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Formation of Ordered Magnetic Nanoparticles Arrays Using Various Obtaining Techniques

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A comparison of the single and multilayers ordered arrays of magnetic nanoparticles (NP) Fe_3O_4, $NiFe_2O_4$ and $CoFe_2O_4$ by the methods of dripping, Langmuir Blodgett and spin coating was presented. Their structure, surface morphology, and the possibility of use for the functional elements of flexible electronics were studied. To investigate the structure of the obtained layers with NPs, we used the methods of transmission and scanning electron microscopy, as well as atomic force microscopy. The formation of the conductive matrix on top of the NP array occurred by the thermal evaporation of Cu or Ag in the vacuum chamber at a residual atmosphere pressure of 10^{-3} – 10^{-4} Pa. Without annealing, the size of the nanoparticles is too small, and they are in a superparamagnetic state. In the case of $NiFe_2O_4$, annealing at a temperature of 1100 K leads to the formation of several phases (Fe, Ni, $FeNi_3$), whereas Fe_3O_4 NPs become Fe-nanoparticles. It was established that after high-temperature annealing at 1100 K, traces of α-Fe_2O_3 oxides are observed, which indicates the formation of a thin oxide shell on the surface of single phase particles. Directly heat treatment leads to the enlargement of NP, which provides for an increase in the amount of magnetic material in a separate particle and, as a consequence, an increase in their magnetic moment. The method Langmuir - Blodgett showed the best efficiency for the formation of perfectly ordered single and multilayers. However, the technique is the most difficult to use, low-productive and not feasible for manufacturing on an industrial scale. At the same time, the dripping method showed its effectiveness when an ideal monolayer is not a necessity. Spin coating allows to obtain a variety of structures, controlling the speed of rotation and concentration of nanoparticles. Therefore, the use of the method is justified if the presence of the monolayer is not critical, because even at low concentrations of nanoparticles the formation of the monolayer is not observed. The maximum value of the magnetoresistance, which was obtained in the Ag matrix is 12 %.

Keywords: Nanoparticles, Fe_3O_4, $NiFe_2O_4$, $CoFe_2O_4$, Dripping, Langmuir-Blodgett, Spin-coating, Magnetoresistance.

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1. INTRODUCTION

Chemical methods of obtaining metal nanoparticles with a small dispersion of technological parameters, such as size and shape have been well developed [1, 2]. Nanoparticles (NPs) can be used as separate functional units for the precise delivery of drugs [3, 4], and as blocks for constructing complex structures [5], or for further introduction into thin metal films, for example, for systems of ultra-dense magnetic recording of information.

Magnetic nanoparticles are most widely used and are usually found in organic or polymeric matrices. Separately, it is worth highlighting the methods of applying nanoparticles to substrates of different types, which is an important stage in the technology of manufacturing functional elements of different nature. There are a many of methods, both purely physical and chemical methods [6]. In addition, the methods are both vacuum and vacuum free. Magnetic nanoparticles of metal oxides are interesting precisely because they are resistant to oxidation, and therefore do not require the presence of a vacuum. The most widely used methods for applying thin layers of NPs are Langmuir-Blodget, spray-pyrolysis, spin coating, chemical vapor deposition. In addition, it is worth highlighting the method of simply dripping the solution from the NPs to the surface.

Separately, it is worth noting the use of nanoparticles in flexible electronics. This technology is increasingly used in some cases when light weight, favorable dielectric properties, reliability, and high density of electrical circuits are needed. To replace conventional solid substrates, flexible substrates should offer properties such as transparency, dimensional stability, low thermal expansion coefficient, elasticity, etc. The main limiting factor is the high temperature of most of the usual technological processes inherent in traditional electronics. According to this, the use of simple and efficient non-vacuum methods of applying nanoparticles is ideal for devices of flexible electronics. That is why the article presents three widely used methods that allow one to obtain single and multilayers of nanoparticles under atmospheric conditions and over large areas of the substrate.

The purpose of the work was to make a comparative assessment of some of the methods of applying nanoparticles to the substrate. The nanoparticles were applied from a solution of chloroform, which quickly evaporates in the air.

2. EXPERIMENTAL DETAILS

Nanoparticles of metal oxides were obtained by the method of chemical synthesis by the authors of work [7] and used unchanged. As application methods, the modified Langmuir-Blodgett technique, the method of simply dripping the solution of NP to the substrate surface and the method of spin coating were used. These methods obtained monolayers from nanoparticles for further introduction into the conducting matrix, and subsequent use in instrumental structures of the spin-valve type. In the fol-

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lowing sections of the article, the conditions for obtaining for each method will be described in more detail.

To study the structure of the obtained layers with NPs, we used the methods of transmission and scanning electron microscopy, as well as atomic force microscopy. The formation of a conductive matrix on top of the NP array occurred by the thermal evaporation of Cu or Ag in the vacuum chamber at a residual atmosphere pressure of 10^{-3}-10^{-4}Pa. The thickness of the deposited material was controlled using a quartz resonator. We used monocrystalline silicon plates with orientation (100) with a layer of silicon dioxide SiO_2 (500 nm).

2.1 The Technique of Dripping the Solution on the Substrate

The technique of dripping the solution is simple and effective for applying a layer of nanoparticles from solution. In our case, the nanoparticles were in chloroform solution. Due to its high volatility, chloroform evaporates very quickly in air after dripping onto the substrate. Both silicon substrates and carbon films were used as substrates for examination in a transmission electron microscope. Fig. 1 shows the structure and diffraction patterns of the nanoparticle layer. In addition, the effects of annealing up to 1100 K on the layer properties are shown. This temperature is optimal for observing the effect of giant magnetoresistance (GMR) after applying a conductive matrix. Without annealing, the size of the nanoparticles is too small, and they are in a superparamagnetic state. The results for flow annealing temperatures were discussed in our paper [8], in which it was shown that the magnetoresistance begins to manifest itself from 600 K and reaches its maximum at 1100 K. In order to minimize the occurrence of diffusion processes between the layers, prior to its application, thermal processing of the NPs arrays was carried out. In the case of $NiFe_2O_4$, annealing at a temperature of 1100 K leads to the formation of several phases (Fe, Ni, $FeNi_3$), whereas Fe_3O_4 NPs become Fe-nanoparticles. It was established that after high-temperature annealing at 1100 K, traces of α-Fe_2O_3 oxides are observed, which indicates the formation of a thin oxide shell on the surface of single phase particles. Directly heat treatment leads to the enlargement of NP, which provides for an increase in the amount of magnetic material in a separate particle and, as a consequence, an increase in their magnetic moment. NPs increase in size by almost 3-4 times (from 10 nm to 40 nm).

2.2 Modified Langmuir-Blodgett Technique

Despite the fact that the dripping method is the simplest and at the same time satisfactory from the point of view of obtaining homogeneous layers of nanoparticles, it is possible to obtain high-quality homogeneous layers using special equipment. One such method is the Langmuir-Blodgett method [9, 10]. In our studies, we used a modified Langmuir-Blodgett technique developed by the authors [11].

The method makes it possible to obtain ideally ordered single and multi layers of nanoparticles at the liquid/air interface over a relatively large area of the substrate under atmospheric conditions. This becomes possible due to the constant computer control of such parameters as surface tension P from the active surface area of the formed nanoparticle array on the water surface S in the process of obtaining samples [12].

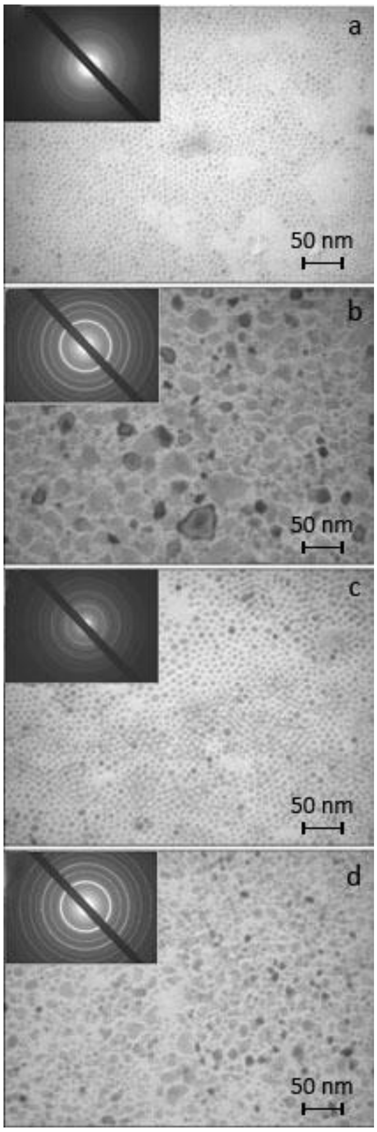

Fig. 1 – Structure and diffraction images of a monolayer of nanoparticles Fe_3O_4 (a, b) and $NiFe_2O_4$ (c, d) obtained by the dripping method before annealing (a, c) and after annealing (b, d) up to 1100 K

Using this technique, layers of nanoparticles Fe_3O_4, $NiFe_2O_4$ and $CoFe_2O_4$ were obtained. The SEM images of the resulting nanoparticle arrays are shown in Fig. 2.

As can be seen from Fig. 2, the layers obtained by this method are more uniform, and also completely fill the surface, in contrast to the dripping method. Annealing of such structures leads to a similar method of dripping results.

2.3 Spin-Coating Methods

The Langmuir-Blodgett technique loses its effectiveness when using substrates with a hydrophobic surface, since not all materials can be equally applied to them. The nanoparticles Fe_3O_4, $CoFe_2O_4$, and $NiFe_2O_4$ are used in studies.

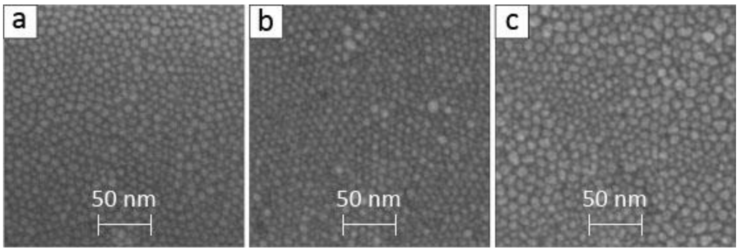

Fig. 2 – SEM images of ordered arrays of Fe_3O_4 (a), $CoFe_2O_4$ (b) and $NiFe_2O_4$ (c) nanoparticles formed on the surface of the water/air separation by the Langmuir-Blodgett method and deposited on a SiO_2(500 nm)/Si substrate

In this case, if it is necessary to deposit a layer of NPs on a hydrophobic surface, it is appropriate to apply the spin coating technique [13, 14]. This technology consists in the distribution of the solution over the surface of the substrate under the action of centrifugal forces.

The nature of this distribution depends on the speed of rotation, the density of the solution, the type of solvent and the surface. In our case, the SCI-10 spin coater was used.

Before applying the NPs, a series of experiments was carried out to establish the optimal rotation speed and concentration to obtain a single layer of NPs over the entire surface of the substrate.

For this purpose, solutions of Fe_3O_4, $CoFe_2O_4$ and $NiFe_2O_4$ NPs with concentrations of 1, 5, 10, 25, 50, 75, 100 μg / ml in chloroform were prepared. Before using the NPs was in a solution of toluene. For a better distribution on the substrate surface, it must be replaced with chloroform, which has a high evaporation rate and is ideal for applying NPs.

The study of the distribution of NPs on substrates showed the possibility of the formation of various nanostructures from small nanoclusters to continuous networks. Fig. 3 illustrates the AFM images obtained by the method of spin coating of nanostructures.

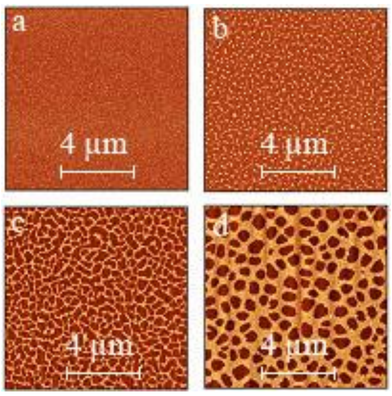

Fig. 3 – AFM images obtained by the spin coating technique of $CoFe_2O_4$ nanoparticle layers using different parameters: 1 μg/ml, 50 rev/s (a); 25 μg/ml, 50 rev/s (b); 50 μg/ml, 25 rev/s (c); 75 μg/ml, 10 rev/s (d)

At high rotational speeds, nanostructured layers of a predominantly cluster character are observed. An increase in the concentration of nanoparticles in chloroform solution leads to the formation of networks with low frequencies uniformly distributed over the substrate surface even at high rotational speeds. In our studies, the formation of clusters with NPs was observed at concentrations of less than 10, 25, 50, 75 μg/ml for rotational speeds of 10, 25, 50, 75 rev/s, respectively. Moreover, at a constant rotational speed and when using solutions with a high concentration, the cluster size increases with decreasing distance between them. Figs. 4 and 5 show the results of the study of the contact angle and roughness as a function of the rotational speed of the spin coater and the concentration of nanoparticles obtained using Brewster microscopy method [15].

3. COMPARATIVE EVALUATION OF LAYERS OBTAINED BY DIFFERENT TECHNIQUES

Research allows us to talk about the possibility of using the method for certain technological tasks and under certain conditions. Table 1 shows the comparative characteristics for different techniques of producing single

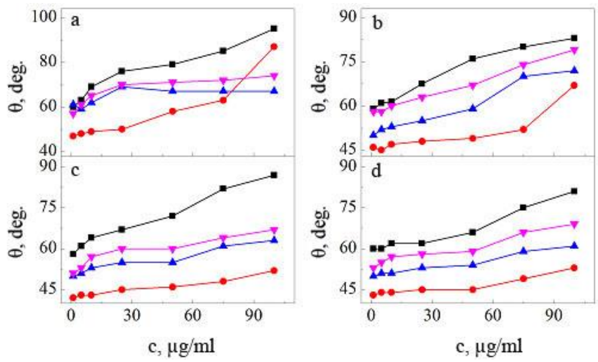

Fig. 4 – Generalized measurement results of changes in the contact angle from the concentration of the NP solution for a rotation speed, rev/s: 10 (a), 25 (b), 50 (c) and 75 (d) immediately after application (■) and after annealing at 520 K (●), 900 K (▲) and 1100 K (▼)

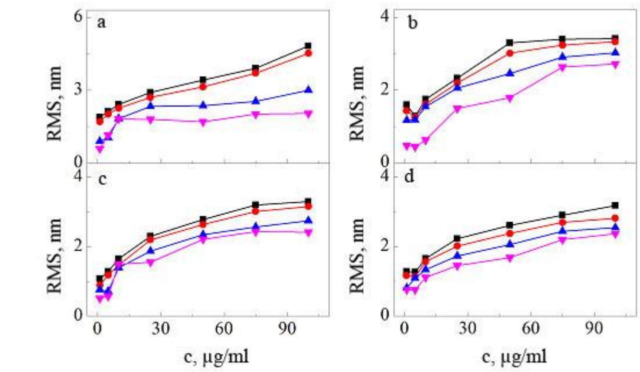

Fig. 5 – Generalized measurement results of the roughness value from the concentration of the NP solution for a rotation speed, rev/s: 10 (a), 25 (b), 50 (c) and 75 (d) immediately after application (■) and after annealing at 520 K (●), 900 K (▲) and 1100 K (▼)

Table 1 – Comparison of parameters of nanoparticles layers obtained by different techniques

Method / Parameters	Dripping	Langmuir-Blodgett	Spin Coating
Substrate surface filling, %	80-85	99	50-80
Relative receiving rate	Fast	Slow	Medium
Vacuum	Not required	Not required	Not required
Simplicity	Simple	Hard	Relatively simple
Opportunity to use on large substrates	Not limited	Limited installation area	Available when using industrial centrifuges
Type of structure formed	Ordered monolayers and disordered multilayers	Ordered monolayers and multilayers	Clusters and wires
Using flexible substrates	Not limited	Only possible for hydrophilic substrates.	Not limited
Maximum value of magnetoresistance of ordered single layer arrays of nanoparticles in the conducting matrix Ag according to the data of the work [16]	Fe_3O_4 – 6% $NiFe_2O_4$ – 10% $CoFe_2O_4$ – 12%		The method is not applied

and multilayers of nanoparticles. From data analysis it becomes clear that the most effective technique for obtaining homogeneous layers is the Langmuir-Blodgett. However, the technique is the most difficult to use, low-productive and not feasible for manufacturing on an industrial scale. At the same time, the technique of simple dripping of a nanoparticle solution onto the surface of a substrate is the simplest and most effective, allowing to obtain ordered single and unordered multi layers of NPs with the right choice of their concentration in solution. The disadvantage is incomplete filling of the surface.

Separately, we single out the spin coating method. With its relative simplicity, depending on the parameters used (concentration of NPs and rotational speed), structures of completely different types with different distribution on the substrate can be obtained. However, we did not succeed in obtaining a homogeneous layer of nanoparticles, since even at low concentrations of NPs in solution, the formation of clusters of different sizes was observed.

4. CONCLUSIONS

The parameters of layers of ferromagnetic metals NPs were analyzed depending on the method used. It is shown that the Langmuir-Blodgett method makes it possible to obtain the most qualitative homogeneous single and multi layers over a relatively large area of the substrate. However, it is complicated and low-productive. On the other hand, the dripping method allows to obtain single and multi layers with satisfactory parameters controlling only the concentration of nanoparticles in the final solution.

Spin coating also showed the impossibility of forming uniform layers of nanoparticles, since even at low concentrations of nanoparticles, the formation of clusters of different sizes is observed. On the other hand, this method allows to obtain a variety of structures, controlling the speed of rotation and concentration of nanoparticles. Therefore, the use of the method is justified if the presence of a monolayer is not critical.

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Формування впорядкованих масивів магнітних наночастинок з використанням різних методів отримання

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Представлене порівняння одно- і багатошарових упорядкованих масивів магнітних наночастинок Fe_3O_4, $NiFe_2O_4$ та $CoFe_2O_4$ отриманих методами капання, Ленгмюра-Блоджет і спін-коатингу. Вивчена їх структура, морфологія поверхні, можливість використання у функціональних елементах гнучкої електроніки. Для дослідження структури отриманих шарів з НЧ використовувалися методи просвічуючої і скануючої електронної мікроскопії, а також атомно-силової мікроскопії. Формування провідної матриці зверху масиву НЧ відбувалося при термічному випаровуванні Cu або Ag у вакуумній камері при залишковому тиску атмосфери 10^{-3}–10^{-4} Па. Без відпалу розмір наночастинок занадто малий, і вони знаходяться в суперпарамагнітному стані. У випадку $NiFe_2O_4$ відпал при температурі 1100 K призводить до утворення декількох фаз (Fe, Ni, $FeNi_3$), тоді як НЧ Fe_3O_4 стають наночастинками Fe. Встановлено, що після високотемпературного відпалу при 1100 K спостерігаються сліди оксидів α-Fe_2O_3, що вказує на утворення тонкої оксидної оболонки на поверхні однофазних частинок. Безпосередня термічна обробка призводить до збільшення НЧ, що забезпечує збільшення кількості магнітного матеріалу в окремій частинці і, як наслідок, збільшення їх магнітного моменту. Метод Ленгмюра-Блоджет показав кращу ефективність для формування ідеально впорядкованих моно- і мультишарів. Однак цей метод є найбільш складним у використанні, малопродуктивним і нездійсненним для виробництва в промислових масштабах. У той же час метод капання показав свою ефективність, коли ідеальний моношар не є необхідністю. Метод спін-коатингу дозволяє отримувати різні структури, контролюючи швидкість обертання і концентрацію наночастинок. Отже, використання методу виправдано, якщо присутність моношару не є критичним, оскільки навіть при низьких концентраціях наночастинок утворення моношару не спостерігається. Максимальне значення магнітоопору, яке було отримано в матриці Ag, становить 12 %.

Ключові слова: Наночастинки, Fe_3O_4, $NiFe_2O_4$, $CoFe_2O_4$, Капання, Ленгмюр-Блоджет, Спін-коатинг, Магнітоопір.