Fabrication of planar iron oxide nanocomposite films and investigation of their optical and magnetic properties

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ABSTRACT

Iron oxide nanoparticles and polymer planar films with different number of layers of iron oxide nanoparticles have been fabricated by the layer-by-layer alternating adsorption technique. It was established that the thickness of the PAH/iron oxide film and its refractive index increases with the increase of the layer number. The microwave irradiation affects the thickness of the PAH/iron oxide film and their refractive index. The increase of refractive index and decrease of thickness of nanocomposite films were observed. The electronic paramagnetic resonance (EPR) spectra of planar films were measured. It was found that parameters of the EPR spectra are sensitive to the number of nanoparticles layers.

Keywords: Layer-by-Layer adsorption, nanocomposite, thickness, refractive index, volume fraction

1. INTRODUCTION

In recent years the research of polymer materials with magnetic nanoparticles started [1-3]. Nanocomposite materials are brand new and promising due to the manifold of their unique properties: electronic [4-6] biomedical [7], optical [8-10]. For example, nanoparticle layers have been successfully applied for fabrication of super-hydrophilic biocompatible coatings [7] and solar cells [9].

Nanocomposite multilayers with embedded layers of iron oxide particles also have good perspectives such as fabrication of magnetic data storage media and structures for spin electronics [1-3, 5,11] or as development of new microwave-absorbing materials [3,12]. The layer-by-layer self-assembly (LbL) method can be applied for fabrication of planar nanocomposite films and microcapsules [13-21]. Layer-by-layer self-assembly is based on subsequent dipping of a substrate in solution of oppositely charged species. Multilayer assemblies are held together by the combination of attractive electrostatic and dispersive forces [3, 13].

The microwave oven is used in our daily life to heat or warm our food. However, microwave (MW) radiation can also be used to control parameters and properties of nanocomposite coatings which contain iron oxide nanoparticles. A short exposure to MW irradiation led to a marked improvement of the in-plane ordering of nanoparticles in such layers adsorbed on silicon substrate [3].

In this paper the properties of polyelectrolyte/iron oxide nanoparticles nanocomposite films were studied by ellipsometry and EPR methods and the possibility to use MW irradiation to control their parameters is discussed.

2. METHODOLOGY

2.1 Materials

The poly(allylamine hydrochloride) (PAH, MW ~70000), polyethylenimin (PEI, MW~600000-1000000) (Fig. 1) and sodium chloride were purchased from Sigma. Magnetic fluid from “Berlin Heart”, an aqueous suspension of iron oxide nanoparticles (Fe_3O_4), was employed for fabrication of nanoparticulate layers. The average size of iron oxide

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nanoparticles (Fig. 2) measured by dynamic light scattering (DLS, Malvern HPPS5001) was 10±1 nm (PDI = 0.23) and was in good agreement with the transmission electron microscopy (TEM, Zeiss EM 912 Omega transmission electron microscope) data (8 nm) [22]. The nanoparticles were stabilized by citric acid and had therefore a negative charge (Zeta-potential of the nanoparticles in aqueous suspension at pH 6.9±0.2 was -47.4 mV).

2.2 Planar nanodimensional film preparation

Chemically cleaned n-type (111) silicon wafers with specific resistance of 5 Ω·cm were used as substrate. The silicon plates were cleaned by boiling CCl_4 for 15 min. After that substrates were etched in HF acid and thoroughly washed with deionised water. As a result, the silicon wafers were covered by a silicon oxide layer of about 2–3 nm thickness. Due to this layer, the wafer surface became negatively charged in water at neutral pH, and no special chemical treatment was necessary to charge it [23]. One precursor layer of PEI was deposited by dipping a substrate in the corresponding polyelectrolyte solutions. Such pretreatment led to higher stability of PAH/iron oxide multilayers deposited later on the same substrate [24]. The thickness of the PEI precursor layer assumed approximately 2.5 nm [25]. All polyelectrolytes were used at a concentration of 2 mg/ml. PAH solutions were prepared in 0.5 M NaCl. Because the surface charge of the iron oxide nanoparticles dispersed in water at pH = 6.9 was negative, PAH, a cationic polyelectrolyte, was used for alternation with these nanoparticles during L-b-L preparation. Iron oxide nanoparticles were adsorbed from their water suspension with the gross content of 3.2 mg/ml. Subsequent PAH and iron oxide layers were formed by subsequent dipping in polyelectrolyte solution and in nanoparticles suspension by automatic setup (Polyion-1M, Saratov, Russia) (Fig. 3) [26]. Nine specimens containing 12, 22, and 32 layers were produced (Fig. 4).

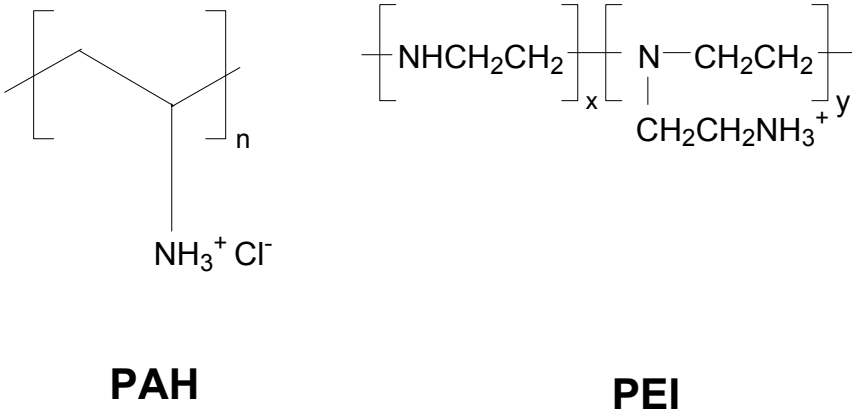

Fig. 1. Structural formulas of polyelectrolytes

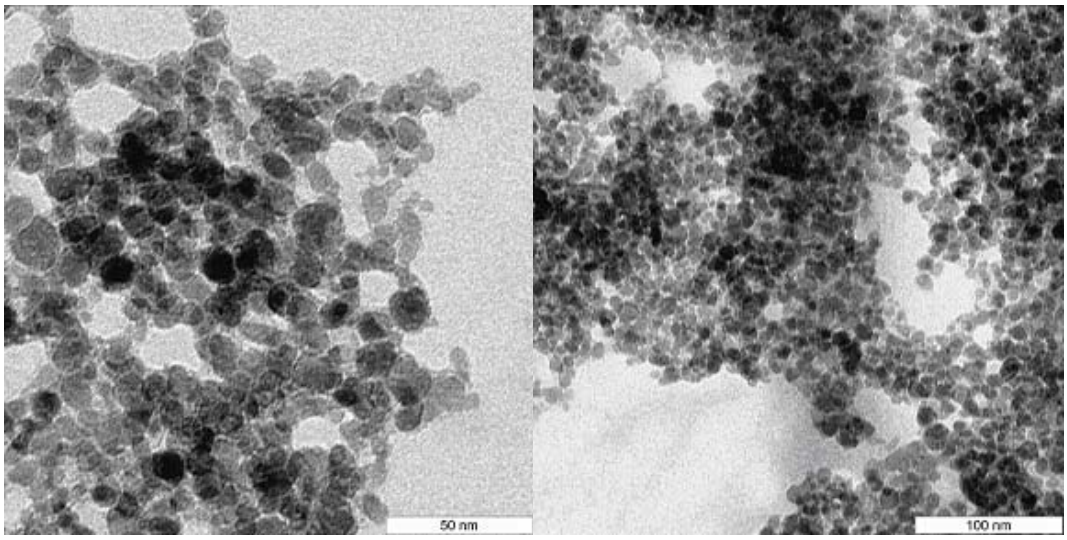

Fig. 2. Transmission electron micrographs of Fe_3O_4 nanoparticles

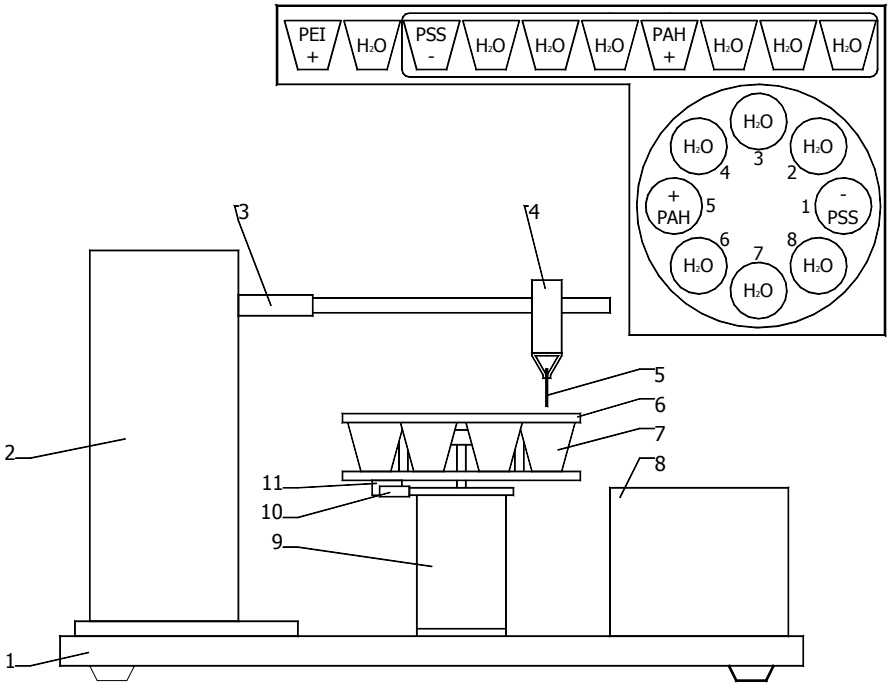

Fig. 3. Schematic drawing of the POLYION-1M automatic setup: (1) base, (2) crane (device for vertical displacement of substrates), (3) crane's rod, (4) substrate's holder, (5) substrate, (6) barrel (holder of vessels), (7) vessels with liquids, (8) electronic control system,(9) stepper motor of the barrel, (10) microswitch (barrel's position sensor), and (11) stop. The inset shows the holder with vessels [26].

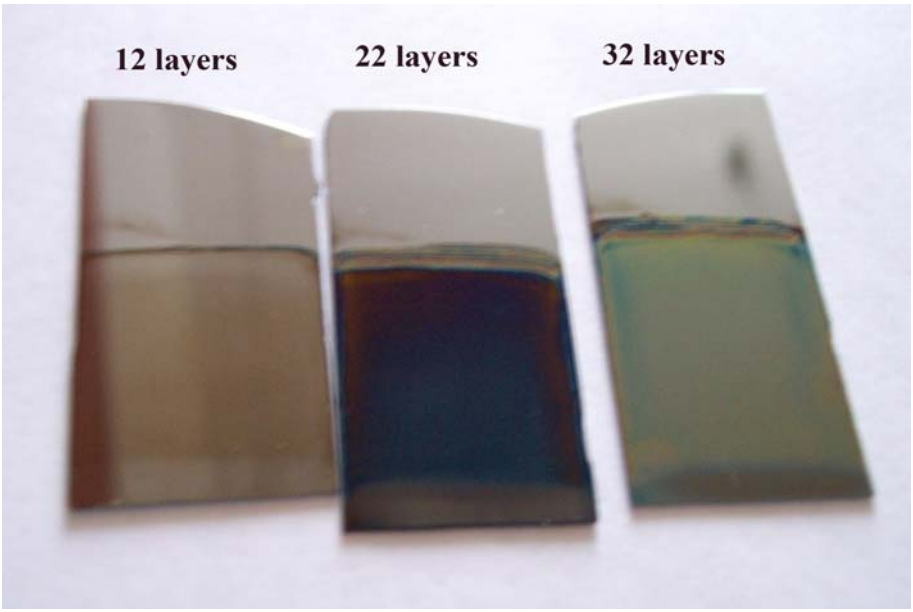

Fig. 4. Specimens of polyelectrolyte layers with iron oxide nanoparticles on silicon substrates

2.3 Methods

2.3.1 Ellipsometric measurements

The ellipsometry method was used to measure the optical constants of the nanocomposite layers deposited on plates. The measurements of polarization angles Ψ and Δ were performed at three different arbitrary chosen points on the surface coated with a film and at a single point on the substrate free. An LEF-3M null-ellipsometer (wavelength of 632.8 nm) was used at angles of incidence of 60° and 70°. Refractive index *n* and film thickness *d* were determined from the experimentally obtained polarization angles Ψ and Δ on the basis of Ψ-Δ nomograms calculated with the use of the model of a nonabsorbing isotropic film on an absorbing isotropic substrate [26, 27]. The nomograms were calculated and plotted by means of a program developed in the MATLAB environment. Refractive index *n* of the substrate of each specimen was determined ellipsometrically, and this value was used in the calculations of the refractive index and thickness of nanocomposite films [27, 28].

2.3.2. EPR measurement

The Varian E-4 EPR X-band spectrometer operating at 9.2 GHz was used. The room temperature signal of absorption derivation from the spectrometer was digitized and processed by a personal computer. The films (N=2÷12) were oriented perpendicular to the magnetic field. For other orientations the resonance cavity was overloaded, probably, due to strong electric component absorption, and measurements were impossible. The effective g-factor, the effective resonance field H_{RES}, the signal peak-to-peak amplitude A, the peak-to-peak line width ΔH_{pp} were determined for each resonance line. The intensity I_{EPR} of the line was estimated as a product $I_{EPR} \approx A \cdot \Delta H^2_{pp}$.

3. RESULTS

The result of ellipsometric investigation of nanocomposite films with and without iron oxide nanoparticles as well as before and after MW irradiation was presented in the Table 1.

The refractive index of polyelectrolyte films without iron oxide nanoparticles didn't depend neither on the number of layer N nor their thicknesses. The refractive index is n = 1.48±0.02. The thickness per layer is 2.1±0.3 nm.

These data agree with result obtained by some other authors [4, 5, 13]. It was established that incorporation of iron oxide nanoparticles into polymeric matrix led to increase refractive index and thickness of nanocomposite films. Thickness d and refractive index n of polyelectrolyte/Fe_3O_4 multilayer nanocomposite are presented in Figs 5 and 6 as functions of N, respectively. The thickness d of the nanocomposite increases linearly with increase of N (Fig. 5) with an increment of 2.8 nm. This thickness behavior shows the regularity of the multilayer structure in the direction normal to the substrate.

Table 1. Results of ellipsometric studies of polyelectrolyte layers with iron oxide nanoparticles on silicon substrates, without and after microwave irradiation

Characteristics of coatings	PEI/(Fe_3O_4/PAH)			PEI/(Fe_3O_4/PAH) after microwave irradiation			PEI/(PAH/PSS)		
Number of layers *(N)*	12	22	32	12	22	32	12	22	32
n	1.58	1.66	1.86	1.64	1.69	1.91	1.46	1.48	1.50
σn	0.01	0.01	0.01	0.01	0.01	0.01	0.02	0.01	0.01
d, nm	49.0	72.7	103.9	47.1	71.7	101.1	28.3	41.6	61.8
σd, nm	2.2	1.1	1.7	1.5	1.1	1.4	2.4	1.3	1.5

Dependence of refractive index on the number of layers had nonlinear behavior (Fig. 6). This may be caused by nonlinear growth of volume fraction of iron oxide nanoparticle with the number of layers N due to increasing interdigitation of the neighboring nanoparticulate layers in the nanocomposite. This was conformed by the decrease of thickness increment with increase N.

EPR spectra of all films (Fig. 7) contain strong resonance line with $g_{eff} \approx 1.5$ as well as more weak line with $g_{eff} \approx 2.3$ (excepting the sample with N=2). The ratio of EPR intensities of these signals are not correlated with N. The line widths of both lines are nearly the same (ΔH_{pp} = 700-800 Oe) in all samples. It is interesting that for a film with N=2 the line with $g_{eff} \approx 2.3$ was not detected and the effective resonance field for the line with $g_{eff} \approx 1.5$ is shifted to lower magnetic fields by $\Delta H_{RES} \approx 100$ Oe in comparison with the same lines in films with different N. It should be noted that EPR signal of iron nanoparticles in non-planar (three-dimensional) matrixes is characterized by a $g_{eff} > 2.0$ [29]. The small value (1.5) of the g-factor of the main resonance line in composite films containing iron-oxide nanoparticles can be due to the high value of the sample magnetization and significant demagnetized factor. The second line with $g_{eff} \approx 2.3$ can be explained by the existence of various defects disturbing planar structure – individual large-scale particles or their agglomerates. For these non-planar objects the demagnetized factor is not as important as for plane films. The data of atomic force spectroscopy showed that surface roughness become more prominent with N increasing. The most perfect structure is anticipated for films with N=2. Hence the absence of the signal with $g_{eff} \approx 2.3$ is correlated with film quality.Thus physical parameters of nanocomposite films could be controlled by change of N.

The other method for modification of nanocomposite coatings is the treatment by MW irradiation. MW irradiation led to the sufficient improvement of nanocomposite films structure, e.g. to decrease of film roughness. It was also established, that MW treatment of the poly(dimethyldiallylammonium chloride) layer prior to the iron oxide nanoparticle adsorption improves the packing density of the particles in the nanocomposite. MW exposure led to cross-linking of the polymer chains. In principle the process of free radical polymerization and cross-linking of polymer chains result in increase of the density and stability of the polymer substance [3].

A MW source used for MW irradiation had frequency 2.45 GHz. Duration of irradiation was 1 minute. It was shown that in case of polyelectrolyte/iron oxide nanoparticles nanocomposite its refractive index is increased and its thickness, on the contrary, is inconsiderably decreased.

The investigation of MW radiation effect on silicon plates with and without coatings (polyelectrolyte and polyelectrolyte/nanoparticles) showed that the most significant influence is observed for polyelectrolyte/nanoparticles coatings. It was shown that this influence is not connected with heating of substrate. MW energy absorbed by iron oxide nanoparticles and converted in thermal energy. This led to their heating and to the increase of nanocomposite films density, in particular because of thermal desorption of water.

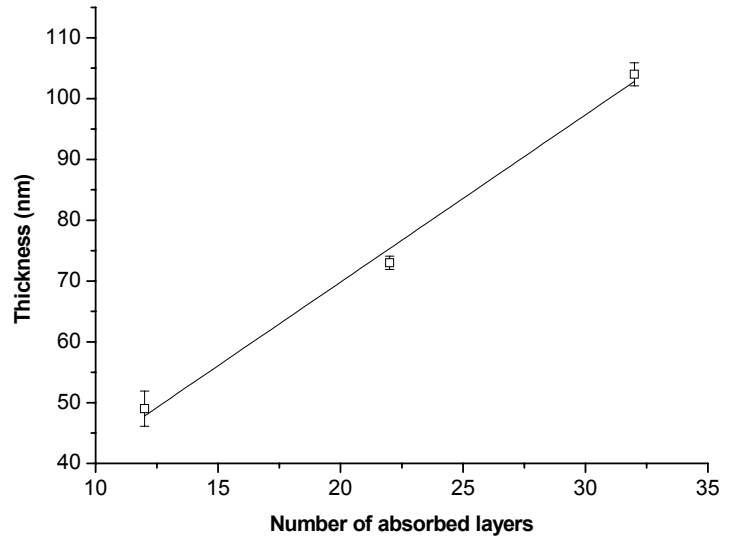

Fig. 5. Thickness d of polyelectrolyte/Fe_3O_4 nanoparticle multilayers as function of total layer number N.

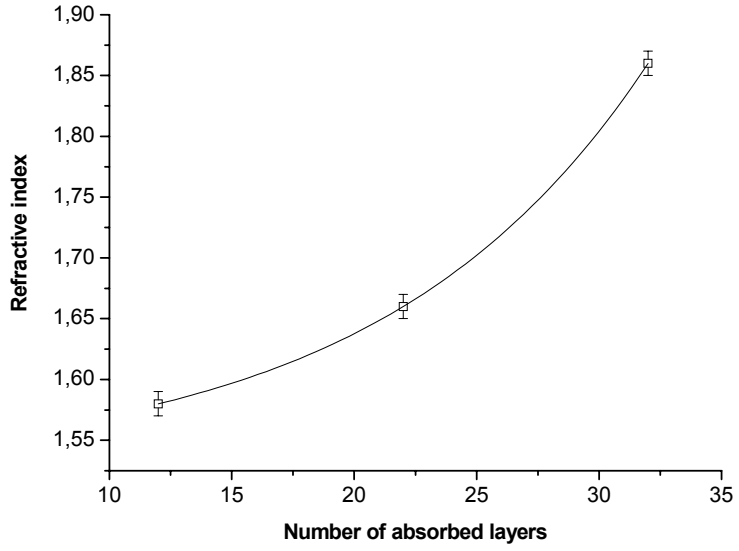

Fig. 6. Refractive index n of polyelectrolyte/Fe_3O_4 nanoparticle multilayers as function of the total layer number N.

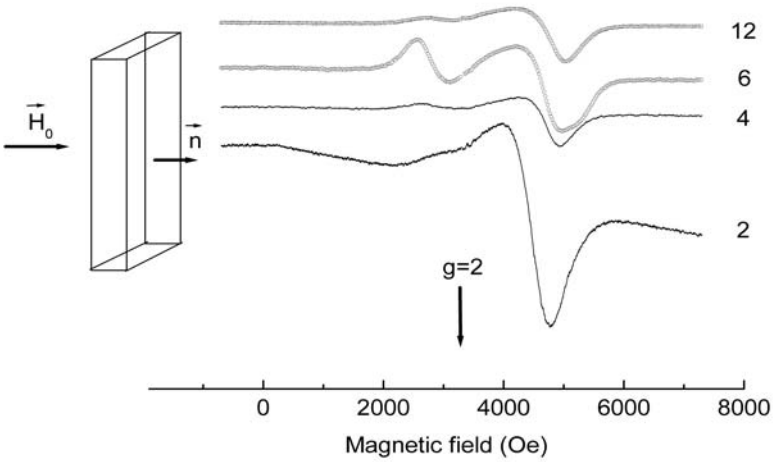

Fig. 7. The electronic paramagnetic resonance (EPR) spectra of polyelectrolyte/Fe_3O_4 nanoparticle multilayers

4. CONCLUSIONS

It was established that using iron oxide nanoparticles as building blocks of negatively charged layer led to the increase of the refractive index as compared to the polyelectrolyte layers without magnetite nanoparticles. Dependence of refractive index on the total number of layers had nonlinear behaviour. This could be explained by nonlinear growth of volume fraction of iron oxide nanoparticle with the total number of layers. We found also that film quality can be modificated to some extent by microwave irradiation.
The magnetic resonance spectra show to significant film magnetization.
Thus, the found dependences of physical parameters of nanocomposite films on the number of layers and their modification upon microwave irradiation may be applied to control magnetic and optical properties of nanocomposite coatings.

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