

Formation factors of stable nanocrystalline thin films

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Experimental data on concentrations and temperature stability of intergrain boundaries and stacking faults in thin metal films of nanocrystalline structure are considered. The defect formation in the course of condensation has been concluded to decrease the thin film free energy.

Анализируются экспериментальные данные о концентрации и температурной стабильности межзеренных границ и дефектов упаковки в тонких пленках металлов с нанокристаллической структурой. Сделан вывод, что образование этих дефектов в процессе конденсации уменьшает свободную энергию тонких пленок.

It is commonly adopted that the higher is the phase transformation rate or a physical factor variation rate, the more non-equilibrium structure is formed and the more probable are the subsequent spontaneous or stimulated relaxation processes in the respective materials. The application results of "express" methods in material synthesis and treatment being in wide use today, however, indicate that the above standpoint is to be corrected. First of all, it is just the thin film preparation techniques in vacuum using the electron beam, magnetron, and laser sputtering that are the matters in question. A characteristic feature of such "express" techniques consists in that the substance flow from the vapor plasma zone to the condensation one on the substrate exceeds substantially the diffusion flows within the condensate bulk being formed.

In contrast to the common concepts, thin films prepared by the above-mentioned express techniques and comprising structure imperfections in high concentrations are often very stable; that is why those techniques are used widely. It becomes obvious that the express techniques give rise (for

reasons still unknown) some specific structure state that will be referred to as extreme ones in what follows. In this work, some kinds and properties of such extreme structure states are considered and thermodynamic and kinetic factors causing them are analyzed.

Polycrystalline films of metals and metal compounds with nanodispersed grains are typical examples of extreme structure materials. The trend to grain subdispersity in thin films can be so pronounced that it is difficult to distinguish definitely amorphous films and polycrystalline ones [1]. A clearly manifested dependence of the grain dispersity in vacuum condensates on the pressure and composition of the residual gases in vacuum chambers [2, 3].

An increased imperfection of thin films, first of all, an anomalous high density of intergrain boundaries, is interpreted usually as an inevitable result of the extremely nonequilibrium conditions during their formation. This predominating point of view is reflected in the fact that concepts of the vacuum condensate non-equilibrium extent and the grain dispersity level therein are

used widely as synonyms. Large amounts of the residual gas particles from the vacuum chamber atmosphere is believed to be among the formation reasons of the non-equilibrium structure films. As a result, the gas content in the condensates may exceed considerably its solubility limit. The commonly used terms "the residual gas particle capturing" or even "immuring" reflect the concept of the quenching nature of the film saturation with gas [4]. The experimental data accumulated today, however, give rise to doubts about the validity of that interpretation in all cases.

First of all, anomalous high size stability of subdispersed grains in thin films draws an attention. In bulk materials of metallurgical origin, the crystalline grains are known to be of several tens of micrometers in size. The material trend to the grain recrystallization and growth under annealing increases as the initial grain size is reduced. The grain size reduction down to tenths of micrometer is possible only using some special methods involving intense plastic deformation [5]. In contrast, in thin vacuum condensates, it is a complicated technologic problem to obtain grains of micrometer size. Moreover, in many case, the higher is the initial dispersity state, the less intense is the recrystallizing grain growth in nanocrystalline films.

As an example, the Table 1 presents the grain size changes in aluminum films condensed in vacuum of 10^{-3} Pa onto an unheated substrate (glass with NaCl interlayer). The purity of the metal evaporated is 99.999 %. The texture-free films of different thickness were obtained simultaneously using different condensation rates from 0.5 nm/s to 2.5 nm/s at the thickness range of 15 to 75 nm. Therefore, the relative amount of residual gas particles was higher in thinner films. The films separated from substrates were annealed for 30 min directly in an electron microscope using a resistive heater.

Qualitatively similar results were obtained when annealing tin films in vacuum: the grain growth (25 nm in the initial state) is not observed up to annealing temperatures of $0.8T_m$. Bearing in mind that the effective diffusion and grain recrystallizing growth occur usually at 0.4 to $0.5T_m$, then it is seen clearly that the intergrain boundaries in such films are not the thermodynamic non-equilibrium factors. In contrast, it is to be concluded that their formation in the course of non-equilibrium crys-

Table 1. Grain size (nm) in annealed aluminum films

Annealing temp., K	Film thickness, nm			
	15	40	55	75
300	22	26	29	31
400	20	25	27	32
550	20	28	27	37
700	24	30	34	43

tallization favors the formation of less non-equilibrium and more stable condensate than it would be in their absence.

It follows from the above that the intergrain boundaries formed in a finished material (e.g. by deformation) differ substantially from those formed during the film preparation, i.e., during its "atom-by-atom assemblage". There are also other specific defects in the thin film crystalline structure that are formed during its "assemblage" and favor a reduced thermodynamic non-equilibrium of the film. In this sense, we will characterize the extreme structure films as materials with "assembled structures".

In our opinion, the nanocrystalline films with impurity particles of a specific kind are localized at the intergrain boundaries are a model of such "assembled structures". During the vacuum condensate crystallization, some particles of residual gases can really be "immured" in the growing grain bulk, as is commonly believed. But a specific kind thereof forms at the growing grain surface bidimensional layers that reduce the specific surface energy as this is done by adlayers at the free surface of any solid. This may be due to a significant chemical affinity between intrinsic and impurity atoms of a specific kind as well as to the possible local relaxation of elastic and Coulombian forces due to interaction of intrinsic and extrinsic point defects.

This standpoint is confirmed also by characteristic changes of intergrain boundary shapes. Fig. 1a presents the morphology of 50 nm thick Ni films condensed in $5 \cdot 10^{-4}$ Pa vacuum onto glass ceramics with NaCl interlayer at 500 K and then annealed at 850 K after separation from the substrate. In Fig. 1b, presented is the morphology of Ni films differing from the above only in that a flow of simultaneously evaporated SiO (about 2 % vol.) was mixed to that of evaporated Ni. It is seen clearly that the rectilinear pattern of intergrain bounda-

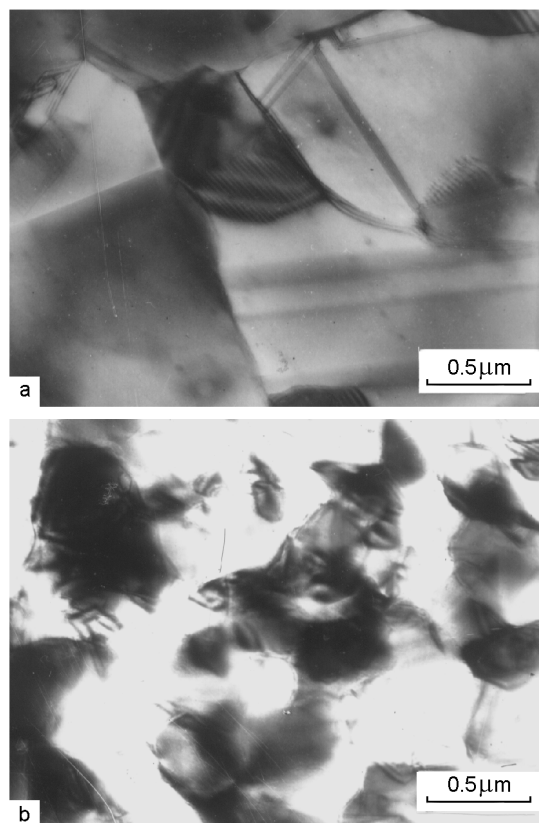


Fig. 1. Grain morphology in Ni (a) and Ni-SiO (b) films.

ries in pure Ni condensates is changed by rounded and blurred grain contours in Ni-SiO films. Thus, introduction of SiO into Ni condensate weakened its trend to rectify the intergrain boundaries and to reduce respectively their total surface area.

If chemical bonds are formed between the condensate grain surface atoms and residual gas particles sorbed thereon, the grain surface energy becomes lowered approximately by the chemisorption energy value. Moreover, submonolayers of foreign atoms at the free solid surfaces can form ordered 2D structures as well as provoke the surface rebuilding of the base material itself [6]. We believe that similar relaxation processes may occur at inner surfaces of solids, too. The impurity particles in such 2D aggregates at intergrain boundaries have a higher binding energy as compared to individual impurities chemisorbed at the free solid surface. Therefore, a fine-grained polycrystalline condensate where the impurities are localized at intergrain boundaries may have a lower free energy than a coarse-grained material that would be a homogeneous supersaturated solid solution formed

due to the "immuring" of impurity particles in the grain bulk.

The model of nanocrystalline structure films with intergrain boundaries relaxed due to impurities explains the temperature stability of grain sizes in such materials. Let a polycrystalline material has the Gibbs free energy increased as compared to that of a single crystal by $\Delta\Phi_b$ due to the intergrain boundary energy:

$$\Delta\Phi_b = \Delta H_b - \Delta(TS)_{or}. \quad (1)$$

Here, ΔH_b and $\Delta(TS)_{or}$ are changes in enthalpy and bound energy, respectively, due to presence of intergrain boundaries and grain disordering in the material.

In Fig. 2a, the curve 1 presents the Gibbs free energy Φ change when the thermodynamic system transits from the vapor phase to the supersaturated solid solution with coarse grains. The curve 2 answers to the transition to the fine-crystalline condensate where the impurities are localized at intergrain boundaries. It follows from the Figure that in the second case, an energy gain is attained

$$\Delta\Phi_i = \Delta H_i - \Delta(TS)_i. \quad (2)$$

Here, $\Delta H_i = \Delta H_{b1} - \Delta H_{b2}$ is the enthalpy lowering due to the "extrinsic relaxation" of intergrain boundaries and $\Delta(TS)_i = \Delta(TS)_{or2} - \Delta(TS)_{or1}$, the entropy term increase due to a wider orientation variety in the system containing grains of a higher dispersity. This lowered thermodynamic nonequilibrium extent (by $\Delta\Phi_i$) reduces thermodynamic stimulus to the subsequent relaxation of nanodispersed films with impurity-loaded intergrain boundaries of the type mentioned. According to [7], the quantity $\Delta F = F_f - F_e$ (Fig. 2b) is the "thermodynamic force of transformation". Moreover, the recrystallization induced displacement of an intergrain boundary with chemisorbed impurities is impossible in essence, while dissolution of the grain-boundary impurities in the nanodispersed grain bulk (followed by the solid solution recrystallization) would result in an increased (by $\Delta\Phi_i$) solid free energy. Therefore, the recrystallizing grain growth in such materials is possible only at high annealing temperatures when the impurity solubility in the grains approaches their physical content averaged over the whole film volume. This explains also the reduced recrystallization effect in films consisting of higher grain dispersity

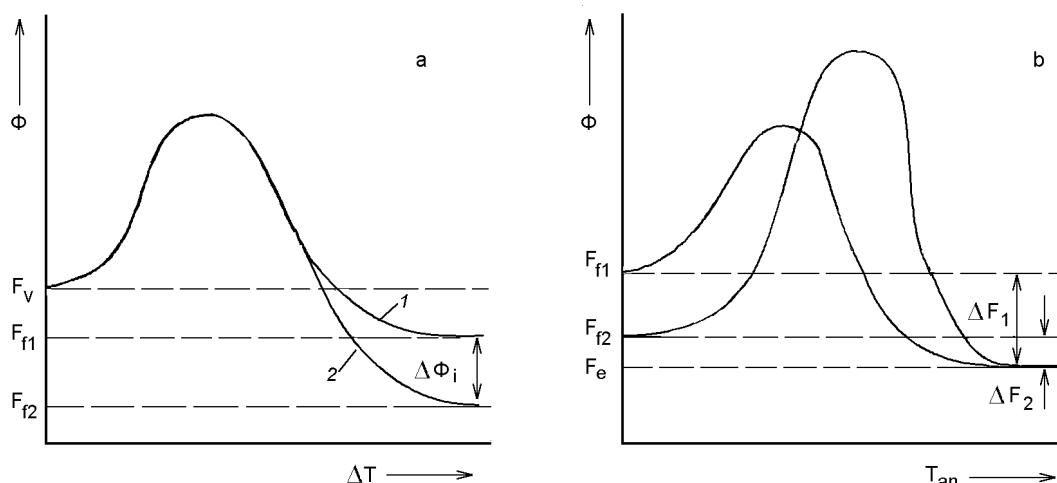


Fig. 2. Change of the Gibbs free energy Φ at vapor condensation into various metastable structure states (a) and at subsequent condensate transformation into equilibrium structure state due to annealing (b). $\Delta T = T_v - T_s$ is the supercooling; T_v , T_s , and T_{an} are the vapor, substrate, and post-condensation anneal temperatures, respectively.

where the intergrain boundary displacement would require a transition to a more super-saturated state that in the case of coarser grains.

From the standpoint of the intergrain boundary model under consideration, data on relative efficiency of different residual gas components are of importance. We determined the composition of gases in niobium films using an Auger electron spectrometer (RIBER). The 70 nm thick Nb films with 5 to 15 m grain size were obtained in 10^{-3} Pa vacuum under electron beam evaporation of 99.9 % pure Nb bar degassed previously at 1850 K in 10^{-5} Pa vacuum for 12 h. It is seen from Fig. 3 that it is oxygen that shows the higher content among the gases found in the films, with nitrogen and carbon occupying the next positions. For our consideration, it is of importance that these gases are arranged in the same sequence according to their chemical activity against metals [8]. The total amount of the above gases in Nb films varies from several atoms per cent up to several tens (maximum about 40) atoms per cent, depending on the condensation conditions. This exceeds by two orders the solubility of those gases at room temperature.

Taking such high impurity concentrations into account, the data on the film electron diffraction are of considerable interest. The interplane distances calculated from electron diffraction patterns correspond to the bcc Nb lattice and only the films heated up to 700 K show diffraction

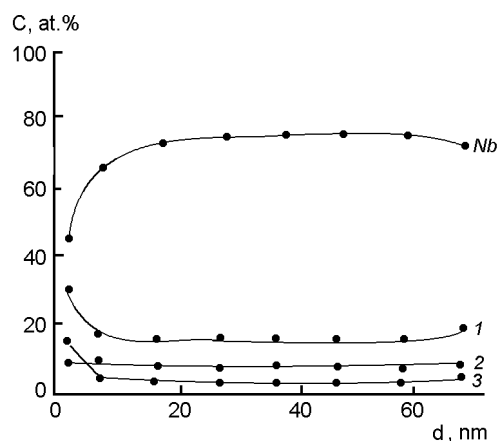


Fig. 3. Concentration profiles of oxygen (1), nitrogen (2), and carbon (3) across the Nb film.

lines of $\text{NbO}_{0.8}$ suboxide. The data evidence clearly that the residual gas impurities in the Nb films are localized mainly in the intergrain boundaries and not in the grain lattice.

If nitrogen dominates in the residual gas, the impurity effect on the intergrain boundary extent in the Nb condensate is observed to be pronounced, too. The electron microscope image (Fig. 4a) presents the structure of a sample obtained in $5 \cdot 10^{-5}$ Pa vacuum on fluorophlogopite at 870 K. The samples presented in Fig. 4b were prepared by Nb condensation at the same temperature but after nitrogen bleed-in up to $5 \cdot 10^{-3}$ Pa to the chamber evacuated

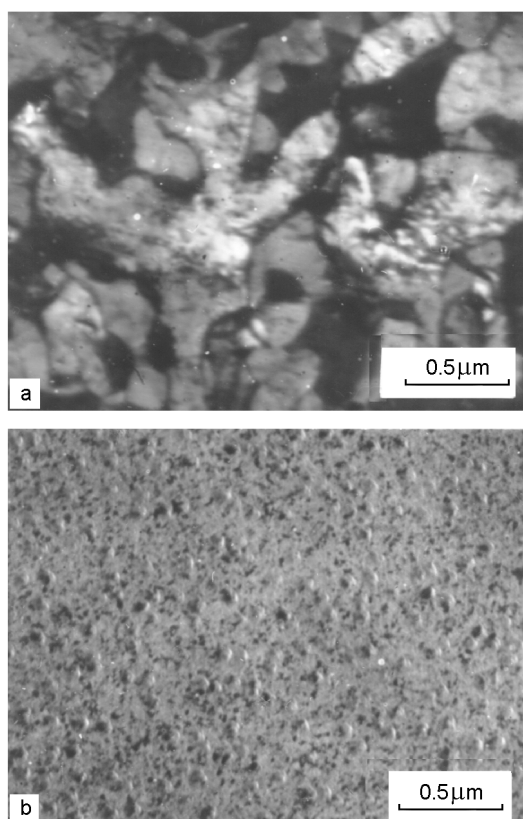


Fig. 4. Grain morphology in Nb films condensed under different vacuum conditions: at the residual pressure $5 \cdot 10^{-5}$ Pa (a) and after nitrogen bleed-in up to $5 \cdot 10^{-3}$ Pa (b).

previously down to $5 \cdot 10^{-5}$ Pa. As a result, the crystal size in the nitrogen-containing Nb films is 20 to 35 nm while in the nitrogen-free films, the crystal grow up to 150 to 500 nm, the evaporation regime and condensation temperature being the same. We believe that the nitrogen presence caused a decrease in the intergrain boundary energy resulting in a substantially increased length thereof. Moreover, there is no predominant grain orientation in the Nb films with respect to the substrate in the presence of nitrogen. This evidences also a reduced energy of the condensate-fluorophlogopite interface energy.

Now let another imperfection type be considered related to the "assembled structures" in vacuum condensates and showing a temperature stability. The matters of question are twin boundaries and stacking faults. A high concentration of such structure defects in vacuum condensates is noted by numerous authors, in particular considering chemical compounds. For example, even grains of less than one micrometer size in semiconductor films show usually a

"stack morphology", that is, those are subdivided by twin boundaries and stacking faults into many tens of parallel plates having nanoscale thickness [9]. In fcc metal films, the stacking faults and twins are observed usually in nanoscale grains even at the island stage of the condensate growth [10] when distances between islands, and thus the atomic diffusion paths, are comparable with the island sizes.

We studied the stacking fault concentrations in Al and Ag films condensed in $5 \cdot 10^{-3}$ Pa vacuum on unheated substrates (glass with NaCl interlayer). The metal evaporated were of 99.999 % purity. The films of two thickness values (40 and 130 nm for Al, 45 and 160 nm for Ag) were prepared simultaneously using a shield. The films were cut into 15×10 mm² sections which were assembled into several micrometers thick stacks. The stacks were examined using a DRON-4M X-ray diffractometer with the Bragg-Brentano focusing. The coherent scattering region dimensions were determined basing on the diffraction line broadening. The broadening fraction due to geometry and microstrains was taken into account by approximation [11]. The stacking fault concentration was determined under account for both displacement of specific diffraction lines and their broadening using the procedure described in [11].

The analysis has shown that there are no stacking faults in Al films, since the angular dependence of the Bragg reflection broadening β is linear in coordinates

$$\beta \cos \theta = f(\sin \theta \cdot E_{111} / E_{hkl}). \quad (3)$$

Here, θ is the Bragg reflection angle; E , the normal elastic module in the corresponding crystallographic direction. In contrast, for Ag films, two parallel straight lines are seen clearly in the plots, namely, one for (200) and (400) reflections and another, for (111) and (222) ones. This is due to the extra broadening of the (200) and (400) diffraction lines caused by the stacking faults. The structure characteristics of Ag films in the as-prepared state and after vacuum anneal are presented in Table 2.

We believe that the high stacking fault concentration in the films may be due to a purely dimensional effect. The specific Gibbs free energy in thin films exceeds that in bulk solids by $\Delta \Phi_s \sim h^{-1}$ due to a substantial surface energy contribution to the enthalpy change ΔH_s . The specific free energy

increment due to this dimensional factor

Table 2. Grain size L and stacking fault concentration α in Ag films

Film thickness, nm	T_{anneal} , K	L , nm	α , per cent
45	300	45	2.4
	400	70	3.2
	500	120	2.5
160	300	90	1.7
	400	120	1.9

can be compensated by increased entropy term $\Delta(TS)_{surf}$ due to formation of stacking faults and twins in the film:

$$\Delta\Phi_s = \Delta H_s - \Delta(TS)_{sf}. \quad (4)$$

The stacking faults in fcc lattice are the fcp phase plates of nanoscale thickness. The specific energy values for fcc and fcp modifications differ only by tenths per cent. But such defects increase significantly the crystal entropy because its translation symmetry becomes deteriorated when passing a stacking fault plane or a twin boundary. Therefore, the total energy change $\Delta\Phi_s$ in thin films caused by formation of those structure defects can be insignificant as compared to a bulk solid free of stacking faults. This explains not only the formation of stacking faults in the films in large amounts but also their temperature stability (Table 2). The stacking faults, while being a thermodynamically necessary factor for the Gibbs free energy decrease at early film growth stages, lose their compensating role as the film thickness increases; their subsequent removal, however, is difficult. Crossing the whole crystal (Fig. 5), those are in the indifferent equilibrium state with respect to any virtual plane-parallel displacement. Moreover, such a displacement would require coordination rebuilding in a substantial fraction of the film volume. The trend to recrystallizing grain growth under annealing is more pronounced in Ag films than in Al ones. Perhaps this results from a lower chemical reactivity of silver against the main residual gases present in vacuum chamber.

Thus, numerous experimental data show that two classes of structure imperfections are to be distinguished in solids from the standpoint of their origin and influence.

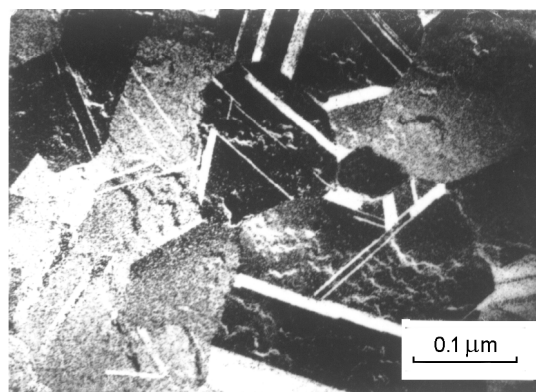


Fig. 5. Stacking faults in Ag films.

The first can be formed in finished materials due to subsequent treatments such as straining, irradiation, etc. Formation of such structure defects results in an increased free energy of a solid body. The second defect type includes those capable of spontaneous formation in the course of condensation, i.e., "atom-by-atom assemblage" of the material. Such defects provide a reduced free energy of the solid body under formation as compared to the case when those are absent. Taking into account the principal distinction in the defect formation causes and its influence on the structure and the structure-sensitive properties of materials, we use the term "assembled structure" to denote the second defect class. Since many of physical properties caused by such structures are very useful and prospective [5], it would be not logical to use the terms "defects" or "imperfections".

It is obvious that it is just the assembled structure films that are of practical interest. In particular, an intentionally created gas atmosphere during vacuum condensation of films can be used as a technologic factor to control the film properties, such as mechanical, electrical, sorption, magnetic, superconductive ones, etc. There is an analogy with providing of the required conduction type and level in semiconductors using the intentionally and controllably introduced impurities.

Result of importance concerning gas content in vacuum condensates are presented in the review [4]. In the works cited here, the gases "captured" and "immured" in the films are considered as a factor of non-equilibrium but not as that favoring thermodynamic relaxation of the growing films. In our opinion, those factors are both of significance and studied aimed at discrimination of their effects are actual. It is impor-

tant also to elucidate how those factors interact with other ones influencing the grain size, e.g., the nucleation center density in the condensate. The general selection criteria for selection of chemical elements to control the quality of films having the properties defined by the grain high dispersity consist in that the impurity particles are to be poorly soluble in the main material and to have high chemisorption energy.

The structural variety is very wide. In addition to the above-mentioned intergrain boundaries where impurities and stacking faults are localized compensating the excess surface energy of thin films, these structures include intergrain boundaries in multiposition epitaxial films, crystallographic planes consisting of the excess component atoms in non-stoichiometric films (latent non-stoichiometry free of point defects [9]), intergrain boundaries in films of single-block thickness, and perhaps many others that are not identified to date. Their studies can provide novel opportunities for material quality control.

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Фактори формування стабільних нанокристалічних тонких плівок

П.О.Панчева, А.Г.Басов

Аналізуються експериментальні дані про концентрацію і температурну стабільність міжзеренних границь і дефектів упаковки у тонких плівках металів із нанокристалічною структурою. Зроблено висновок, що утворення цих дефектів під час конденсації зменшує вільну енергію тонких плівок.