A Study of PVDF Langmuir-Blodgett Thin Film Using Quartz Crystal Microbalance

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ABSTRACT: Poly(vinylidene fluoride) (PVDF) was deposited onto a quartz crystal microbalance (QCM), using a standard Langmuir–Blodgett (LB) thin film deposition procedure. QCM technique was used to monitor the reproducibility of the LB film monolayer, and the fabricated QCM sensor was employed to detect the dimethyl methyl phosphonate (DMMP) vapor, a simulant of nerve agents. The results show that PVDF was successfully deposited from the water surface onto the quartz crystal substrate. The PVDF LB film is found to be highly sensitive to DMMP vapor, and frequency shifts are linear to the concentrations. The response of the sensor against DMMP is fast, large, and reversible. © 2007 Wiley Periodicals, Inc. J Appl Polym Sci 106: 1024–1027, 2007

Key words: QCM sensor; PVDF; DMMP; Langmuir–Blodgett (LB)

INTRODUCTION

Among lethal chemical weapon (CW) agents, the nerve agents have had an entirely dominant role since the Second World War.[1] Nerve agents are stable and easily dispersed, highly toxic, and have rapid effects both when absorbed through the skin and via respiration. Nerve agents can be manufactured by means of fairly simple chemical techniques, and the raw materials are inexpensive and generally readily available. So the *in situ* detection of nerve agents is necessary and urgent.

Since the ultrahigh sensitivity of quartz crystal microbalance (QCM) sensors can accurately detect mass uptake on the order of nanograms, QCM has been widely exploited in the field for various chemical sensors, such as organic vapor detection,[2,3] environmental monitoring,[4] and biosensing applications[5,6] in gases or liquids. It is widely recognized that a QCM is useful to evaluate the deposition processes of ultrathin films, including Langmuir–Blodgett (LB) films and this method has also been used for the precise detection of vapors.

Poly(vinylidene fluoride) (PVDF) is a fluorinated polymer with good physical and chemical properties. It exhibits high chemical inertness, nontoxicity, thermal and mechanical stability, and pyroelectric and piezoelectric properties. These properties lead to PVDF wide application in physical sensors.[7–9] But PVDF hasn't been used as sensitive material for chemical sensors.

The most important nerve agents included in modern CW arsenals are tabun, sarin, soman, and VX. Because of high toxicity it was impossible to work with these compounds in ordinary laboratory. Therefore our study was carried out with dimethyl methyl phosphonate (DMMP), the simulant of nerve agents. DMMP was chosen as a simulant for it conforms with those nerve agents to the structure
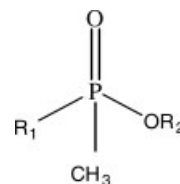
where R_1 and R_2 are differing functional groups. For DMMP, $R_1 = OCH_3$ and $R_2 = CH_3$; for nerve agents, they are other bonds.[1]

In this article, the sensing characteristics of the QCM gas sensor based on PVDF LB film have been reported. The QCM technique can be easily applied to monitor the successive deposition of monolayers and to confirm the reproducibility of the LB film deposition process. The QCM system was also employed to display the kinetic response of PVDF LB film coated sensor against DMMP vapors. The variation of the frequency changes was monitored as a function of time when the sensor was exposed to DMMP vapors.
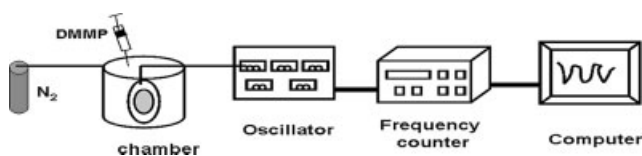
Figure 1 Schematic diagram of the measurement system.

EXPERIMENTAL

The LB films were prepared with a KSV5000 computer-controlled LB trough on a pure water subphase (25°C, resistance 18 MΩ cm, pH 5.6). PVDF (average molecular weight ∼ 534,000, Aldrich) was dissolved in dimethyl formamide. The solution was spread onto the pure water surface, and after a time period of 15 min for the solvent to evaporate, the area enclosed by the barriers was reduced. The monolayer was compressed with a barrier rate of 5 mm/min up to a surface pressure of 25 mN/m. The single layers were deposited onto the different sensors with a vertical dipping rate of 1 mm/min. After a proper drying, the films deposited were ready for gas-sensing experiments.

The resonant frequencies of the commercial QCMs used in this experiment were 6, 8, and 12 MHz, respectively. The measurement set up is given in the schematic diagram of Figure 1. The measurement was conducted in a sealed glass vessel having a volume of 100 mL. The QCM sensors were attached at the inner side of the glass vessel lid. The resonant frequency shifts of QCM sensors due to vapor adsorption were monitored employing a counter (SUING, SS7200 intelligent counter, the Fourth Radio Factory, China), and the recorded data were transferred to the computer versus GPIB interface. QCM-5 Oscillator (Shengyang Vacuum Technology Institute, China) was used to oscillate the QCM device.

Since the vapor pressure of DMMP at 25°C is 112 Pa,[10] it exists as a low-volatility liquid at room temperature. Different concentrations of DMMP vapor were obtained by multiple dilutions.[11] Saturated DMMP vapor was collected in a 60-mL syringe from the headspace above the liquid solvent in a closed container. The vapor was diluted by injecting the vapor sample with different volume into a 100-mL dilution chamber containing clean N_2. When repetitive dilutions were carried out, the aimed concentration was obtained. In operation, N_2 was passed through the test chamber between each vapor injection.

RESULTS AND DISCUSSION

Mass changes of QCM sensor

The relation between the mass changes due to absorbed/desorbed gas molecules and the frequency

shifts was described in detail by Sauerbrey, and the following equation describes the resonant frequency of the QCM[2,12]:

$$\Delta f = \frac{-2f_0^2}{\rho_q^{1/2}\mu_q^{1/2}A}\Delta m \qquad (1)$$

where Δf is the measured frequency shift, f_0 is the resonant frequency of the uncoated QCM, Δm is the mass change per unit area (g/cm^2), A is the piezoelectricity active area, ρ_q is the density of quartz (2.648 g/cm^3), μ_q is the shear modulus of quartz (2.947 × 10^{11} dyn cm^2). The QCM measurements can confirm the reproducibility of LB film multilayer using the relationship between the frequency shifts against mass change. For an LB film, Δf should be related directly to the mass of the layers. The shift in resonant frequency for LB films is given by:

$$\Delta f = \frac{-2f_0^2\Delta m}{K_q}N \qquad (2)$$

where N is the number of deposition layers, Δm is the mass per unit area per layer and $K_q = (\rho_q\mu_q)^{1/2}$. Through this equation, a linear relationship between the mass, the number of layers and the shift in resonant frequency for LB films was clearly indicated.

To investigate the mass sensitivity of the QCM sensors, various LB layers were applied onto the surface of the sensors with different frequencies. Figure 2 shows the resonant frequency shifts measured as a function of the number of the LB layers for three QCM sensors oscillating at 6, 8, and 12 MHz. The results indicate a frequency shift increasing linearly with the number of deposited layers for each QCM device. The slope of the linear relationship gives the sensitivity to the mass loading effect. We have measured a mass sensitivity of 45.08, 73.13, and
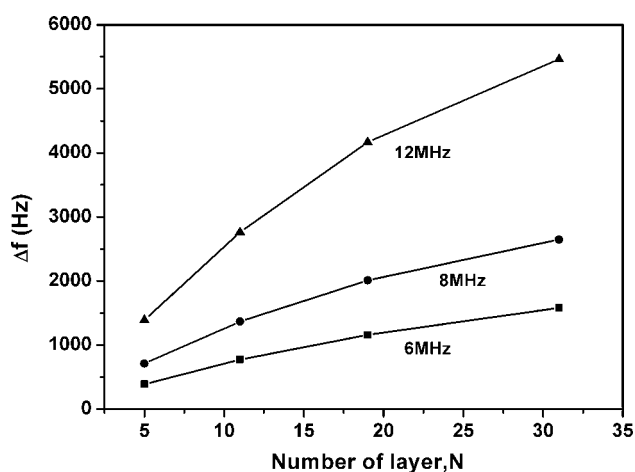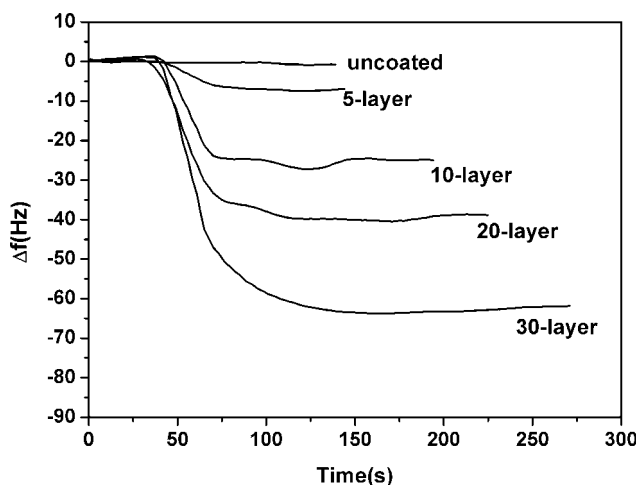

Figure 2 The frequency shifts observed as a function of the number of LB layers applied to the surface of the QCMs.

Figure 3 The frequency shifts of QCM coated with different layers of PVDF LB films as a function of the exposure time to 40 ppm DMMP vapor.

154.20 Hz/layer for the 6, 8, and 12 MHz QCM device, respectively, with a mass sensitivity increasing with the resonance frequency, as theoretically expected.

DMMP vapor sensing properties

Effect of film thickness

The response of the LB films to the DMMP vapor was investigated with the change in film thickness. Figure 3 shows the frequency shift of the 12M QCM sensor coated with different layers of PVDF LB films, and the concentration of the DMMP vapor is 40 ppm. It can be found the frequency response of the uncoated reference QCM is negligible, almost equal to zero. The time to reach the stable level increases with the number of the LB layers, which is due to the longer time it takes for DMMP molecules to diffuse in the films as the thickness increases. However, even for 30-layer films, after exposed to DMMP vapor, the reaction between DMMP vapor and PVDF film was still fast. In the other hand, the response magnitude increases with the film thickness. This fact suggests that a compromise must be made between response magnitude and response time to optimize the performances of PVDF LB films.
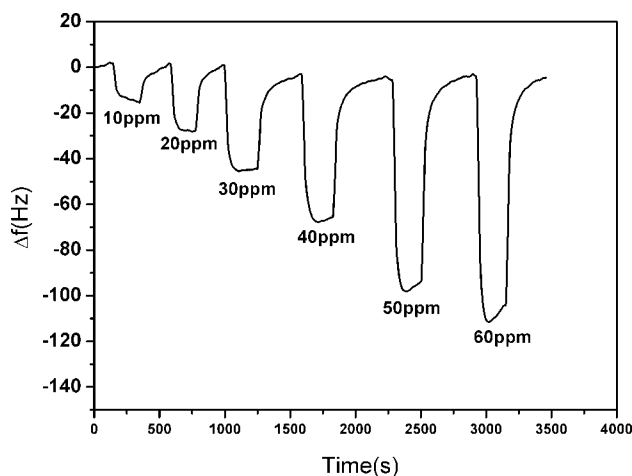
Effect of the DMMP vapor concentration

Figure 4 shows the real-time frequency shifts of the 12M QCM sensor coated with 30-layer PVDF LB films as a function of the exposure time to DMMP vapor at different concentrations. It is obvious that as the concentration increased, the frequency shift also increased. It exhibits good and fast response,

negligible baseline drift, and excellent reversibility. The frequencies of the PVDF-coated QCM sensor can return to the original values after desorption processes, especially at low vapor concentrations. The reason is ascribed to the relatively weak interaction between DMMP molecules and PVDF films. With respect to the nature of interaction between PVDF and DMMP, it is assumed that the quasi-hydrogen bonding[13] occurs due to the fact that the hydrogen atoms of PVDF and oxygen atoms of DMMP have acid and basic properties, respectively. Since the P = O is also existed in the nerve agents, we expect the same absorption will occur with the actual nerve agents.

The frequency increases sharply with time at first when LB film contacts with DMMP vapor, which may be due to the surface adsorption effect, and then increases slowly, which may be due to the bulk diffusion effect.[14] The interaction process between LB film and the adsorbed vapor is a dynamical process. When the LB film is exposed to DMMP vapor, the adsorption and desorption processes will simultaneously occur. After reaching dynamic equilibrium, the number of the adsorbed gas molecules will be equal to the number of the desorbed gas molecules. Then the frequency attains a stable value. The recovery also shows a rapid decrease followed by a slower decrease of frequency when the DMMP vapor is removed, which also can be explained by the surface effect and bulk effect.

The responses are shown in Figure 5 by plotting the frequency shifts against the concentrations of DMMP vapor. The data points were frequency shifts from the DMMP vapor injected-in to the response equilibrium state. It can be seen that the frequency shifts of the sensors are linear to the vapor concentrations.

Figure 4 The frequency shift of QCM coated with 30-layer PVDF LB films as a function of the exposure time to DMMP vapor at different concentration.
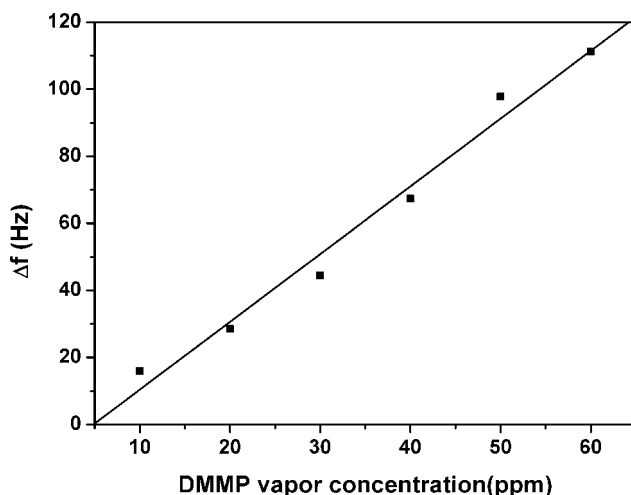
Figure 5 The frequency shift of QCM coated with 30-layer PVDF LB films as a function of the different concentration of DMMP vapor.

CONCLUSION

It is suggested from this study that PVDF is able to form stable monolayer on pure water at room temperature. Deposition onto a QCM substrate using the LB thin film is feasible. The response of frequency shift due to the exposure of DMMP vapor is fast, large and reversible. For the same concentration, the sensitivity increases with the increasing number of LB layers coated onto QCMs. The frequency shifts versus concentrations of the DMMP exhibit a linear correlation. PVDF film has an excellent sensitivity for DMMP vapor and may find potential applications in the development of sensing devices for nerve agents.

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