Structure and Thermal Stability of $NiFe_2O_4$ Nanoparticles Functional Structures

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Abstract—**The structure of monolayers of $NiFe_2O_4$ nanoparticles at their deposition by Langmuir-Blodgett methods and the method of dripping onto the substrate is shown. The high efficiency of obtaining homogeneous monolayers of nanoparticles is proved by using both methods. The effect of annealing on the structure and phase composition of the samples is shown.**

Index Terms—**nanoparticles, Langmuir-Blodgett, annealing TEM, SEM, AFM.**

I. Introduction

In recent years, there has been a great interest in the synthesis and study of the properties of new nanomaterials. Nano-objects and electronic devices working on their basis can provide radically new properties of familiar materials. New methods of obtaining are actively studied and processes are optimized in the already familiar methods. There are a large number of methods, both purely physical and chemical methods[1,2]. Widespread methods for obtaining nanoparticles arrays (NP) include the use of chemical compounds where metal-containing compounds and metal salts are used as starting materials for chemical synthesis. The following techniques are used for synthesis: thermolysis or decomposition of metal compounds under the action of ultrasound, magnetic materials restoration, sol-gel method, magnetic synthesis on the interface of the distribution of the gaseous and liquid phases and heterometal nanoparticles [3-6]. The main condition remains the homogeneity of the particles obtained and the minimum scatter in size. Of particular interest are nanoparticles of ferromagnetic metals, which have unique magnetic properties. Structures based on them can be used as active elements of sensors or in systems of ultra-dense magnetic data recording.

Separately it is necessary to say about the methods of applying nanoparticles on the substrate. Most of the above methods are quite expensive and are not suitable for large surface areas, which makes them unsuitable for mass production. At the same time, nanoparticles of ferromagnetic metal oxides are an ideal candidate for implementing simple and effective methods of application because of their resistance to oxidation. Such methods include the Langmuir-Blodgett method (LB). The method makes it possible to obtain homogeneous ordered mono- and multilayers of nanoparticles over a relatively large area of the substrate[7-10].

The aim of the work is to investigate the structure and thermostability of nanoparticle monolayers, using the example $NiFe_2O_4$ nanoparticles.

II. Method and technique of experiment

The $NiFe_2O_4$ nanoparticles were obtained by the method of chemical synthesis by the authors of work [11] and used unchanged.

The results of the structure investigation immediately after deposition of nanoparticles on the substrate, as well as after the stepwise annealing to 600, 900 and 1100 K are presented. The layers of nanoparticles were obtained by two methods. The first method is the modified Langmuir-Blodgett technique [10]. Authors of the methodology applied a modified vertical LB technique which allows an improved control of the homogeneity and ordering of nanoparticle arrays. In addition, the structure of nanoparticles obtained by the method of dripping onto a substrate is shown. The method is incredibly simple, since it does not require a vacuum chamber and special equipment. For this, a microdoser was used, which made it possible to obtain a drop of the required volume. The optimal concentration was determined experimentally.

The studies used two types of substrates. Samples obtained by the drop method were applied to a carbon film preliminarily deposited on NaCl crystals. For further investigation by transmission electron microscopy (ПЭМ-125K), the film was applied to microscopic grids. Due to the technological features of the Langmuir-Blodgett method, it is impossible to study the layers obtained in this way. Here we used Si / SiO2 substrates (500 nm). The surface structure of the samples obtained by this method was studied using an atomic force microscope (AFM) and a scanning electron microscope (SEM) In our studies, the Dimention Edge atomic force microscope of Bruker was used. The AFM module makes it possible to measure in two modes: contact and semi-contact (tearing). In the study of NP films, the semi-contact mode was used, which greatly reduces the effect of the scanning probe on the surface of the sample. The maximum scanning area is 100 μm, which allows a qualitative study of the ordering and quality of the NP arrays. Along with this, in the study of nanoobjects with dimensions close to the radius of the curvature of the probe, the effect of the convolution [12] always holds, which prevents the receipt of accurate data on the geometric dimensions of the objects under study. For such tasks ideally suited scanning or transmission electron microscopy.The research also used the scanning electronic microscope JEOL JSM 7500F. Annealing of the samples was carried out in a vacuum 10^{-4} Pa.

III. Results

At the first stage, the structure of the samples obtained by the dripping method on a substrate was studied. Figure 1 shows the TEM images of nanoparticles at different annealing temperatures.

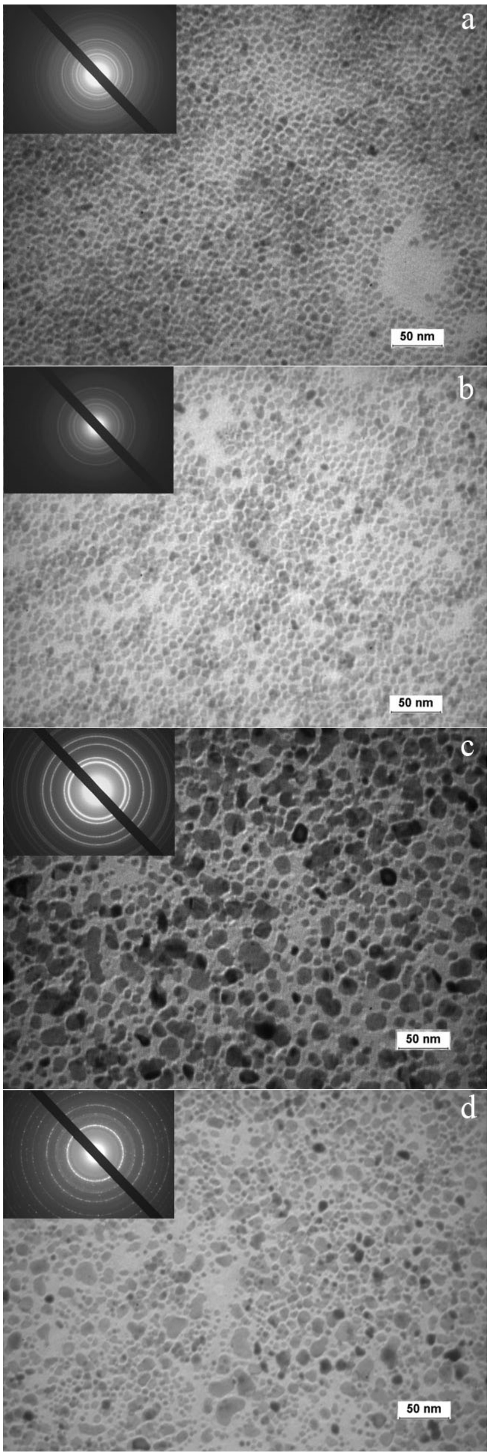

Figure 1. TEM images of the structure of $NIFe_2O_4$ samples obtained by the method of dripping onto a substrate and their electron diffraction patterns at 300 (a), 600 (b), 900 (c) and 1100 K (d)

The results of the study of the structure and morphology of the surface of the samples (Fig. 1) show the high efficiency of the method used to obtain single-layered ordered arrays of magnetic $NiFe_2O_4$ nanoparticles. Results of electron diffraction are given in the insets of Fig. 1. The average of the particle size distribution (given in the histogram in Fig. 2a) is equal to d = 7 nm. Also, the spread is small in size. Annealing up to 600 K does not introduce a change in the size of nanoparticles and the structure remains close to homogeneous.

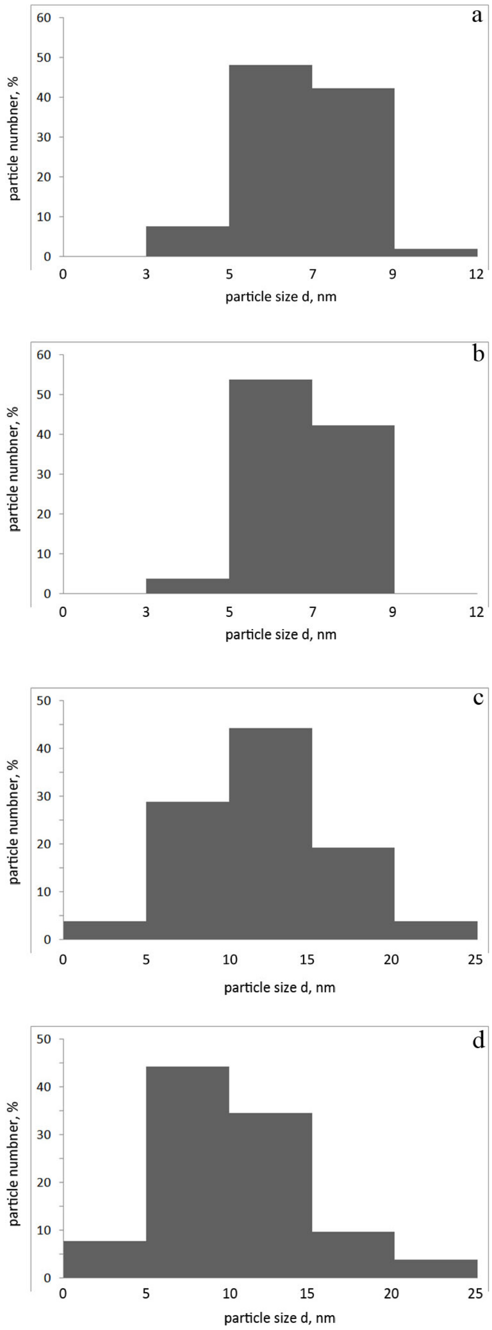

Figure 2. The size distribution of $NiFe_2O_4$ NPs without annealing (a) and after heat treatment to temperatures of 600 (b), 900 (c) and 1100 K (d)

Beginning at 900 K, the nanoparticle size grows rapidly to a value d = 15 nm. With further annealing up to 1100 K, the particle size remains the same as the particle size for annealing up to 900 K. However, there is a preferential orientation of the crystals on the substrate, which is confirmed by the contrast of TEM and reflexes on the electron diffraction pattern. In addition, annealing at a temperature of 1100 K leads to the formation of several phases (Fe, Ni, $FeNi_3$), which is also shown in [12]. In the remaining cases, the $NiFe_2O_4$ phase is conserved.

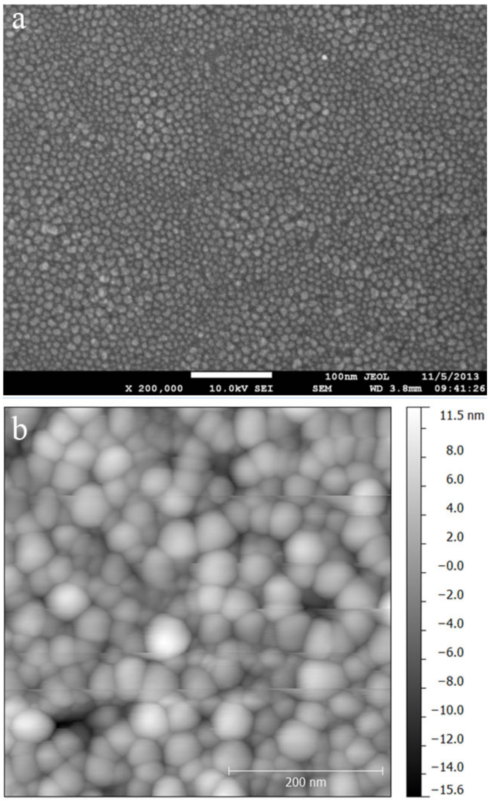

Figure 3. SEM image of a sample obtained by the Langmuir-Blodgett method prior to annealing (3a) and AFM image after annealing to 1100 K (3b)

Figure 3a shows the structure of samples obtained by the Langmuir Blodgett method. The image was obtained by the SEM method. The study of samples by the AFM method does not give a clear picture due to the small particle sizes (in comparison with the diameter of the rounding of the probe). The figure also shows that a homogeneous monolayer without defects was obtained. Figure 3b shows the structure of the sample obtained by the Langmuir-Blodgett method after annealing up to 1100 K. It is evident from the AFM image that after annealing the sample ceases to be a monolayer, and individual particles are layered and collected into larger crystals.

IV. Conclusion

The study shows the high efficiency of the Langmuir-Blodgett technique for obtaining a homogeneous monolayer without defects, with the possibility of incarnating over a large area of the liner. On the other hand, a simple and easy-to-use method of dripping proved to be effective for obtaining a monolayer of nanoparticles in selecting the desired concentration and size of the droplet.

It was shown that when annealing to a temperature of less than 900 K, the layer retains its uniformity, and the nanoparticles retain their size. At higher temperatures, nanoparticles begin to integrate into larger crystals. At a temperature of 1100 K, the $NiFe_2O_4$ phase ceases to exist, and the Fe, Ni, $FeNi_3$ phases are formed.

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References

[1] A.V. Lukashin, A. A. Eliseev, “Physical methods of synthesis of nanomaterials,” Moscow, 2007.

[2] Namita Rajput “Methods of preparation of nanoparticles – a review,” International Journal of Advances in Engineering & Technology, Vol. 7, Issue 4, pp. 1806-181, Jan., 2015.

[3] S.P. Hubin, Yu.A. Koshkarov, G.B. Khomutov, G.Yu. Yurkov, Usp.-Khimii 74, 539 (2005).

[4] Yongai Zhai, Fengqi Liu, Oing Zhlang, Ge Gao, “Synthesis of magnetite nanoparticle aqueous dispersions in an ionic liquid containing acrylic acid anion,” Colloid. Surf. A: Physicochem. Eng. Aspects, vol. 332, pp. 98 – 102, 2009.

[5] S.K. Giri, N.N. Das, G.C. Pradhan, “Synthesis and characterization of magnetite nanoparticles using waste iron ore tailings for adsorptive removal of dyes from aqueous solution,” Colloid. Surf. A: Physicochem. Eng. Aspects, vol. 389, pp.43 – 49, 2011.

[6] S.S. Andrade, D. Rabelo, V.K. Garg, A.C. Oliveira, P.C. Morais, “Synthesis of magnetite nanoparticles in hydrophobic styrene divinylbenzene copolymer templates,”J. Magn. Magn. Mater., vol. 289, pp. 25 – 27, 2005.

[7] Gennes P.G., “Deposition of Langmuir–Blodgett layers,” Colloid. Polym. Sci., V.264, №5, pp.463 – 465,1986.

[8] Laura J. Cote, Franklin Kim, Jiaxing Huan, “Langmuir-Blodgett assembly of graphite oxide single layers,” J. Am. Chem. Soc., V.131, №3, pp.1043 – 1049, 2009.

[9] Xiaolin Li, Guangyu Zhang, Xuedong Bai [et. al.], “Highly conducting graphene sheets and Langmuir–Blodgett films,” Nat. Nanotechnol, V.3, №9, pp. 538 – 542, 2008.

[10] L. Chitu, P. Siffalovic, E. Majkova, M. Jergel et al., “Modified Langmuir-Blodgett deposition of nanoparticles – measurement of 2D to 3D ordered arrays,” Measurement Science Review, Volume 10, No. 5, 2010

[11] Ivanco J., Luby S., Jergel M. [et. al.], “Nitric dioxide and acetone sensors based on Iron Oxide nanoparticles,” Sensor Lett., V.11, №12, pp.2322 – 2326, 2013.

[12] V.A. Zlenko, M.H. Demydenko, S.I. Protsenko, “Determination of the nanoparticle sizes using AFM images and simulation of their magnetooptical properties,” J. Nano- Elec. Phys., V.5, №3, pp.03055–1 – 03055–7, 2013.