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HIGH PRECISION INTERFEROMETRIC THICKNESS ANALYSIS OF SUB-MICROMETERS SPIN-COATED POLYEPOXYPROPYLCARBAZOLE FILMS

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Abstract. This paper deals with the interferometric thickness measurements of the spin-coated submicrometer polymer films based on polyepoxypropylcarbazole. The measuring system including the conventional microinterferometer MII-4 with attached webcamera and software for the high precision measurement of the submicrometer thicknesses of films was designed and developed. Different concentrations of polymer solution and spin speed were used in order to obtain thin films with thicknesses in the range from 160 nm to 960 nm. It was shown that there was a linear dependence of obtained film thickness on polymer solution concentration, but the significant effect of spin speed on film thickness wasn't observed.

Keywords: spin-coating, microinterferometer MII-4, thickness measurement system, digital interferograms processing, submicrometer thin films

ПРЕЦИЗІЙНИЙ ІНТЕРФЕРОМЕТРИЧНИЙ АНАЛІЗ ТОВЩИНИ СУБМІКРОННИХ ПОЛИТИХ ПОЛІМЕРНИХ ПЛІВОК

А. Ю. Мєшалкін, В. Г. Абашкін, А. М. Прісакар, Г. М. Трідух, И. С. Андрієш, Л. П. Бєц, Е. А. Акімова

Анотація. У статті розглядається інтерферометричне вимірювання товщини субмікронних полімерних плівок на основі полиепоксипропілкарбазола, отриманих методом поливу на скляну підкладку, яка обертається в центрифузі. Для прецизійного виміру субмікронних товщин запропонована система, що включає мікроінтерферометр МИИ-4 із установленою веб-камерою

і з обробкою інтерферограм за допомогою розробленого програмного забезпечення. Для одержання тонких полімерних плівок різної товщини (від 160 нм до 960 нм) використали різні концентрації розчину полімеру і швидкості обертання підкладки. Показано, що існує лінійна залежність отриманої товщини плівки від концентрації розчину полімеру і незначний вплив швидкості обертання підкладки на товщину плівки.

Ключові слова: покриття, отримане методом центрифугування, мікроінтерферометр МИИ-4, система виміру товщин, цифрова обробка інтерферограм, субмікронні тонкі плівки

ПРЕЦИЗИОННЫЙ ИНТЕРФЕРОМЕТРИЧЕСКИЙ АНАЛИЗ ТОЛЩИНЫ СУБМИКРОННЫХ ПОЛИТЫХ ПОЛИМЕРНЫХ ПЛЕНОК

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Аннотация. В статье рассматривается интерферометрическое измерение толщины субмикронных полимерных пленок на основе полиэпоксипропилкарбазола, полученных методом полива на вращающуюся в центрифуге стеклянную подложку. Для прецизионного измерения субмикронных толщин предложена система, включающая микроинтерферометр МИИ-4 с установленной вебкамерой и с обработкой интерферограмм с помощью разработанного программного обеспечения. Для получения тонких полимерных пленок различной толщины (от 160 нм до 960 нм) использовали различные концентрации раствора полимера и скорости вращения подложки. Показано, что существует линейная зависимость полученной толщины пленки от концентрации раствора полимера и незначительное влияние скорости вращения подложки на толщину пленки.

Ключевые слова: покрытие, полученное методом центрифугирования, микроинтерферометр МИИ-4, система измерения толщин, цифровая обработка интерферограм, субмикронные тонкие пленки

1. Introduction

Nowadays polymers play a critical role in the advancement of the microelectronics and optoelectronics industry. They serve as photoresists in microlithography and as insulating dielectric materials in chips, displays, interconnectors, and photonic devices [1, 2]. A large number of different deposition techniques are used for the production of thin polymeric films for optical applications. The most important categories are thermal vaporization, sputtering, and chemical deposition. It is obvious, that for each polymer is required suitable deposition technique [3]. Properties of thin films including optical, mechanical, electrical and thermal properties are depend on deposition parameters such as temperature, viscosity, evaporation velocity. The self-assembly [4], the co-extrusion [5] and the spin coating [6, 7] is used for fabrication of the layer structures based on polymers. However, obtaining of thin polymer films with required uniform thickness and accurate control of the layer thickness remains the important problem in thin film researches. Spin coating is one of the technological and well controlled and accessible method of obtaining polymeric thin films. Kimura M. et al. [8] first fabricated multi-layered structures using polystyrene and polyvinylalcohol. Recently, A.L. Alvarez et al. [9] also demonstrated polymeric multi-layered structures obtained by spin coating of polyvinylcarbazole and polyvinylalcohol. In both cases, accurate control of the optical thickness up to a quarter wavelengths was not achieved. So, the measurement of the thickness of transparent films becomes one of the important problems in optics research and in industry. This is especially important in the case of optical applications (e.g. interference filters), where the optical properties of the construction element are mainly determined by the film thickness of the deposited material. The most common methods of thickness measurement available commercially

are ellipsometry [10], the spectral reflectance/ transmittance method [11], interferometry [12], profilometry [13] and atomic-force microscopy [14]. Each of them has its advantages and disadvantages, but the interferometry combines high precision with nondestructive measurement. The choice of polyepoxypropylcarbazole as material for thin film obtaining was based on its importance as optical recording media and its photoinduced optical properties [15-16].

The main task of the work was to study the influence of spin-coating conditions (concentration of polymer solution and angular velocity) on the thickness of polyepoxypropylcarbazole (PEPC) thin films measured by modified microinterferometer MII-4 with developed soft for interferogram analysing.

2. EXPERIMENTAL

Synthesis of polymer. PEPC was selected since it was known as having excellent film forming properties and its photoinduced properties. PEPC used in this investigation was synthesized by polymerization of epoxypropylcarbazole at the presence of 1-3% potassium methylate on the anionic mechanism at temperature 100˚C during the course of 4 hrs. For the full drying it was stored in a drying chamber at 50˚C up to constant mass was achieved. The molecular weight was obtained within the range 2000-3000 from the characterization of polymer viscosity using calibrated standards. The scheme of synthesis of monomer epoxypropylcarbazole and chemical structure of polymer PEPC are presented on Fig. 1.

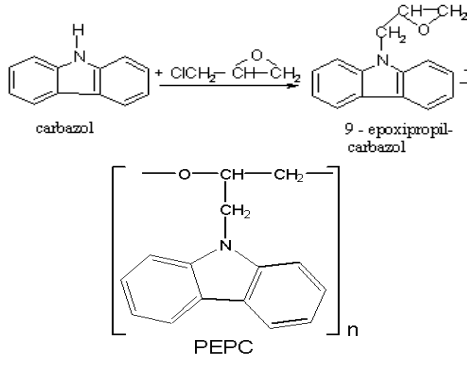

Fig. 1. The scheme of synthesis of monomer epoxypropylcarbazole and chemical structure of polymer PEPC used in this study.

Formation of polymer films from solution.

The thin polymer films were prepared from homogeneous polymer solution by spin coating procedure using programmable spin-coater "SGS Spincoat G3P-8". There are several major factors affecting the resulting polymer film thickness during coating process: angular velocity, viscosity, acceleration, spin time and exhaust.

Operation conditions for depositing of polymer solution on 50mm diameter flat optical glass disk (BK7) were as follows: 1 ml of liquid polymer solution was dispensed on the disk at rest, subsequently accelerated in about 10 s up to angular velocity in the range of 500÷7000 rpm and spun for 20 s. To remove the remaining solvent films were solidified inside Petri dish at room temperature (22ºC). Time of drying was about 24 hours.

The used coating cycle of angular velocities and accelerations is shown on Fig. 2.

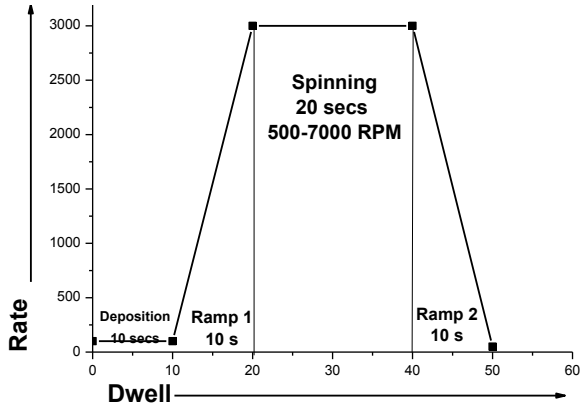

Fig.2 Rate/time schedule of spin-coating for polymer films

Film thickness measurement.

For the determination of film thickness the MII-4 interference microscope was applied which has been modified by webcam. It gives us the possibility to connect the microscope with PC for digital processing of interferograms.

A thickness determination of the samples was achieved by a MII-4 interference microscope with webcam micrographs recorded. The interference pattern of light reflected from a glass reference surface and from the polymeric one was acquired by webcam in PC throughout USB port. We used the magnification of interferometer as much 490^{x}.

The area of film was at 0.3mm dia circle from which interference pattern analysis was performed.

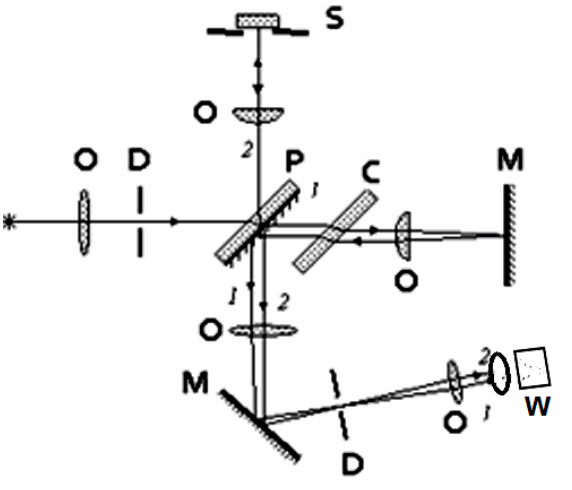

Fig.3. Optical scheme of modified MII-4 inter-ference microscope. 1 — reference beam, 2 — object beam, O — objectives, D — diaphragms, M — mirrors, P — beam-splitting plate, C — com-pensating plate, S — sample, W — webcamera with optics.

The optical scheme of MII-4 is shown in Fig.3.

The interference fringe shift in interferogram introduced by different height of layer is shown in Fig. 4.

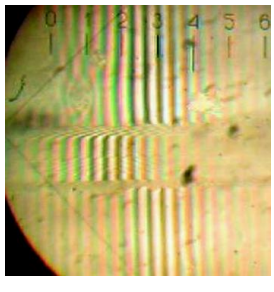

Fig.4. Achromatic interference fringe shift c in interferogram introduced by different height of layer. Photo of interferogram obtained by webcamera and computerized MII-4.

In case of the interferometer microscope MII-4 the value of calculated thickness h of opaque or transparent layer is proportional to shift c of interference fringes (Fig. 5a) and inverse proportional to their width b

$$h = \frac{\lambda}{2} \cdot \frac{c}{b}, \quad h = \frac{\lambda}{2} \cdot \frac{c}{b(n-1)}, \qquad (1)$$

where λ is the wavelength of light, n – refractive index of the film material. The first expression refers to the opaque films, and the second – to the transparent films. Using the software for interferogram processing in order to determine the parameters b and c allows on the one hand to greatly improve the accuracy of this determination, compared with the visual method, and on the other hand to facilitate the implementation of the measure. In addition, it is possible to process and store the measurement results in electronic form.

With aim to achieve these advantages the software tool named OpticMeter has been elaborated for computer processing of inter-ferograms. It permits to fit the interference patterns in an analytical form and precisely calculate the lines shift corresponding to thickness of sub-micrometer films.

The tool's methods are based on the mathe-matical model of interferograms and the least squares method of fitting the lines of minima and maxima in interferogram. In order to determine b and c it is necessary to construct the extremes lines (minimum or maximum).

As seen in Figure 4, in order to accurately determine the parameters b and c the extreme lines (minima or maxima) for the biased and unbiased central interferogram bands must be build up to the appropriate precision. For this purpose, the set of extreme points of a given type (min or max) are defined in three rectangular areas N_1, N_2 and N_3 the selected in an interactive mode (Fig. 5b).

It is important that each rectangle covers only one type of extreme lines pre-selected in the interactive mode (regions of the minima in Fig. 5). The rectangles are positioned in areas with the best image quality of the central achromatic fringes. To improve the quality of the image pre-processing techniques are provided, especially smoothing and filtering for noise removal.

In the simplest case it is assumed that the interference fringes are strictly parallel to the frame borders (i.e. borders of the pixel's matrix) and, therefore, the lines of extreme points should be parallel to the vertical borders of the frame (Fig. 5c). In this approximation the values of the coordinates J for all extreme lines can be carried out as the average values of the extreme points coordinates j (one per horizontal line in

the rectangle). Thus, the coordinates J_1, J_2 and J_3, representing the average coordinates of extreme points for rectangular areas N_1, N_2 and N_3 respectively, are determined.

Rectangles N_1 and N_2 are arranged in such a way that they covered the sets of adjacent extreme points of the same type and allow to determine the width of the interference fringes b as the difference in absolute coordinates of lines $|J_1 - J_2|$. The rectangle N_3 is positioned so that it covers the shifted set of the extreme points with respect to the N_2 area, so that the difference in absolute value $|J_3 - J_2|$ determines the shift c of the interference fringes. Thus the desired thickness h is defined by the formula:

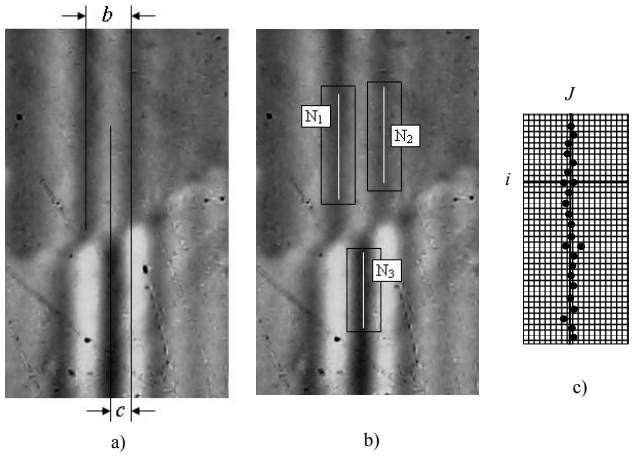

Fig.5 Example of the interferogram processing: a) b – the distance between two adjacent interference fringes; c – shift of the interference fringe; b) Interactive selection of N1, N2 and N3; c) Determination of coordinates of extreme points of lines in the Ni area.

$$h = \frac{\lambda}{2} \cdot \frac{c}{b} = \frac{\lambda}{2} \cdot \frac{|J_3 - J_2|}{|J_1 - J_2|}. \qquad (2)$$

In the real measuring process a strict parallelism can not be achieved (Fig. 6a) and the set of extreme points (one per line) is located along the slope to the vertical boundary line (Fig. 6b). Analytical determination of the slope line position can be carried out using mathematical methods of linear fitting approximation in frame of the least-squares method.

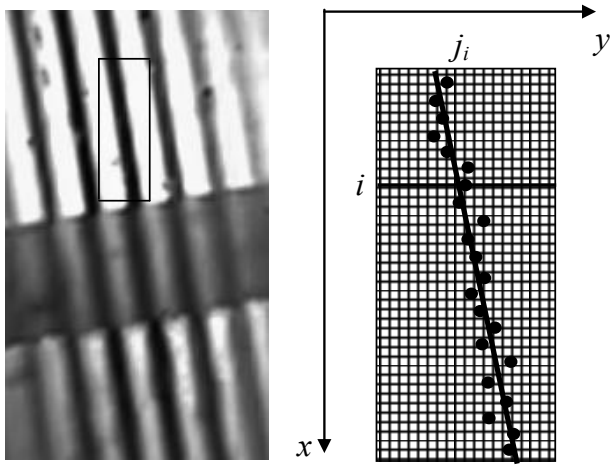

Fig. 6. a)-Example of fringes nonparallel to the boundaries of frame and b) slope line of extreme points.

For this purpose, for each rectangle the approximation function of extreme line in form $y = ax + b$ is searched, where a and b are the unknown parameters. In this notation, the x-axis is perpendicular to the rows of pixels, and y - parallel (Fig. 6b). Following the standard least squares method, we can obtain analytical expressions for the extreme lines in all three rectangles N_1, N_2 and N_3:

$$\begin{aligned} y_1 &= a_1 x + b_1, \\ y_2 &= a_2 x + b_2, \\ y_3 &= a_3 x + b_3. \end{aligned} \qquad (3)$$

These lines should be parallel to each other in compliance with the physical condition, so the distance δ between them in a common coordinate system is defined by the formula (4):

$$\delta = \frac{|b_1 - b_2|}{\sqrt{a_1^2 + 1}}. \qquad (4)$$

The final expression for the desired thickness h has the following form:

$$h = \frac{\lambda}{2} \cdot \frac{c}{b} = \frac{\lambda}{2} \cdot \frac{|b_3 + Y_3 - b_2 - Y_2|}{|b_1 + Y_1 - b_2 - Y_2|}. \qquad (5)$$

Here, the distances Y_1, Y_2 and Y_3 are introduced,

for which the corresponding rectangles are separated from the left vertical frame borders.

3. RESULTS AND DISCUSSION

Optical grade of surface quality and uniformity of the films was confirmed by the smooth interference fringes in the interferogram obtained by MII-4. Several samples were prepared out of the same solution. To check the reproducibility of observed structures, the several samples were prepared in the same conditions and examined. In sample series A, PEPC concentration of the solution was kept fixed (10 wt% solutions of the PEPC polymer in chloroform $CHCl_3$, boiling point is 62°C) and set of angular velocities was chosen in range pointed above. In sample series B, the PEPC concentration was varied (2.5, 5, 7.5,10, 12.5 wt% solutions in chloroform) and deposition carried out at fixed angular velocity.

In this experiment a very accurate surface cleaning was carried out, and it was confirmed by many repetitions of the preparation that manifest the same morphology. Though each individual sample shows a different surface features the statistical features of the film morphology remain the same.

The interferograms of the polymer films spin-coated from solutions with different polymer concentrations taken by webcamera are shown in Fig. 7.

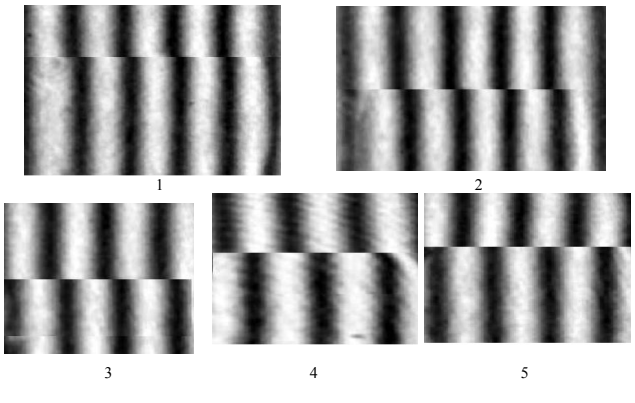

Fig. 7. Interference fringe shift in interferograms MII-4 introduced by step of different thickness of series B layers obtained from following concentrations of PEPC solution: 1 — 2.5 wt%; 2 — 5.0wt%; 3 — 7.5 wt%; 4 — 10.0 wt%; 5 — 12.5 wt%.

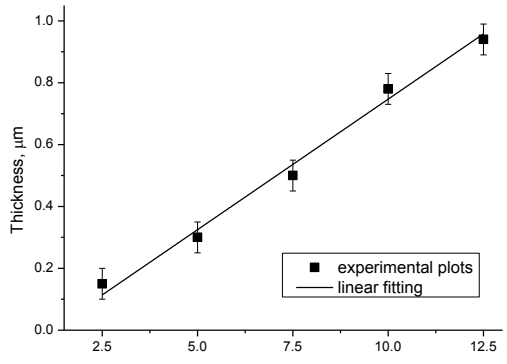

Fig. 8. Film thickness as a function of concen-tration of PEPC solution.

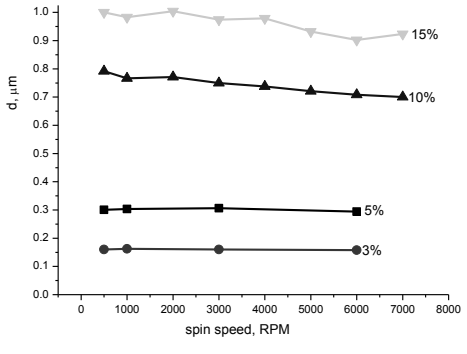

Fig. 9. Film thickness as a function of spin speed for percent concentrations of PEPC into solutions.

The thickness of series B films determined from the fringe pattern in the interferogram was found to be increased with the increase of polymer concentration in solution. It was shown that by raising the polymer concentration from 2.5 to 15.0 wt%, the final film thickness increase from 160 to 960 nm at a spin speed of 3000 rpm during 20s. Applied method of thickness measurements showed a quasi-linear thickness dependence on polymer concentration. (Fig.8.).

Influence of angular velocities in pointed above range of sample series A on polymer film thickness was controlled. Weak influence no much as 8% was found (Fig. 9). It should be noted that thickness measurement was carried out in the center of the substrate and no edge effects were studied.

Therefore, smooth polymer films can be fabricated just by controlling the polymer concentration in solution.

4. SUMMARY AND EVALUATION

It was investigated the process of thin PEPC polymer films deposition with desired thickness by spin coating procedure. Changing the concentration of the solution PEPC from 2.5% to 12.5% leads to a change in the thickness of the obtained films from 160 nm to 960 nm, and this dependence is quasi-linear, which can be used to produce submicron films PEPC with desired thickness. It was shown that the angular velocity of the substrate under irrigation has no more than 8% effect on the resulting film thickness. Thus, it is optimal to choose a suitable concentration of the PEPC solution in conditions of our trial.

Working with computerized MII-4 interference microscope and elaborated software has shown that precise determination of layer thickness of thin films can be user-friendly. Software can process the interferograms in the case of interference fringe angles deviation.

In contrast to conventional layer thickness measuring devices such as profilometers or scanning force microscopes (AFM), this technique provides the full field analyzing specimens, is more rapid, noncontact, and does not require complicated specimen preparation. Thanks to these advantages, the modernized MII-4 interference microscope has great potential as a combined analysis system (optical microscope and layer thickness measurement device), particularly in thin-film engineering. Moreover, the cheaper USB webcamera with more than 1mln pxs is a good alternative to CCD camera connected to framegrabber.

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