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TECHNICAL NOTE

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Spun thin films of poly(methyl methacrylate) polymer for benzene sensing

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Abstract
Thin films of poly(methyl methacrylate) (PMMA) were deposited on suitably prepared substrates by spinning the spreading solution in chloroform at 3000 rpm for atomic force microscopy and surface plasmon resonance studies. Four different types of PMMA were used within a range of molecular weight between 540 and 760 kg mol^{-1}. The film surface was found to be uniform. Values of refractive index for PMMA film were found to exist in the range of 1.50 ± 0.04 to 1.53 ± 0.02. All films exhibited fast response to the exposure of benzene vapour but the sensitivity of detection depended upon the molecular weight.

1. Introduction

Poly(methyl methacrylate), commonly known as PMMA, is a transparent, hard and rigid plastic material, often used as a shatterproof replacement for glass and a low temperature non-viscous solvent for lubricating oils and hydraulic fluids. PMMA derivatives find uses as a bone graft template and a femoral window plug in total hip replacement and also in orthopaedic surgery to fix prosthetic components [1, 2]. Intraocular lenses are frequently made of PMMA [3]. The property of optical loss less than 4% due to reflection at the polymer/air interface makes PMMA a suitable material for the cores of communication grade polymer optical fibres and also substrates for polymer optoelectronic devices and integrated waveguides [4, 5]. A PMMA-based interconnection scheme was proposed using index alignment for the realization of MT(TM)-compatible direct connectorized modules [6]. Modified PMMA materials were known to exhibit excellent spectral transmission and a twofold increase in measured laser damage thresholds was attained over conventional PMMA [7]. Using the proton implantation technique, PMMA waveguides are formed at the depths where the stopping power reaches the maximum value [8]. Low optical loss in the visible spectrum, low lateral shrinkage, high scratch hardness, and no glass transition temperature were achieved for PMMA-based transparent organic–inorganic hybrid materials by optimizing the interacting variables of acid catalyst concentration, polymer molecular weight, polymer composition, and thermal treatment [9].

Electrical properties of PMMA films were exploited for sensing applications. An increase in resistance of two to three orders of magnitude was observed for composite thin films of PMMA with carbon nanotubes when exposed to dichloromethane, chloroform and acetone. The sensing mechanism is explained on the basis of volume expansion and polar interaction of various vapours on the nanotube surface [10, 11]. Spin coating is regarded as being a cost-effective, convenient technique for depositing thin films of PMMA on solid substrates. Ellipsometric measurements indicated that the films spun from the spreading solution in toluene were approximately fourfold thinner, but more uniform and of higher quality, than those produced using chloroform as

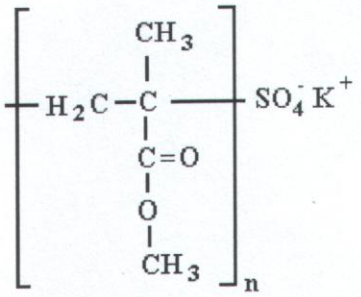

Figure 1. Chemical structure of poly(methyl methacrylate) derivatives: (a) $n = 18\,536$ for PMMA-1, (b) $n = 15\,609$ for PMMA-2, (c) $n = 14\,146$ for PMMA-3 and (d) $n = 13\,170$ for PMMA-4.

a solvent. This attribute was acquired presumably because of the lower volatility and slower evaporation of toluene [12, 13]. It was observed from surface plasmon resonance (SPR) studies on spun films of a PMMA derivative that the film thickness shows a power-law dependence on the spin speed but the thickness increases almost linearly with the concentration of the spreading solution. The room temperature response under dynamic conditions of PMMA films to benzene vapours is found to be fast, highly sensitive and reversible. The sensitivity of detection of toluene, ethyl benzene and *m*-xylene was found to be much smaller than that of benzene [14].

The present article reports the results of SPR measurements on spin coated thin films of modified PMMA polymer with different molecular weights (a schematic structure is given in figure 1). These series were synthesized using the emulsifier-free emulsion polymerization method [15]. The effect of the molecular weight on the film thickness, optical constants and benzene vapour exposure was investigated.

2. Experimental details

Microscopic glass slides were ultrasonically cleaned and then were coated with thermally evaporated 40 nm thick gold at a rate of 1 nm s^{-1} under a vacuum of 10^{-4} Pa. Using a photoresist spinner (model 4000 from Electronic Microsystem) at 3000 rpm, organic overlayers were prepared on gold-coated glass substrates from the spreading solution of the concentration of 1 mg ml^{-1} of PMMA molecules in chloroform. The morphology of the AFM measurement was studied at room temperature in air using a Nanoscope III a (Digital Instruments) microscope in the standard tapping mode. The spring constant of the cantilever was 40 nm^{-1} and the resonant frequency was 300 kHz. The AFM image was taken in an area of 1 μm × 1 μm.

A p-polarized monochromatic He–Ne laser light source (wavelength $\lambda = 632.8$ nm) was employed to excite the surface plasmons using a semi-cylindrical prism (of refractive index $n_p = 1.515$) in a Kretschmann type optical system (see figure 2(a)). Values of the dielectric constant ε and thickness d of the PMMA film were determined from the following expression of resonance shift $\Delta\theta_i$ due to the polymer overlayer

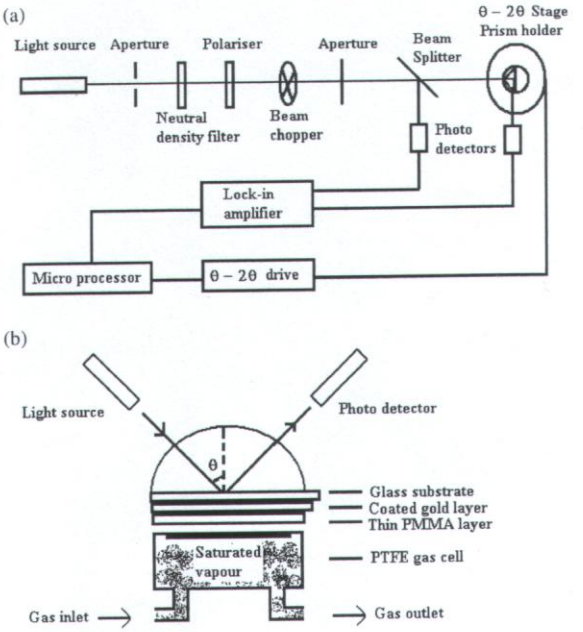

Figure 2. SPR measurement system for film characterization and gas sensing: (a) Kretschmann type optical interrogation; (b) PTFE gas cell.

on the gold-coated glass substrate [16]:

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

where $|\varepsilon_m|$ is the modulus of the complex dielectric constant of the gold film. ε_i is the dielectric constant of the medium in contact with the PMMA thin layer (air and water in this case).

To study the adsorption properties of PMMA thin films on exposure to benzene vapour, the substrates were placed with the sensing membranes facing the top of a specially designed poly(tetrafluoroethylene) (PTFE) gas cell in a leak-proof environment using a rubber O-ring system (see figure 2(b)). For the kinetic measurements the SPR signal was recorded as a function of time at the angle of incidence of 46° near the resonance angle. The photodetector response is measured as a function of time when the sample was exposed to benzene vapour and was allowed to recover by injection of fresh air.

3. Results and discussion

Table 1 summarizes the average particle diameters and average molecular weights of the PMMA polymers at the temperature of 75 °C and the ionic strength of the aqueous phase in terms of the concentration of NaCl. The particle diameters of PMMA beads were found to increase with the rise in the NaCl concentration in the reaction.

Figure 3 shows an atomic force microscopy image of a spin-coated PMMA-1 film on a glass substrate. Pores, 30–60 nm in diameter and 1–4 nm deep, were found to be randomly scattered over the otherwise smooth surface. The pore density was estimated to be in the order of 10^{12} m^{-2}. The rms value of roughness was found to be 2.4 nm.

Table 1. Properties of PMMA molecules.

PMMA type	Molecular weight (kg mol^{-1})	Diameter of PMMA beads (μm)	NaCl concentration (%)	$\Delta\theta_i$ (deg) Resonance shift due to PMMA overlayer on gold substrate	$\Delta\theta_r$ (deg) Resonance shift when PMMA overlayer exposed to benzene vapour	Film thickness, d (μm)		Dielectric constant, ε		Partition coefficient	Sensitivity (%)
						Before exposure	After exposure	Before exposure	After exposure		
1	760	0.22	0	2.238	0.126	7.701	8.202	2.33	2.51	112	93
2	640	0.26	5	3.239	0.458	6.908	7.374	2.31	2.46	115	91
3	580	0.32	10	1.602	0.154	4.970	6.540	2.26	2.90	542	90
4	540	0.35	20	2.061	0.100	1.579	2.023	2.32	2.61	484	90

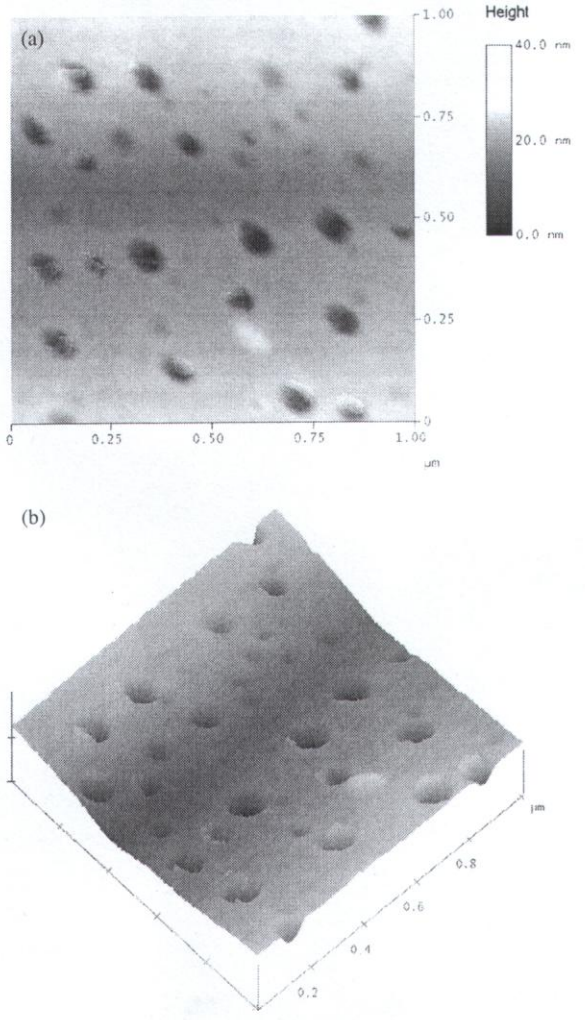

Figure 3. AFM images of PMMA-1 film spun on glass substrates: (a) two- and (b) three-dimensional view.

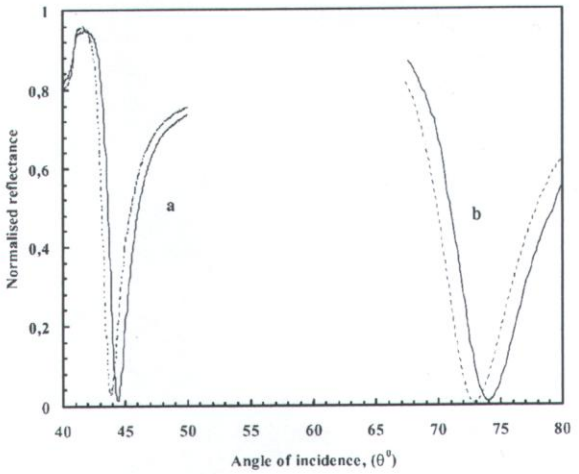

Figure 4. Observed SPR shifts due to the overlayer of PMMA-1 on gold-coated glass substrates: PMMA films in contact with (a) air and (b) water; broken curves were obtained for bare gold films. The spin speed is 3000 rpm.

Figure 4 shows a set of SPR curves obtained for four-layer (glass/gold/PMMA-1/ambient) systems. These curves were produced by the least squares fitting of experimental data to the Fresnel equations of reflection. When the ambient was changed from air to water, the resonance was found to have increased from 44.42° to 74.01°. The substitution of these values in equation (1) gave rise to two equations [17], the graphical solution of which produced the unique values of 7.701 nm and 1.527 for the thickness and refractive index of the polymer film (PMMA-1), respectively. Similar calculations were performed for the remaining three PMMA molecules and the results are summarized in figure 5. The thickness of spin-coated PMMA films was found to increase with the molecular weight increases but the values of refractive index are very similar, varying between 1.496 and 1.550. These values are close to one reported for bulk PMMA [18] and also agree well with the ellipsometric data within the range of 1.499–1.553 at the same wavelength for similarly produced spun PMMA films [13].

A typical SPR curve obtained for the PMMA-3 film before and after the exposure of benzene vapour is shown in figure 6. It can be seen that a large shift, $\Delta\theta_r = 0.154°$, in the SPR minimum occurred due to the adsorption of saturated benzene vapour on the PMMA film (see curves (a) and (b)). Benzene is a planar molecule and has zero dipole moment. The refractive index of benzene is 1.5011, a value close to that of the PMMA film [19] and the effect of benzene adsorption on the refractive index is not expected to be significant. The dissolution of benzene in the bulk of the polymer film is, therefore, believed

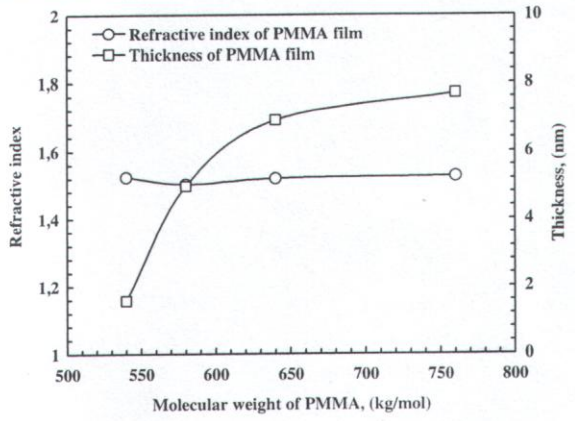

Figure 5. Refractive index and film thickness of PMMA films as a function of molecular weight. The spin speed is 3000 rpm.

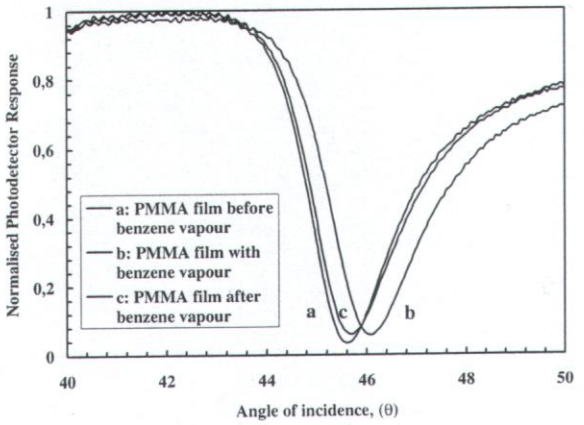

Figure 6. SPR curves for PMMA-3 thin films (a) before, (b) in the environment of and (c) after exposure to benzene vapour.

to form a heterogeneous layer, primarily giving rise to the swelling of the film [20]. A reasonable degree of recovery was also observed with the withdrawal of the organic vapour followed by the injection of dry air. It can be seen that the response of PMMA to benzene is fast and reversible. The theoretical fit of equation (1) to SPR data for the treated PMMA 1 sample gives an increase in thickness, d, from 7.701 nm before exposure to 8.202 nm after exposure. The initial value of the volume fraction ν of the benzene molecules is, therefore, estimated to be 0.065. The partition coefficient f_{pg} is defined as the ratio of the concentration of benzene molecules in the PMMA spun film matrix to that in the gas phase. It has been shown that f_{pg} is related to the volume fraction ν through the following expression [21]:

$$f_{pg} = \frac{\nu \rho RT}{cPM} \tag{2}$$

where ρ, c and M are the density, concentration and molecular weight, respectively, of the organic solvent and P, T and R are the pressure, temperature and universal gas constant, respectively. Assuming values of $\rho = 0.81$ kg m^{-3}, $P =$ 10 kPa and $M = 78.1$, the value of f_{pg} is estimated to be 112.

The kinetic response of PMMA films with different molecular weights to the benzene vapour was recorded by measuring the reflectivity at a fixed angle $\theta^* = 46°$. Figure 7 shows the normalized photodetector response as a function of time when PMMA films were exposed to the benzene vapour for 2 min followed by the injection of dry air for a further 2 min period. All spin-coated PMMA film with different molecular weights show a fast response to the benzene vapour. As soon as the air was injected into the gas cell, PMMA films were found to recover almost fully. The sensitivity σ of the PMMA spun film to benzene is defined as the ratio of $\frac{\Delta I}{I_0}$ where ΔI is the deviation of the photo-detector signal for a vapour relative to the base line signal I_0 obtained in dry air. The sensitivity of PMMA-3 was found to be 89.7. Similar calculations were carried out for the three remaining PMMA derivatives and the results are summarized in table 1.

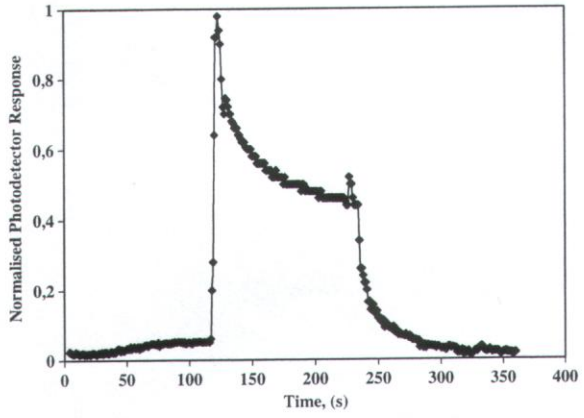

Figure 7. Kinetic response of PMMA-3 thin films to the exposure of benzene vapour.

4. Summary

A series of PMMA molecules with different molecular weights were formulated in thin films using spin coating method. AFM is employed to investigate their surface morphology and film surface is homogeneous and smooth. The value of surface roughness is found to be 2.40 nm. The refractive index of PMMA films is estimated between 1.503 and 1.527 from the SPR experimental results. The film thickness increases with the molecular weight. It can be clearly seen that the sensitivity of benzene detection is dependent on the molecular weight, exhibiting the largest sensitivity for the greatest molecular weight. These films have a fast and reversible response to the benzene vapour. Our results show the potential of PMMA films for application as vapour sensing membranes.

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