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Optical properties of thin PMMA films for sensor application

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In this paper we present results from the study of the optical properties of thin poly (methyl methacrylate) (PMMA) films deposited by conventional spin coating technique and their change during exposure to vapors of some solvents of PMMA, such as chloroform, acetone, methanol and ammonia. The optical constants (refractive index, n and extinction coefficient, k) and the thickness, d were calculated using the measured reflectance spectra, R of the thin films deposited on the Si wafer. The thickness dependence of the optical properties of the thin PMMA layers was investigated. The results for the optical constants showed that the refractive index of PMMA films thicker than 110 nm are independent of the film's thickness. The reflectance changes, $\Delta R/R$ of the thin films from poly (methyl methacrylate) following exposure to vapors of chloroform and methanol were investigated. The obtained results for $\Delta R/R$ were used to calculate the thickness changes of the thin PMMA films after exposure to vapors of different liquids. To explain the resulting change in the optical properties, the dissolution rate of PMMA film in different solutions (chloroform, acetone, methanol and ammonia) was investigated. It was found that the dissolution rate in chloroform and acetone was greater than 63 nm/s, while in methanol and ammonia, the thickness changes were within the experimental error for times greater than 60 min. On the basis of the results obtained the potential application of PMMA layers as building coatings in quarter wavelength optical stack working as optical sensor is discussed.

Key words: optical properties, thin films, PMMA, sensor properties

INTRODUCTION

The presence of volatile organic compounds (VOCs) in the environment as a result of their extensive use in industrial and commercial applications is not negligible. They are toxic and carcinogenic for human health. Detection of these vapors and gases in atmosphere has become an important environmental issue [1–3].

In gas sensing applications one of the most important parameters is the sensing layer which produces a signal during exposure to a toxic gas. In the last decade polymeric thin films have attracted interest for gas sensing applications because of their high sensitivity and selectivity [4, 5].

In terms of its gas sensing performance poly (methyl methacrylate) (PMMA) is a promising chemical material. It has recently been found that PMMA thin films obtained by spin coating and self-assembly are suitable candidates for the detection of several VOCs [6–8]. From the literature it is known that upon contact with chloroform thin PMMA films increase their thickness by $\Delta d = 13.6 - 19.7\%$ [6]. In previous works [9, 10] the possibility was shown for preparation of a Bragg stack from $As_{30}Ge_{10}S_{60}$/PMMA for the infrared spectral range and the potential for gas sensing application.

The subject of the investigation of the present work is to summarize the results of a study on the optical properties of PMMA and their changes during exposure to vapors of some liquids which are solvents of the PMMA such as chloroform, acetone, methanol and ammonia. The potential application as building coatings in 1D photonic crystal working as optical sensor was probed in a three-layered coating consisting from chalcogenide film/PMMA/chalcogenide film.

EXPERIMENTAL DETAILS

The stock solution of the polymer was prepared by dissolution of PMMA (Poly (methyl methacrylate)) in 20 ml of Dichloroethane (Aldrich) at ambient temperature using magnetic stirrer for accelerating the process. The polymer films with different thicknesses were obtained by the method of spin coating using the stock solution further diluted by adding dichloroethane. Polymer layers with thicknesses of 180 nm were obtained by dripping a drop of 0.3 ml of 3.2%w/v polymer solution on a preliminarily cleaned substrate. The speed and duration of spinning were 2500 rpm and 30 s. To remove the extra solvent the samples were annealed at 60 °C for 30 minutes.

The three-layered coatings consisting from chalcogenide film/PMMA/chalcogenide film were prepared by layer-by-layer deposition of As_2S_3 and PMMA. The bulk As_2S_3 glass was synthesized in

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a quartz ampoule by the method of melt quenching from elements of purity 99.999% [11]. The chalcogenide layers were deposited by thermal evaporation at a deposition rate of 0.5–0.7 nm/s in vacuum of 10^{-3} Pa. The X-ray microanalysis shows that the film composition is close to that of the bulk samples. The thickness was controlled in situ by quartz oscillator monitoring and ex situ by optical and profiler measurements.

Transmittance, T and reflectance, R spectra of single layers and three-layered stacks were measured at normal and oblique incidence of light with a high precision UV-VIS-NIR spectrophotometer Cary 5E (the accuracy in T and R at normal incidence are 0.3% and 0.5%, respectively).

The spectrophotometer is equipped with a gas cell which allows in-situ measurements of the spectrophotometric quantities in the presence of a given gas.

RESULTS AND DISCUSSION

Reproducible deposition of the polymer layers by spin-coating technique necessary to create a calibration curve for the dependence of the thickness of the resulting layer on the concentration of the solution employed for the deposition. The knowledge of the optical parameters of the polymer films is very important for the adaptability of the material for different applications. The refractive index, n and extinction coefficient, k and the thickness, d of the spin-coated PMMA films deposited on Si wafer were determined through minimization of a function consisting of the discrepancies between measured and calculated R spectra using multi-wavelength nonlinear curve fitting [12]. For description of the refractive index the Sellmeier's equation was applied:

$$n^2(\lambda) = 1 + \frac{A_1\lambda^2}{\lambda^2 - A_2^2}, \qquad (1)$$

where A_1 and A_2 are the Sellmeier's coefficients. The dispersion of the extinction coefficient was described by the following exponential dependence:

$$k = B_1 \exp(B_2/\lambda), \qquad (2)$$

where B_1 and B_2 are dispersion coefficients The results for the calibration curve for the film's thickness are presented in Fig. 1. It is seen that the thickness of the spin-coated PMMA films depends on the concentration of the solution following a linear approximation.

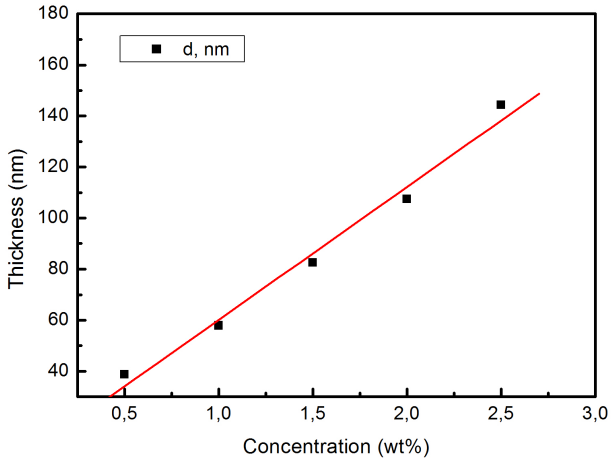

Fig. 1. Dependence of the thickness of the spin-coated PMMA film on the solution concentration.

The obtained dependence of the refractive index on the thickness of the polymer films is plotted in Fig. 2.

It is seen that the refractive index of thin PMMA films increase with the increasing of the thickness following an exponential low of the type $n = n_0 + A_1(1 - \exp(-d/d_1))$, where n_0 is the initial value of the refractive index, $A_1 = -0.90$ and $d_1 = 31.91$ are parameters. The values of the refractive index for films with thicknesses greater than 110 nm are close to that of the bulk material ($n_{\text{bulk}} \sim 1.49$) [13, 14]. It can be expected that with the increasing of the film's thickness the film's density increases, which is the most likely cause for the observed trend of the curve.

It is well known that PMMA swells when exposed to organic vapors [8, 15], which results in a shift of the reflection spectrum. Our next step was

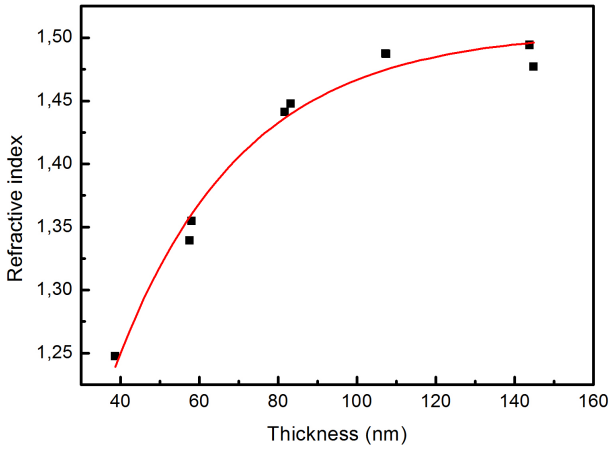

Fig. 2. Dependence of the refractive index on the thickness of thin spin-coated PMMA films at wavelength of 600 nm.

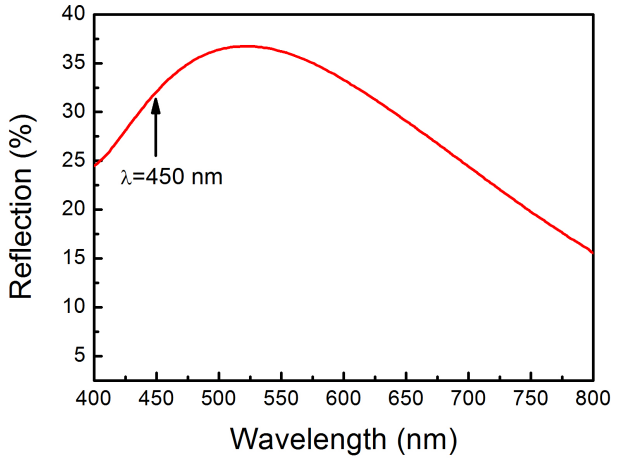

Fig. 3. Reflection spectra of a spin-coated PMMA film with thickness 180 nm on a glass substrate.

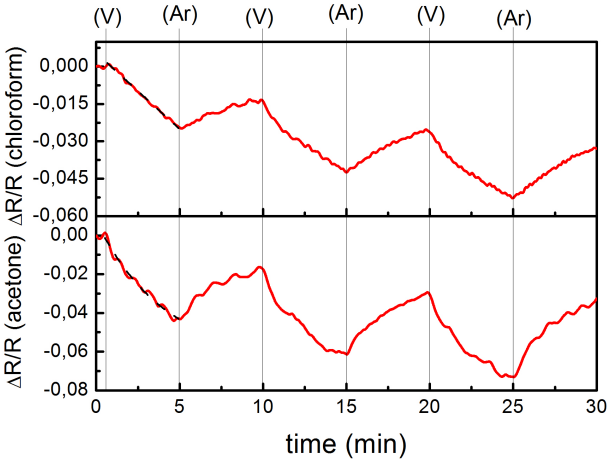

Fig. 4. Changes in the reflection at $\lambda = 450$ nm of a single PMMA film with thickness 180 nm exposed to methanol (a) and ammonia (b) vapors in argon atmosphere at temperature 0°C (V) and subsequent treatment with argon (Ar).

to investigate the changes of the optical properties of thin PMMA films during exposure to vapors of different substances in order to determine their ability for sensing of different vapors. We measured how the reflectance from PMMA films at a fixed wavelength changes as a result of the induced increasing of the thickness. The working wavelength was chosen to be in the steep part of the interference extreme where the value of the reflectance depend strongly on the wavelength and maximum changes in R can be expected (Fig. 3). We traced the change of the reflection at a wavelength of $\lambda = 450$ nm in dependence on the time of exposure to vapors. The reflectance measurement was performed in-situ, consecutively introducing vapors of liquid solvent putted at 0°C of the substance with argon and argon only in a gas cell for 5 minutes. We have performed three and more cycles for each substance. The results are plotted in Figs. 4 and 5.

It is seen in Fig. 4 that the time dependence of $\Delta R/R$ follows an exponential law of the type $y = y_0 + A_1 \exp(-x/t_1)$, where y_0 is the initial value of the reflectance, A_1 and t_1 are parameters. The determined values for A_1 were 0.072 and 0.020 for methanol and ammonia, respectively. The parameter t_1 has a physical meaning of diffusion coefficient of the vapors in the PMMA film. The values for t_1 were 0.64 min and 0.33 min for methanol and ammonia respectively.

After the third repetition of exposure to different vapors the changes in the reflection continued. The argon treatment following treatment with methanol Fig. 4 (a) and ammonia Fig. 4 (b) vapors is sufficient to restore the initial state of the reflectance spectra. From Fig. 4 it is seen that the changes in the reflection are $\Delta R/R = 3.7\%$ after exposure to methanol and $\Delta R/R = 1.3\%$ after exposure to ammonia.

The exposure of the PMMA films to the vapors of chloroform and acetone also leads to changes in the reflection (Fig. 5).

But in this case the argon treatment cannot restore the original state of the polymer film.

It is seen in Fig. 5 that the time dependence of $\Delta R/R$ follows again an exponential law of the type $y = y_0 + A_1 \exp(-x/t_1)$.

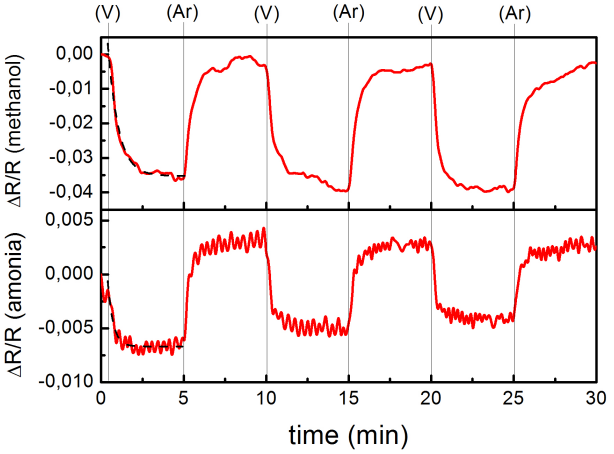

Fig. 5. Changes in the reflection at $\lambda = 450$ nm of a single PMMA film with thickness 180 nm exposed to chloroform (a) and acetone (b) vapors in argon atmosphere at temperature 0°C for 5 minutes (V) and subsequent treatment with argon for 5 minutes (Ar).

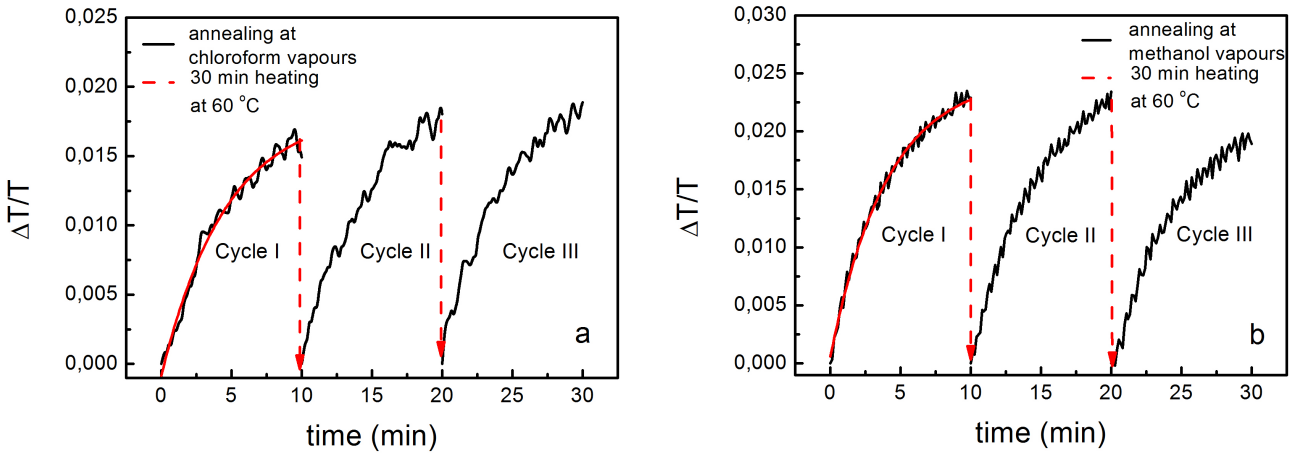

Fig. 6. Time dependence of the transmittance of three-layered coatings from As_2S_3 and PMMA with thicknesses 54 nm and 180 nm respectively exposed to chloroform (a) and methanol (b) vapors in argon atmosphere at 0°C. The annealing procedures at 60°C for 30 minutes are only signed with dot lines.

The determined values for A_1 were 0.32575 and 0.072 for chloroform and acetone, respectively. The diffusion parameter t_1 is estimated at 4.74 min and 4.13 min for chloroform and acetone respectively. The vapors of chloroform and acetone demonstrated significantly higher values for t_1 than those for methanol and ammonia.

The results plotted on Fig. 5 show changes in the reflection, $\Delta R/R$ of 2.5% at exposure to chloroform vapors (a) and $\Delta R/R = 4.5\%$ at exposure to acetone vapors (b). It is seen that the treatment with argon recovers about 50% of the initial state of the polymer film.

Considering the type of the curves following treatment two groups of reagents of the chosen substances may be distinguished. It is known that all of the investigated substances – methanol, ammonia, chloroform and acetone are solvents of PMMA. To determine how they reacted with the PMMA films we investigated the dissolution rate of 180 nm polymer film in liquid solvents. The experiment consists in immersing the film in a given solvent for an exact time. The reflection spectrum of treated film was collected afterwards and the thickness and optical constants were calculated by the above-described procedure. The dissolution rate was determined as:

$$V = |d_1 - d_0| / \tau, \qquad (3)$$

where d_0 and d_1 are the film's thicknesses before and after immersion in the solvent, respectively, τ is the duration of the treatment. For methanol and ammonia, we established that the thickness changes are within the experimental error for treatment longer than 60 min, while the dissolution rate of films from the second group (chloroform and acetone) is 63 nm/s.

In a prior work [16, 17] we demonstrated the potential application of the thin PMMA layers as building coatings in a quarter wavelength optical stack working as optical sensor and the permeability of the thin As_2S_3 film to chloroform. It is necessary to demonstrate a method to restores the original state of the structure. To this end, three-layer coatings consisting of As_2S_3/PMMA/As_2S_3/glass substrate were prepared. The relative changes of the transmittance in chloroform (a) and methanol (b) vapors are shown in Fig. 6. Since the presence of the As_2S_3 film delays the reaction of the PMMA [17], for removing the absorbed vapors we heated the structure at 60 degrees for 30 minutes.

It is seen in Fig. 6 that the time dependence of $\Delta T/T$ follows an exponential law of the type $y = y_0 + A_1 \exp(-x/t_1)$, where A_1 is -0.019 and -0.024 for chloroform and methanol respectively. The values for t_1 are 4.59 min for chloroform and $t_1 = 4.06$ min for methanol.

After exposure of the three-layer system to vapors it was found that the changes after the third iteration are similar for both kinds of vapor and also that the thermal treatment restores the original state of the coating. It is seen in Fig. 6 that the relative change of the transmittance is $\Delta T/T = 1.7\%$ after exposure to chloroform vapors and after exposure to methanol vapors – 2.2%.

CONCLUSIONS

In the present work the optical properties of thin PMMA films and their changes due to exposure to vapors of some solvents of PMMA are investigated. It was found that the refractive index is thickness dependent for values of $d < 110$ nm. For thin films with thickness greater than 110 nm the coatings possess refractive index close to that of the bulk. The changes of the optical properties during exposure to vapors of chloroform, acetone, methanol and ammonia were followed. When the thin polymer films were exposed to vapors of methanol or ammonia and subsequently treated in argon restoration of their initial state was observed for many cycles. In the case of treatment with chloroform or acetone, again cyclic changes were displayed but the treatment with argon restores only 50% from the initial state of the reflectance spectrum. The obtained changes in the reflectance spectrum were in the range of 1.3–4.5%. Maximal values were observed after exposure to vapors of methanol and acetone. The potential application of a three-layered coating consisting from chalcogenide film/PMMA/chalcogenide film as building stack for 1D photonic crystal working as optical sensor was probed. It was found that the changes after exposure of the multilayered coatings to the vapors of the chloroform and methanol showed good cyclic properties as the treated films must be annealed at 60^{o}C for 30 minutes. The magnitude of the obtained changes observed in the reflectance of the three layered coatings was the similar (1.7–2.2%) to that of the single polymer films.

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ИЗСЛЕДВАНЕ НА ОПТИЧНИТЕ СВОЙСТВА НА ТЪНКИ PMMA СЛОЕВЕ ЗА ПРИЛОЖЕНИЕТО ИМ КАТО СЕНЗОРИ

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(Резюме)

В настоящата работа са представени резултати от изследването на оптичните свойства на тънки ценрофужно отложени тънки филми от poly (methyl methacrylate) (PMMA) и тяхната промяна при взаимодействие с пари на хлороформ и метанол. Оптичните константи (показател на пречупване, n и коефициент на поглъщане, k) и дебелината, d са изчислени от измерените спектри на отражение R, за слоеве, отложени върху силициева подложка. Резултатите показват, че показателят на пречупване за тънките филми с дебелина над 110 nm съвпада с този на обемния материал. Проследена е относителната промяната на коефициента на отражение $\Delta R/R$ при излагане на тънки филми от poly(methyl methacrylate) на пари на хлороформ и метанол. От получените резултати за $\Delta R/R$ са пресметнати промените в дебелината на тънките слоеве след третирането им. За да бъдат обяснени получените промени в оптичните свойства е изследвана скоростта на разтваряне на тънки слоеве от PMMA в различни разтворители (хлороформ, ацетон, метанол, амоняк). Установено е, че в хлороформ и ацетон скоростта на разтваряне на покритията е по-голяма от 63 nm/s, докато в метанол и амоняк промените в дебелината са в рамките на грешката за времена по-големи от 60 min. На основа на получените резултати е обсъдено потенциалното приложение на слоеве PMMA, като градивен елемент в четвърт вълнови оптични стекове, работещи като оптични сензори.