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Role of carbon in the formation of the structure and magnetic properties of Ni@CN$_x$ nanoclusters under reactive magnetron deposition

R. V. Shalayev, V. N. Varyukhin, A. M. Prudnikov, A. I. Linnik, V. V. Syrotkin

Donetsk Institute for Physics and Engineering named after A. A. Galkin,
R. Luxembourg str. 72, 83114, Donetsk, Ukraine

sharos@donfti.ru

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Nanostructured hybrid Ni–CN$_x$ films were grown by magnetron sputtering of a composite graphite-nickel target. Atomic force microscopy showed the clustered nature of the films deposition on the substrate surface: a relatively high pressure in the low-temperature magnetron plasma made it possible to form the Ni@CN$_x$ nanoclusters type "core-shell", where metallic nickel is the core and carbon nitride is the shell. When studying the role of carbon in the formation of the structure and properties of Ni@CN$_x$ nanoclusters, it was established that the saturation magnetization $4\pi M_s$ of nanoclusters drops sharply with a carbon content above 30 at.%. The reason is the formation of an increasingly saturated solid solution of carbon in nickel. At a carbon concentrations above 38 at.%, amorphous Ni–CN$_x$ nanoclusters are formed in the magnetron plasma, which are deposited on the substrate. An increase in the substrate temperature leads to the crystallization of Ni atoms, and the C and N atoms are forced out onto the surface of the nickel core, forming an array of Ni@CN$_x$ elements.

Keywords: carbon nitride, nanoclusters, magnetron sputtering.

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1. Introduction

Carbon nanomaterials have unique physical and chemical properties [1, 2]. In recent years, attention has been drawn to the so-called hybrid nanomaterials with metal encapsulated in a carbon shell (Me@C) [3]. The carbon coating covering the ferromagnetic metal not only provides protection against mechanical damage, but also protects it from oxidation. Due to this, the limits of the potential application of such materials are expanding [4]. Areas of use of material such as Me@C: as magnetic recording devices, medical diagnostics and "transportation" of drugs in the human body [5], nanocontainers for the storage of metallic materials [6], etc. There are many methods for obtaining metallic materials coated with a carbon shell: laser ablation, arc method, chemical vapor deposition, evaporation by condensation from the gas phase, plasma-chemical deposition [7,8]. The above methods of obtaining Me@C hybrid structures are mainly high-temperature. In this paper, we propose a magnetron sputtering method (compatible with semiconductor technologies) that does not require high temperatures. Its positive factor is the relatively high pressure of the buffer gas, which leads to the formation of nanoclusters [9]. The use of a composite target makes it possible to obtain nanocluster type "core-shell". In this case, the metal is the core, and the carbon is the shell. The physical and chemical properties of such nanoclusters are strongly dependent upon the structure of the core and the shell.

The purpose of this work was to study the role of carbon in the formation of the structure and magnetic properties of Ni@CN$_x$ nanoclusters at reactive magnetron deposition on a cold substrate, and also its modification upon heating during growth.

2. Experiment

Nanostructured film structures of the Ni–C system doped with N were obtained by magnetron sputtering of a composite nickel-carbon target in an argon atmosphere with nitrogen admixture on quartz and cover glass substrates. The plasma power did not exceed 20 W, the buffer gas pressure was 26 Pa. The surface morphology of the films was investigated by atomic force microscopy (AFM) using the Ntegra probe nanometer laboratory of the energy dispersive spectrometer INCA Penta FETx3. X-ray analysis of the obtained samples was carried out on a DRON-3 installation in CoKα-radiation. The saturation magnetization of the material of the films was measured by means of an induction-frequency installation by the change in the resonant frequency $\Delta F \propto \Delta M = f(H)$ of the oscillatory circuit into the coil of which the sample was placed [10]. The use of an inductive-frequency method makes it possible to directly measure the saturation magnetization of $4\pi M_S$ of a ferromagnetic sample [11]. The saturation magnetization of all samples was determined at room temperature.

3. Results and discussion

Atomic force microscopy was used to investigate nucleation processes on the growth surface and the morphology of the surface of growing films. For this purpose, we used polished quartz glass substrates with a roughness of the order of 1 nm. This made it possible to control the complex morphology of the surface of the obtained samples with an accuracy also comparable to 1 nm.

As can be seen from Fig. 1a, at the initial stage of growth the substrate surface is covered by cluster elements of $\sim$ 10 nm in size in a chaotic order. With increasing growth time, the entire surface of the substrate is covered by such cluster elements.

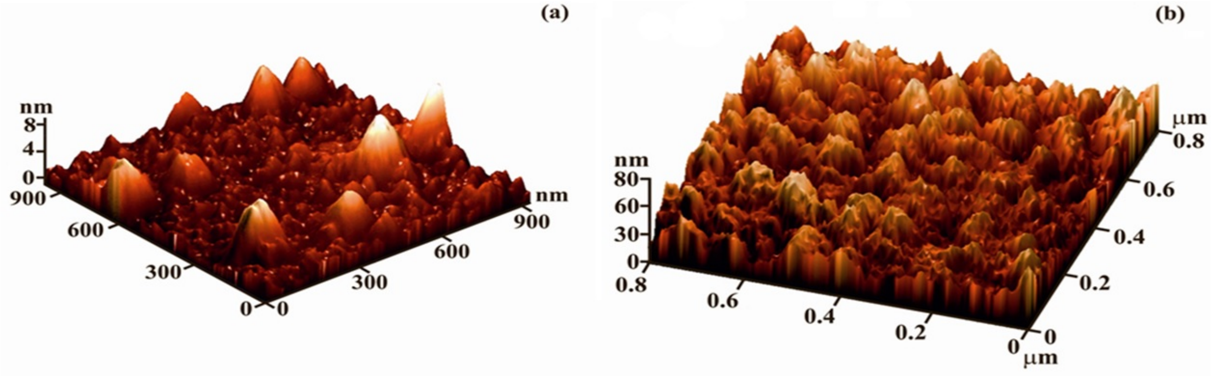

FIG. 1. AFM image of the Ni–C film surface after 10 seconds of growth (a) and after 300 seconds of growth (b)

Thus, the study of nucleation processes on the substrate surface shows that in the case of magnetron sputtering, there is a cluster character of the deposition of Ni–C films: nanosized clusters of sputtering material already formed in the plasma are deposited on the substrate surface.

The occurrence of clusters is due to the rather high pressure of the buffer gas [9], in our case about 150 mTorr. This pressure is almost an order of magnitude higher than that usually used in magnetron sputtering experiments at low powers ($\sim$ 20 W) for the magnetron plasma. As a result, a small region of plasma is characterized by a sufficiently high concentration of atomized atoms. Due to this, at a relatively low temperature, self-organization processes begin to occur – the clusters formation in the plasma from the target material and the buffer gas.

When the flow of charged clusters hits a relatively cold substrate, relative to the plasma and the clusters temperature, there is its "congealing" with the transfer of thermal energy to the substrate. In this case, nucleation centers of the film are formed, which is observed in AFM studies.

This result requires a rethinking of the growth processes of nanostructured films by the method of magnetron sputtering and the construction of new models, in particular, growth models of nanocolumns from charged nanoclusters. Figure 1b shows 3D images of the surface of the film obtained after 300 sec of growth. A "sharp" acicular nanocolumnar structure formed by individual nanoclusters is clearly visible.

To determine the role of carbon in the formation of the structure and properties of Ni@CN$_x$ nanoclusters, a series of films differing in carbon content (from 10 to 40 at.%) with an admixture of nitrogen of 5 at.%, was grown at a constant growth time of 10 min (thickness $\sim$ 100 nm) without heating substrate.

Analysis of the diffractograms of the obtained films showed that only reflections corresponding to (111), (200) and (220) planes of the FCC nickel lattice are present. The lattice constant is 3.529 Å, which is close to the value for the bulk nickel (3.56 Å). The only difference is in some broadening of the X-ray reflexes. This indicates a relatively small amount of Ni-crystallites, of which films are built. At the same time, the presence of carbon in the film composition and the absence of nickel oxide indicate, as shown in [3], the presence of a carbon shell around nickel nanocrystallites. Thus, we obtain in the magnetron plasma nanoclusters of the "core-shell" type Ni@CN$_x$ – a ferromagnetic metal (Ni) coated carbon with an admixture of nitrogen. Nitrogen is necessary for curving graphene planes, because the presence of nitrogen leads to the formation of pentagons.

Figure 2 shows the dependence of the crystallite size D (determined from the broadening of X-ray reflections) and the saturation magnetization $4\pi M_S$ (measured at room temperature) on the carbon concentration in Ni@CN$_x$ nanoclusters ($N_x = 5$ at.%). We note that the magnetization dependence has a sharply nonlinear character – with an increase in the carbon concentration ($\geq$ 30 at.%) the magnetization $4\pi M_S$ falls very rapidly. The crystallite size also decreases with increasing carbon concentration, but is practically linear. Extrapolation of the $4\pi M_S = f(C)$

curve to the zero magnetization value yields $C = 37.5$ at.%, at which the film is not magnetically ordered at all. The crystallite size is about 8 nm. With an increase in carbon concentration (~ 38 at.%) the films become X-ray amorphous.

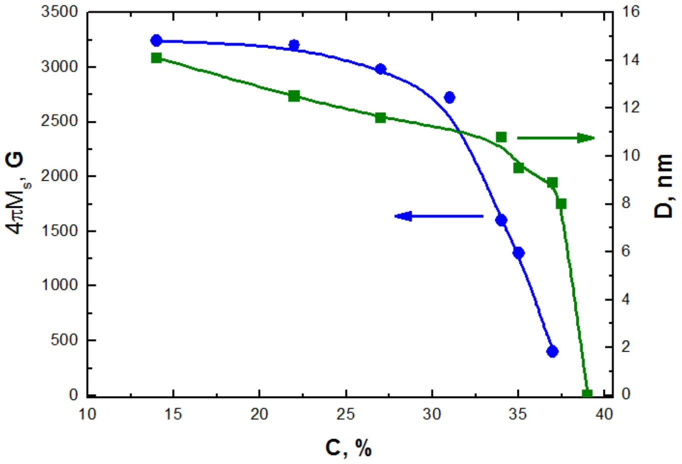

FIG. 2. Dependence of the crystallite size D and the saturation magnetization $4\pi M_S$ on the carbon concentration C in nanoclusters Ni@CN$_x$

To determine the effect of substrate temperature on the structure and magnetic properties of Ni@CN$_x$ nanoclusters, three series of films were grown, differing in the ratio of C/Ni atoms (A series – 30/70, B series – 40/60 and C series – 60/40) up to 100 nm thick.

Figure 3a shows the dependences of the Ni nanocrystallites size D (estimated from the broadening of X-ray reflections by the Debye-Scherrer formula) of nickel-carbon films of series A from the substrate temperature T_S. With increasing T_S, the crystallite size D increases smoothly and has different values for reflexes (111) and (200). It should be noted that there is practically no such difference at low temperatures. This indicates that at low temperatures the clusters deposited on the substrate have a predominantly spherical shape. And also, an increase in the size D of nanocrystallites in comparison with their size at a lower temperature makes it possible to state that the growth is due to diffusion processes during the temperature effect of the substrate.

Figure 3b shows the dependence of the Ni nanocrystallites size D of nickel-carbon films of series B on the substrate temperature. It can be seen that with increasing temperature, the size of nanocrystallites also increases. There is some specific substrate temperature T_{cr} of about 80 °C, below which the size of the nickel particles approaches zero. It should be noted that in the temperature range of the substrate T_S 125...220 °C, the size of the crystallites practically does not change, and then sharply goes up, presumably due to the fusion of individual clusters due to diffusion processes.

Figure 3c demonstrates the effect of substrate temperature T_S during film growth on the saturation magnetization $4\pi M_S$ for the films of A, B and C series. As we can see, films of group A exhibit ferromagnetism even when deposited on a cold substrate. A slight increase in $4\pi M_S$ with an increase in the substrate temperature T_S can also be easily explained by the size effect [11] associated with the growth of the crystallite size D (Fig. 3a). These results are in good agreement with the notion that, at low carbon concentrations, clusters deposited on the substrate have a structure of the “Ni-nanocrystallite/C-shell” type [3]. Moreover, they are formed in a magnetron plasma by crystallization of nickel atoms inside an amorphous nickel-carbon cluster. With increasing substrate temperature, the size of the nickel core of the cluster grows, due to diffusion processes on the substrate surface (see Fig. 3a) and the saturation magnetization of crystallites $4\pi M_S$ also increases (see Fig. 3c). It is clear that when the size of Ni crystallites at a temperature $T_S \approx 300$ °C reaches macroscopic values, the value $4\pi M_S$ approaches the magnetization of bulk nickel.

At the same time, the films of group B and C with higher carbon contents were non-magnetic when deposited on a cold substrate. They began to exhibit ferromagnetism only when deposited on heated substrates. Moreover, with an increase in the C/Ni ratio, the specific temperature T_{cr} of the onset of ferromagnetism increases: at C/Ni $= 40/60 T_{cr} \approx 80$ °C, at C/Ni $= 60/40 T_{cr} \approx 160$ °C.

We see that as the carbon concentration in the series B and C films increases, the magnetization decreases, in full accordance with the model [12–14], suggesting the formation of an increasingly saturated solid solution of carbon in nickel. Subsequently, as the substrate temperature rises, the nickel phase in the nanoclusters crystallizes

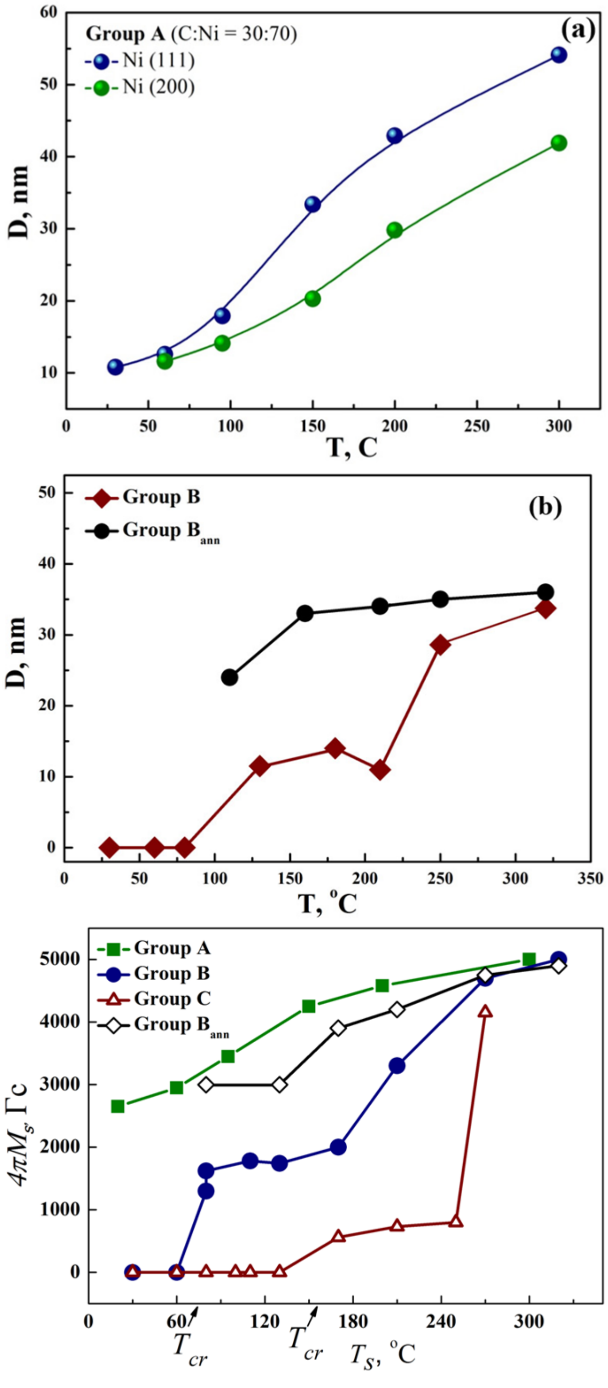

FIG. 3. Influence of substrate temperature on the nickel nanocrystallites size in films of various groups (a, b). Dependence of the saturation magnetization $4\pi M_S$ on the substrate temperature (c). B_{ann} – films of group B after annealing

first, and the more carbon in the cluster, the smaller the magnetization of the nickel crystallite and its smaller size (see Fig. 2, Fig. 3b and Fig. 3c). This process takes place in the temperature range of the substrate T_S 80 – 180 °C for B-group films and T_S 160. . . 250 °C for C-group films. At higher T_S, due to the diffusion processes on the substrate and the release of carbon from the saturated solid solution of carbon in nickel, a fusion of separate clusters occurs into a common nickel core covered with a carbon shell and, correspondingly, an increase in the magnetization. To confirm such a model, we performed an experiment on annealing samples of group B. The experiment was carried out in air at a temperature of 350 °C for 10 min. The experimental results are shown in Fig. 3c (curve B_{ann}). As we see, the curve B_{ann} fixes the increase in magnetization after annealing for samples obtained at low substrate temperatures. Thermal annealing of the samples to accelerate the decomposition of the supersaturated solid solution of Ni(C) confirms the diffusion mechanism of growth of nickel crystallites at high substrate temperatures. An increase in the size of the Ni crystallites is also evidenced by calculations based on X-ray data of the characteristic size D for samples of group B subjected to the above annealing. These data are presented in Fig. 3b, the curve B_{ann}.

Thus, at a low carbon concentrations, a metastable supersaturated solid solution of Ni(C) is formed first in the magnetron plasma. The supersaturated solid solution decomposes into nickel and pure carbon with the displacement of C atoms to the surface of the nickel crystallite, forming a nickel nanocluster with a carbon shell Ni@C [12–14].

4. Conclusions

The obtained results make it possible to draw the following conclusions. At high C/Ni ratios, the nickel-carbon clusters formed in the plasma are amorphous formations in the form of a mixture of Ni and C atoms. When deposited on a cold substrate, such clusters form nonmagnetic films. At substrate temperatures above T_{cr}, a weakly magnetic supersaturated solid solution of Ni(C) begins to form. Then, the supersaturated solid solution decomposes into nickel and carbon doped with nitrogen, forming a nickel nanocluster with a carbon shell. In this case, the solid solution can partially or completely decay, reducing the concentration of carbon in the metallic core [12, 14]. Further annealing, as shown by our experiments, leads to a significant additional decay of the system.

At low C/Ni ratios, ferromagnetic nickel-carbon nanoclusters of the "core-shell" type are already formed in the plasma. The mechanism of formation for such nanoclusters is caused by the formation of supersaturated solid solutions based on Ni(C) and its subsequent disintegration into pure nickel in the core and the formation of a carbon coating on the surface of the nanoparticles.

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