I = \frac{G}{V} = \frac{\sigma A}{l}$$

(32)

where $G$ is the conductance, $\sigma$ the conductivity, $A$ the cross-sectional area perpendicular to the electric current, and $l$ the length along the direction of the electric current.

4.3. Choice of solvent

Various solvents are chosen in the post-treatment for a 100-nm PbPc thin film, as shown in Fig. 6. Solvents such as ethanol (EtOH), water, acetonitrile, acetone, isopropanol, and n-hexane are used. It is noticed that all post-treated films possess lower currents as compared to that of the untreated one, which results from the morphological reforma-
tion from an amorphous to a more crystal structure that will be discussed in a later section. The other reason for lower response current is presumably due to the strong ad-
sorption between PbPc and solvent molecules rather than NO molecules, even when operated at an elevated tem-
perature of 170 °C. Another possible reason may be due to the dissolution of PbPc films in organic vapor environments.

Among all solvent-treated films, the one with ethanol-
treated possesses the highest current response. Moreover, a faster response time is also achieved as compared to the un-
treated one. This brings a promising possibility for sensing applications.

4.4. Sensing performance with ethanol-treated films

From previous discussion, our attention is focused on ana-
lyzing the performance of ethanol-treated PbPc thin films. A
typical sensing curve for a 300-nm film is shown in Fig. 7. The
corresponding full log plot of the maximum current change
versus inlet NO concentration for the ethanol-treated films
is shown in Fig. 8. The fitted $\gamma$ values for 100, 200, and
300 nm PbPc films are 0.65, 0.39, and 0.66 (also summa-
rizied in Table 1), respectively. Except for film thickness of
200 nm, $\gamma$ value increases almost twice as compared to those of untreated films. This means that the Freundlich adsor-
tion isotherm model is altered after ethanol-treatment. The increase in $\gamma$ value enhances the adsorption process (as Eq.
Fig. 7. The current responses of an EtOH-vapor-treated PbPc film exposed to different NO concentrations. Film thickness: 300 nm, evaporation rate: 0.5 nm/s, substrate temperature: 25 °C, operating temperature: 170 °C, flow rate: 200 ml/min.

(8) depicts, which results in a faster response time during the sensing process.

4.5. Morphology

Fig. 9 is the XRD analyses for a 300-nm PbPc thin film before and after ethanol treatment. The increase in the XRD intensity represents the transformation from amorphous to α-phase crystal structure (2θ = 12.5–12.7°). The SEM images, as shown in Fig. 10, also support the crystalline formation after 24-h post-treatment. The increase grain size after post-treatment could cause decrease in the adsorptive surface area which offers binding sites for NO adsorption. That is one of the reasons that the current responses are always lower for solvent-treated films as compared to those of untreated films in Fig. 6.

Fig. 8. The full log plot of the maximum current change vs. inlet concentrations of EtOH-vapor-treated PbPc films. Evaporation rate: 0.5 nm/s, substrate temperature: 25 °C, operating temperature: 170 °C, flow rate: 200 ml/min.

Fig. 10. SEM micrographs of a 300-nm PbPc film (a) before and (b) after ethanol-treatment for 24 h.

4.6. Data fitting

Based on Eqs. (12) and (29), an attempt has been made to fit the sensing data by a numerical means. Several parameters are required for the numerical procedure, such as γ (obtained from Figs. 5 and 8 and summarized in Table 1), µ...
(=6.0 × 10^{-10} \text{m}^2\text{V}^{-1}\text{s}^{-1}) (29) ), q (=1.6 \times 10^{-19} \text{C}), V (=10 \text{V}). The maximum adsorbed concentration or trap concentration, N0, can be obtained from Eq. (8) when concentration is C0. The fitting results, both for untreated and treated films, are shown in Figs. 11 and 12, respectively. The calculated parameters both for untreated and treated films are summarized in Tables 2 and 3, respectively.

According to the fitting data, it can be found that the value of N0 (the trap concentration) for an ethanol-treated film is smaller than that of the untreated one. This is consistent with the morphological evidence, because the surface area available for adsorption after ethanol-treatment is smaller due to the diffusion inside a PbPc thin film. Thus, a response time, t80, which is defined as the time needed to attain 80% of its steady-state value, can be determined from the fitting results in Figs. 11 and 12. The diffusion depth at t80 is denoted as δt80, which can be obtained through Eq. (20). Similarly, an averaged diffusion depth can also be evaluated by \( \sqrt{D \tau_{e}} \), whose values are generally on the same order of magnitude as that of δt80. The diffusion depths are different when comparing the film treated with ethanol and that without treatment. The treatment does result in the morphology change. As a matter of fact, the calculated diffusion depth (δt80) is on the same order of magnitude as the averaged diffusion depth (\( \sqrt{D \tau_{e}} \)), which suggests that the ethanol treatment process may not be able to alter the diffusion mechanism, but does improve the adsorption kinetics (larger y value).

### Table 2
<table>
<thead>
<tr>
<th>C0 (ppm)</th>
<th>( k ) (m^{-1} \text{s}^{-1})</th>
<th>( D ) (m^2/s)</th>
<th>N0 (m^{-3})</th>
<th>( D_0 ) (m^2/s)</th>
<th>( \tau_0 ) (s)</th>
<th>( \delta_{0} ) (nm)</th>
<th>( \sqrt{D \tau_{e}} ) (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>20</td>
<td>1.92 × 10^{-11}</td>
<td>5.18 × 10^{-12}</td>
<td>1.42 × 10^{-16}</td>
<td>0.49 × 10^{-16}</td>
<td>318</td>
<td>7.74 × 10^{-8}</td>
<td>12.48 × 10^{-8}</td>
</tr>
<tr>
<td>40</td>
<td>2.06 × 10^{-11}</td>
<td>5.37 × 10^{-12}</td>
<td>2.04 × 10^{-16}</td>
<td>0.73 × 10^{-16}</td>
<td>219</td>
<td>7.76 × 10^{-8}</td>
<td>12.60 × 10^{-8}</td>
</tr>
<tr>
<td>60</td>
<td>2.03 × 10^{-11}</td>
<td>4.59 × 10^{-12}</td>
<td>2.27 × 10^{-16}</td>
<td>0.83 × 10^{-16}</td>
<td>201</td>
<td>7.93 × 10^{-8}</td>
<td>12.89 × 10^{-8}</td>
</tr>
<tr>
<td>80</td>
<td>2.16 × 10^{-11}</td>
<td>5.26 × 10^{-12}</td>
<td>2.72 × 10^{-16}</td>
<td>1.05 × 10^{-16}</td>
<td>156</td>
<td>7.88 × 10^{-8}</td>
<td>12.80 × 10^{-8}</td>
</tr>
<tr>
<td>100</td>
<td>2.12 × 10^{-11}</td>
<td>4.77 × 10^{-12}</td>
<td>2.96 × 10^{-16}</td>
<td>1.11 × 10^{-16}</td>
<td>141</td>
<td>7.73 × 10^{-8}</td>
<td>12.53 × 10^{-8}</td>
</tr>
<tr>
<td>Average</td>
<td>2.06 × 10^{-11}</td>
<td>5.03 × 10^{-12}</td>
<td></td>
<td></td>
<td></td>
<td>7.81 × 10^{-8}</td>
<td>12.66 × 10^{-8}</td>
</tr>
</tbody>
</table>

Film thickness = 100 nm, film type = amorphous, \( \gamma = 0.36 \).

### Table 3
<table>
<thead>
<tr>
<th>C0 (ppm)</th>
<th>( k ) (m^{-1} \text{s}^{-1})</th>
<th>( D ) (m^2/s)</th>
<th>N0 (m^{-3})</th>
<th>( D_0 ) (m^2/s)</th>
<th>( \tau_0 ) (s)</th>
<th>( \delta_{0} ) (nm)</th>
<th>( \sqrt{D \tau_{e}} ) (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>20</td>
<td>1.54 × 10^{-11}</td>
<td>5.95 × 10^{-13}</td>
<td>4.49 × 10^{-16}</td>
<td>1.06 × 10^{-16}</td>
<td>90</td>
<td>7.84 × 10^{-8}</td>
<td>9.77 × 10^{-8}</td>
</tr>
<tr>
<td>40</td>
<td>1.42 × 10^{-11}</td>
<td>3.99 × 10^{-13}</td>
<td>6.43 × 10^{-16}</td>
<td>0.98 × 10^{-16}</td>
<td>102</td>
<td>8.06 × 10^{-8}</td>
<td>10.00 × 10^{-8}</td>
</tr>
<tr>
<td>60</td>
<td>1.49 × 10^{-11}</td>
<td>3.88 × 10^{-13}</td>
<td>8.84 × 10^{-16}</td>
<td>1.04 × 10^{-16}</td>
<td>96</td>
<td>8.08 × 10^{-8}</td>
<td>9.92 × 10^{-8}</td>
</tr>
<tr>
<td>80</td>
<td>1.44 × 10^{-11}</td>
<td>4.75 × 10^{-13}</td>
<td>1.03 × 10^{-16}</td>
<td>1.46 × 10^{-16}</td>
<td>71</td>
<td>8.21 × 10^{-8}</td>
<td>10.18 × 10^{-8}</td>
</tr>
<tr>
<td>100</td>
<td>1.48 × 10^{-11}</td>
<td>4.67 × 10^{-13}</td>
<td>1.23 × 10^{-16}</td>
<td>1.51 × 10^{-16}</td>
<td>67</td>
<td>8.10 × 10^{-8}</td>
<td>10.05 × 10^{-8}</td>
</tr>
<tr>
<td>Average</td>
<td>1.47 × 10^{-11}</td>
<td>4.65 × 10^{-13}</td>
<td></td>
<td></td>
<td></td>
<td>8.06 × 10^{-8}</td>
<td>9.98 × 10^{-8}</td>
</tr>
</tbody>
</table>

Film thickness = 100 nm, film type = \( \alpha \) phase, \( \gamma = 0.65 \).
All the fitting values shown in Tables 2 and 3 are parts of Eqs. (1) and (8), which involve a diffusion condition coupled with a nonlinear adsorption. Therefore these values can be divided into two categories. One is for the adsorption kinetics, such as the proportional constant for adsorption (k) and the adsorption dependency (γ). The other is for the diffusion process, including diffusivity (D) and δe, diffusion depth (δ80), and diffusion time (τ80). Each value is essential to evaluate a sensing system involving both diffusion and adsorption.

5. Conclusions

In this work, nitric oxide (NO) sensing using PbPc thin films is studied. An optimized temperature of 170 °C was selected at which the highest current response was attained. Ethanol vapor was found to be the most promising solvent for post-treating PbPc thin films. It was found that the response current after ethanol treatment was lower than that of the untreated one, because of surface area reduction caused by α-phase crystal structure formation. Based on a nonlinear diffusion/adsorption theory, the slope of the calibration curve in a full log plot of ΔImax versus C0 gives the value of γ, which is a characteristic constant in characterizing film’s properties. The γ value for ethanol-treated film is roughly double when compared to that of the untreated one. This indicates an improved adsorption property (even though the surface area is fewer on the treated film). A higher trap concentration (εα) is obtained, which corresponds to a higher surface area for the untreated film. The calculated diffusion depth, δ80, is close to the averaged diffusion depth √(Dτ80), which suggests that the diffusion process does determine the sensing process. This supports the faster adsorption process assumption made at the beginning of the theoretical section.

Acknowledgements

This work was sponsored by the National Research Council of the Republic of China under grant numbers NSC 92-2214-E-002-037 and NSC 93-ET-7-002-005-ET.

References


Biographies

Kuo-Chuan Ho received BS and MS degrees in chemical engineering from National Cheng Kung University, Tainan, Taiwan, in 1978 and 1980, respectively. In 1986, he received the PhD degree in chemical engineering at the University of Rochester. The same year he joined PPG Industries, Inc., first as a Senior Research Engineer and then, from 1990 until 1993, as a Research Project Engineer. He has worked on the electrochemical properties of various electrode materials, with emphasis on improving the performances of sensor devices. Following a 6-year industrial career at PPG Industries, Inc., he joined his alma mater at National Cheng Kung University in 1993 as an Associate Professor in the Chemical Engineering Department. In 1994, he moved to the Department of Chemical Engineering at National Taiwan University. Currently, he is a Professor jointly appointed by the Department of Chemical Engineering and Institute of Polymer Science and Engineering at National Taiwan University.

Chun-Ming Chen received his BS degree in chemical engineering from National Taiwan Institute of Technology (currently renamed as National Taiwan University of Science and Technology), Taipei, Taiwan, in 1998. He received MS degree in chemical engineering from National Taiwan University in 1998. Currently, he is a Technology Development Engineer at SST Taiwan Ltd., Hsinchu, Taiwan. He is working on new flash memory development and manufacturing. His research interest mainly is in sensor and high functionality flash memory applications.

Jung-Yu Liao received his BS degree in chemical engineering from National Taiwan University, Taipei, Taiwan, in 1999. He received PhD degree in chemical engineering from National Taiwan University in 2004. Currently, he is in the army to fulfill the compulsory military service. His research interest mainly surrounds applications of chemically modified electrodes on sensing and electro-optical devices.