Optical characterization and organic vapor sensing application of perylendiimide Langmuir-Blodgett thin films

Y. ACİKBAS[a,*], R. CAPAN[b], F. YUKRUK[c], M. ERDOGAN[b]
[a] *Department of Material Science and Nanotechnology Engineering, Faculty of Engineering, University of Usak, Turkey*
[b] *Department of Physics, Faculty of Science, University of Balikesir, Turkey*
[c] *Department of Chemistry, Faculty of Science, University of Balikesir, Turkey*

The Langmuir–Blodgett (LB) technique was employed to produce thin LB films using *N,N'*-(glycine tert-butylester)-3,4,9,10-perylenediimide (FY1) material on gold coated glass. The characteristics of the perylenediimide FY1 LB films are assessed by surface plasmon resonance (SPR) measurements. The experimental SPR data are fitted using the Winspall software to evaluate the film thickness and refractive index of this material. Thickness of LB films were determined to be 0.66±0.07 nm per monolayer of FY1, and the refractive index value of FY1 was obtained as 1.41±0.06. FY1 LB thin film sensor element was exposed to chloroform, benzene and toluene vapors. Results show that the response of the FY1 film to chloroform was the largest among organic vapors with the photodetector response change, ΔI_{rf} value of 0.082 au. It can be proposed that these LB films have good sensitivity and selectivity for saturated chloroform vapor.

1. Introduction

The effects of Volatile Organic Compounds (VOCs) exposure depends on several parameters including the type of VOCs, the amount of VOCs and the length of time a person is exposed. High concentration exposure to some VOCs over a short or long term may cause diseases or serious irreversible effect [1,2]. Therefore, the detection of VOCs is one of the most important issue for the protection of human health and enviroment. The development of new sensors based on chemical [3] or opto-chemical [4,5] investigation techniques has generated a considerable international interest for decades. The chemical sensors have been extensively investigated for possible applications because of their response times, low cost, portability, ease of use and a continuous real time signal. The nanocomposite materials [6], p-type oxide semiconductor materials [7], polymers [8-10], graphene [11], calix[n]arene [12-14], phthalocyanine [15], porphyrin [16] and perylenes (PDIs) [17] are selected as sensor materials for chemical sensor application.

These sensors can be investigated by using interferometry, ellipsometry, or surface plasmon resonance (SPR) techniques [18-20]. Among them, SPR has recently attracted a large interest due to its potential applications such as thin film optical characterization [21] and gas sensor applications [22]. For the purpose of sensing gas molecules, the thin film must be functionalized with a gas sensitive layer. Perylene diimides and their derivatives are excellent materials to organize as a monolayer on the water surface, due to being aromatic molecules with an extensive π-system and considerable planarity. The

Langmuir-Blodgett (LB) technique is a suitable method for the fabrication of thin films with perylenediimides and most organic compounds [23,24].

There is little information about the sensing properties of perylene and its derivatives using SPR technique in literature. Therefore, the purpose of the present work is to use *N,N'*-(glycine tert-butylester)-3,4,9,10-perylenediimide (FY1) as an active material for producing thin LB films and to investigate the quality of LB films during the deposition process using SPR. The thickness and refractive index of the LB films are determined and sensing properties against various vapors are studied. The sensitivity for the SPR signal to the exposure of chloroform vapor is found to be quite high, stable and reversible.

2. Experimental details

The chemical structure of the *N,N'*-(glycine tert-butylester)-3,4,9,10-perylenediimide $(C_{36}H_{32}N_2O_8)$ molecule is shown in Fig. 1. The synthesis process of this material is given in our previous study [25]. Solutions of FY1 in chloroform with a concentration of ~0.1 mg ml^{-1} were spread onto ultra pure water subphase to investigate the behavior of FY1 molecule at air-water interface. The floating monolayers at the air-water interface was found to be stable at a surface pressure of 22.5 mN m^{-1}; therefore, this surface pressure value was selected for LB film deposition. The deposition mode for LB film was of the Y-type and vertical dipping procedure was performed at the selected surface pressure with a speed of 25 mm min^{-1} for

both the down and up strokes. FY1 LB film samples were left to dry after each up stroke. Different numbers of FY1 monolayer were deposited onto 50-nm thick gold-coated glass at room temperature for SPR measurement.

SPR technique allows us to evaluate the thickness and the refractive index of thin films. The SPR system that was employed also has a transparent plastic flow cell, which was made in-house for vapor measurements. The photodetector response was monitored as a function of time during periodic exposure of the sample to organic vapor for at least 2 min, the cell was then flushed with dry air allowing the sample to recover.
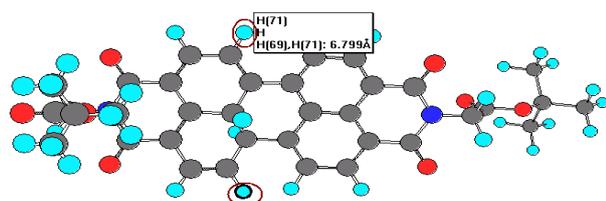
Fig. 1. Chemical structure of FY1 molecule.

3. Result and discussion

Fig. 2 represents a set of experimental SPR curves with the variation of reflected intensity as a function of internal angle for FY1 LB film. The SPR curve of the bare gold is also included as a reference. The SPR curves of FY1 LB film of five different thicknesses get shifted to larger angles as the number of layers increase. The multilayer thickness was found to be linearly related to the number of layers deposited, as seen by the linear increase in the shifting of SPR angles with the number of layers shown in the inset in Fig. 2 for FY1 LB film.
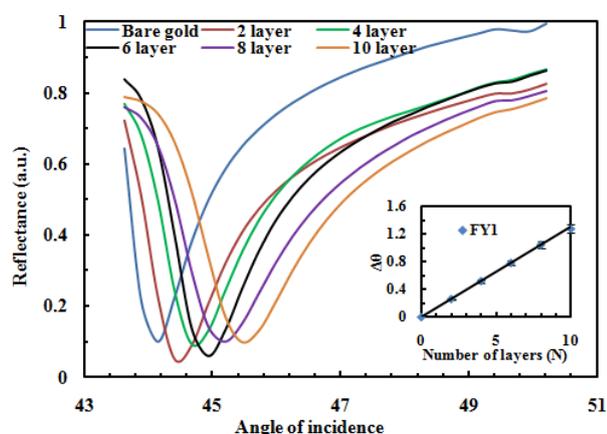
Fig. 2. SPR curves of FY1 LB films with increase in thickness. Inset: linear increase of thickness as a function of number of bilayers.

The experimental SPR data were fitted using the Winspall software (written by Wolfgang Knoll, developed

at the Max-Plank- Institute for Polymer Research, Germany) [26] to evaluate the film thickness (d) and its refractive index (n). It was assumed that k=0 for our LB films, since they are transparent at $\lambda = 633$ nm [27]. Values of the thickness (d) and the refractive index (n) of FY1 LB film are presented in Table 1. The fitting calculations produce a mean value of 0.66±0.07 nm per monolayer of FY1 for the thickness, and the refractive index value of FY1 was obtained as 1.41±0.06. In comparison, when the 3-D chemical structure of FY1 molecule (Fig. 1) was modeled using Chem office 5 (Cambridge soft.), the thickness of the FY1 molecule was determined as 0.68 nm. The thickness value for FY1 material is almost the same and it may be concluded that the material is perpendicular to the substrate.
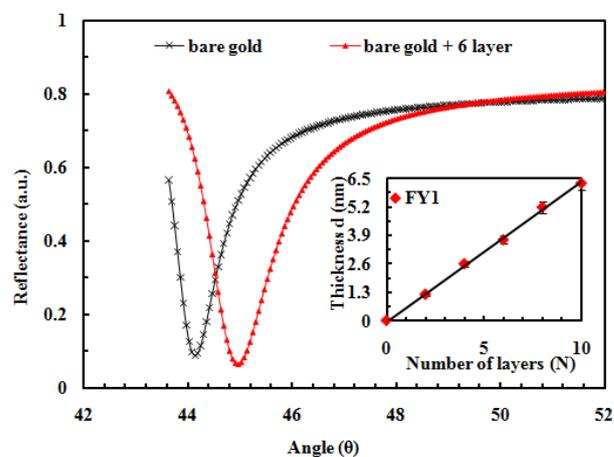
Fig. 3. Complete measured (dots) and fitted (lines) SPR curves for clean bare gold and 6 layer FY1 LB film. Inset: Modeled layer thickness as a function of number of layers for FY1 LB layers.

The inset in Fig. 3 shows that the thickness of FY1 LB film increases linearly with the number of layers. Cui and his group investigated the optical device applications of the perylene tetracarboxylic acid diimide (PTDI) derivatives. UV results showed that the thickness of the PTDI film increased linearly according to the number of bilayers and the thickness of the single bilayer could be calculated as 1.6 nm [28]. Another study by Gordon et al. [29] utilized 3,4,9,10-perylene tetracarboxylic dianhydride (PTCDA) to investigate their optical properties using spectroscopic ellipsometry and the thickness of the single layer for PTCDA films on SiO_2 / Si substrate was determined as 0.5 ± 0.4 nm.

PTCDA films were fabricated on Au-coated substrates by Fuchigami et al. [30] and the refractive index was measured as 1.51. PTCDA films' optical properties were also investigated by Alonso using ellipsometry. The values of the refractive index were calculated to be between 1.55 and 1.60 for single crystals [31] and 1.49 to 1.53 for monoclinic of PTCDA [32]. Similar studies have been conducted for perylenediimide (PDI) organic

semiconductor thin films and the refractive index was found as 1.53 [33].

Table 1.The film thickness and refractive index of the FY1 LB thin films with respect to number of layers deposited, and the photodetector response change of FY1 LB films against organic vapors.

Thin film sensors	Organic vapors	Photodetector response change ,ΔI_{rf} (au)	Number of layers	Thickness (nm)	Refractive index
			2	1.2	1.37
	Chloroform	0.082	4	2.6	1.42
FY1	Benzene	0.045	6	3.7	1.45
	Toluene	0.024	8	5.2	1.41
			10	6.3	1.55

In general, the mechanism of gas permeation into the sensing material can be considered to take place in a three stage "solution-diffusion"mechanism. More information on the gas sensing mechanism can be found in our previous studies [25]. Fig. 4 displays the photodetector response as a function of time as the FY1 LB film sensor was periodically exposed to several organic vapors for 2 min, followed by injection of dry air for a further 2 min period. Response of the LB thin film to these organic vapors is fast, reproducible and reversible. Table 1 shows the photodetector change of the response of FY1 LB film against organic vapors. FY1 LB film sensor material is found to be reasonably selective and significantly sensitive to chloroform vapor than other organic vapors. All the response measurements of the FY1 LB film to organic vapors were run three times, and the results showed that the sensor responses are reproducible.

The interaction of the produced thin films with VOCs' molecules can be explained by physical properties of organic vapors such as molecular weight and molar volume. The molecular weights of organic vapors is ordered as chloroform (119.38 g mol^{-1}) > toluene (92.14 g mol^{-1}) > benzene (78.11 g mol^{-1}). A larger molecular weight of vapor leads to higher sensitivity, which is in good agreement with the previous findings in the literature [34]. However, the sensitivity of FY1 LB film sensor against benzene vapor is larger than toluene vapor. This can be explained with the molar volumes of organic vapors. The molar volume of benzene (86.36 cm^3 mol^{-1}) is smaller than toluene (107.00 cm^3 mol^{-1}). While benzene molecule can easily penetrate into FY1 LB film, the diffusion of toluene molecules into the same LB films is slower.

In our previous study, using the QCM measurement system, vapor sensing properties were investigated and FY1 [25] novel material showed similar results. The response of FY1 LB film in the form of QCM or SPR response to same organic vapors is reproducible and reversible, which is ordered as chloroform > benzene > toluene.
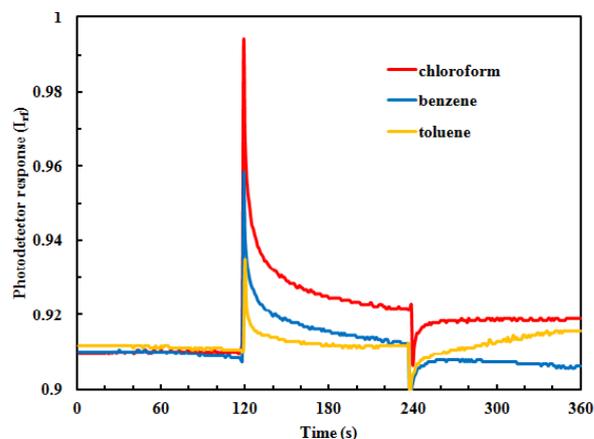
Fig. 4. Kinetic response of sensor coated with FY1 (10 layers) to injection of volatile organic vapors into working cell.

Fig. 5 shows the photodetector response as a function of time as the FY1 LB film sensor was periodically exposed to chloroform vapor for 10 min, followed by injection of dry air for a further 10 min period. Response of the LB thin film to this organic vapor is fast, reproducible and reversible. Fig. 5 also displays the mechanism of gas permeation into the sensing material. In the initial step, FY1 LB film sensor expose to dry air for nearly 600 seconds and the response was a stable value in this period of time. The initial response of FY1 LB film in the SPR system for chloroform vapors increased sharply between 600 and 605s due to surface adsorption effect. When the vapor molecules moved into the FY1 LB film sensor, the response decreased exponentially, which resulted from bulk diffusion effect. In the 1200s, after flushing dry air, a rapid decrease of response was observed and then recovery process occured between 1200 and 1204s for chloroform vapors due to desorption of vapor. After 1205s, the response of FY1 LB film sensor reached a stable value and the sensor obtained initial baseline. This process was applied three times and all the response measurements of the FY1 LB film to chloroform vapors showed that the sensor responses were fast and reproducible.
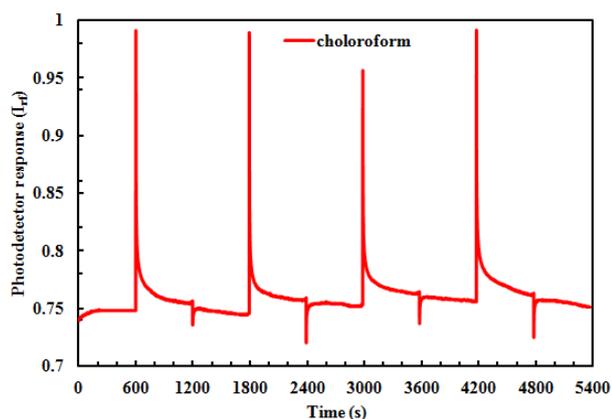
Fig. 5. Kinetic response of sensor coated with FY1 to injection of chloroform vapors into working cell for 10 min period.

4. Conclusion

The LB film and sensing properties of FY1 material is studied in this present article. SPR results show that the FY1 LB film transfer onto a gold-coated substrate is found to be successful and monolayers are transferred uniformly onto gold-coated glass substrates with a linear relationship between number of layer and $\Delta\theta$. This relationship suggests that equal mass per unit area is deposited onto the gold-coated glass substrate during the transfer of FY1 LB film layers. The film thickness and refractive index of FY1 LB films is found to be 0.66±0.07 nm/deposited layer and 1.41±0.06, respectively. FY1 LB film sensor was periodically exposed to organic vapors for 2 min or 10 min, followed by injection of dry air for a further 2 min or 10 min period. The potential application of FY1 LB film as a vapor sensing material using chloroform, benzene and toluene vapors is investigated and the kinetic measurement of this LB film shows fast, reproducible and reversible response to all used vapors (for 2 min or 10 min period). A larger response to chloroform occurred compared to the other organic vapors. The FY1 material can be used as a sensing material and may find potential applications in the development of room temperature organic vapor sensing devices.

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[*]Corresponding author: yaser.acikbas@usak.edu.tr