Ellipsometric *Ex-Situ* study of fluorescent oligoperoxide nanolayers with europium complexes adsorbed on a glass surface. Formation and structure

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Abstract

Structure of nanolayer and kinetics of its formation during the adsorption process are studied for novel metal complexes composed of oligoperoxide copolymer ligands and Eu^{3+} ions (OP-Eu). The adsorbed layers are deposited from water-ammonium solution on a glass surface. Time dependences of the thickness of adsorption layer obtained from ellipsometric measurements indicate rapid adsorption followed by a gradual desorption. Optical parameters of the OP-Eu nanolayers derived on the basis of our ellipsometric data testify that the layer structure depends on the properties of solution and the adsorption duration.

1. Introduction

Modification of material surfaces via depositing polymers with fluorescent properties has recently found a wide range of applications in nanotechnology. The approach has also resulted in creation of promising systems for protein detection, bio-labelling and diagnostics of tumour cells [1–5]. Ellipsometric technique is one of the most sensible methods for structural characterisation of material surfaces and study of kinetics of surface processes. It enables one to determine optical parameters of surface layers and their thickness with a high accuracy. Moreover, the technique provides also important information on the structure of those surface layers (roughness, volume fraction of deposited material in the case of its heterogeneous structure, porosity, etc. [6–8]).

In our earlier work [6], we have suggested a method for deposition of polymer layers by means of their adsorption from the water solution. This facilitates successive studies for kinetics of the adsorption using an *ex situ* ellipsometry.

2. Experimental details

2.1. Materials

Carbon chain oligoperoxide (OP) derived from vinyl acetate, maleic anhydride, 2-tertbutylperoxy-2-methyl-5-hexene-3-yne and butylacrylate was obtained through copolymerisation of the solution at 333 K in ethyl acetate, using azobisisobutyronitrile as an initiator [9, 10]. Eu-containing OP complex based on the OP as a ligand was synthesised in the following way: 10%-solution of the OP and solution of the metal salt (EuCl$_3$) in ethanol (or methanol) were put into a three-necked flask equipped with a stirrer. After stirring the content for 0.5 h at 298 K, we precipitated the reacting mixture in distilled water. The OP-Eu precipitate was carefully washed out from the metal cations by water and dried in the vacuum until its weight had become constant. The content of the metal cations was determined using elemental analysis and additionally checked using atom-adsorption spectroscopy.

2.2. Measuring ellipsometric technique

The thickness and optical parameters of the polymer nanolayers adsorbed were obtained experimentally for different concentrations of the OP-Eu solutions, using ellipsometric measurements described in our earlier work [6]. We employed a so-called *ex situ* ellipsometric technique. Glass plates were immersed into the water solution of OP with the concentration of 0.6÷5.0% in a thermostated bath at the temperature of 20.0±0.1°C. The adsorption time was varied from 1 to 120 min. After that the plates were withdrawn from the solution and immediately arranged into a centrifuge for removing the excess solution. Ellipsometric measurements were carried out for each specimen before and after formation of the layer.

Null-ellipsometer LEF-3M produced by the Institute for Semiconductors Physics (Novosibirsk, Russia) and equipped with a PCSA (polarizer–compensator–specimen–analyser) set-up provided the angular setting accuracy of 0.01° for the optical components. Single-mode He–Ne laser with the light wavelength of $\lambda = 632.8$ nm was used as a light source. The polarisation parameters of the light reflected from the sample (the angles Ψ and Δ, according to a standard notification) were determined with the four-zone technique [11], using the incident angles 58÷63° with the step of 1°.

Under optimal experimental conditions, the accuracy for the parameters of the layers under test and the surface model used by us was described by the following errors: $\delta d_f = \pm 0.05$ nm for the thickness and $\delta n_f = \pm 0.001$ for the refractive index of the layer. These values were obtained using computation experiments for the well defined "glass–polymer layer" surface model.

The refractive index of the surface layer may provide information concerning volume fraction of the polymer in the adsorbed surface layer. Therefore the ellipsometric technique allows for estimating the density of macromolecules packed on the solid surface. One can calculate the volume fraction of the polymer in heterogeneous surface

layer using the effective-medium theory by Maxwell-Garnett [11, 12]:

$$q = \frac{V_{pol}}{V_f} = \frac{n_e^2 - n_m^2}{n_e^2 + 2n_m^2} \cdot \frac{n_{pol}^2 + 2n_m^2}{n_{pol}^2 - n_m^2},$$ (1)

where V_{pol} is the total volume occupied by polymer molecules, V_f the total volume of the heterogeneous surface layer, n_e the refractive index of the surface film obtained from ellipsometric measurements, n_{pol} the bulk refractive index of the polymer material obtained from supplementing refractometric data, and n_m the refractive index of surrounding medium (solvent or air) that causes heterogeneity of the nanolayer polymer structure.

The adsorption parameter can be calculated from experimental ellipsometric data on the basis of equation [6]

$$A = \frac{V_{pol}}{V_f} \rho d_f,$$ (2)

where ρ denotes the polymer density and d_f the thickness of the polymer nanolayer. The surface area occupied by a single OP molecule can be also estimated using the data obtained from our experiments.

The bulk refractive indices of the polymer material have been obtained using the refractometric technique and assuming that the refractive index of the solution (n_s) depends linearly on the polymer concentration [6]. The bulk refractive index thus measured for the OP-Eu polymer material is equal to $n_{pol} = 1.51$.

3. Results and discussion

Dependences of the thickness d_f and the refractive indices n of the OP-Eu-films on the duration time of adsorption have been obtained on the basis of our ellipsometric measurements (see Fig. 1 and Fig. 2). It is obvious that, regardless of complicated character of the adsorption curves within the duration range of 0–10 min, these curves agree well with a typical shape of adsorption-desorption curves [13].
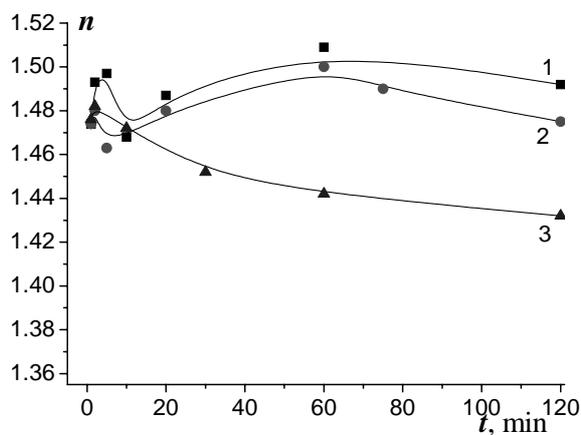

Fig. 1. Dependences of refractive indices (n_f) of the OP-Eu-layers obtained from water-ammoniac solutions on the adsorption time *t*. The solution concentrations are *c* = 2.5% (curve 1), *c*=1.0% (curve 2) and *c* = 0.6% (curve 3).
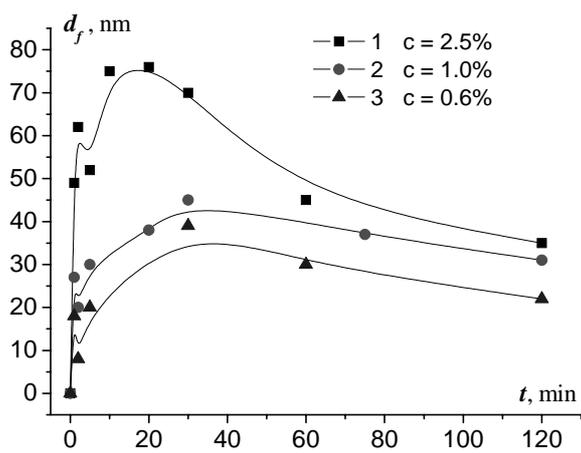
Fig. 2. Dependences of layer thickness d_f on the adsorption time t for the OP-Eu-layers obtained from water-ammoniac solutions. The solution concentrations are $c = 2.5\%$ (curve 1), $c = 1.0\%$ (curve 2) and $c = 0.6\%$ (curve 3).
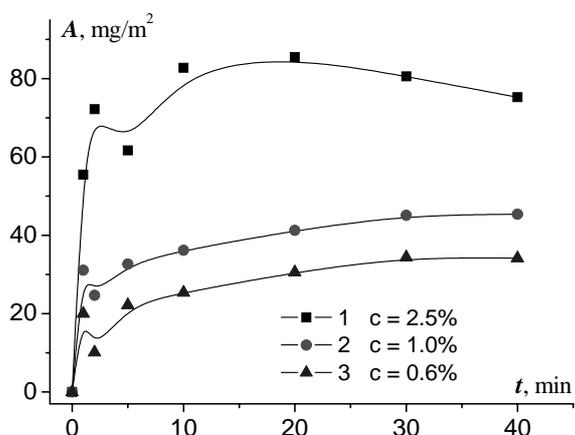

Fig. 3. Time dependences of adsorption for the water-ammoniac solutions of OP-Eu copolymer: $c = 2.5\%$ (curve 1); $c = 1.0\%$ (curve 2) and $c = 0.6\%$ (curve 3).

During several minutes in the beginning, growth of the layer thickness has a jump-like character. The concentration of the solution plays an important part in the adsorption kinetics and affects the structure of adsorbed polymer layer. Afterwards the thickness growth slows down somewhat and the thickness reaches its obvious maxima in the time regions 10–20 min for the solution concentration of 2.5% and 30–40 min for the case of 0.6% and 1.0%.

The results mentioned above suggest the following conclusions. The time dependences of the thickness of adsorption layer point to transitional character of the process. Namely, the adsorption process prevails at the first stage and the parameter *A* increases with increasing solution concentration. Duration of this stage differs from 15 min for the 2.5%–solution up to 40 min for the concentrations 1.0% and 0.6% (see Fig. 2 and Fig. 3). At the second stage the process of desorption becomes more intense, until a steady state is reached in the time interval defined as $t > 120$ min.

The refractive indices of the adsorption layers deposited from the 2.5% – and 1.0% – solutions remain practically invariable at all the stages of the process, being close to the bulk refractive index of the polymer ($n^{pol} = 1.51$). This fact testifies a high packing density of OP molecules in the surface layer. The volume fraction of the polymer in the layer calculated in the approximation of effective medium gives the value $q \sim 0.98$ on

average. Therefore the desorption process in case of the concentrations mentioned leads only to thinning of the layer and does not affect homogeneity of the latter.

The situation is substantively different in the case of layers obtained from 0.6%-solution. Decreasing of refractive index of the layer (see curve 3 in Fig. 1) indicates worsening of layer homogeneity. Then the volume fraction of the polymer calculated from Eq. (1) decreases to $q = 0.88$. It is evident that the desorption leads to worsening homogeneity of the adsorbed layer.

The structure of layers deposited from the solutions with different OP concentrations substantially differs from that corresponding to the region of maximal adsorption (i.e., the time region of 1–40 min). The thicknesses of the layers deposited from low-concentration solutions ($c = 0.6\%$ and 1.0% – see curves 2 and 3 in Fig. 2) are considerably smaller ($d_f = 30$–40 nm) that that referred to high-concentration ($c = 2.5\%$) one (see curve 3 in Fig. 2; $d_f = 75$ nm). The refractive indices and, consequently, the volume fractions of polymer in the layer do not differ so considerably in this time interval.

Using our experimental data, we have calculated the adsorption value in accordance with Eq. (2). The results for the time interval of 0–40 min are shown in Fig. 3. The data obtained by us illustrate well a difference in the characters of adsorption from dilute (0.6% and 1.0%) and concentrated (2.5%) solutions at the initial stages of the process ($t < 40$ min). A rapid adsorption process taking place for several minutes (see Fig. 2 and Fig. 3, curves 1) should imply that for the case of solution concentration $c = 2.5\%$, there is a transition onto the glass surface of not only separate macromolecules but their agglomerates, too.

In order to confirm these results, we have measured the contact angle for the water droplets placed on the same specimens of adsorbed layers. Fig. 4 testifies good agreement of effective fraction x of the glass surface modified by the OP-Eu complexes, which is deduced from the contact angle data, and the effective thickness of the adsorbed layer obtained from the ellipsometric measurements. The slope of this dependence is proportional to the packing density of copolymer substance on the surface. Since the composition of the effective adlayer medium within the ellipsometric model is practically
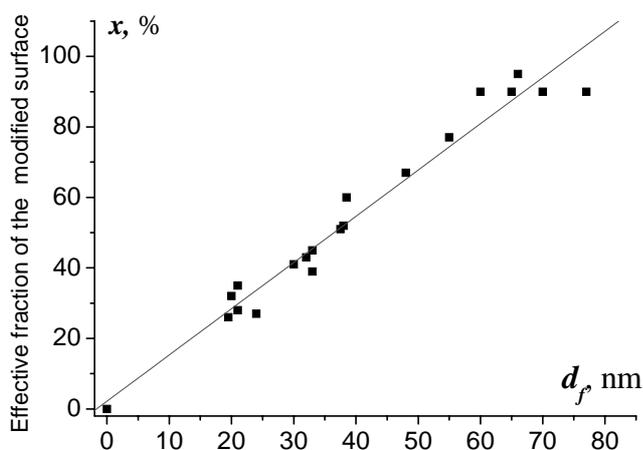

Fig. 4. Thickness of the adsorbed OP-Eu layer versus fraction of the glass surface modification.

constant ($q = 0.88 \div 0.98$), the average adlayer thickness d_f determined above could be a good measure of the adsorption amount typical for OP-Eu.

From the viewpoint of thermodynamics, the kinetic features of the adsorptions observed immediately at the beginning of the process (i.e., in the time interval 0–5 min – see Fig. 1 and Fig. 2) are extremely interesting. It is obvious that fast and intense reconstruction processes occur in the adsorption layer at this stage. Dynamics of these processes is very similar to that peculiar for transient regimes in the radio engineering [14]. Quasi-periodical changes in the thickness and refractive index of the layer represent basic solid manifestation of those reconstructive processes. Rapid increase of the layer thickness at the beginning of the process is followed by its further decrease in the time interval of 2–3 min, which is accompanied by noticeable increase in the refractive index of the layer. At the next stage, the changes occurring in the thickness and the refractive index reverse. This effect is well reproducible.

The peculiarity addressed to above is present on all the three dependences (see Fig. 1 and Fig. 2). More detailed studies are needed for complete understanding of these processes. For this purpose, similar measurements should be carried out in a wider temperature range.

4. Conclusions

The OP-Eu nanolayers have been formed with the aid of adsorption from water-ammoniac solution on the glass surfaces. It is shown that the thickness of nanolayers and their structure depend on the polymer concentration in the solution and the time of adsorption. The maximal layer thickness is achieved for the OP concentration in solution equal to 2.5%. It is plausible that desorption is caused by conformation changes in the macromolecules adsorbed on the surface, or their reorientation. It is quite possible that aggregates of those macromolecules are adsorbed on the surface and so they get partially destroyed.

We conclude finally that the *ex situ* ellipsometric measurements are suitable for studying subtle kinetic effects of adsorption from the polymer solutions on solid surfaces. The results obtained in this work with the ellipsometric technique enable determining the optimal concentration and the time modes needed for reliable modification of the glass surface by the adsorption of layers with the OP complexes.

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Анотація. *Досліджується структура і кінетика формування в процесі адсорбції наношарів нових метало комплексів, які є лігандами олігопероксидного кополімеру та іонів Eu³⁺. Адсорбційні шари формувались на скляній поверхні із водно-аміачного розчину. Часові залежності товщини адсорбованих шарів одержані еліпсометричним методом свідчать про стрімкий процес адсорбції, що змінюється поступовою десорбцією. Структура європійвмісних наношарів залежить від властивостей розчину і тривалості процесу адсорбції. Про це свідчать часові та концентраційні залежності оптичних параметрів олігомерних наношарів.*