INSTITUTE OF PHYSICS PUBLISHING
JOURNAL OF PHYSICS D: APPLIED PHYSICS
J. Phys. D: Appl. Phys. **36** (2003) 1115–1119
PII: S0022-3727(03)56170-8

A04

Poly(methyl methacrylate) films for organic vapour sensing

R Capan[1,4], A K Ray[2], A K Hassan[2] and T Tanrisever[3]

[1] Science Faculty, Physics Department, Balikesir University, 10100 Balikesir, Turkey
[2] School of Engineering, Nanotechnology Research Laboratory, Sheffield Hallam University, City Campus, Pond Street, Sheffield S1 1WB, UK
[3] Science Faculty, Chemistry Department, Balikesir University, 10100 Balikesir, Turkey

Received 15 November 2002, in final form 20 February 2003
Published 16 April 2003
Online at stacks.iop.org/JPhysD/36/1115

Abstract
Optical constants and fabrication parameters are investigated using surface plasmon resonance (SPR) studies on spun films of poly(methyl methacrylate) (PMMA) derivatives in contact with two different dielectric media. A value of 1.503 for the refractive index of PMMA films produced from a solution having concentration of $1\,\mathrm{mg\,ml^{-1}}$ at the speed of 3000 rpm is in close agreement with the data obtained from ellipsometric measurements. 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. These results are in good agreement with the hydrodynamic theory for a low-viscosity and highly volatile liquid. On the basis of SPR measurements under dynamic conditions, room temperature response 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 is much smaller than that of benzene.

1. Introduction

The detection of the BTEX (benzene, toluene, ethyl benzene and *m*-xylene) vapours has been the subject of an intensive investigation in recent years using various optical and acoustic transduction techniques [1]. Among optical methods the surface plasmon resonance (SPR) technique is found to be highly sensitive, offering an accuracy in the order of 10^{-5} per ppm and the glass–silver-polymer (Teflon)–air multilayer system is capable of detecting concentrations lower than 100 ppm of hydrocarbon vapours [2]. Hassan *et al* [3] studied the effect on spun films of amphiphilic calix-4-resorcinarene (C-4-RA) derivatives to exposure of BTEX vapours. The fast and reversible adsorption of ethyl benzene was believed to be associated with the change in the refractive index of the calixarene films due to the host–guest interaction between the cavitand C-4-RA and vapour molecules. Thin films of the schiff base poly(CuMBSH) polymer (where MBSH represents the molecule 5,5′-methylenebis(N-hexadecylsalicylideneamine)) exhibited a reversible shift in the resonance depth and position on exposure to benzene at concentrations as low as 100 ppm [4, 5]. Since the sensitivity of SPR arrangement is related to the refractive index and dipole moment of the detected vapour, the highest detection sensitivity was achieved for benzene with no dipole moment and large refractive index [4]. Assuming a diffusion process of the vapour molecules inside the polymer film, the effect was attributed to the two principal mechanisms of film swelling and increased film density due to the filling of the free volume [5].

In this paper, the optical parameters and organic vapour sensing behaviour of thin films of poly(methyl methacrylate) (PMMA) polymer have been studied using SPR technique. Spin coating method is employed to prepare thin films of PMMA molecules for the measurements. Different types of PMMA derivates were extensively investigated for their electrical properties [6], rheological behaviour [7] and bioactivities [8]. Fluorescence emission from Langmuir–Blodgett thin films of PMMA doped with perylene was exploited for fabrication of selective and robust optical sensors for NO_2 gas with suitable response times for materials aging applications [9]. The chemical structure of a newly modified PMMA which has a head group (SO_4^- K^+) and a long chain

---

[4] Present address: Sheffield Hallam University, School of Engineering, Nanotechnology Research Laboratory, City Campus, Pond Street, Sheffield S1 1WB, UK.

0022-3727/03/091115+05$30.00

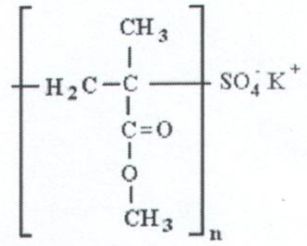

Figure 1. Chemical structure of PMMA derivative.

group is shown in Figure 1 and this derivative is used for this paper. This PMMA is synthesized using the emulsifier-free emulsion polymerization method and the processing of this material was adequately described in a previous publication [10].

2. Experimental details

Ultrasonically cleaned microscopic glass slides coated with 40 nm thick gold films were used as substrates. Gold was thermally evaporated with a rate of 1 nm s^{-1} under vacuum of 10^{-4} Pa and the thickness of the gold film was estimated to be 40 nm using the conventional quartz crystal microbalance method. Gold-coated glass substrates were vacuum held onto a rotating chuck of a photoresist spinner (Microsystem model 4000). Using a micro syringe, a small amount (approximately 50 μl) of the solution of PMMA molecules (molecular weight is 580 000 g mol^{-1} and purity is 98%) in chloroform was dispensed onto the substrate from a distance of 5 mm above the substrate surface. Samples of PMMA thin films were prepared using different concentrations of the solutions and different spin speeds. The concentrations varied between 1 and 12 mg ml^{-1} while a range of spin speeds from 1000 to 6000 rpm was employed.

A Kretschmann type optical set-up system shown in figure 2 was employed for SPR measurements [11]. Prism and sample were mounted on a θ–2θ rotation platform driven by a stepping motor (with a resolution of 0.01°) and controlled by a microprocessor. A *p*-polarized monochromatic (λ = 633 nm) He–Ne laser light source was used to excite surface plasmons. An optical contact between these samples and a semi-cylindrical prism (of refractive index $n_p = 1.515$) was made using an index matching liquid (ethylsalicylate from Aldrich). Optical parameters of spun PMMA thin films were analysed using a least squares algorithm for theoretical fitting of Fresnel's reflection equations to experimental data [12]. PMMA films were produced on silicon wafers for ellipsometric measurements at λ = 633 nm using zero-type instrument (Nanotechnology). The thickness and refractive index were obtained from the numerical solution of the reverse problem using the least squares fitting procedure [13].

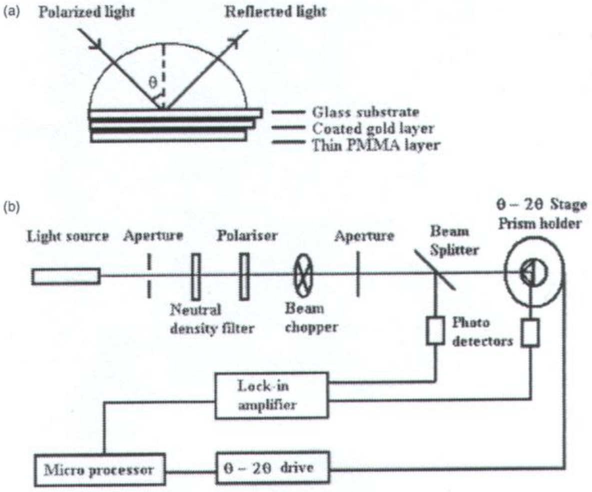

Figure 2. (*a*) A Kretschmann type configuration to measure SPR signals of PMMA thin film. (*b*) Optical set-up system for the SPR measurement.

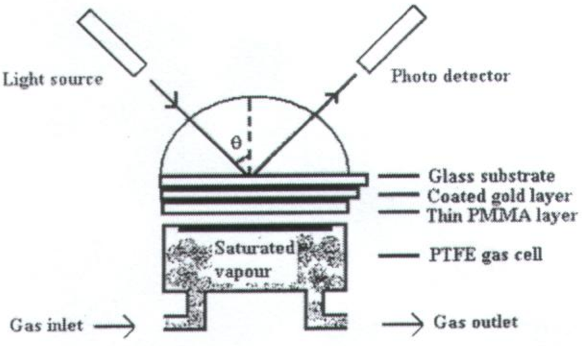

Figure 3. Experimental arrangement of PTFE gas cell.

As shown in figure 3, a special poly(tetrafluoroethylene) PTFE gas cell, which was sealed by the sample through a rubber O-ring system, was constructed to study adsorption properties of PMMA thin film on exposures to benzene, toluene, ethyl benzene and *m*-xylene (BTEX) vapours. Two methods were adopted to obtain dynamic characteristics. In the first method, SPR curves were recorded before and after gas exposures by scanning through the angle range between 39° and 50°. The shift in the position of SPR resonance was employed to determine the sensitivity of vapour interaction with the PMMA film. The second method was concerned with kinetic measurements in which a fixed angle θ^* was chosen near the minimum on the left-hand side of the SPR curve. The reflection intensity at this angle was measured as a function of time when the sample was exposed to an organic vapour for at least 2 min and was then allowed to recover after injection of dry air.

3. Results and discussion

Figure 4 presents the SPR curves showing the variation of reflected intensity as a function of the incident angle θ for a bare gold film and the gold film with a PMMA thin overlayer. The solution concentration of 1 mg ml^{-1} and the spin speed of 3000 rpm were used for producing the PMMA film. SPR measurements were repeated on different points over the PMMA film surface and the results obtained were similar, indicating a reasonable degree of uniformity over the film surface. The minimum of the SPR curve is shifted to a larger angle for the gold film with a PMMA overlayer. The shift $\Delta\theta_a$ depends on the thickness d and complex dielectric constant ε

of the PMMA thin layer and its magnitude can be obtained from Fresnel's equation in the form [14]:

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

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

It is not possible to determine uniquely two unknown quantities d and ε from a single set of measurement of $\Delta\theta_a$. We have recently demonstrated for thin films of tetra-undecyl-tetra-p-nitrophenylazocalix(4) resorcinarene molecules that an additional SPR measurement on organic films in a medium of different known dielectric constant ε_i such as water offers an effective method for simultaneous determination of the film thickness and the dielectric constant [15].

Figure 4 shows another set of SPR curves for PMMA thin film layer in contact with water. The resonance shift $\Delta\theta_w$ is found to be larger than $\Delta\theta_a$. Two values of $\Delta\theta_a$ and $\Delta\theta_w$ gave rise to two sets of equations connecting parameters d and ε of the organic overlayer, the solution of which is given in the form [16]:

$$\varepsilon = \frac{\varepsilon_w^{5/2}\Delta\theta_a\cos\theta_a(|\varepsilon_m| - \varepsilon_a)^2 - \varepsilon_a^{5/2}\Delta\theta_w\cos\theta_w(|\varepsilon_m| - \varepsilon_w)^2}{\varepsilon_w^{3/2}\Delta\theta_a\cos\theta_a(|\varepsilon_m| - \varepsilon_a)^2 - \varepsilon_a^{3/2}\Delta\theta_w\cos\theta_w(|\varepsilon_m| - \varepsilon_w)^2} \qquad (2)$$

where the subscripts w and a refer to water and air as media, respectively. Once ε is known, the value of d can be found from equation (1).

Equations for $\Delta\theta_a$ and $\Delta\theta_w$ were solved in this paper using a graphical method. Values of ε and d were obtained from the least square analysis for theoretical fit of equation (1) to experimental data of $\Delta\theta_a$ and $\Delta\theta_w$. A value of $\varepsilon_m^* = -11.5 + j1.2$ for the complex dielectric constant of the 40 nm thick gold film was used in this calculation [17]. PMMA is transparent at 633 nm and the refractive index of the film is $n = \sqrt{\varepsilon}$. Figure 5 presents two curves showing the variation of refractive index (n) of PMMA film as a function of the thickness d obtained from individual analysis of $\Delta\theta_a$ and $\Delta\theta_w$. The intersection coordinates of two $n(d)$ curves gives the values of 1.503 and 4.97 nm for the refractive index at 633 nm and film thickness of the PMMA film, respectively. A value of 1.516 for the refractive index of PMMA thin film was determined from ellipsometric measurements, indicating an excellent agreement within less than 1% between the results obtained from two independent methods.

In order to investigate the dependence of the thickness of PMMA film on spin speed, six different PMMA films on gold-coated substrates were prepared at different speeds ranging from 1000 to 6000 rpm. The concentration of the spreading solution was always 1 mg ml^{-1}, the same as in the previous SPR experiments. SPR measurements were performed on these samples and the thickness of the PMMA films was deduced from equation (1). Results of calculations are shown in figure 6 in which the thickness d was plotted as a function of spin speed ω on logarithmic scales. The resulting graph shows a linear behaviour and the best linear fit yields a slope of −0.585. In the hydrodynamic theory, the thickness of a spun film is defined as a function of the viscosity η of the spreading solution, the density ρ of the pure solvent and the mass flux ϕ

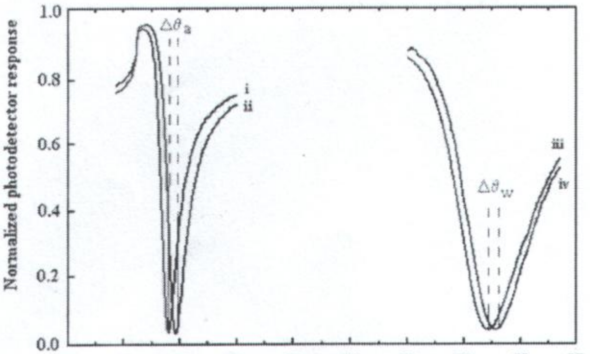

Figure 4. SPR curves with the variation of reflected intensity as a function of the angle of incidence for (i) gold in contact with air, (ii) PMMA thin film layer in contact with air, (iii) gold in contact with water and (iv) PMMA thin film layer in contact with water. The spin speed is 3000 rpm.

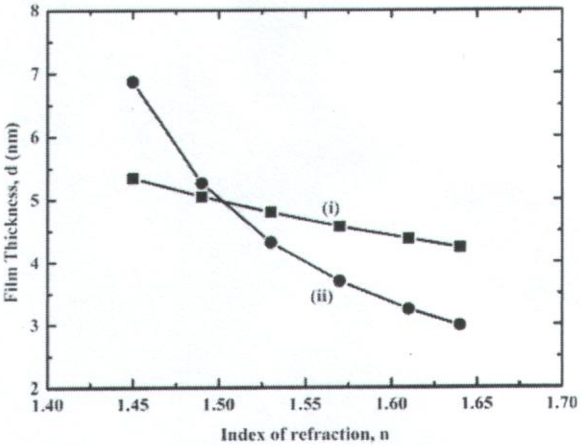

Figure 5. A plot of thickness of a PMMA film as a function of refractive indexes using the theoretical fitting to the SPR curves when PMMA film is (i) in contact with air and (ii) in contact with water. The spin speed is 3000 rpm.

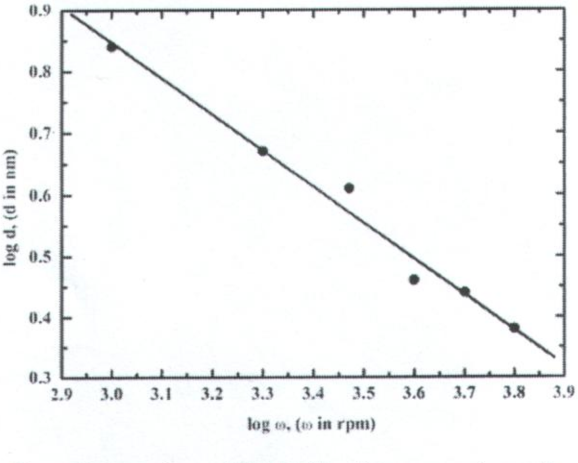

Figure 6. Dependence of PMMA film thickness on spin speeds.

as a result of evaporation in the form [18]:

$$d = \sqrt[3]{\left(\frac{3\eta\phi}{2\rho^2\omega^2}\right)} \tag{3}$$

It is well known that chloroform is one of the highly volatile solvents and the mass flux ϕ can be assumed independent of spin speed in our case because the concentration of 1 mg ml^{-1} was low. If the mass flux is independent of the spin speed for a low concentration, the ratio of (η/ρ^2) also remains invariant for different spin speed. The experimental result of 0.585 is in a good agreement with the value of $(\frac{2}{3})$ theoretically predicted in equation (3).

Measurements were carried out on the samples in which the PMMA overlayers were produced at a fixed spin speed of 3000 rpm using different concentrations of the spreading solutions ranging from 1 to 12 mg ml^{-1}. As before, the thickness was determined from the SPR measurements. Figure 7 shows the trend of monotonically increasing thickness with the concentration of PMMA molecules in chloroform solution. PMMA films are prepared using different amounts of solute in a fixed volume of chloroform solvent in order to vary the concentration of the solution. Chloroform is highly volatile and the loss of the mass is dominantly due to the evaporation of chloroform. The mass flux ϕ is therefore assumed to be constant for different levels of concentration. It can therefore be inferred that the viscosity η increases almost proportionately with the concentrations of spreading solutions.

Figure 8 shows a typical SPR curve obtained for the PMMA film before and after the exposure of benzene vapour. It is clear that a large shift $\Delta\theta_r$ in the SPR minimum occurred due to the adsorption of saturated benzene vapour on the PMMA film (see curves a and b). The shift of SPR minimum is usually explained in terms of an increase in refractive index of the sensitive layer and change in the film thickness due to the film swelling [19]. The refractive index of benzene is 1.5011, a value close to that of the PMMA film [20] and the effect of benzene adsorption on the refractive index is not expected to be significant. It is therefore believed that the resonance shift is primarily caused by the change in the film thickness due to swelling. On injection of clean air into the gas cell, the recovery is found to be almost complete. The response of PMMA to benzene is, therefore, fast and reversible.

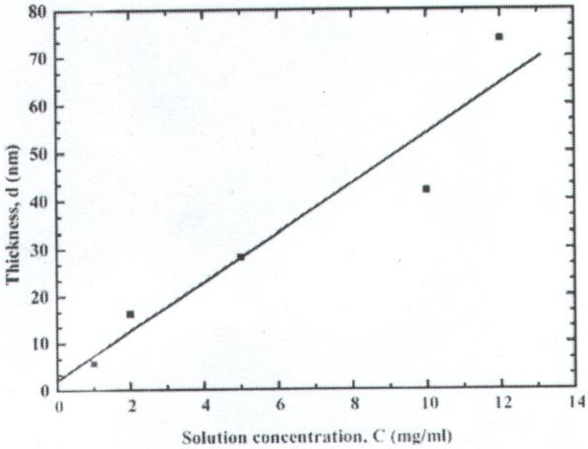

Figure 7. Variation of thickness of PMMA thin film as a function of concentration. The spin speed is 3000 rpm.

Similar investigations were carried out for other BTEX vapours (toluene, ethyl benzene and *m*-xylene) at the nominally same concentrations. Values of $\Delta\theta_r$ which indicates the degree of response are measured with an accuracy of 0.01°. The results of observations were summarized in figure 9 according to the degree of responsivity and it can be seen that PMMA is reasonably selective for benzene. Benzene is a non-polar solvent and toluene, ethyl benzene and *m*-xylene are expected to show stronger solvation than benzene. Dissociated solvent ions may bind a shell of ions, increasing the effective radius for dissolving in the polymer matrix [21]. This dissociation may not occur for benzene, producing the highest SPR response.

Kinetic response of PMMA thin film to the BTEX vapour was recorded by measuring the reflectivity at a fixed angle $\theta^* = 46°$. Figure 10 shows the variation of the intensity signal as a function of time when PMMA films were periodically exposed to the BTEX vapours for 2 min followed by the injection of dry air for a further 2 min period. It can be seen that the response to benzene vapour is the largest of all.

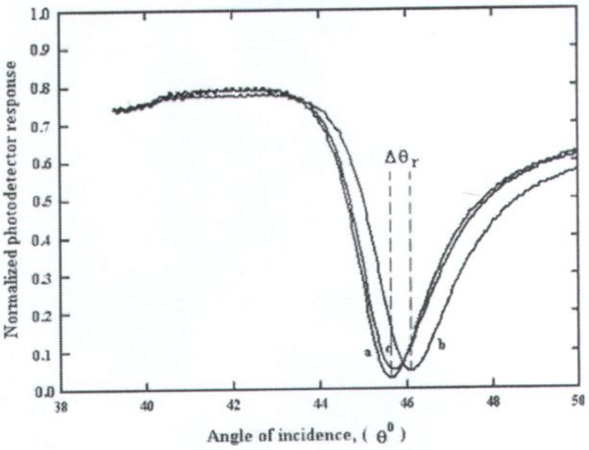

Figure 8. Response of PMMA film to benzene vapour: SPR curves obtained (a) before and (b) after exposure of benzene vapour. Curve (c) recovery after withdrawal of benzene vapour. The spin speed is 3000 rpm.

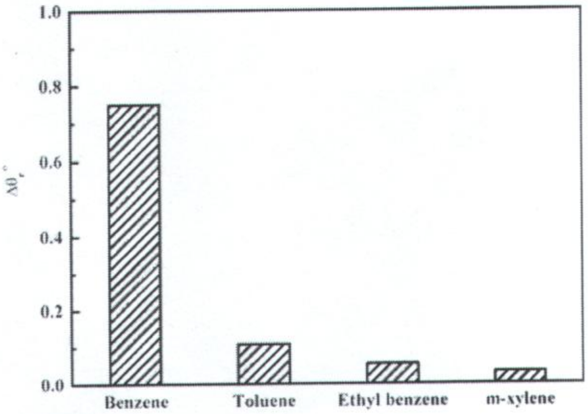

Figure 9. Response of PMMA films on exposure to different members of BTEX family. The spin speed is 3000 rpm.

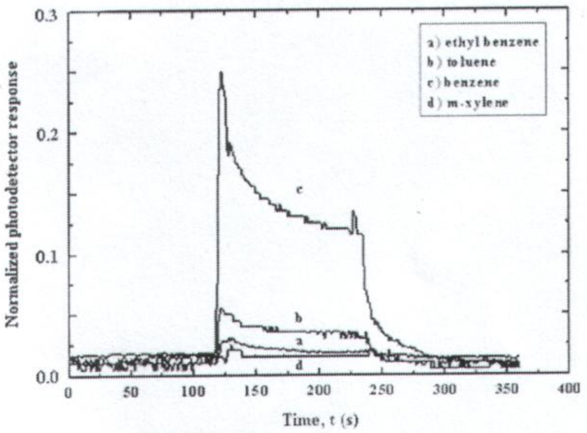

Figure 10. Kinetic response of PMMA film to organic vapours. The spin speed is 3000 rpm.

4. Conclusion

Thin films of PMMA molecules were successfully deposited onto gold-coated substrates by the method of spin coating. A Kretschmann type SPR set-up was employed to investigate the optical parameters and dynamic response of PMMA thin film for the detection of BTEX vapours. SPR measurements indicate that the thickness of the film can be effectively controlled by the spin speed and solution concentration. PMMA film is found to be significantly more sensitive to benzene vapour than other BTEX vapours. The response in terms of resonance shift of the SPR curve to the exposure of benzene vapour is fast, large and reversible. The PMMA film may find potential applications in the development of room temperature optical sensors for benzene vapour.

Acknowledgments

Dr R Capan is grateful to the Leverhulme Trust Foundation for the award of visiting fellow at Sheffield Hallam University. A special thank is due to Dr A V Nabok for his help in ellipsometry measurements. Partial support from the Balikesir University Research Council Foundation is gratefully acknowledged.

References

[1] Schirmer M, Butler B J, Church C D, Barker J F and Nadarajah N 2003 *J. Contaminant Hydrol.* **60** 229–49
[2] Podgorsek R P, Sterkenburgh T, Wolters J, Ehrenreich T, Nischwitz S and Franke H 1997 *Sensors Actuators* B **38–39** 349–52
[3] Hassan A K, Ray A K, Nabok A V and Wilkop T 2001 *Appl. Surf. Sci.* **182** 49–54
[4] Wilde J N, Nagel H and Petty M C 1998 *Thin Solid Films* **327–329** 726–9
[5] Casalini R, Wilde J N, Nagel H, Oertel U and Petty M C 1997 *Sensors Actuators* B **57** 28–34
[6] Rajendran S, Mahendran O and Kannan R 2002 *J. Solid State Electrochem.* **6** 560–4
[7] Chateauminois A and Briscoe B J 2003 *Surf. Coat. Technol.* **163** 435–43
[8] Rhee S H, Hwang M H, Si H J and Choi J Y 2003 *Biomaterials* **24** 901–6
[9] Sasaki D Y, Singh S, Cox J D and Pohl P I 2001 *Sensors Actuators* B **72** 51–5
[10] Tanrisever T, Okay O and Sonmezoglu I C 1996 *J. Appl. Poly. Sci.* **61** 485–93
[11] Kretschmann E 1971 *Z. Physik* **241** 313–24
[12] Hassan A K, Ray A K, Nabok A V and Davis F 2001 *Sensors Actuators* B **77** 638–41
[13] Nabok A V, Hassan A K, Ray A K, Travis J, Hofton M and Dailey A 2000 *IEE Proc.-Sci. Meas. Tech.* **147** 153–7
[14] Pockrand I 1978 *Surf. Sci.* **72** 577–88
[15] Hassan A K, Ray A K, Nabok A V and Panigrahi S 2000 *IEE Proc.-Sci. Meas. Tech.* **147** 137–40
[16] De Bruijn H E, Altenburg B S F, Kooyman R P H and Greve J 1991 *Opt. Commun.* **82** 425–32
[17] Ray A K, Hassan A K, Saatchi M R and Cook M J 1997 *Phil. Mag.* B **76** 961–71
[18] Partridge A, Taussaint S L G, Flipse C F J, Van Ijzendoorn L J and Van Den Oetellar L C A 1996 *J. Vac. Sci. Technol.* B **14** 585–92
[19] Nabok A V, Hassan A K and Ray A K 2000 *J. Mater. Chem.* **10** 189–94.
[20] Bolz R E and Tune G L (ed) 1970 *Handbook of Tables for Applied Engineering Science* (Ohio: The Chemical Rubber Co.) p 68
[21] Wilkop T and Ray A K 2002 *J. Phys. D: Appl. Phys.* **35** 2661–7