

Self-assembly of magnetic multilayer polymer films on the base of polyelectrolytes and magnetic suspensions

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Abstract

Possibility of the manufacturing magnetic ultra-thin multilayer films with exactly controlled thickness of separated polymer layers was considered. Magnetic multilayer nanocomposites based on polyelectrolytes have been prepared by alternate layer-by-layer assembly method. They were investigated by optical, magneto-optical and electron microscopy and electron diffraction methods. It is shown that the planar surface charge sign influences on the magnetic layer density.

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1. Introduction

The investigation of polymer composite materials which can change their size and shape under external magnetic field has been reported in the last years. These are composed of magnetic hydrogels—polymers with cross-linked network filled with 10-nm-large magnetic particles [1,2]. Other materials of this group are the magnetoelastics prepared by dispersion of ultra-fine and large (up to a few microns) magnetic particles in oligomer of the siloxane caoutchouc [3–6], manufacturing in the presence of surface-active substances and plasticizers. The uniaxial deformation induced by the external magnetic field reach 40% in magnetic gels and 200–300% in magnetoelastics.

These materials form inhomogeneous structures with disordered distribution of magnetic particles in the polymer bulk. Their use in optical or magneto-optical transparencies, membranes and filters, is limited because of the aggregation of magnetic particles during the

synthesis of polymer matrices and low reproducibility of their magnetic and mechanical properties.

The aim of this work is study of the possibility of preparing magnetic ultra-thin multilayer magnetic films by the method of layer-by-layer self-assembly. This technique is used for preparing ultra-thin ordered multilayer films of semiconductor nanoparticles [7]. It consists in subsequent alternate adsorption of oppositely charged polyions from appropriate solutions and following electrostatic bonding of neighbor layers. This provides the rigorous control of the thickness of individual polymer layers (0.7–2.0 nm), and also the thickness of whole film.

2. The sample preparation and experimental methods

The self-assembly method is based on the electrostatic attraction of oppositely charged functional groups of the macromolecules of a polyelectrolytes. The oppositely charged polyelectrolytes were Na-poly(styrenesulfonate) (PSS), poly(allylamine) hydrochloride (PAA) and polyethyleneimine (PEI); the magnetic material was the suspension of Fe-nanoparticles. The films were assembled on a clean glass plate or on a copper grid. The first layer with a fixed positive charge was formed

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during 30 min on the substrate into the PEI-solution. The sample washed in distilled water used as a substrate for the deposition of successive layers of PSS-polyanion and PAA-polycation. The adsorption process took 20 min. The superfluous polyions were removed by washing the sample in distilled water. The deposition of a PSS–PAA-bilayer was repeated until the formation of a polyelectrolyte film of a desired thickness. The sign of the surface charge depended on the kind of the polyelectrolyte solution used in the final stage of film formation.

The ultra-sound treatment resulted in dispersion of magnetic particles in water by. An as-prepared polyelectrolyte substrate was dipped into the suspension, and magnetic nanoparticles deposited on its surface.

The optical properties and homogeneity of the multilayer films were studied by the optical transmission and magneto-optical reflection methods. The size of the light spot on the sample was 3×3 mm. The transparency T was determined as the I/I_0 ratio related to $(I/I_0)_{\max}$.

The magneto-optical study were performed using the equatorial Kerr effect (EKE). The method reduced to the change of intensity of linearly polarized light reflected from the sample during its remagnetization described as

$$\delta = I_H - I_{H=0}/I_{H=0},$$

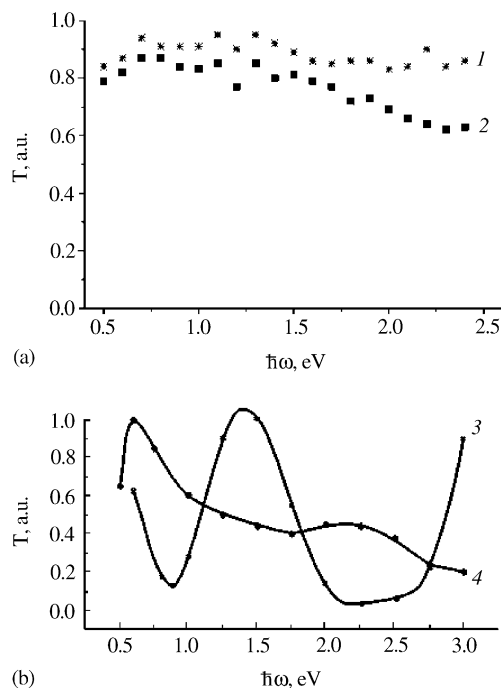


Fig. 1. The typical dependencies T on $\hbar\omega$: (a) self-assembled samples without (1) and with (2) magnetic particles; (b) thin layer of magnetic liquid based on Fe (3) and Fe_3O_4 (4) particles.

where I_H and $I_{H=0}$ are the intensity of light reflected from magnetized and non-magnetized surfaces, respectively. As other odd magneto-optical effects, the EKE takes place only in the presence of a magnetic material on the surface. In the absence of the magnetic phase EKE cannot be revealed in the reflected beam.

3. Results and discussion

Fig. 1 shows the typical dependence of the optical transparency T on the photon energy $\hbar\omega$ measured in the samples prepared by the successive layer-by-layer assembly. No absorption bands characteristic of ultra-dispersed Fe and Fe_3O_4 were detected in the spectra. This indicates the existence of some transparent regions in the film, containing neither Fe nor Fe_3O_4 nanoparticles. The EKE-measurements reveal that the continuous layer of magnetic nanoparticles with effective thickness of 10–20 Å can be prepared only on a positively charged polymer surface on a glass substrate. The corresponding results are shown in Fig. 2a. Fig. 2b shows similar dependencies for the magnetic liquid

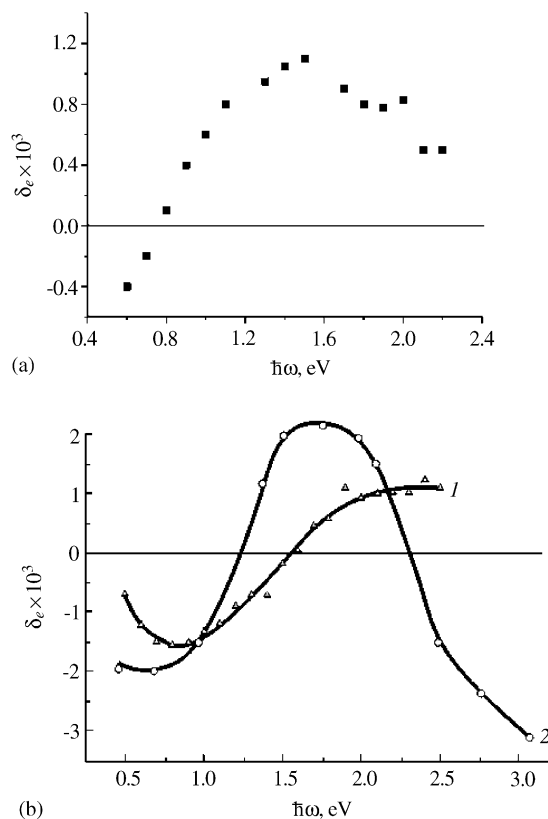


Fig. 2. The EKE dependencies on $\hbar\omega$: (a) positively charged surface with magnetic particles; (b) precipitations of Fe (1) and Fe_3O_4 (2) magnetic fluids.

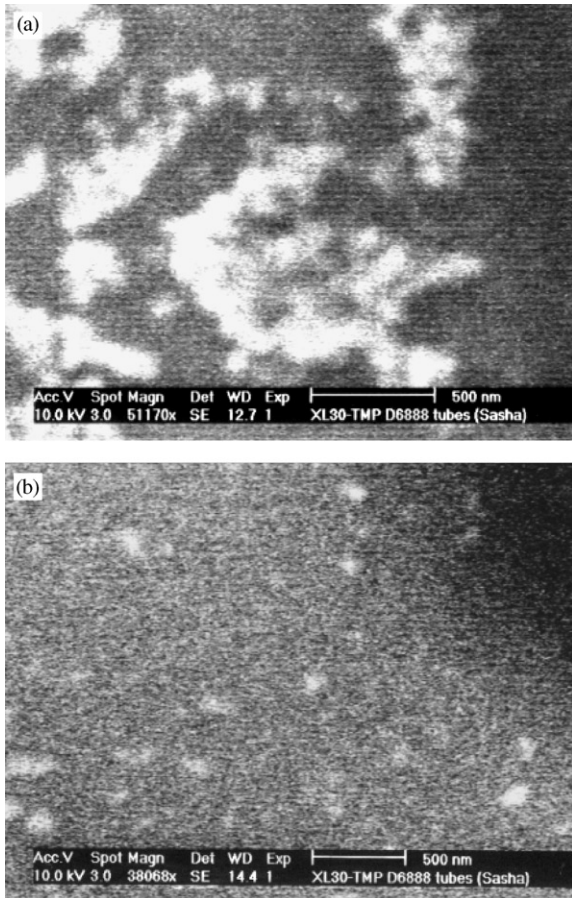


Fig. 3. Electron microscope image of magnetic particles deposited on positive (a) and negative (b) surfaces.

containing Fe and Fe_3O_4 particles. Comparing of these data one can draw the conclusion that the curve in Fig. 2 relates rather to magnetic Fe_3O_4 particles than to any other phase.

The EKE in the films prepared on negatively charged substrates is negligible. This leads one to the conclusion about the film discontinuity and their effective thickness being small ($\sim 5 \text{ \AA}$). These results are consistent with the electron microscopy data.

The self-assembly technique permits to carry out the layer-by-layer magneto-optical control of the deposited film. The magnetic particles are not coated with a thick layer of a polymer as is the case in polymer gels and magnetoelastics. Thus the analysis of bilayer iron films showed that the structures densely populated with magnetic particles is formed according to the scheme Fe–PSS–PAA–Fe (Fig. 3).

The electron diffraction patterns from the monolayers of magnetic particles indicate the presence of polycrystalline Fe_3O_4 particles (Fig. 4). The comparative analysis of shape of reflections in the diffraction patterns shows

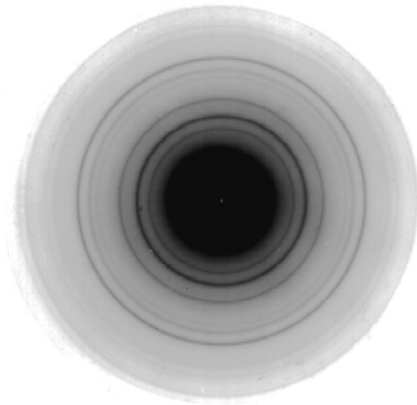


Fig. 4. Electron diffraction pattern from the monolayer of magnetic particles deposited on positively charged surface.

that the size of the magnetic particles deposited onto a positive PAA polymer substrate (150 nm) exceeds the size of the particles deposited onto negative PSS substrate (100 nm).

4. Conclusions

Thus, we have demonstrated that it is possible to manufacture ultra-thin multilayer magnetic films of the controlled thickness of individual polymer layers. These films contain interlayer magnetic particles of the nanometer size. The effect of the charge sign of the plane surface on the density of magnetic deposits was established. It is also shown that the ultra-sound dispersion of the initial magnetic Fe-particles in the water results in the change of their chemical composition. The electron diffraction data shows that the particles deposited onto a polymer substrate have Fe_3O_4 -type lattice. The magneto-optical properties observed also correspond to those of Fe_3O_4 -nanoparticles too.

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