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Self Assembled Thin Films of Poly(Methyl Methacrylate) for Gas Sensing

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Poly(methyl methacrylate) polymer is selected to produce a self assembled thin film onto a quartz crystal using self assembly deposition technique. The deposition of this poly(methyl methacrylate) film layer is characterized by UV-Visible spectroscopy and quartz crystal microbalance. These results show a uniform high quality and reproducible poly(methyl methacrylate) thin film produced onto the Quartz Crystal Microbalance substrate. The interaction of this poly(methyl methacrylate) film against volatile organic compounds is investigated using Quartz Crystal Microbalance measurement system. A fast and reversible response to chloroform vapor is observed using self assembled poly(methyl methacrylate) film. Our results show that self assembled poly(methyl methacrylate) film gives a promising result for the chloroform vapor sensing application.

Keywords: Polymers, Sensors, QCM.

1. INTRODUCTION

High concentrations of volatile organic compounds (VOCs) are very dangerous compounds for human health and environment.[1–3] The detection of VOCs has become a serious task due to stringent environmental standards and regulations on VOCs in many countries of the world and their natural toxicity is dangerous for the environmental and human being. They are highly dangerous and may cause acute, chronic or long-term effects such as affecting the nose, throat, and lungs that asthma-like reactions, eye irritation and cancer.[4] Therefore the detection of VOCs is an important issue and have a big interest for researchers in the field of gas sensing devices.[5,6] When VOCs interact with a sensing material in a Quartz Crystal Microbalance (QCM) measurement system, ossilation frequency changes as a function of mass change. Therefore QCM technique is widely used for the detection of VOCs in the nanogram scale.[7–10]

Organic materials are widely used as gas sensor applications due to their easy synthesis, fabrication, high quality and low cost. Porphyrins,[11–13] phythalocyanines,[14–17] calixarenes[18–19] and polymer materials[20–22] are extensively used as sensing material because of their low operation temperature, fast response and full recovery.

Poly(methyl methacrylate), commonly known as PMMA, is a transparent, hard and rigid plastic material with a low optical loss in the visible spectrum, low lateral shrinkage, high scratch hardness, and no glass transition temperature.[23] Therefore PMMA has a wide range of potential application in the field of optical and sensing devices.[24–25] PMMA thin film prepared by spin coating method is found to be sensitive to benzene with a fast, large and reversible response.[26] Composite thin films of PMMA sensing devices exhibit a particular sensitiveness to the polarity of the molecule of the VOCs.[27] PMMA is used for the detection of phenol in the solution and is found to be very sensitive to phenol due to the adsorption of phenol at the surface of modified electrode.[28]

In this paper, we report an investigation of PMMA polymer deposited with self assembly thin film deposition method onto a quartz crystal and a glass substrate. Deposition process of PMMA layer is monitored using UV-Visible and QCM measurement system. The gas sensing properties of PMMA thin film against several VOCs is also investigated using QCM measurement system. Our results indicate that self assembled PMMA thin film shows a high selectivity and a reversible response to chloroform vapor than others.

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2. EXPERIMENTAL DETAILS

PMMA material was synthesized using emulsifier-free emulsion polymerization method.[29] Potassium persulfate is widely used as a free radical initiator in emulsifier-present and emulsifier-free systems. It is generally accepted that its use results in the incorporation onto the latex surface of charged sulfate and uncharged hydroxyl groups; the latter are produced either by hydrolysis of surface sulfate groups or by initiation by hydroxyl radical.[30] Figure 1 shows the chemical structure of PMMA with a molecular weight of 830 kg/mol. The polymer backbone has 20243 repeating units, which causes a micellization in water solution. Aqueous solution of PMMA molecule was prepared using pure water with a concentration of 5 mg/ml at pH 5.8. For the self assembly deposition process, the glass and quartz crystal substrates were briefly washed with pure water and chloroform, respectively. These substrates were immersed in a PMMA solution for 2 minutes with a withdrawal speed of 41 mm/s. A further 5 minutes was given for the substrate to dry. This process was repeated to fabricate multilayer PMMA films at the room temperature. Deposition steps were controlled using a computer controlled experimental set-up system. A VARIAN CARY 1E UV-Visible spectrophotometer was employed to investigate the deposition of PMMA self assembly layers in the ultraviolet and visible spectral region from 250 nm to 800 nm in the absorbance mode.

QCM measurement system was performed at room temperature using an in-house designed oscillating circuit and standard quartz crystal with a nominal resonance frequency of 4.5 MHz. The frequency was measured with a MOTECHFG-513 model function generator and TEKTRONIX TDS 210 model digital oscilloscope. The QCM technique was applied to monitor the response of self assembled PMMA film on exposure to organic vapors using a special gas cell. The variation of the QCM frequency was recorded as a function of time when the sample was periodically exposed to the organic vapors for at least 2 minutes and was then allowed to recover after injection of dry air. The organic vapors were injected into the gas cell in liquid form with the amount of 20 μl using a Hamilton syringe. Figure 2 shows a schematic diagram of QCM system and gas cell unit. The baseline frequency in air (stable to ± 0.1 Hz) was recorded before and after the deposition of PMMA materials onto a quartz crystal substrate.

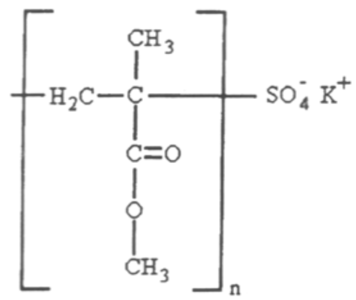

Fig. 1. Chemical structure of PMMA molecules.

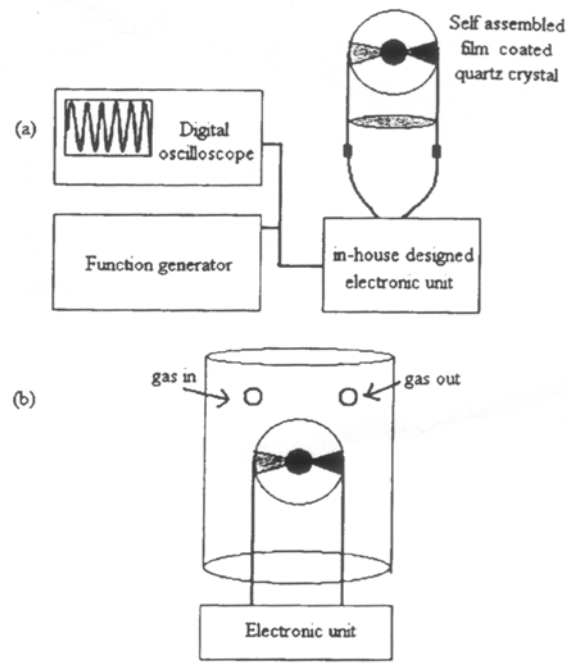

Fig. 2. Schematic diagram of (a) QCM system and (b) gas cell.

3. RESULTS AND DISCUSSION

Figures 3 and 4 show the typical UV-Visible spectrum of PMMA molecule in the chloroform solution and the UV-Visible spectra of PMMA thin film on the glass substrate respectively. An absorption peak for the PMMA

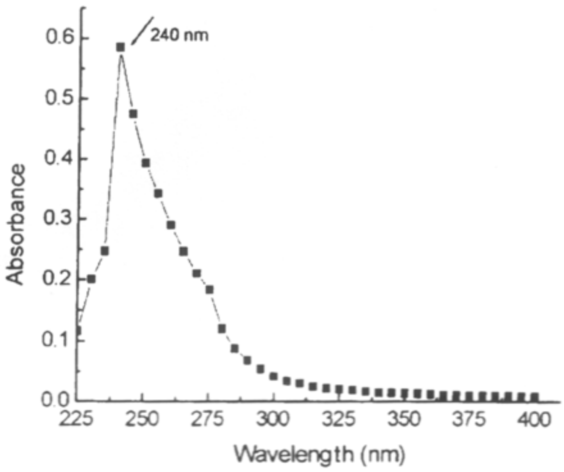

Fig. 3. UV-Visible spectrum of the PMMA solution in chloroform between the range 225–400 nm.

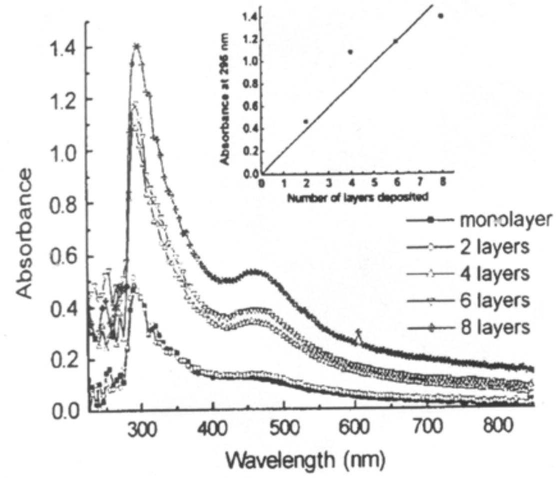

Fig. 4. UV-Visible spectra of up to 8 deposited layers on glass substrate with the inset of absorbance at maximum absorbance value versus number of layers deposited.

solution is observed at 240 nm which is in good agreement with the previous result.[31] It can be seen that PMMA thin film gives absorption peaks around 295 and 460 nm. This difference between PMMA in chloroform and PMMA thin film could be due to a solution effect and inter-molecular interaction in the film or aggregation behaviours of the PMMA molecules on the glass substrate.[32–33] The inset in Figure 4 shows a linear dependence of absorbance intensity of the peak at 295 nm versus number of deposited layers which indicates the uniform and reproducible PMMA film occurred during the deposition process.

In order to investigate the deposition of PMMA thin films onto a quartz crystal, the variation of a resonance frequency is measured as a function of mass change. The relationship between the resonance frequency shift and the deposited mass is described in detail by Sauerbrey;[34]

$$\Delta f = -C_f \Delta m \qquad (1)$$

where Δf is the measured frequency shift (Hz), Δm is the mass change on the quartz crystal (g). C_f is given by:

$$C_f = \frac{2nf_0^2}{\sqrt{\rho_q \mu_q} A} \qquad (2)$$

where n is the number of the harmonic at which the crystal is driven, f_o is the resonance frequency of the fundamental mode of the crystal (Hz), ρ_q is density of quartz (2.648 g cm^{-3}), μ_q is shear modulus of quartz (2.947×10^{11} g cm^{-1} s^{-2}) and A is the piezo-electrically active area (cm^{-2}).

Figure 5 shows the frequency shift of self assembled PMMA film onto a quartz crystal substrate as a function of number of layers. This linear dependence of frequency shift indicates that the deposited self assembled layers contain equal amount of PMMA molecules. This process is repeated several times and the results was found to be highly reproducible.

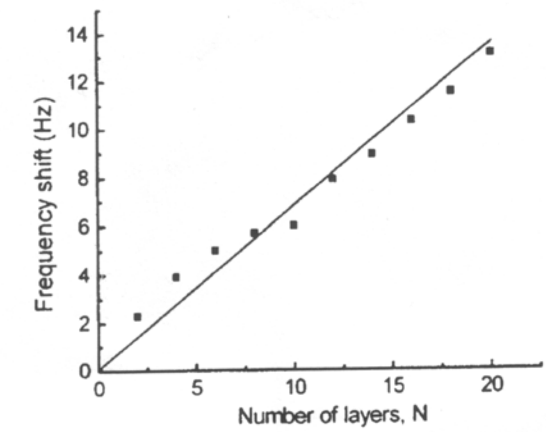

Fig. 5. Frequency shift versus number of deposited self assembled layers.

QCM measurement system is also used to monitor the response of PMMA film against several VOCs such as benzene (C_6H_6), toluene (C_7H_9), chloroform ($ClCH_3$) and isopropyl alcohol (C_3H_8O). All measurements were performed exposure of organic vapor for 2 minutes followed by the injection of dry air for a further 2 minutes period. Figure 6 shows the resonance frequency dependence of PMMA thin film as a function of time to organic vapors. Results presented in the figure are one of the three similar measurements with a relative standard deviation of 10–12%. Self assembled PMMA film is found to be much more selective to chloroform vapor than the others. The response and recovery times are quite large, fast and almost fully reversible. Sensing properties of this PMMA film were compared by sensitivity which is usually defined as $S = (\Delta f / f_o) \times 100$ where Δf is the frequency change as a result of interaction with the organic vapour and f_0 is the initial frequency before that interaction. The value of sensitivity was calculated to be 0.03, 0.008, 0.007, 0.003 for chloroform, toluene, benzene, and isopropyl alcohol

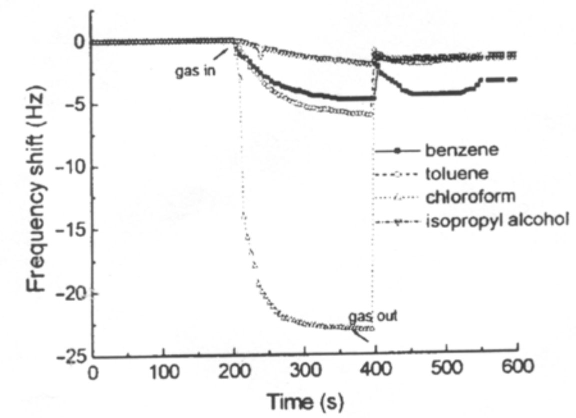

Fig. 6. Kinetic study of PMMA film due to exposure to benzene (■), toluene (o), chloroform (Δ) and isopropyl alcohol (∇) vapors.

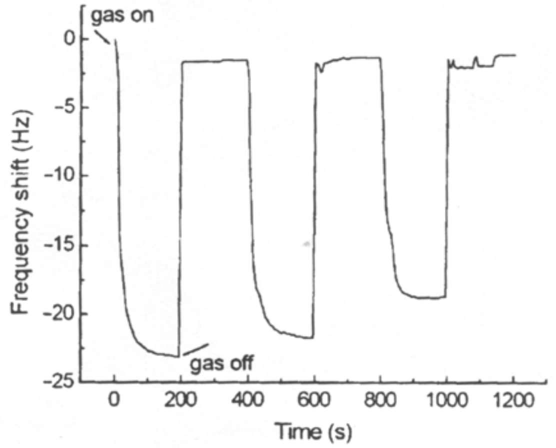

Fig. 7. Kinetic response of PMMA film due to exposure to chloroform vapor for 3 cycles.

vapors respectively. Similar results have been found in other organic vapour sensing studies for polymeric thin films[35–37] as well as phthalocyanine[38] and carbon nanotube thin films.[39] It should also be noted that the nominal frequency of the quartz substrates were found to be effective on the gas sensing performances.[40]

Figure 7 shows a plot of the response of PMMA film against chloroform vapor for 3 cycles. The reproduction of the PMMA response to chloroform vapor is stable with the response and recovery times around 3 and 5 seconds. Despite some baseline instability observed which can be attributed to temperature fluctuations, sensor responses were not significantly affected and quite resonable reproducibility was observed from one sample to another.

4. CONCLUSIONS

A PMMA molecule was successfully deposited onto the glass and quartz crystal substrates using self assembly deposition method and the deposition process of PMMA molecule was monitored using UV-Visible spectroscopy and QCM measurement technique. Our results showed that a high quality self assembly PMMA film was occurred onto the glass and quartz substrates. The organic vapor sensing properties of PMMA film for three different groups named as aromatic (benzene and toluene), chloroorganic (chloroform) and alcohol (isopropyl alcohol) were investigated in this work. It was found that self assembled PMMA film gives a high selectivity to chloroform vapor than the others. The response of PMMA film to chloroform was large, fast and fully reversible. Self assembled PMMA film could have a potential application in the development of room temperature volatile organic vapor sensing device for the chloroform vapor. Future studies will concentrate on improving the sensor performances.

References and Notes

1. C. W. Lee, Y. T. Dai, C. H. Chien, and D. J. Hsu, *Environ. Res.* 100, 139 **(2006)**.
2. H. Mielke, A. Gundert, K. Abraham, and U. G. Remy, *Toxicology* 214, 256 **(2005)**.
3. Y. M. Kim, S. Harrad, and R. M. Harrison, *Environ. Sci. Technol.* 36, 5405 **(2002)**.
4. A. L. Hinwood, C. Rodriguez, T. Runnion, D. Farrar, F. Murray, A. Horton, D. Glass, V. Sheppeard, J. W. Edwards, L. Denison, T. Whitworth, C. Eiser, M. Bulsara, R. W. Gillett, J. Powell, S. Lawson, I. Weeks, and I. Galbally, *Chemosphere* 66, 533 **(2007)**.
5. B. Matthews, J. Li, S. Sunshine, L. Lerner, and J. W. Judy, *IEEE Sens. J.* 2, 160 **(2002)**.
6. L. H. Huo, X. L. Cheng, H. Zhao, S. Gao, Y. Xu, and J. G. Zhao, *Coll. Surf. A* 257–258, 137 **(2005)**.
7. A. Fort, S. Rocchi, M. B. Serrano-Santos, N. Ulivieri, V. Vignoli, G. Pioggia, and F. Di Francesco, *Sens. Actuators, B* 111–112, 193 **(2005)**.
8. S. Muñoz-Aguirre, T. Nakamoto, and T. Moriizumi, *Sens. Actuators, B* 105, 144 **(2005)**.
9. H. Ding, V. Erokhin, M. K. Ram, S Paddeu, and C. Nicolini, *Mat. Sci. Eng. C* 11, 121 **(2000)**.
10. X. Wang, J. Zhang, and Z. Zhu, *Appl. Surf. Sci.* 252–6, 2404 **(2005)**.
11. C. D. George, T. Richardson, M. E. Hofton, C. M. Vale, M. G. M. Neves, and J. A. S. Cavaleiro, *Mat. Sci. Eng. C* 8–9, 559 **(1999)**.
12. H. Ding, V. Erokhin, M. K. Ram, S. Paddeu, L. Valkova, and C. Nicolini, *Thin Solid Films* 379, 279 **(2000)**.
13. J. M. Pedrosa, C. M. Dooling, T. H. Richardson, R. K. Hyde, C. A. Hunter, M. T. Martin, and L. Camacho, *Langmuir* 18, 7594 **(2002)**.
14. A. Altindal, Z. Z. Öztürk, S. Dabak, and Ö. Bekaroğlu, *Sens. Actuators, B* 77, 389 **(2001)**.
15. H. Q. Xiang, K. Tanaka, and T. Kajiyama, *Langmuir* 18, 9102 **(2002)**.
16. D. Xie, W. Pan, Y. D. Jiang, and Y. R. Li, *Mat. Lett.* 57, 2395 **(2003)**.
17. L. Valli, *Adv. Coll. Inter. Sci.* 116, 13 **(2005)**.
18. B. Pignataro, S. Conoci, L. Valli, R. Rella, and G. Marletta, *Mat. Sci. Eng. C* 19, 27 **(2002)**.
19. I. A. Koshets, Z. I. Kazantseva, Y. M. Shirshov, S. A. Cherenok, and V. I. Kalchenko, *Sens. Actuators, B* 106, 177 **(2005)**.
20. R. Capan, A. K. Ray, T. Tanrisever, and A. K. Hassan, *Smart Mater. Struct.* 14, N11 **(2005)**.
21. D. N. Debarnot and F. P. Epaillard, *Anal. Chim. Acta* 475, 1 **(2003)**.
22. B. Adhikari and S. Majumdar, *Prog. Polym. Sci.* 29, 699 **(2004)**.
23. J. H. Harreld, A. Esaki, and G. D. Stucky, *Chem. Mat.* 15, 3481 **(2003)**.
24. W. J. Wadsworth, S. M. Giffin, I. T. McKinnie, J. C. Sharpe, A. D. Woolhouse, T. G. Haskell, and G. J. Smith, *Appl. Optics* 38, 2504 **(1999)**.
25. J. H. Harreld, A. Esaki, and G. D. Stucky, *Chem. Mat.* 15, 3481 **(2003)**.
26. R. Capan, A. K. Ray, A. K. Hassan, and T. Tanrisever, *J. Phys. D* 36, 1115 **(2003)**.
27. C. P. de Melo, B. B. Neto, E. G. de Lima, L. F. B. de Lira, and J. E. G. de Souza, *Sens. Actuators, B* 109, 348 **(2005)**.
28. A. Mirmohseni and A. Oladegaragoze, *Sens. Actuators, B* 98, 28 **(2004)**.
29. T. Tanrisever, O. Okay, and I. Ç. Sönmezoğlu, *J. of Appl. Poly. Sci.* 61, 485 **(1996)**.
30. A. R. Goodall and J. Hearn, *J. Poly. Sci.* 1019–1037, 1019 **(1979)**.
31. R. Srinivasan, B. Braren, and K. G. Casey, *Pure Appl. Chem.* 62, 1581 **(1990)**.
32. S. Acharya, D. Bhattacharjee, and G. B. Talapatra, *Chem. Phys. Lett.* 352, 429 **(2002)**.
33. S. Acharya, D. Bhattacharjee, J. Sarkar, and G. B. Talapatra, *Chem. Phys. Lett.* 393, 1 **(2004)**.

34. G. Sauerbrey, Z. *Phys.* 155, 206 **(1959)**.
35. M. Giannetto, V. Mastria, G. Mori, A. Arduini, and A. Secchi, *Sens. Actuators, B* 115, 62 **(2006)**.
36. H. Nanto, N. Dougami, T. Mukai, M. Habara, E. Kusano, A. Kinbara, T. Ogawa, and T. Oyabu, *Sens. Actuators, B* 66, 16 **(2000)**.
37. György Barko and Jozsef Hlavay, *Anal. Chimica Acta* 367, 135 **(1998)**.
38. Y. Acıkbas, M. Evyapan, T. Ceyhan, R. Capan, and O. Bekaroglu, *Sens. Actuators, B* 123, 1017 **(2007)**.
39. M. Consales, S. Campopiano, A. Cutolo, M. Penza, P. Aversa, G. Cassano, M. Giordano, and A. Cusano, *Sens. Actuators, B* 118, 232 **(2006)**.
40. R. D. Williams, A. K. Upadhyayula, and V. R. Bhethanabotla, *Sens. Actuators, B* 122, 635 **(2007)**.