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XPS and ESR study of tantalum nanoparticles

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The electron structure of the films formed by ensemble of tantalum nanoparticles has been studied using XPS and EPR methods. Spectra of internal atomic levels of the film surface have been obtained using step-by-step annealing in vacuum. Using Ta4*f* spectra decomposition into components, the kinetics of phase formation processes has been investigated.

Методами РФС и ЭПР исследована электронная структура пленок, сформированных из ансамбля наночастиц тантала. Получены спектры внутренних уровней атомов поверхности пленок при ступенчатом отжиге в вакууме. По результатам разложения Ta4*f*-спектров на компоненты изучена кинетика процессов фазообразования.

Ensembles of nanoparticles are thermodynamically nonequilibrium dispersed systems with a highly developed surface which tend to realize physicochemical processes resulting in decreased free energy. One of such processes can be the agglomeration of nanoparticles. The agglomeration speed can be decreased by creation of a matrix which disjoints nanoparticles. However, interaction of such matrix with the particles is necessary to be taken into account. The agglomeration in films consisting of tantalum nanoparticles under annealing in vacuum has been investigated to study the processes occurring on the material surfaces.

The electron structure of films consisting of 1 to 10 nm size tantalum nanoparticles was investigated by XPS and ESR. The thickness of tantalum nanoparticles films prepared by aerosol method was 1000 nm [1]. To initiate the phase transformations on the film surface and in its bulk, the annealing was carried out in the temperature range of 300 to 700 K (t = 30 min) in vacuum.

The electron structure of Ta nanoparticles was studied using an enhanced EC-2402 electronic spectrometer (E MgK_α = 1253.6 eV, P = 300 W). The absolute resolution as measured for the $Au4f_{7/2}$ gold peak was 1.0 eV, the measurement accuracy for $Ta4f_{7/2}$-line maximum, ±0.05 eV. The operating vacuum was $2 \cdot 10^{-7}$ Pa. ESR spectra were obtained using a SE/X-2544 spectrometer under simultaneous control of magnetizing force H and working frequency ν. The XPS-spectra were obtained for internal levels of tantalum atoms. To consider the spin-orbit splitting of component pairs, the $Ta4f_{7/2}$-lines were decomposed into pairs of components. The area of components was determined after background subtraction by Shirly method [2]. The integrated intensities of components obtained in such a way are proportional to the content of nonequivalent tantalum phases on the film surface.

The spectra of Ta4*f* atomic level of the particle ensemble obtained at room temperature and under step-by-step annealing of the samples are shown in Fig. 1. The main components of Ta4*f* spectra of the films under study can be correlated with *n*-TaC nanoparticles in a polymer matrix (D-D′), agglomerates of *n*-TaC nanoparticles (C-C′), and nanoparticles of tantalum oxides *n*-Ta_nO_m (E-E′) and *n*-Ta_2O_5 (F-F′). The binding energy (E_b) values of Ta4*f* spectrum components F-F′, B-B′′, and A-A′ coincide with E_b for bulk Ta_2O_5 (26.8 eV), TaC (22.6 eV) and Ta (21.8 eV) respectively.

Thus, the studied particles surface are formed by two different groups of tantalum

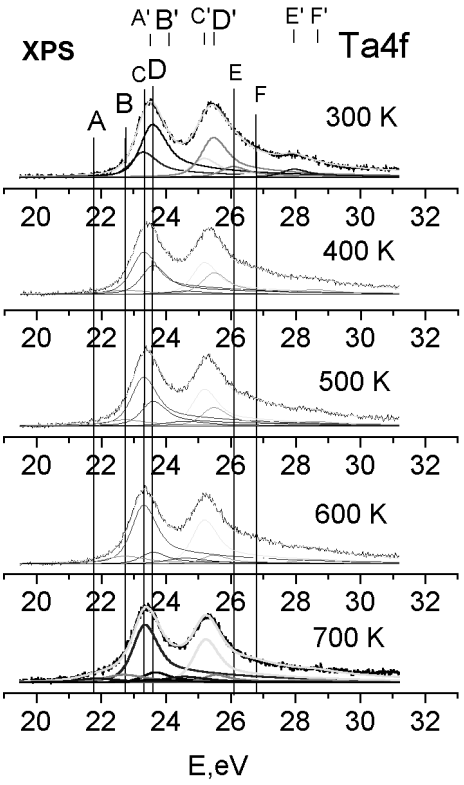

Fig. 1. The XPS spectra of tantalum 4*f*-levels from an initial film (300 K) and after its annealing up to 400 K, 500 K, 600 K and 700 K decomposed onto componenets.

particles: group 1 — *n*-TaC nanoparticles stabilized by the polymer matrix, (D-D′), agglomerates of *n*-TaC nanoparticles (C-C′), n-Ta_nO_m (E-E′) and *n*-Ta_2O_5 (F-F′) nanoparticles. Group 2 — TaC macroparticles (B-B′).

It is just the D-D'components (58.1 %, Fig. 1, 300 K) corresponding to *n*-TaC nanoparticles in a polymer matrix that make the main contribution to the initial film spectrum. The contribution of agglomerated *n*-TaC (C-C′) nanoparticles to the initial film spectra is 27.6 %, the total contribution of tantalum oxide nanoparticles (E-E′, F-F′) amounts about 14 %. As the temperature increases, a redistribution of integrated intensity of components in D-D′ → C-C′ direction occurs that can be explained by transformation of *n*-TaC nanoparticles stabilized by polymer matrix to agglomerates thereof (Fig. 2). Under heating up to 400 K, the content of oxide nanoparticles E-E′ decreases at simultaneously increasing contribution from Ta_2O_5 oxide nanoparticles (F-F′) and those of TaC macrophase (B-B′). The disproportionation effect can be caused by presence of the OR

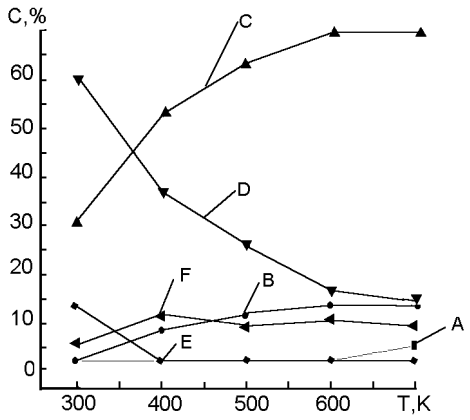

Fig. 2. Changes of integrated intensity of components of XPS tantalum spectra from an initial film (300 K) after its annealing up to 400 K, 500 K, 600 K and 700 K.

type reactive centers (where R is a carboniferous fragment of the matrix) on the surface and also by the *n*-TaC agglomeration. Formation of TaC phase at temperature 400 K evidences a high reactivity of nanoparticles.

At heating up to 700 K, the contribution of *n*-TaC agglomerates (C-C′) becomes dominating. Appearance of A-A′ components at 700 K in the region of low E_b values can be connected with existence of a metallic core in some nanoparticles. Registration of a signal from a particle core is possible because of decreasing thickness of a polymeric capsule due to its decomposition. Reduction of a fraction of macroparticles in the films at T = 700 K up to metal Ta by the polymer matrix pyrolysis products is hardly probable. As a whole, the change character of the integrated intensities from the components corresponding to nanophase particles (C-C′, D-D′, E-E′, F-F′) and macrophases (B-B′) under annealing is considerably different. It is to note that the contributions ratio from particles of nano- and macrophases in films changes not only at heating, but also at variations in conditions of the nanoparticle synthesis and their assembling into a film. In the case of high macrophase TaC content (B-B′) in initial films, the shift of the Ta4$f_{7/2}$ line maximum in relation to the metal tantalum E_b was decreased down to ΔE_b = 1.4 eV.

The signal resulting from superposition of two isotropic lines having about equal integrated intensities with parameters g^{I}_{ef} = 1.902, ΔH_I = 140 mT and g^{II}_{ef} = 1.980, ΔH_{II} = 70 mT is observed in the ESR spectra.

Table. Binding energy of Ta4$f_{7/2}$ and Ta4$f_{5/2}$ components (eV), their half-height width (eV), and integrated intensities of the components (per cent) at different annealing temperatures

E_b Ta4$f_{7/2}$-Ta4$f_{5/2}$ (eV)	A-21.76 A′-23.64 (eV)	B-22.74 B′-24.62 (eV)	C-23,32 C′-25.2 (eV)	D-23.58 D′-25.46 (eV)	E-26.08 E′-27.96 (eV)	F-26.8 F′- 28.68 (eV)
300 K	0		27.6	58.1	11.0	3.3
400 K	0	6.5	50.5	34.2	0	8.8
500 K	0	8.7	60.8	23.6	0	6.9
600 K	0	11.5	67.0	13.3	0	8.2
700 K	3.1	11.5	66.7	11.6	0	7.1
Precision	±0.9	±0.9	±0.9	±0.9	±0.9	±0.9

At 77 K, the signal amplitude remains constant, symmetry and g_{ef} values of lines are also kept. However, the g^{II}_{ef} 1.980 line width increases up to ΔH_{II} = 90 mT. The presence of a signal with such ΔH values specifies an odd number of electrons in nanoparticles which collective behavior reveals in the exchange interaction.

The value g^{I}_{ef} = 1.902 testifies to a significant contribution from spin-orbit interaction that is typical in the case of ionic bond, while g^{II}_{ef} = 1.980, for systems with a higher contribution from covalent bond. The formation of a polymer matrix isolating nanoparticles at room temperature is possible to describe by catalytic reaction of alcohol transformation $C_2H_5OH \rightarrow H_2O + CH_2 = CH_2 \rightarrow (CH_2–CH_2)_n$- in the presence of tantalum. The decomposition of polymeric matrix under annealing can be explained both by nanoparticle agglomeration and increased involvement of nanoparticles into exchange magnetic interactions.

Thus, dynamics of phase formation in the films is investigated using the Ta4*f*-spectra decomposition into components. The surface of initial films is formed by *n*-TaC nanoparticles isolated by a polymeric matrix, agglomerates of *n*-TaC, and nanoparticles of tantalum oxides. Under heating, *n*-TaC agglomerates are formed, the process rate being the highest at the initial stages of heating process.

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Дослідження наночастинок танталу методами РФС та ЕПР

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Методами РФС та ЕПР досліджено електронну будову плівок, сформованих з ансамблю наночастинок танталу. Отримано спектри внутрішніх рівнів атомів поверхні плівок при відпалі у вакуумі. За результатами розкладання Ta4*f*-спектрів на компоненти вивчено кинетіку процесів фазоутворювання.