Investigation of the adsorption behavior of polymethacrylic acid on silicon substrates.

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Abstract

Thickness and optical parameters of the adsorption polymer layers of polymethacrylic acid (PMAA) from water solution was investigated. Null-ellipsometry technique is used for *in-situ* determination of the adsorbed layer parameters. Two calculation methods are used for solving of the inverse ellipsometry problem for the suggested two-layer model of the surface. Adsorbed amount in the equilibrium state of the layers is calculated for the polymers with different molecular characteristics and corresponding adsorption isotherms are obtained.

Introduction.

The adsorption of linear polymer chains has been extensively studied [1,2] since this is the subject of great practical and fundamental interest. Common theoretical treatment of the polymer adsorption predicts that the adsorbed amount and geometric parameters of the adsorbed layer are mainly controlled by the quality of the solvent and the molecular characteristics of chains.

In this work, the adsorption of polymethacrylic acid is investigated by means of null-ellipsometry. The adsorption studies are performed both in water solution (*in situ*) and in void for control the adsorbed layer optical parameters. The substrates used in this work are silicon wafers.

In order to verify theoretical predictions, the polymer samples are synthesized with different molecular characteristics and different number of functional groups.

Experimental section.

The measurement was performed with a serial null ellipsometer LEF-3M in PCSA (polarizer-compensator-sample-analyzer) arrangement.

The light source was a He-Ne laser (λ=632.8 nm).

All adsorption measurements were made in the specially built glass cell, which has the stress free entrance and exit windows and fixed slope angle of 60°.

The cell was filled with 30 ml of pure solvent, kept at the constant temperature of $20.0 \pm 0.1\ ^{\circ}\mathrm{C}$ by the thermostat and the ellipsometric angles were measured. Then a small volume (0.3 - 3 ml) of the concentrated polymer solution was added and stirred for 2 min. Subsequently, every 2 min a pair of ellipsometric angles, Δ and Ψ, was recorded. Measurements were performed over 12 h. After about 6 h, constant values of ellipsometric angles were reached.

For the data interpretation the layer model of the adsorbed homogeneous isotropic polymer layer on a silicon substrate is proposed (fig. 1)

In this layer model, the substrate is well-defined by means of ellipsometry. It is composed of Si (index of refraction $N_3 = 3.865 - \mathbf{i}\,0.023$) and a top native SiO_2 layer typically 5nm thick ($n_2 = 1.462$) determined through ellipsometric measurements.
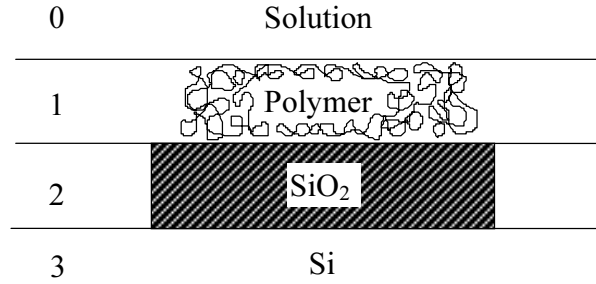
Fig. 1 Layer model used for ellipsometric data interpretation. The adsorbed polymer layer is assumed to be homogeneous.

The accuracy of the SiO_2 layer thickness determination must be very high ($\Delta d_2 = \pm 0.05$nm). More essential inaccuracies in the surface model ($\Delta d_2 = \pm 0.5$nm) cause significant errors of the sought parameters (n_1, d_1) and lack of the physical sense for the obtained results in special cases.

The refractive index of the solution is measured with Abbe refractometer. Optical parameters (n_1) and thickness (d_1) of the adsorbed polymer film can be obtained from ellipsometric measurements. The relationship between these parameters and the ellipsometric angles can be expressed as

$$e^{i\Delta} \tan \Psi = R_p / R_s = f(n_k, d_k, \lambda, \varphi) \qquad (1)$$

where R_p and R_s represent the overall reflection coefficient for the basic p – and s – polarized waves. They are the function of n_k and d_k, which refer to the indices of refraction and the thickness of each layer of the model, the wavelength λ, and the angle of incidence φ. Measurements of Δ and Ψ allow the evaluation of two unknown parameters, the polymer layer thickness- d_1, and its refractive index- n_1.

Due to the nonlinear and transcendental nature of equation (1), it is not possible to obtain a direct solution for d_1 and n_1. For that reason, two solution methods of the inverse ellipsometry problem were used. Iterative numerical calculations are performed for minimizing an error function defined as follows [3]:

$$G = \sum_{i=1}^{n} \left[\frac{(\Psi_i^m - \Psi_i^c)^2}{\sigma \Psi} + \frac{(\Delta_i^m - \Delta_i^c)^2}{\sigma \Delta} \right] \qquad (2)$$

where n is the number of ellipsometric measurements performed in different condition, Ψ_i^m, Δ_i^m are the measured ellipsometric angles, Ψ_i^c, Δ_i^c are the calculated ones for the chosen model of investigated surface and $\sigma\Psi$, $\sigma\Delta$ are experimental errors of ellipsometric angles. Minimizing procedure was performed by the Hoock-Jeeves calculation method [4].

Since the adsorbed polymer layer is not absorbing in visible region, and its refractive index consists only of real part ($k_1=0$), it is possible to use a nomograme technique for the solution of the inverse ellipsometry problem [3]. The nomograme is a graphic representation of the lines of constant film parameters (n_1, d_1) in (Δ, Ψ) coordinates.

The contours of n_1=const and d_1=const form a distorted scale in (Δ, Ψ) coordinates. Such joint covering of both (n_1, d_1 and Δ, Ψ) scales allow to find immediately for each pair of experimental ellipsometric angles (Δ, Ψ) the corresponding pair of sought parameters (n_1, d_1).

Results and discussion

Null ellipsometry is a very accurate technique to investigate adsorption phenomena and to detect ad-sorption processes *in situ* from dilute solution of a given substance on reflecting substrates. When the adsorption process takes place, an adsorbed layer is observed as a change in ellipsometric angles Δ and Ψ. This change is related to the refractive index and to the thickness of the adsorbate. The ellipsometric angles measured for different silicon wafers

with pure solvent or in the void are not always the same due to small differences in the thickness of SiO_2 layer.

Changes in the ellipsometric angles as a function of time measured during the adsorption are showed in the Fig. 2 for one set of the substrate samples.

The polymer samples used in the ellipsometric measurements have different molecular characteristics which are mainly predicted by the molecular weight of the polymer substance. We use three samples of

polymethacrylic acid with molecular weights 190000, 66000 and 10000 g/mol. After 6 hs the equilibrium is reached in all three cases. The concentration of polymer in measured solutions was in the region 0,1÷5 mg/ml.

Followed from the ellipsometric data, the difference in refractive indices of water solution and adsorbed layer is insignificant. In such measurement conditions, small errors in the measured ellipsometric angles Δ and Ψ can result in significant inaccuracy of the sought parameters (n_1, d_1).
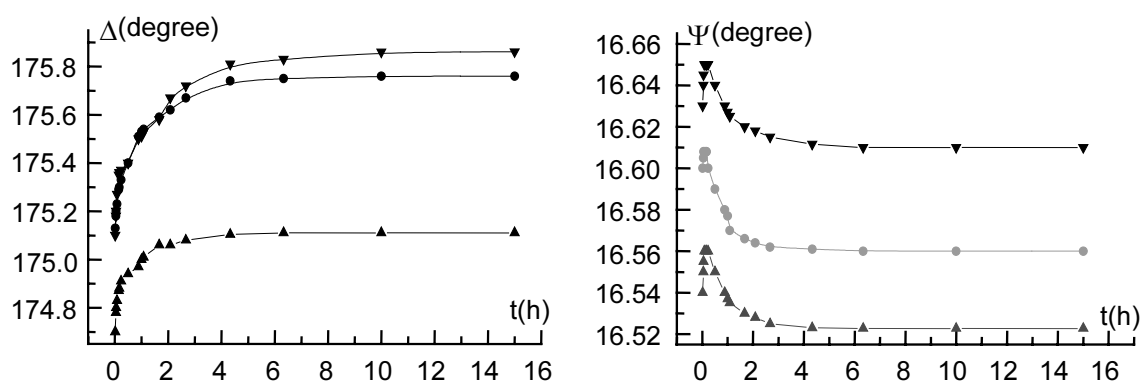

Fig. 2 Ellipsometric angles Δ and Ψ measured as a function of adsorption time for a water solution of PMAA (c=1.0 mg/ml, angle of incidence φ=60°). -•- M=66000g/mol; -▲- M=10000g/mol; -▼- M=190000g/mol;
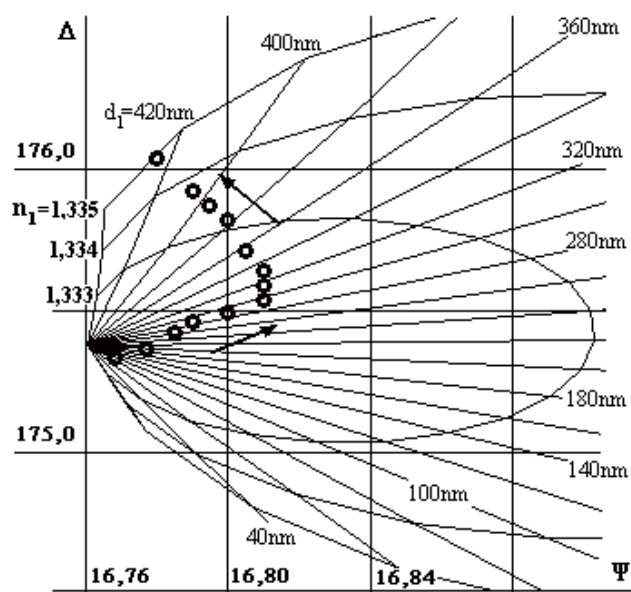

Fig. 3 $\Delta\Psi$-nomograme calculated for a two-layer surface model. (N_{Si}=3.865-i0.023 is the complex refractive index of substrate; N_2=1.46 – i0.0, d_2=7.1 nm are the parameters of native SiO_2 layer).

As it can be seen from the typical nomograme calculated for the presented surface model (Fig. 3), the error of the layer thickness is not smaller than 5÷10 nm for the attainable accuracy of the ellipsometry angle measurement (0.01^o). The errors of the layer refractive index (n_1) are essentially smaller ($0.0001÷0.0003$). It may be explained by significant values of the partial derivatives $\partial\Psi/\partial n_1$, $\partial\Delta/\partial n_1$ in the region of experimental data for the presented model of the surface. Experimental data are presented in the nomograme as a sequence of points. The direction of the data change is shown by arrows.

In all cases the refractive indices of adsorbed layers change in a very small range and remains very close to the refractive index of the solution ($n_1=1.334÷1.336$). It allows to make some conclusions on the composition, structure of the layer and dynamics of their changes during the adsorption. Therefore, we can make a conclusion that the layer composition is very close to the solution consistence. It is possible to consider the adsorbed layer as a layer of solution with insignificantly larger concentration of polymer. The thickness of those layers increase to the values $d_1=150–450$ nm (for the polymers with different molecular characteristics and different concentration of solution) in the equilibrium stage. Great values of the adsorbed layers thickness are caused by the aggregation of polymer macromolecules. On the solid surface not only separate macromolecules but also aggregates of the polymer molecules are adsorbed [5].

The adsorbed layer parameters obtained from the values of ellipsometric angles Δ and Ψ are used to calculate the amount of adsorbed substance- A (mg/m^2), using the following equation:

$$A = d_1 c_1 = \frac{d_1(n_1 - n_0)}{(dn/dc)} \qquad (3)$$

where n_1 and d_1 are polymer layer parameters measured at equilibrium, n_0 is the index of refraction of the solution measured with Abbe refractometer, dn/dc is the increment of the refractive index determined with refractometric measurements for different concentration of solutions and c_1 is the average polymer concentration within the adsorbed layer.

As it can be seen form Fig. 2, the equilibrium is reached after 6–7 hs from the beginning of the experiment. Then the adsorbed amount is calculated. The ellipsometric measurements are performed for different solution concentration in the range 0.1–5.0 mg/ml. The values of refractive index increment (dn/dc) obtained by means of refractometric measurement are the following for each polymer type: 0.0012 (mg/ml)$^{-1}$ for M=190000 g/mol; 0.00085 (mg/ml)$^{-1}$ for M=66000 g/mol and 0.00065 (mg/ml)$^{-1}$ for M=10000 g/mol. It allows to obtain adsorption isotherms (dependencies of adsorption amount versus the solution concentration for constant temperature) for these three polymers with various molecular characteristics. The isotherms showed in the Fig. 4. are very similar. The adsorbed amount A increases as the concentration raises, reaching a plateau value where A does not depend on the solution concentration within the experimental error.

Multiple angle of incidence ellipsometry technique was used for the determination of the polymer layer parameters in the void after the adsorption. Typical thickness of such layers (2–7nm) are remarkably smaller than those thickness in water solution (150–450 nm). Therefore we can make a conclusion that strong adsorptive interaction between the polymer functional groups and the solid surface is the cause of the decrease of the macromolecules hydrodynamic volume when the solvent disappears. Pushing out the solvent molecules from the polymer macroclews result in such significant reduction of the layer thickness.
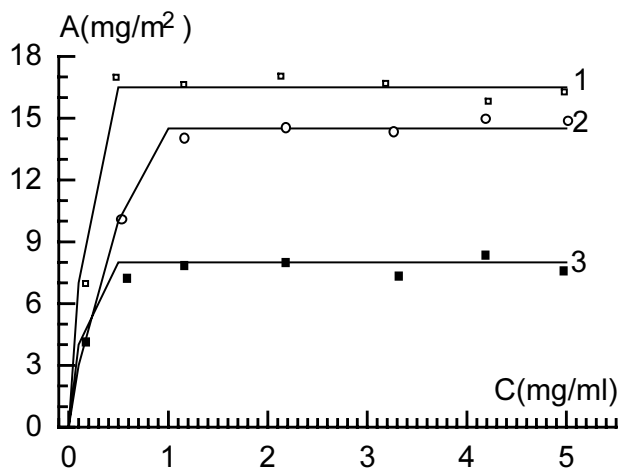
Fig. 4 Adsorption isotherms for the PMAA with molecular weights:
1– M=10000 g/mol; 2– M=66000 g/mol; 3– M=190000 g/mol.

Conclusions.

The adsorption of polymethacrylic acid on Si-SiO_2 substrates from water solution and the dynamics of this process was investigated by means of ellipsometry technique. It is shown that the presented null-ellipsometry technique is a very sensitive method for the *in-situ* investigation of such process. The low contrast between the adsorbed layer and solution is not obstacle for the obtaining of the adsorption process characteristics. Results obtained in this work allow to make a set of well-founded conclusions about the influence of the polymer molecule size on its adsorbed amount, at about the aggregation degree of the polymer macromolecules in solution and other characteristics of adsorption behavior.

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