Phthalimide Thin Film for Methanol Vapor Detection

Article *in* Sensor Letters · April 2008

DOI: 10.1166/sl.2008.048

6 authors, including:

Sevde nur Şen
Gediz University

Rifat Capan
Balikesir University

M.E. Ozel
Fatih Sultan Mehmet Vakif Üniversitesi

A.K. Hassan
Sheffield Hallam University

SENSOR LETTERS
Vol. 6, 261–265, 2008

Phthalimide Thin Film for Methanol Vapor Detection

S. Şen[1], R. Çapan[2,*], M. E. Özel[1], A. K. Hassan[3], O. Turhan[4], and H. Namli[4]

[1]Science Faculty, Physics Department, Onsekiz Mart University, Çanakkale, Turkey
[2]Science Faculty, Physics Department, Balikesir University, Balikesir, Turkey
[3]Materials and Engineering Research Institute, Sheffield Hallam University, Sheffield, UK
[4]Science Faculty, Chemistry Department, Balikesir University, Balikesir, Turkey

(Received: 13 September 2007. Accepted: 30 October 2007)

The thin film and sensing properties of a novel (*N*-phthalimido)-*p*-aminobenzoic acid (FIABA) compound against methanol vapor is investigated using Atomic Force Microscopy (AFM) and Surface Plasmon Resonance (SPR). AFM results indicated that FIABA molecule is a suitable material to produce thin films by spin coating method, with compact and granular morphology. SPR results showed that thin films of this material are highly selective for methanol vapor with fast response and recovery times. Vapor exposure tests using SPR measurements clearly show that the novel FIABA molecules demonstrate a promising material in the development of room temperature vapor sensing application.

Keywords: Phthalimide, Surface Plasmon Resonance, Vapor Sensors, Thin Films.

1. INTRODUCTION

Methanol is a light, volatile, colourless, flammable and poisonous liquid. It is used as an antifreeze, solvent, fuel, dye, drug and as a denaturant for ethyl alcohol.[1,2] It is toxic by its breakdown (toxication) by the enzyme alcohol dehydrogenase in the liver by forming formic acid and formaldehyde, which cause blindness by destruction of the optic nerve.[3,4] The initial symptoms of methanol intoxication are those of central nervous system depression such as headache, dizziness, nausea, and lack of coordination, confusion, drowsiness, and with sufficiently large doses, unconsciousness and death.[5] These potential applications, toxicity and clinical implications of methanol attracts most researchers to study of reliable, selective and sensitive methanol sensors[6] and there has been increasing efforts towards the design and synthesis of new molecules to detect and identify methanol vapor at low concentration.[7–9]

Phthalimide and their derivatives have a wide range of applications in the fields of chemistry, biomedical and pharmacological research such as in the synthesis of pesticides, activated drug-binding materials, antimicrobial activity, antiandrogen, tumor treatment and against HIV cells.[10–14] These materials are largely investigated in the field of sensor research and a few publications are reported in the literature.[15–17] A donor–acceptor molecule was synthesized by bonding tercarbazole to phthalimide through flexible bridge and it was found that the relative intensity of the long wavelength emission depends on the solvent polarity, which implied that this D–A dyad might be used as solvent polarity sensor.[16] *N*-trifluoromethylsulfonyloxy-phthalimide and *N*-trifluoromethylsulfonyloxy-1,8-naphthalimide were investigated for the mechanisms and efficiencies of photoacid generation using acid sensor and an actinometer.[17]

In this work, a novel (*N*-phthalimido)-*p*-aminobenzoic acid (FIABA) molecule is synthesized for the study of the thin film preparation and the methanol vapor sensing properties using atomic force microscopy (AFM) and surface plasmon resonance (SPR).

2. EXPERIMENTAL DETAILS

o-Phthaloyl dichloride (2.03 g, 10 mmol) was dissolved in tetrahydrofurane (25 ml). A suspension of *p*-hydrazinobenzoic acid (1.52 g, 10 mmol) and triethylamine (2.02 g, 20 mmol) in 15 ml tetrahydrofuran (THF) was added dropwise to the former solution with a vigorous mixing. The reaction mixture was stirred for 6 hours at 60 °C. The ammonium salts of the Et_3N as white precipitate was filtered off, then the crude product was obtained by evaporating the rest solutions. Pure product was received by re-crystallization from ethanol-water mixture (8:2). Yield: %61. The synthesis route of FIABA is given in Figure 1.

*Corresponding author; E-mail: rcapan@balikesir.edu.tr

1546-198X/2008/6/261/005
doi:10.1166/sl.2008.048

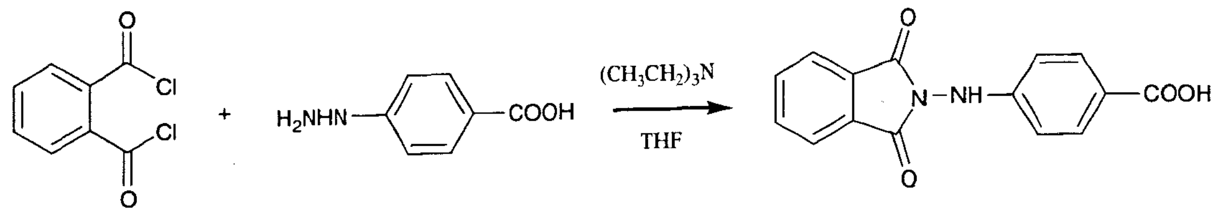

Fig. 1. The chemical structure of (N-phthalimido)-p-aminobenzoic acid (FIABA).

In order to prepare samples for SPR measurements, microscopic glass slides were ultrasonically cleaned and gold was thermally evaporated onto these glass slides with a rate of 1 nm s^{-1} under vacuum of 10^{-4} Pa. The thickness of the gold film was estimated to be 45 nm using the conventional quartz crystal microbalance method. Gold-coated glass substrates were vacuum held onto a rotating chuck of a photoresist spinner (Microsystem model 4000). Using a micro syringe, a small amount of FIABA solution in ethane was dispensed onto the substrate from a distance of 5 mm above the substrate surface. Samples of FIABA thin films were prepared using different spin speeds from 1000 rpm to 5000 rpm.

A Kretschmann type optical set-up system with a $\theta-2\theta$ rotation platform driven by a stepping motor (with a resolution of 0.01°) and controlled by a microprocessor was employed for SPR measurements. A p-polarised monochromatic ($\lambda = 633$ nm) He—Ne laser light source was used to excite surface plasmons and the obtained SPR data were analysed using a least squares algorithm for theoretical fitting of the Fresnel's reflection Equations.[18] A special PTFE gas cell, which was sealed by the sample through a rubber O-ring system, was constructed to study the response of FIABA thin films on exposures to methanol vapor. For the kinetic measurements, a fixed angle θ^* was chosen from the SPR curve and the reflection intensity at this angle was measured as a function of time when the sample was exposed to methanol vapor for at least 2 minutes and was then allowed to recover after injection of dry air.

The AFM measurement was performed on samples deposited onto silicon substrates at room temperature using a Nanoscope III a (Digital instruments) microscope in the standard tapping mode. A standard silicon nitride tip was used to obtain the images and the spring constant of the cantilever was 40 nm^{-1}. The AFM image was taken in an area of 5 μm × 5 μm.

3. RESULTS AND DISCUSSION

The surface morphology of FIABA thin film deposited onto a silicon substrate is carried out using AFM in tapping mode. Figure 2 shows an AFM picture of FIABA film deposited at a rate of 2000 rpm spin speed. The surface of the film has a compact and granular morphology with a root-meansquare (rms) value of 4.72 nm. This granular morphology could have an advantage for the detection of methanol vapor during the physical interaction between the film and methanol molecules.[19] AFM images of N-dodecylphthalimide thin films obtained by Langmuir-Blodgett method indicated a smooth, compact, uniform and void-free film morphology.[20] The LB film is shown to possess a more uniform structure compared to the spin coated films, however the LB method is proved to be more difficult and less practical for thin film deposition of this phthalimide material.

Figure 3 presents the SPR curves showing the variation of reflected intensity as a function of the incident angle θ for a bare gold film and the gold film with a FIABA thin overlayer spun from a 2 mg/ml solution of FIABA in ethane at the speed of 2000 rpm. The minimum of the SPR curve is shifted to a larger angle when the gold substrate is coated with FIABA material. SPR measurements were repeated on different points over the FIABA film surface and the results obtained were quite similar, indicating a reasonable degree of uniformity over the film surface. A refractive index value of $n_p = 1.62$ of phthalimide derivative was obtained from the literature,[21] and used for the fitting of the SPR measured curves to the theoretical Fresnel equation, giving a thickness value $d = 7.41$ nm for films spun at 2000 rpm.

In order to investigate the dependence of FIABA film thickness on the spin speed, five different films were prepared onto gold-coated substrates at different spin speeds ranging from 1000 rpm to 5000 rpm. SPR measurements were used to evaluate the thickness of FIABA films and are given in Figure 4, in which the thickness d was plotted as

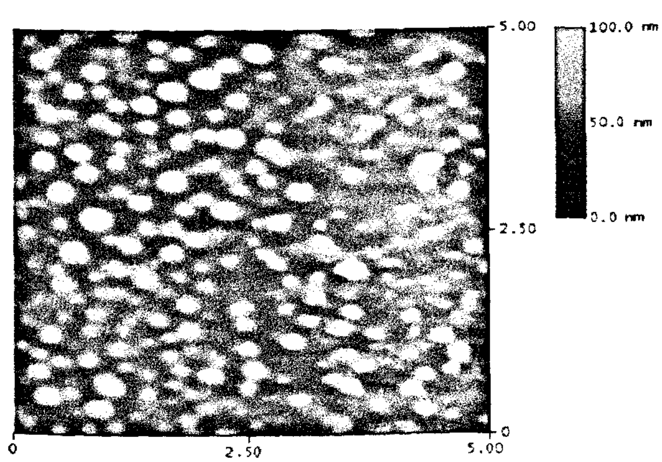

Fig. 2. AFM image of FIABA thin film.

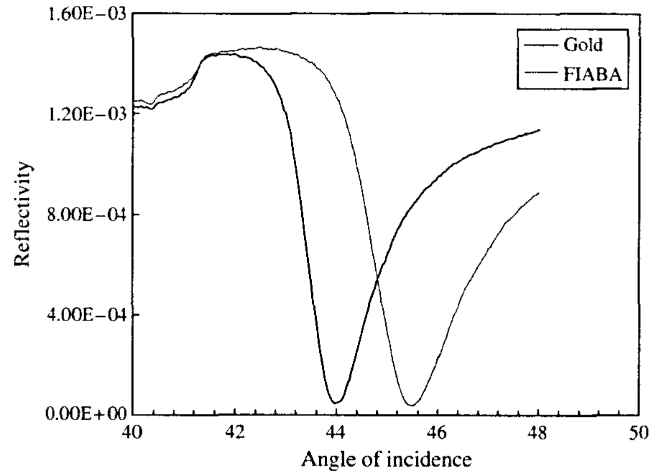

Fig. 3. SPR curves of the FIABA thin film.

a function of spin speed ω on the logarithmic scales. This graph yields a linear behaviour with a slope of -0.577. In the hydrodynamic theory, the thickness of a spun film is defined as a function of the viscosity η of the spreading solution, the density ρ of the pure solvent and the mass flux ϕ as a result of evaporation in the form:[22]

$$d = \sqrt[3]{\left(\frac{3\eta\phi}{2\rho^2\omega^2}\right)} \tag{1}$$

It is well known that ethane is one of the highly volatile solvents and the mass flux ϕ can be assumed independent of spin speed in this case because the concentration of 2 mg/ml of FIABA molecules in ethane is considered to be low. If the mass flux is independent of spin speed for such low solution concentration, the ratio of (η/ρ^2) also remains invariant for different spin speeds. The experimental result of 0.577 is in a good agreement with the value of (2/3) theoretically predicted by Eq. (1).

Figure 5 shows the SPR curve obtained for the FIABA thin film before and after the exposure of methanol vapor and a large shift in the SPR minimum occurred due to the

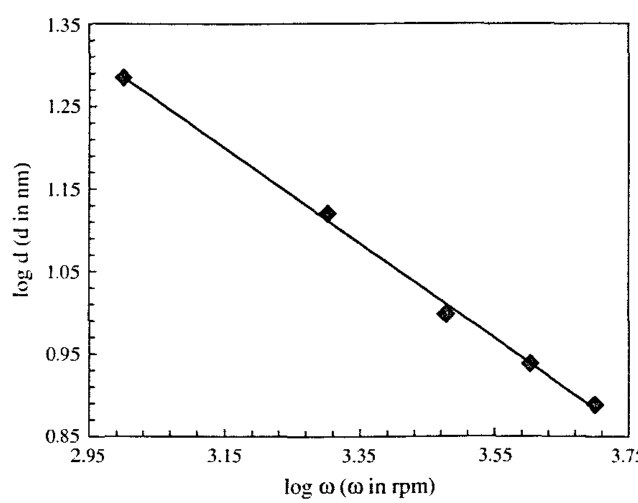

Fig. 4. Dependence of FIABA film thickness on spin speeds.

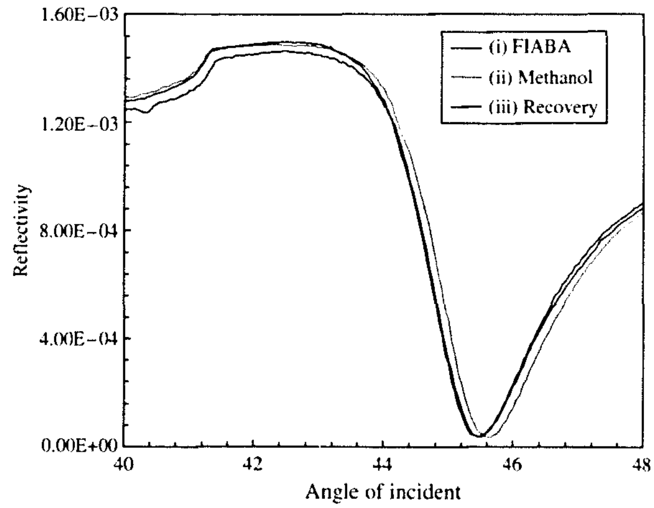

Fig. 5. Response of FIABA thin film to methanol vapor: SPR curves obtained (i) before, (ii) after exposure of methanol vapor and (iii) recovery after withdrawal of methanol vapour.

adsorption of methanol vapor on the FIABA film. This shift can be explained in terms of an increase in refractive index of the sensitive layer and a change in the film thickness due to the film swelling.[23-24] The methanol vapor could interact with FIABA film via hydrogen bonding due to the presence of the —OH group. Similar results were obtained for poly(3-butoxythiophene)/stearic acid thin film when the film exposed to methanol vapor.[25] After clean air injected into the gas cell, the recovery of the FIABA film is found to be fully complete with a fast and reversible response.

When a sensing material is exposed to selected vapor molecules, adsorption and desorption process of the detected vapor molecules will occur simultaneously. This adsorption and desorption process as a function of time is known as the kinetic response of the sensing material. Kinetic response of FIABA thin film to methanol vapor was recorded by measuring the SPR reflectivity at a fixed angle of incidence of $\theta^* = 45.2°$. Prism and FIABA thin film were mounted on a $\theta - 2\theta$ rotation platform driven by a stepping motor (with a resolution of 0.01°) and controlled by a microprocessor. Figure 6 shows the kinetic response as a function of time when the sample was periodically exposed to methanol vapor for a period of 2 min followed by injection of dry air for a further 2 min period. The reflectivity increased sharply with time at first when the spun film was exposed to methanol vapor. The response of FIABA thin film is quite large, fast and a completely reversible when the gas cell is flushed with dry air. Response and recovery times of about 4.7 and 2.8 seconds respectively are observed. Furthermore, the new FIABA thin film is shown to possess excellent reproducibility in its interaction with methanol vapor exposures.

The concentration dependence of the SPR response for FIABA thin film is important to establish the sensitivity of the materials for calibration proposes. Figure 6 gives

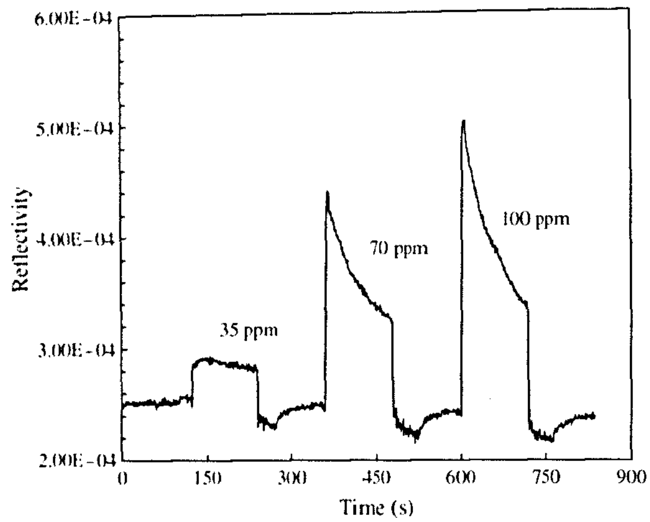

Fig. 6. Kinetic response of FIABA thin films on exposure to step changes in the concentration of methanol vapor at room temperature.

the dynamic variation of the reflectivity of the FIABA film when increasing concentrations of methanol were introduced in the test chamber at the room temperature. In each cycle, the FIABA film were exposed to a given concentration of methanol for 2 min and then flushed with air for 2 min. The response is very high for all vapor concentrations tested and FIABA film is stable with a completely recovery of the signal when the air flux is restored after the vapor test. The calibration curves for the FIABA film is given in Figure 7 by plotting the reflectivity as a function of concentration of the methanol vapor. The response is linear over the vapor concentration range measured (35–140 ppm). The slope of this straight line can be regarded as the sensitivity of the FIABA thin film to methanol vapor. The vapor sensitivity is given by:[23,26]

$$S = \frac{\Delta R}{c} \tag{2}$$

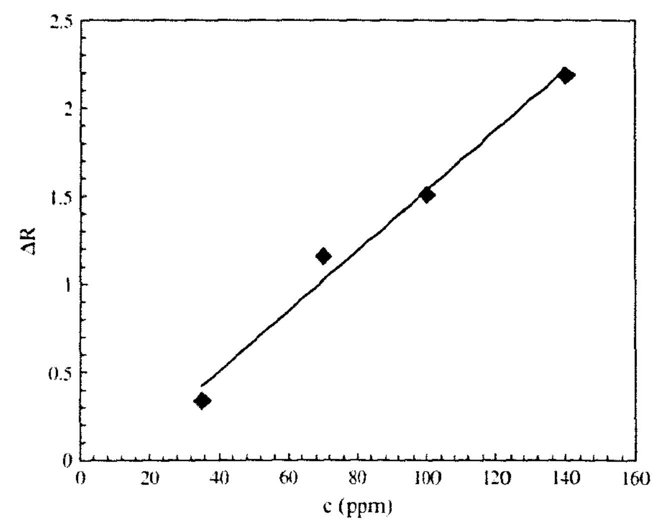

Fig. 7. The reflectivity change of the methanol vapor against concentration.

where ΔR, c are the reflectivity change and the concentration respectively. Using Figure 7 and Eq. (2), a value of 1.7% per ppm is calculated from the slope of a linear approximation to experimental data.

In order to test the stability of FIABA film, kinetic measurements repeated several times using the same experimental conditions at room temperature. The film was stable without significant losses in its sensitivity.

4. CONCLUSION

Preparation and properties of thin films of a novel (*N*-phthalimido)-*p*-aminobenzoic acid molecule and its interaction with methanol vapor were evaluated using AFM and SPR measurements. The AFM image indicated that FIABA thin film is characterised by a compact and granular surface morphology. rms value of the film surface is obtained 4.72 nm. SPR measurements showed that this FIABA material is suitable to produce sufficiently homogeneous thin films on a gold surface. The film thickness showed a power-law dependence on the spin speed in good agreement with the hydrodynamic theory for a low-viscosity and highly volatile liquid. This can be concluded that the thickness of the film can be effectively controlled by the spin speed. The thickness of FIABA film at 2000 rpm is found to be 7.41 nm.

FIABA film is used as a sensing element for the detection of methanol vapor and it yields a large and fast shift in the SPR minimum to the exposures of methanol vapor. The recovery of this shift is found to be fully complete with a fast and reversible response. On the basis of SPR measurements under dynamic variations, the room temperature response of FIABA film to methanol vapour is found to be fast, highly sensitive, reversible and reproducible. The concentration dependence of the SPR response for FIABA film shows a linear relationship with a sensitivity value of 1.7% per ppm. This new FIABA material is stable during the measurements without significant losses in the sensitivity. These results can be concluded that this FIABA film may find potential applications in the development of room temperature optical sensors for methanol vapor.

Acknowledgment: This work was supported by Onsekiz Mart University Research Council Foundation under Project number 2005/111.

References and Notes

1. Z. P. Shao, S. M. Haile, J. Ahn, P. D. Ronney, Z. I. Zhan, and S. A. Barnett, *Nature* 435, 795 (**2005**).
2. P. P. Shah and C. J. Roberts, *J. Phys. Chem. B* 111, 4467 (**2007**).
3. D. G. Barceloux, G. R. Bond, E. P. Krenzelok, H. Cooper, and J. A. Vale, *J. Toxicol., Clin. Toxicol.* 40, 415 (**2002**).
4. R. Rajamani, A. Muthuvel, M. Senthilvelan, and R. Sheeladevi, *Toxicol. Lett.* 165, 265 (**2006**).
5. M. Shelby, C. Portier, L. Goldman, J. Moore, A. Iannucci, G. Jahnke, and S. Donkin, *Reproductive Toxicology* 18, 303 (**2004**).

6. N. G. Patel, P. D. Patel, and V. S. Vaishnav, *Sens. Actuators, B* 96, 180 **(2003)**.
7. L. Palummo, I. Fratoddi, M. V. Russo, and A. Bearzotti, *Sensor Letters* 2, 205 **(2004)**.
8. J. M. Bertolo, A. Bearzotti, P. Falcaro, E. Traversa, and P. Innocenzi, *Sensor Letters* 1, 64 **(2003)**.
9. N. Stevens and D. L. Akins, *Sens. Actuators, B* 123, 59 **(2007)**.
10. L. M. Ching, W. L. Browne, R. Tchernegovski, T. Gregory, B. C. Baguley, and B. D. Palmer, *British J. Cancer* 78, 336 **(1998)**.
11. H. Miyachi, A. Azuma, T. Kitamoto, K. Hayashi, S. Kato, M. Koga, B. Sato, and Y. Hashimoto, *Bioorganic & Medicinal Chem. Lett.* 7, 1483 **(1997)**.
12. Y. Lingappa, S. S. Rao, R. V. S. S. N. Ravikumar, and P. S. Rao, *Radiat Eff. Defects Solids* 162, 11 **(2007)**.
13. A. Takami, M. Iwakubo, Y. Okada, T. Kawata, H. Odai, N. Takahashi, K. Shindo, K. Kimura, Y. Tagami, M. Miyake, K. Fukushima, M. Inagaki, M. Amano, K. Kaibuchi, and H. Iijima, *Bioorganic Medicinal Chem.* 12, 2115 **(2004)**.
14. W. G. Verschueren, I. Dierynck, K. I. E. Amssoms, L. L. Hu, P. M. J. G. Boonants, G. M. E. Pille, F. F. D. Daeyaert, K. Hertogs, D. L. N. G. Surleraux, and P. B. T. P. Wigerinck, *J. Medicinal Chem.* 48, 1930 **(2005)**.
15. M. E. Vazquez, D. M. Rothman, and B. Imperiali, *Org. Biomolecular Chem.* 2, 1965 **(2004)**.
16. Y. Xing, H. Lin, F. Wang, and P. Lu, *Sens. Actuators, B* 114, 28 **(2006)**.
17. F. Ortica, J. C. Scaiano, G. Pohlers, J. F. Cameron, and A. Zampini, *Chem. Mater.* 12, 414 **(2000)**.
18. I. Pockrand, *Surf. Sci.* 72, 577 **(1978)**.
19. S. B. Patil, P. P. Patil, and M. A. Moreb, *Sens. Actuators, B* 125, 126 **(2007)**.
20. M. Evyapan, R. Çapan, H. Namlı, O. Turhan, and G. A. Stanciu, *Mater. Lett.* 60, 2371 **(2006)**.
21. http://www.texloc.com/closet/cl_refractiveindex.html.
22. R. Capan, A. K. Ray, A. K. Hassan, and T. Tanrisever, *J. Phys. D: Appl. Phys.* 36, 1115 **(2003)**.
23. R. P. Podgorsek, T. Sterkenburgh, J. Wolters, T. Ehrenreich, S. Nischwitz, and H. Franke, *Sens. Actuators, B* 38–39, 349 **(1997)**.
24. A. V. Nabok, A. K. Hassan, and A. K. Ray, *J. Mater. Chem.* 10, 189 **(2000)**.
25. L. Xu, X. Hu, Y. T. Lim, and V. S. Subramanian, *Thin Solid Films* 417, 90 **(2002)**.
26. A. K. Hassan, A. K. Ray, A. V. Nabok, and F. Davis, *Sens. Actuators, B* 77, 638 **(2001)**.