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Gas-Phase Synthesis of Film Structures of Ni–N System

R. V. Shalaev

O. O. Galkin Donetsk Physicotechnical Institute, N.A.S. of Ukraine,
72 Rosa Luksemburg Str.,
83114 Donetsk, Ukraine

As shown, the magnetron sputtering is effective for the synthesis of various nanostructured phases of nickel nitride (solid solution of nitrogen in nickel, Ni_4N, Ni_3N, and Ni_2N). The regularities of formation of globular or nanocolumnar film structures are determined, depending on the concentration of nitrogen in the buffer gas.

Показано, що магнетронне розпорошення є ефективним для синтези різноманітних наноструктурних фаз нітриду ніклю (твердий розчин Нітроґену у ніклі, Ni_4N, Ni_3N та Ni_2N). Визначено закономірності утворення наноколонарних або ґлобулярних плівкових структур системи Ni–N залежно від концентрації азоту у буферному газі.

Показано, что магнетронное распыление эффективно для синтеза различных наноструктурных фаз нитрида никеля (твёрдый раствор азота в никеле, Ni_4N, Ni_3N и Ni_2N). Определены закономерности образования наноколонарных или глобулярных плёночных структур системы Ni–N в зависимости от концентрации азота в буферном газе.

Key words: nickel nitride, nanocolumnars, globules, magnetron sputtering, atomic force microscopy.

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1. INTRODUCTION

Last years, nitrides of transition metals, such as Fe, Co, Ni, attract major interest of the scientists because of their unique physical properties—mechanical, optical, electrical, and magnetic ones. These materials have a high potential of practical application in such fields of a science and technique, as semiconductor technics, magnetooptics, sensor devices, and magnetic devices of storing of information [1, 2]. As known, a nitrogen introduction in structure of transition metals allows to actively control their properties, in particular, magnetic ones (coercivity, magnetic moment) [3]. Unfortunately, nitrides of such metals as Ni and Co are frequently metastable and not all their phases are uniquely identified, despite the complicated phase diagram. First, it falls into nickel: nickel nitrides, in comparison with other nitrides of metals, are insufficiently studied, their properties, and methods of production are not well observed, until now the confirmed data for some phases of Ni–N are absent.

At the same time, numerous experiments on synthesis of film nickel nitrides have shown that the composition of films is an intermixture of various nitride phases up to the pure nickel [4, 5], though there is an obvious dependence on the nitrogen contents: the higher nitrogen content—the more nitrogen saturated nitride phases enter into the composition of film. During the gradual increase of the nitrogen content in a material, pure nickel with the f.c.c. lattice sequentially transfers in nickel nitride Ni_4N (f.c.c.), further in Ni_3N (h.c.p.) and at the maximum concentrations of nitrogen in Ni_2N (body-centred tetragonal—b.c.t.) [6]. All these phases under certain conditions exist in the material simultaneously.

Nickel nitrides are usually produced by such methods as reactive spraying and ion-beam implantation. Implantation of ions sometimes is more preferable for the precise stoichiometry control and production of various unstable phases of nickel nitride [7]; however, it usually demands rather complicated procedures. Reactive magnetron spraying is also one of the popular methods of metals nitrides films production. For instance, Dorman and co-authors [5] produced nickel nitrides (Ni_4N, Ni_3N and Ni_2N) by the direct current reactive spraying at various fractional pressure of nitrogen. Phase Ni_3N can be produced at nickel heating in a stream of ammonia NH_3 at 781 K [8]; however, it is not stoichiometrically pure. Ni_3N is also produced using high pressure (20 GPa) and temperatures (2000 K) from the intermixture of nickel and sodium nitride NaN_3 [9]. Besides, in the literature, there are mentions of such phases as Ni_3N_2 and NiN_6 [10], which were not confirmed in later works.

Thus, frequently contradictory information concerning diversiform phases of nickel nitride and insufficiently studied behaviour of Ni–N (in particular, in the form nanostructured films) demand the additional investigations devoted to production of various phases of Ni–N system.

In the present work, a number of phases of nickel nitride (Ni with a nitrogen solid solution, Ni_4N, Ni_3N, and Ni_2N) are synthesized by a method of magnetron sprayings of a nickel target in an argon–nitric intermixture, which is confirmed by the X-ray diffraction studies.

2. EXPERIMENT AND DISCUSSION

Process of magnetron sputtering allows to precipitate films of a wide spectrum of materials with a variation of a thickness from tens nanometres to several micrometres. Magnetron spraying falls into the methods of spraying of materials with the ionic bombing of a surface. In the present work, films of nickel and nickel nitride are produced on the VUP-5M installation with a standard magnetron direct current attachment. Plasma is produced by means of a magnetron of a planar design with a flat cathode and an orificed anode. Power of discharge of the magnetron did not exceed 20 W, a discharge current—40 mA. The nickel (very high purity grade) target of 40 mm in diameter is fixed on the cathode of the magnetron and sputtered on substrates from a cover or quartz glass at the temperature of ≅ 240°C in Ar atmosphere with adding from 2% to 70% N_2. Gas mixture is preliminary prepared in external gas system and pumps down in vacuum volume through the piezoelectric inlet valve. Pressure of gas in the chamber is controlled by devices of the vacuum post and comprises 24 Pa. Substructures are preliminary cleaned in an intermixture of solvents and their vapours. The distance from the cathode to the substructure is 2.5 cm. Time of growth of films was 20 minutes; the thickness thus varied from 0.2 to 0.5 micrometres (measurements were performed using MII-4 interference microscope).

The X-ray diffraction analysis of the produced specimens is performed using of DRON-3 diffractometer in CoK_α radiation, and also using Panalytical X'Pert MPD α1 Bragg–Brentano diffractometer equipped with the scintillation counter, in CuK_α radiation. Morphology of a surface of films and their thickness is analysed by field emissive scanning electron microscopy using JEOL JSM-6490 LV device, and an atomic force microscopy (AFM) with the help of the Ntegra Aura probe nanostation. Magnetic properties of the films are studied using inductive-frequency installation [11]. X-ray diffraction patterns of Ni–N system films produced with adding of 0–8 vol.% of nitrogen in a growth atmosphere at CuK_α radiation are presented in Fig. 1. Identification of the specified structure has been performed and the information concerning phase composition of films is obtained (see Table 1).

The analysis of X-ray spectra of the specimens produced in nitrogen-free atmosphere and at insignificant concentrations of nitrogen (less than 2%), has shown the presence of lines, close to lines of the f.c.c. lattice of nickel (see Fig. 1, *a*). Difference consists only in some broadening and shift of lines towards smaller angles. Besides, in the specimen No. 252, the presence of traces of the ferromagnetic phase of Ni_4N nitride is observed. Shift of Bragg reflexes directly points to the increase of f.c.c. lattice parameter of nickel that is indicative of nitrogen solid-solution formation in nickel.

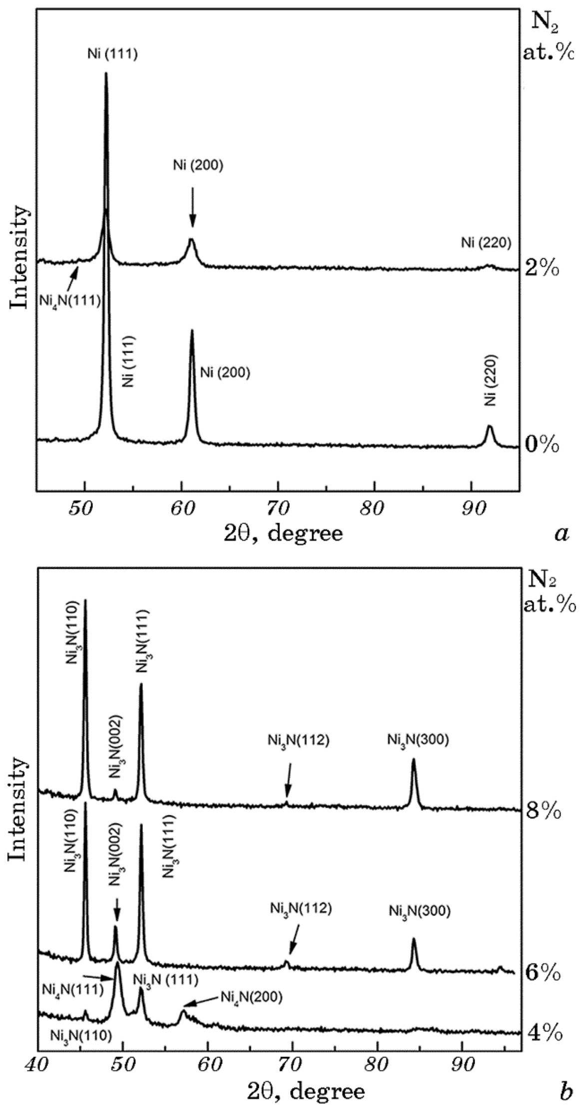


Fig. 1. X-ray diffraction patterns (CoK_α radiation) of Ni–N films produced with the contents of 0–2% N_2 (*a*) and 4–8% N_2 (*b*).

Thus, at concentrations of nitrogen in the gas phase lower than 2%, the films are made as the pure nickel phase or the nitrogen solid solution in nickel. The ferromagnetic phase of Ni_4N nickel nitride (f.c.c.) is sustainably formed at nitrogen concentrations in the growth atmosphere less than 2–4% (see Fig. 1, *b*) and, at the further increase of nitrogen content, is substituted by the Ni_3N phase (h.c.p.). Intensive reflexes from (110) and (111) planes, in comparison with tabular etalon

TABLE 1. Phase composition of Ni–N films produced with the contents of 0–8% vol. of N_2 in the gas phase.

Number of specimen and N_2 content	$2Q_{exp.}$, deg.	$2Q_{tab.}$, deg.	*hkl*	Phase
No. 250 0% N_2	52.17	52.17	111	Ni
	61.04	61.01	200	Ni
	91.79	91.76	220	Ni
No. 252 2% N_2	49.28	48.92	111	Ni_4N
	52.15	52.17	111	Ni
	61.05	61.01	200	Ni
	91.8	91.76	220	Ni
No. 253 4% N_2	45.62	45.54	110	Ni_3N
	49.39	48.92	111	Ni_4N
	52.13	52.15	111	Ni_3N
	57.18	57.15	200	Ni_4N
No. 255 6% N_2	45.62	45.54	110	Ni_3N
	49.14	49.316	002	Ni_3N
	52.18	52.178	111	Ni_3N
	69.21	69.16	112	Ni_3N
	84.29	84.293	300	Ni_3N
No. 251 8% N_2	45.6	45.54	110	Ni_3N
	49.12	49.316	002	Ni_3N
	52.16	52.15	111	Ni_3N
	69.2	69.16	112	Ni_3N
	84.31	84.29	300	Ni_3N

patterns for equioriented crystallites, allow to speak about preferential orientation of growing Ni_3N crystallites in these two directions.

X-ray diffraction patterns of films of Ni–N system, produced with adding of 27–70% of nitrogen in the growth atmosphere, at CuK_α radiation are presented in Fig. 2. Identification has been made and the information about phase composition of films is obtained (see Table 2).

As seen, at concentrations of nitrogen in a gas phase approximately from 6% to 30% in growing structure only one Ni_3N phase is observed, that is unequivocally identified by a number of reflexes. Preferential orientation of (110) and (111) planes is preserved. At the further nitrogen concentration increase, the appearance of a new phase reflexes is observed (see Fig. 2, *a*, *b* and Table 2), which has been identified by us as Ni_2N (b.c.t.). This phase is mentioned in references in very rare cases [5, 12] and by now is studied insufficiently. Intensity of its reflexes increases at the further increase of nitrogen concentration in the growth atmosphere.

Nevertheless, the specimen produced at 70% of nitrogen still contains a small amount of Ni_3N phase, which is seen from the correspond-

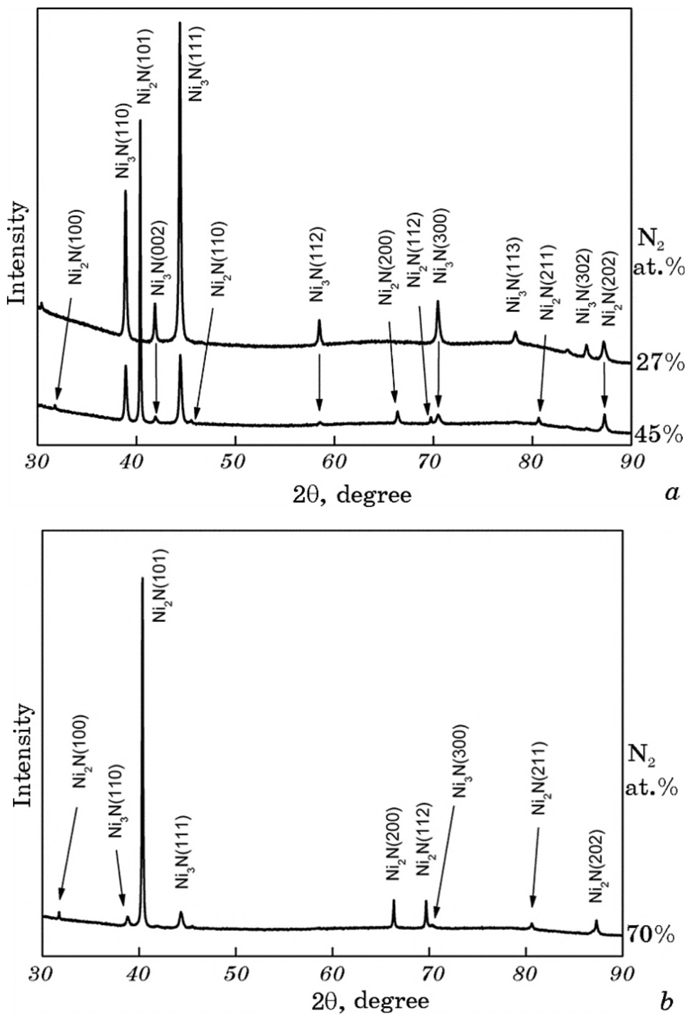


Fig. 2. X-ray diffraction patterns (CuK_α radiation) of Ni–N films produced with the N_2contents of 27%, 45% (*a*) and 70% (*b*).

ing X-ray diffraction pattern (see Fig. 2, *b*). Hence, at concentrations of nitrogen in a gas phase above 30%, heterophase system $Ni_3N + Ni_2N$, with a dominance of the last phase, is formed at the nitrogen concentration increase.

Thus, as seen from the presented spectra and the tables, the produced specimens for the most part are heterophase, as several Ni–N phases are present in their compositions simultaneously, and their ratio varies with a change of specimens' production conditions (change of nitrogen concentration in the growth atmosphere). The X-ray structural analysis demonstrates for produced specimens successive transi-

TABLE 2. Phase composition of Ni–N films produced with the N_2 contents of 27–70% in the gas phase.

Number of specimen and N_2 content	$2Q_{exp.}$, deg.	$2Q_{tab.}$, deg.	*hkl*	Phase
No. 233 7% N_2	38.89	38.94	110	Ni_3N
	41.87	42.111	002	Ni_3N
	44.38	44.48	111	Ni_3N
	58.45	58.51	112	Ni_3N
	70.44	70.6	300	Ni_3N
	78.27	78.38	113	Ni_3N
	85.48	85.665	302	Ni_3N
	87.21	87.39	221	Ni_3N
No. 234 45% N_2	38.9	38.94	110	Ni_3N
	40.37	40.79	101	Ni_2N
	41.9	42.111	002	Ni_3N
	44.42	44.48	111	Ni_3N
	45.56	45.79	110	Ni_2N
	58.54	58.51	112	Ni_3N
	66.36	66.76	200	Ni_2N
	69.73	70.60	300	Ni_3N
	70.45	70.67	112	Ni_2N
	80.62	81.28	211	Ni_2N
	87.27	88.38	202	Ni_2N
No. 237 70% N_2	31.74	31.94	100	Ni_2N
	38.81	38.94	110	Ni_3N
	40.36	40.79	101	Ni_2N
	44.33	44.48	111	Ni_3N
	66.35	66.76	200	Ni_2N
	69.68	70.67	112	Ni_2N
	80.59	81.28	211	Ni_2N
	87.29	88.38	202	Ni_2N

tion from formation of pure metal nickel (the cubic phase) and the nitrogen solid solution in nickel to the nickel nitrides of various stoichiometry: Ni_4N, Ni_3N, and Ni_2N at the increase of gaseous nitrogen concentration in the growth atmosphere from 0% to 70% (Figs. 1 and 2). At concentrations of nitrogen in a gas phase above 50%, dominancy of Ni_2N phase in the structure of films (see Fig. 2) is observed.

The broadening of reflexes observed in produced spectra can indicate a comparatively small size of crystallites from which the film is built. The estimate of this size by the Scherrer formula provides amplitude 10 times smaller than full thickness of produced films, *i.e.*, ten nanometres. Sizes of crystallites L (more exactly, coherent scattering region—CSR) have been determined for all phases of the produced specimens by maximally intensive reflexes. The diffraction reflection

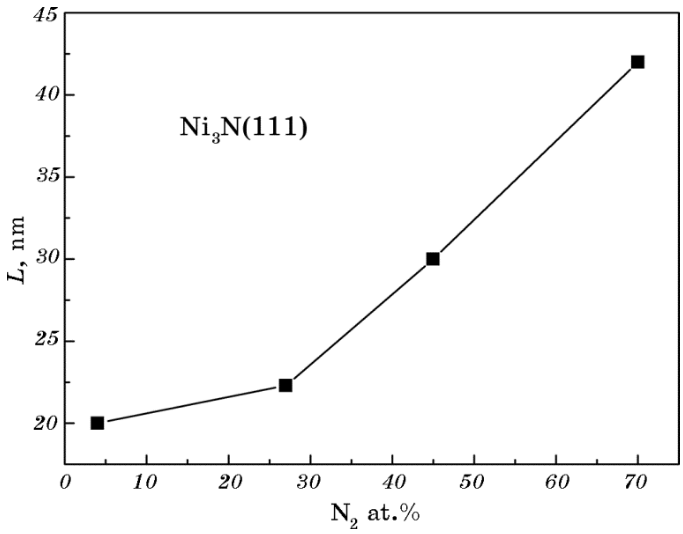


Fig. 3. Dependence of the typical sizes of crystallites of Ni_3N phase in the films produced at various nitrogen concentrations in the growth atmosphere.

peak width at half-height of the peak intensity and angles of diffraction for each phase of specimens are measured, and calculation is performed by the Scherrer formula:

$$L = \frac{0.9\lambda}{B\cos Q},$$

where λ is wavelength of X-rays (λ = 1.7902 Å for CoK_α radiation, λ = = 1.54056 Å for CuK_α radiation), Q is diffraction angle, B is the width of the diffraction reflection at half-height of the peak intensity. The dependence of change of CSR of Ni_3N crystallites calculated by reflexes of (111) orientation, depending on concentration of nitrogen in the growth atmosphere in which specimens are grown, is presented in Fig. 3. The distinctive growth of crystallites sizes of Ni_3N phase with growth of nitrogen concentration is observed.

The complicated relief of a surface of grown nickel nitride specimens is confirmed by the 3*D*-images obtained by the means of AFM. In Figure 4, the 3*D*-images of a surface of films produced in the pure Ar atmosphere (see Fig. 4, *a*) and in atmosphere with adding of 75% of nitrogen (see Fig. 4, *b*) are presented. In Figure 4, *a*, the specimen is represented by the film of pure nickel (with a small amount of the dissolved atoms of nitrogen). 'Sharp' needle structure formed by the separate thin nanocolumns is well seen. Heterophase Ni_3N + Ni_2N film in Fig. 4, *b* differs by smoother differences of a surface profile, typical for globules.

AFM data also correlate with high-resolution SEM investigation (see Fig. 5). As seen, the films grown at low concentrations of nitrogen (nitrogen solid solution in nickel and Ni_4N phase) consist of close packed nanocolumns with the effective diameter ≅ 50–70 nm (see Fig.

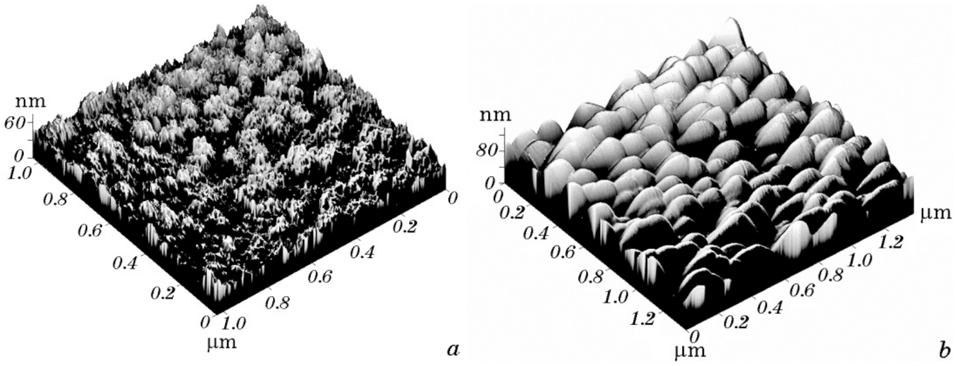
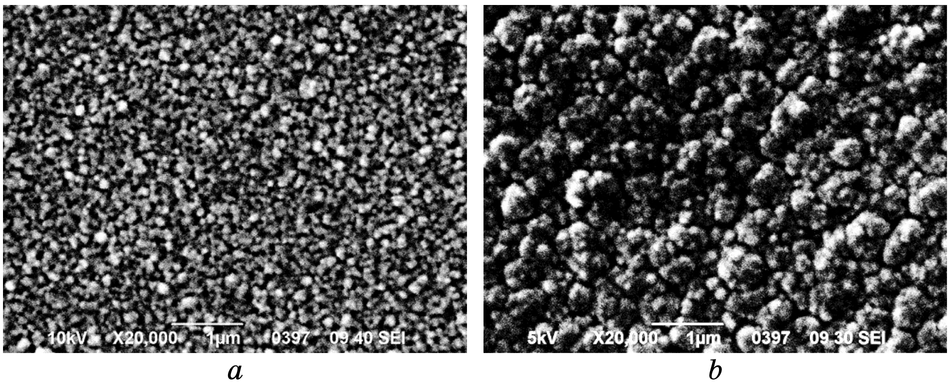


Fig. 4. AFM 3*D*-images of the surface of films of Ni–N system grown in 100% Ar (*a*) and with adding of 75% N_2 (*b*) in the growth atmosphere.



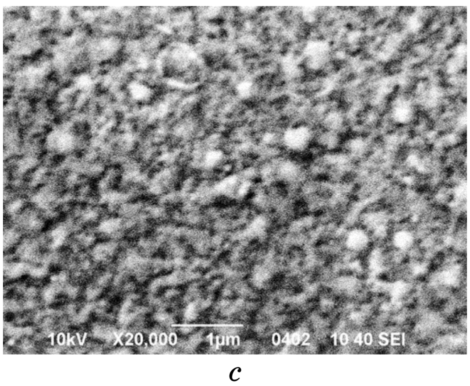


Fig. 5. SEM images of the surface of films of Ni–N system grown with adding of 2% N_2 (*a*), 27% N_2 (*b*) and 75% N_2 (*c*) in the growth atmosphere.

5, *a* and paper [11]). With growth of the nitrogen content in the gas phase in the films containing Ni_3N and Ni_2N phases, appreciable structural change of films is observed (see Fig. 5). They have the typical globular structure with the effective size of elements ≅ 20–40 nm, and incorporation of separate globules in aggregates with a size lower than 400–500 nm (see Fig. 5, *b*, *c*). It correlates with AFM data. It should be noted that the specimens produced at nitrogen concentrations of 2% and 27% have predominantly metal type of conductivity. It is well seen by the quality of the SEM image. At the same time, the specimen produced at 75% N_2 (Ni_2N major phase) is characterised by considerably smaller conductivity. It is seen from SEM image deterioration (see Fig. 5, *c*).

3. CONCLUSIONS

As shown in this work, the magnetron spraying is effective method of synthesis of various nanostructured phases of Ni–N system. With growth of nitrogen concentration in the growth atmosphere of magnetron plasma, consequent formation of phases Ni, Ni_4N, Ni_3N and Ni_2N (at present, the last phase is insufficiently investigated) on the substrate is observed. The typical sizes of crystallites of nickel nitride phases comprise tens nanometres. It is revealed that the films produced at high concentrations of nitrogen (Ni_3N and Ni_2N phases) have the globular structure, whereas films of pure nickel and the nitrogen solid solution in nickel with small additions of the Ni_4N phase are nanocolumnar. Thus, depending on growth parameters (in particular, on nitrogen concentrations in a buffer gas), one of the processes is observed: nucleation of nanocolumns growing perpendicularly to the substrate surface or the films growth with the globular character, *i.e.* processes of self-organising of substance on the substrate, provided by the non-catalytic mechanism, take place.

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