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p-phthalimidobenzoic thin film for volatile organic vapor detection

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Thin films of the molecule of p-phthalimidobenzoic acid (FIBA) have been deposited by spin coating and are studied for application as sensing membrane for the detection of alcohols. Atomic force microscopy (AFM) and surface plasmon resosnance (SPR) were used for the characterisation of the FIBA films. Alcohol sensing properties of the obtained films were examined using SPR measurements. AFM images show that FIBA films have the large surface roughness with an estimated roughness RMS value of 6.3 nm. Films with such compact and granular morphology are believed to provide improved sensitivity when used in sensor applications. The measured SPR curves were analysed by applying a least square fitting procedure using Fresnel's reflection theory. FIBA film used as a sensing element for the detection of saturated 2-propanol, ethanol and methanol vapors. Fast response and recovery for all studied analytes have been obtained. These results show that thin films made with this FIBA molecule are demonstrating good suitability for room temperature vapor application.

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1. Introduction

Determination of alcohols, in particular 2-propanol, methanol and ethanol is of great interest in food, fermentation and different industrial processes as well as in clinical chemistry and cleaning. Those three organic compounds are mono alcohols that have one -OH group. These compounds are colourless, flammable and toxic [1]. Several methods such as Surface Plasmon Resonance (SPR), Quartz Crystal Microbalance (QCM) and UV-visible have been used for the detection of volatile organic compounds (VOCs) in the field of gas sensor applications [2-4]. SPR technique is based on the registration of the coupling of the incident electromagnetic wave into the surface plasmons (i.e., vibrations of free electrons in thin metal films near the metal-dielectric interface) and thus provides fast and reliable detection means of changes taking place onto thin film surfaces [5]. It is therefore widely used in the characterization of different types of thin films and their interaction with ambient air [6-11]. A broad range of materials, both inorganic and organic, have been used as thin films for the monitoring of alcohols [4, 12-14]. Phthalimide and their derivatives have a wide range of applications in the fields of chemistry, biomedicine and pharmacology, such as in the synthesis of pesticides, activated drug-binding materials, antimicrobial activity and others [16-20]. These materials have also been investigated as sensing elements for the detection of different gases and VOCs [21-24].

In the present work, we report the morphological and optical characterization of spin coated thin films made of p-phthalimidobenzoic acid (FIBA) molecule by using Atomic Force Microscopy (AFM) and SPR measurements. The sensing properties of the new FIBA molecule for the detection of alcohols are discussed in details in this paper.

2. Experimental details

Phthaloyl dichloride (2.03 g, 10 mmol**)** was dissolved in 100 ml tetrahydrofuran. 4-aminobenzoic acid (1.37 g, 10 mmol) and triethylamine (2.02 g, 20 mmol) was added dropwise into this solution. White precipitate was obtained. The reaction mixture was stirred for 8 hour at 60 ^{o}C. Formed white triethylamine hydrochloride salt was filtered. Filtrate was evaporated and product was recrystallised from acetonitrile. Yield: %61. The synthesis route and the chemical structure of FIBA material is given in Fig. 1. The AFM measurements were performed on samples deposited onto silicon substrates at room temperature using a Nanoscope IIIa (Digital Instruments) 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 5μm × 5μm. For SPR measurements, microscopic glass slides were first ultrasonically cleaned and gold films, 45 nm in thickness, were thermally evaporated onto these glass slides, with an evaporation rate of 1 nms^{-1} under vacuum with

background pressure of 10^{-4} Pa. The gold-coated slides were placed onto a rotating chuck of a photoresist spinner (Microsystem model 4000) and 10 μl of FIBA dissolved in ethanol with a concentration of 2 mg ml^{-1} was injected onto the substrate from a distance of 5 *mm* when the spin speed reached 2000 *rpm*. For the AFM measurements, ultrasonically cleaned silicon slides were used as the substrate and FIBA thin films were produce at 2000 *rpm*.

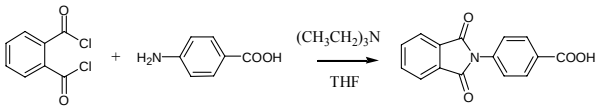

Fig. 1. The synthesis route and the chemical structure of p-phthalimidobenzoic acid (FIBA) molecule.

A Kretschmann's type SPR set-up with a $\theta - 2\theta$ rotation platform driven by a stepping motor (with a resolution of 0.01°) was employed to investigate the optical parameters and the vapor sensing properties of FIBA thin films. The surface plasmon was excited by a p-polarised monochromatic (λ=633 nm) He-Ne laser light source. The SPR data were analysed to obtain the refractive index and film thickness using a least squares algorithm for the theoretical fitting of the Fresnel's equations [25]. The response of FIBA thin films on exposures to 2-propanol, ethanol and methanol vapors were studied using a special PTFE gas cell, sealed by the sample through a rubber O-ring system, specially constructed for this purpose. An angle θ^* was chosen on the SPR curve to perform the kinetic measurements at a fixed angle. The reflection intensity at this angle of incidence was recorded as a function of time when the sample was exposed to each one of the three studied vapors for at least 2 minutes. The samples were allowed to recover for another 2 minutes after injection of dry air into the gas cell. Concentration ranges of 2-propanol, ethanol and methanol were 12000-44000 ppm, 22000-55000 ppm and 52000-130000 ppm respectively.

3. Results and discussion

The surface morphology of FIBA thin film deposited onto a silicon substrate was studied using AFM in tapping mode. An AFM image of a FIBA film deposited at the spin speed of 2000 rpm is shown in Fig. 2. This image shows that the film surface is not uniform with a root mean square (RMS) roughness estimated as $6.3\,nm$. This type of morphology is considered as an advantage for improved sensitivity when such membranes are used in vapor detection [26- 28]. Fig. 3 presents the SPR curves showing the variation of reflected intensity as a function of incident angle θ for a bare gold layer and a FIBA thin film deposited on the Au-coated slides. The minimum of the SPR curve was shifted to a larger angle when the gold substrate was coated with FIBA material.

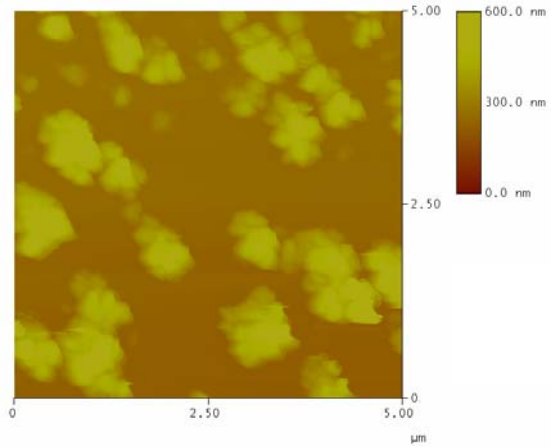

Fig. 2. AFM image of FIBA thin film spun at 2000 rpm.

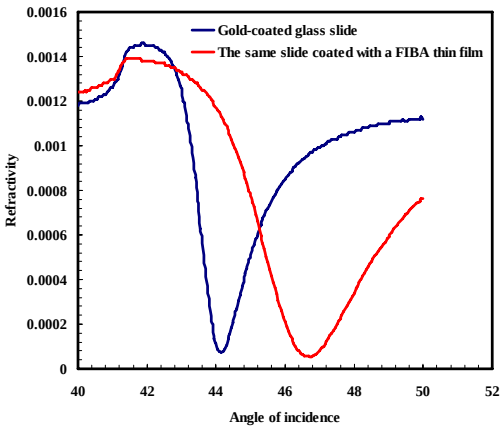

Fig. 3. SPR curves at 2000 rpm.

The SPR curve shift $\Delta\theta$ depends upon the complex dielectric constant ε and thickness d of the organic layer, as given by the following equation [25]:

$$\Delta\theta = \frac{(2\pi/\lambda)(|\varepsilon_m|\varepsilon_i)^{3/2} d}{n_p \cos\theta(|\varepsilon_m| - \varepsilon_i)^2 \varepsilon}(\varepsilon - \varepsilon_i) \qquad (1)$$

here n_p and λ are the refractive index of prism and wavelength of the p-polarised monochromatic (λ=633 nm) respectively. ε_m is the modulus of the real part of the dielectric constant of the gold film and ε_i is the dielectric constant of the medium in contact with the FIBA layer (in this case air). These measurements were repeated on different points over the FIBA film and the results were quite reproducible. A refractive index value of n = 1.62 for phthalimide derivative was taken from the literature [29], and was used for the fitting of the measured SPR curves to the theoretical Fresnel equation. A film thickness value of $d = 12.45\,nm$ is derived for FIBA thin film spun at 2000 rpm. Because of difficulties of simultaneous evaluation of

n and d for thin transparent films [30], Table 1 are obtained by fixing the refractive index ($n=1.62$) of the organic thin film. Also, we assumed an extinction coefficient of zero for both films, since they are transparent at λ=632.8 *nm*, the wavelength of HeNe laser used for the surface resonance. This response is the result of alcohol adsorption process. The mechanism of adsorption process included swelling of the film and even condensation of adsorbate within the film. The alcohol molecules penetrate through the nanoporous matrix of FIBA film and accumulate within the bulk of the film. This mechanism was previously discussed by Nabok at al, 1999 [31]. The data presented in Table 1 show consistent increase in the thickness of layers following the adsorption sequence for the three vapors and it was shown that resonance shift same degree with change of thickness of the films. A similar behaviour has been observed for similar phthalimide compound [21].

Table. 1. Changes in FIBA spun film thickness and sensitivity of the film on exposure to different organic vapors (Vapuor concentrations of 2-propanol, ethanol and methanol used those measurements were 44000 ppm, 55000 ppm and 130000 ppm respectively.).

Exposed gases	$\Delta\theta$ (deg) Resonance shift when FIBA overlayer exposed to gas vapor	Film thickness (nm)		Δd (nm)	Sensitivity
		Before exposure	With exposure		
Ethanol	0.35	12.45	12.91	0.46	91
2-propanol	0.3	12.54	12.72	0.18	97
Methanol	0.15	12.10	12.19	0.09	89

Fig. 4 shows the SPR curve obtained for the FIBA thin film before and after exposure of 2-propanol vapor. The interaction between 2-propanol and the FIBA film has resulted in a large shift of the SPR minimum of about $\Delta\theta = 46^{o}$. This shift could possibly be explained by a change in the film refractive index as well as by a change in the film thickness due to the film swelling [32-34]. This kind of host molecules can possibly interact with -OH groups of VOCs. Similar effects were also observed for FIBA films on exposures to ethanol and methanol vapors. When clean air is injected into the gas cell, fast and complete recovery of the SPR curves are observed. Similar results were obtained for the assembled monolayer of Cu(II) meso-tetra(4-sulfanatophenyl) porphyrin (CuMTSP) when exposed to 2-propanol vapor [31].

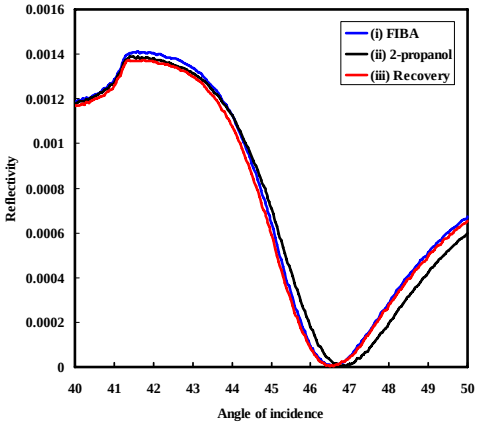

Fig. 4. Response of FIBA thin film to an exposure of 2-propanol vapor: SPR curves obtained for (i) a freshly deposited FIBA film, (ii) the FIBA film after exposure of 2-propanol vapor and (iii) the same film after withdrawal of 2-propanol vapor.

When a sensing material is exposed to vapor molecules, adsorption and desorption processes will occur simultaneously. This is known as kinetic response of the sensing material, a process that is studied here by monitoring the SPR reflectivity at a fixed angle of incidence of $\theta^{*} = 45.75^{0}$ as a function of time. Fig. 5 shows the kinetic response when a FIBA thin film was periodically exposed to the alcohol vapors for a period of $2\,\text{min}$, followed by injection of dry air for a further 2 min period. The SPR signal increases sharply when the FIBA film was exposed to the alcohol vapors. The response is quite large, fast and completely reversible. Response and recovery times of FIBA film were a few second for all vapors. All SPR responses yield a large signal and increase as a function of vapor concentration. Furthermore, the response of FIBA films is shown to be stable and characterised by full recovery of the signal when air is injected into the gas cell. Furthermore, the SPR signal is shown to increase sharply in the first few seconds of vapor injection, followed by decay, with a time constant of a few tens of seconds.

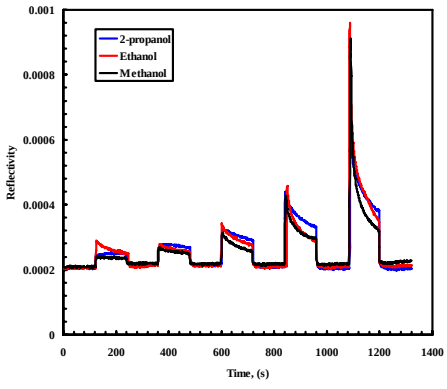

Fig. 5. Kinetic response of FIBA thin films on exposure to step changes in the concentration of 2 – propanol, ethanol, methanol vapors at room temperature.

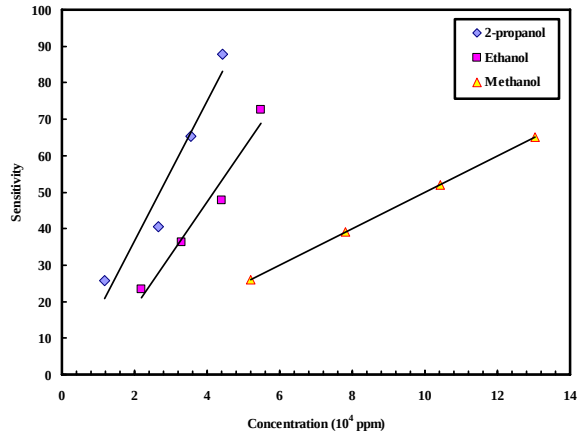

Fig. 6. Calibration curves of FIBA thin films exposed to different concentration of 2-propanol, ethanol and methanol vapors.

The concentration dependence of the SPR response of FIBA thin film is important to establish the sensitivity of the materials. Fig. 6 shows a plot of the sensitivity as a function of concentration of the vapors. The film sensitivity S is given by the following relation [33]:

$$S = \frac{R_{gas} - R_{air}}{R_{air}} \times 100 \qquad (2)$$

where R_{gas} is the response of the sensor during gas exposure and R_{air} is the response during air exposure. The responses are linear over the investigated range of vapor concentrations. The gradient of the straight lines can be considered as the sensitivity of the FIBA thin film to alcohol vapors. The response is found to increase with increasing vapor concentration for each vapor and the highest sensitivity was obtained for 2-propanol. Using Eq. (2) the sensitivity of FIBA film was calculated and the results were presented in Table 1.

In order to test the stability of FIBA film, kinetic measurements were repeatedly performed using the same experimental conditions at room temperature. The film was found rather stable without significant losses in its sensitivity.

4. Conclusions

Thin films of a p-phthalimidobenzoic acid molecule were prepared using spin coating method and its vapor sensing properties are studied using SPR technique. The thickness of FIBA film spun at $2000\,\mathrm{rpm}$ is found to be $\mathrm{d} = 12.36\,\mathrm{nm}$.

The response of FIBA film on exposures to 2-propanol, ethanol and methanol vapors yields a large and fast shift in the SPR minimum. A complete recovery of the SPR curves was observed when the films were flushed with dry air. Among the three studied alcohols, the highest FIBA films sensitivity was obtained for 2-propanol. It can finally be concluded that thin films fabricated using FIBA molecule are expected to find potential applications in the development of room temperature optical sensor for various alcohol vapors.

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