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Growth Morphology and Structure of PdCu Ion-Plasma Condensate in the Pores of SiO_2 and Al_2O_3 Amorphous Matrices

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Abstract:

The features of the growth morphology and structure of ion-plasma palladium-copper condensate both on the surface and in the pores of amorphous SiO_2 and Al_2O_3 matrices were studied by scanning electron microscopy and high resolution transmission electron microscopy. Differences in the morphology and crystal structure of the metallic ion-plasma condensate obtained by magnetron sputtering deposition of the PdCu alloy on the surface and in a limited pore volume were shown and substantiated. The main regularities of the ion-plasma condensates formation on a developed surface with a high open porosity were discussed.

Keywords: A1: Crystal morphology; Crystal structure, Nanostructures; A2: Growth from vapor; A3: Physical vapor deposition processes; B1: Alloys

Highlights:

- PdCu films on SiO_2 and Al_2O_3 porous matrices were produced by magnetron sputtering.
- SEM, SAED and HRTEM studies of ion-plasma PdCu condensate were carried out.
- Differences of PdCu structure on surface and in pores of SiO_2, Al_2O_3 were defined.
- Main regularities of the PdCu formation in a limited pore volume were determined.

Introduction

A number of knowledge-intensive branches and technologies are developing with the growth of hydrogen energy, which increases the interest in efficient and low-cost ways of extracting high-purity hydrogen from gas mixtures through selective membranes based on palladium alloys [1–6]. To reduce the proportion of precious metal, reduce the thickness of the membrane, and to ensure the reliability (mechanical strength) use composite porous (the basis is a porous glass of SiO_2, Al_2O_3, B_2O_3, ceramics, stainless steel, obtained by pressing the powder) membrane elements with a thin foil of palladium alloy as selective layer [7–11]. The foil of the palladium alloy is produced by chemical methods, cold rolling or vacuum condensation [12–15]. And taking into account the actively developing innovative direction - the development of the physical and technological foundations for creating matrix hybrid structures (metal clusters in nanopores of an amorphous matrix) for sensors and spintronics [16–19], the problem of synthesis of thin films of palladium alloys on the surface of a porous material is very actual.

It should be noted that the solid solutions of the PdCu system belong to the group of alloys recommended for the production of selective membranes for deep hydrogen purification and CO oxidation [20–23]. Taking into accaunt the passivity of this alloy to hydride and the possibility of forming an ordered structure with a crystal lattice of the CsCl type. The formation of an ordered structure is of practical interest in various aspects: a low specific resistance as compared to a disordered structure; for membranes, a small value of the activation energy of hydrogen diffusion (0.035 eV), which is almost an order of magnitude less than in a disordered solid solution (0.325 eV) and in Pd (0.23 eV) [24]

The fabrication and exploitation of the membrane (PdCu alloy on a porous base) for ultra-purification of hydrogen and CO oxidation are associated with heating and mechanical stresses, so the purpose of this work is to establish the mechanism for filling open pores and the conditions for the formation of an ordered structure in the condensed PdCu layer as a function of from the size of the open pore; establishment of a size effect on phase formation. Thus, in this work thin films of PdCu alloy on a surface of SiO_2 and Al_2O_3 porous matrices studied by scanning electron microscopy (SEM) and high resolution transmission electron microscopy (HRTEM) to reveal the main regularities in the synthesis of ion-plasma condensates of metals and alloys.

Methods

The porous silica matrix was created by irradiating samples Si/SiO_2 on a linear accelerator DC-60 (Astana, Kazakhstan) with ions of ^{209}Bi with an energy of 175 MeV, a fluence of 5×10^7 cm^{-2} fluence and with the following oxide etching in 1.4 % HF solution [25]. Heterostructure Si/SiO_2 characterized by the vertical arrangement of the array with a lateral distribution of exposed pores in

the oxide ~ 5 × 10^7 cm^{-2}, all pores have the same shape - an overturned cone; the diameter and the depth of the pore were set by the etching time in HF (bigger depth corresponds to a smaller pore diameter). For the experiment were prepared two types of samples Si/SiO_2: **I** – pore depth 400 nm, diameter from the side of silicon is 150 nm and 450 nm at the free surface of the oxide: **II** - pore depth 300 nm, diameter from 100 to 300 nm).

Porous alumina was synthesized by anodic oxidation of rolled aluminum foil (thickness 50 μm), which was pre-annealed in vacuum for increasing of the grain size (isothermal annealing at 770K, 1h). Anodic oxidation was carried out in the potentiostatic mode according to the methods [26]. Al_2O_3 samples were prepared with an array of open cylindrical pores with a diameter of 60 - 80 nm ordered over the entire thickness of the sample.

The PdCu layer was simultaneously grown on porous surfaces of Al_2O_3 and SiO_2 at a substrate temperature (T_s) ~ 670K by magnetron sputtering (MS) (working gas – argon, P=3×10^{-1} Pa) alloy target with composition Cu+47 ат.% Pd (specific magnetron power 20 W/cm^2; build speed ~1.0 nm/s).

For the SEM studies the Si/SiO_2/PdCu and Al_2O_3/PdCu heterostructures were prepared by fracture and delamination (due to low adhesion). To analyze the degree of filling of pores with a condensate material (PdCu), micro- and nanostructure layers SiO_2/PdCu, Al_2O_3/PdCu was used the method of focused ion beam (FIB) of gallium for the preparation of transverse sections of heterostructures Si/SiO_2/PdCu, Al_2O_3/PdCu, their visualization in secondary electrons using an immersion lens. Study of the grain structure and morphology of pore filling in SiO_2, Al_2O_3 with solid solution PdCu, carried out jointly by FIB and TEM methods, wherefore the electron-transparent samples were prepared (Lateral dimensions 12x6 μm, thickness from 10 to 50 nm), representing the cross sections of heterostructures SiO_2/PdCu, Al_2O_3/PdCu, extracted from sample volume. This allowed direct TEM methods (Titan 80-300) determine the morphology, crystal structure, phase composition and obtain a direct resolution of the planes of the PdCu crystal lattice in the pores of SiO_2, Al_2O_3. Use of the attachment of energy-dispersive X-ray spectroscopy (EDX), allowed to estimate the elemental composition of PdCu and the stoichiometry of SiO_2, Al_2O_3. TEM images were obtained in two ways: a light-field TEM with recording of electrons scattered at small angles (amplitude, diffraction, and phase contrast); registration of electrons elastically scattered on the nuclei of the atoms of the crystal lattice at large angles (Z - contrast). The first allowed to obtain data on the grain structure of composites SiO_2/PdCu, Al_2O_3/PdCu, phase composition from the analysis of selected area electron diffraction (SAED), direct resolution of crystalline planes (phase contrast), to realize the Fourier transformation of the image of grains PdCu. The second method, in addition to the amplitude contrast, forms a significant Z-contrast, which allowed to reveal the morphology of the pores, grain boundaries and agglomerates of PdCu grains in SiO_2 and Al_2O_3 pores.

Results and discussion

Si/SiO_2/PdCu system. On the SEM image of the samples **I** (fig. 1) it was found that the surface of SiO_2 after peeling off the PdCu film has open pores practically free of the condensate material. A small fraction of the PdCu remaining in the pores is due to mechanical destruction of the "imprint" extracted from the pore (see the inset in fig. 1), which accurately replicates the geometry of the pore and indicates a weak interphase interaction of ion-plasma condensate with an amorphous matrix. The absolutely smooth surface of the PdCu film on the substrate side and the columnar relief of its fracture confirm the weak interfacial interaction of the condensate with the matrix. The morphology of the growth front of the film does not inherit the porous topography of the substrate, even small deposition of a film 1.5 μm thick above the depth of 0.4 μm. The lateral dimensions of the crystallites at the outer surface of the condensate are from 140 to 170 nm, and at the interphase boundary with the substrate is an order of magnitude smaller. As the thickness of the ion-plasma condensate increases, the morphology of the compact nanocrystalline “pedestal” layer realized at the stage of film formation at the interphase boundary with the substrate, nanocrystals form a fibrous and then columnar structure with a high proportion of internal pores.

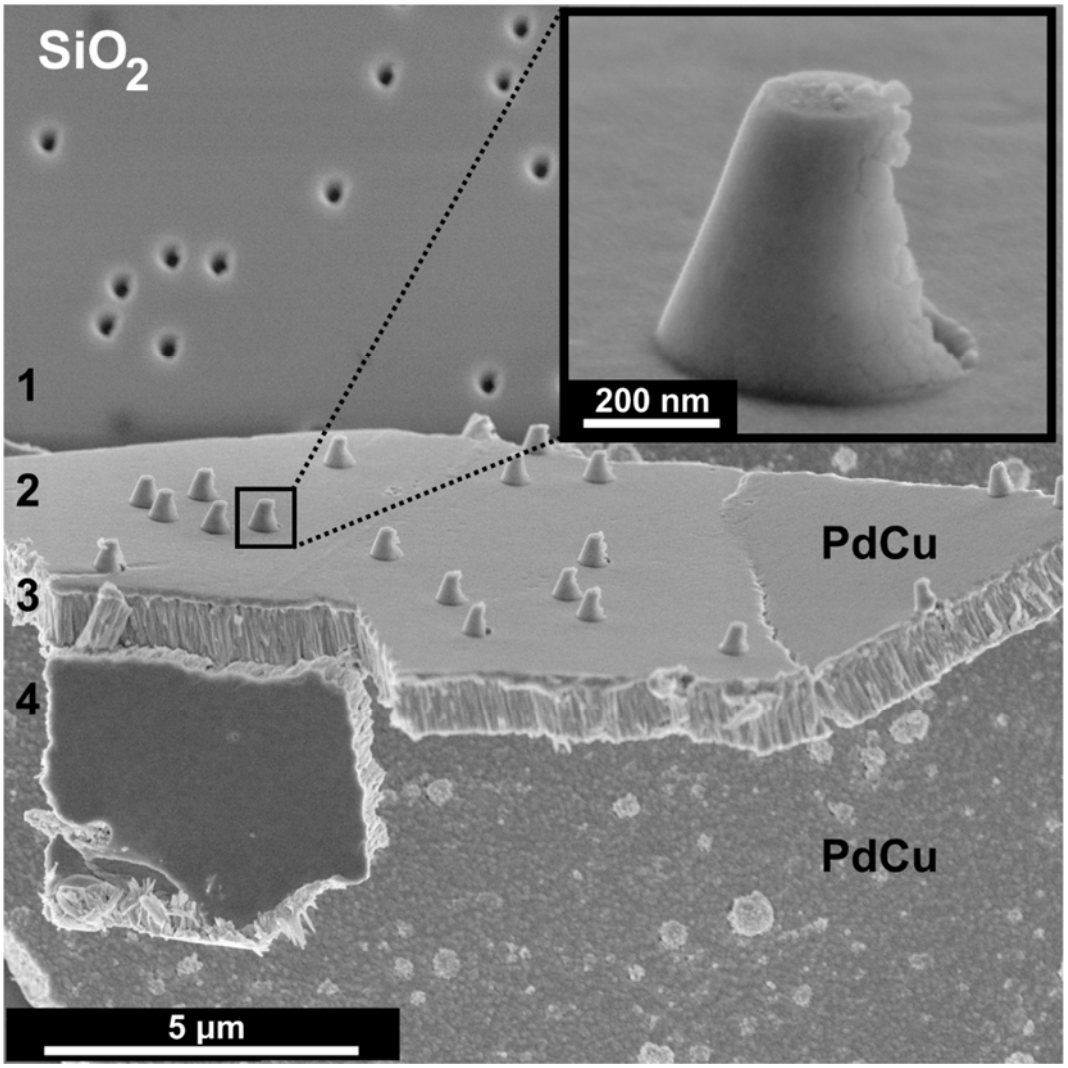

*Fig. 1 SEM image of the sample type **I**: porous surface of SiO_2 after peeling of the PdCu film (1), the surface of the PdCu film on the substrate side (2), its fracture (3) and growth front (4).*

Figure 2 shows the SEM images of the sample type **II**. As in the previous case, the smooth surface of the PdCu film on the substrate side, the columnar relief of its fracture (fig. 2a), and the exact copy of the "imprint" pore geometry (fig. 2b) show a weak interaction of the condensate with the matrix. The morphology of the film growth front does not inherit the porous topography of the substrate. Sequentially from the interphase boundary to the substrate nanocrystalline “pedestal” of PdCu is formed, then a fibrous and columnar morphology of growth with a high proportion of interior surfaces.

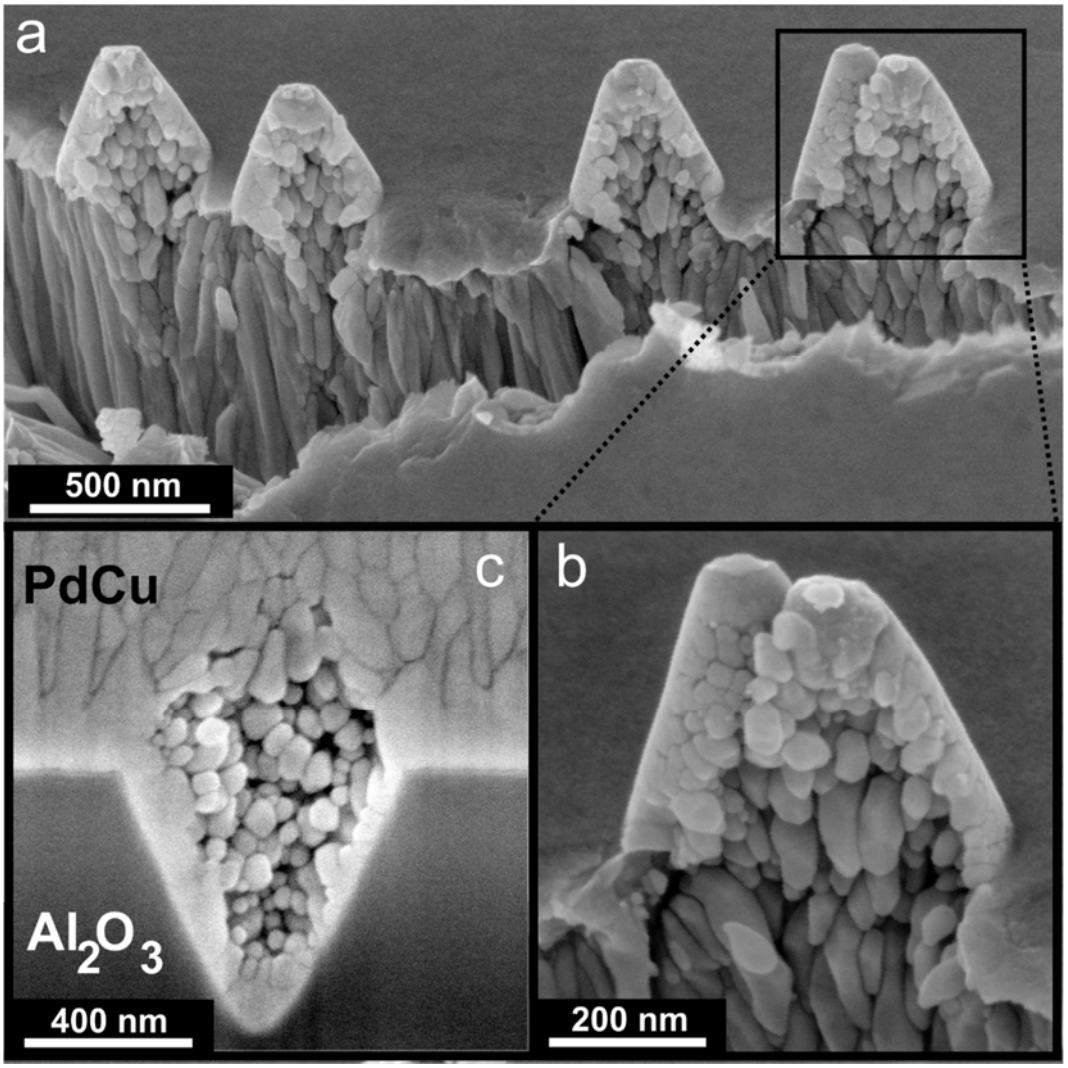

*Fig. 2 SEM images of the sample type **II:** the interphase surface of PdCu from the SiO_2 side (a); extracted "imprint" of pores (b); cross section of FIB heterostructure Si/SiO_2/PdCu (c).*

For type **I** and **II** samples, the character of the fracture surface morphology shows that the bond between the crystals within one column is substantially higher than that between neighboring columns. Cross section of the heterostructure Si/SiO_2/PdCu prepared by the FIB method (fig. 2c) confirms the significant anisotropy of the crystalline structure of the ion-plasma condensate – individual grains in the direction of growth are larger by a factor of magnitude than in the lateral direction. At the interphase boundary with a substrate at a thickness of ~ 40 nm, intercrystallite boundaries are not revealed, it shows the formation of an amorphous-nanocrystalline layer or the "pedestal" of the ion-plasma condensate. This transition layer is formed inside the SiO_2 pore. In the pore volume of SiO_2, the PdCu crystallites are isotropic, separated and highly dispersed (sizes from 15 nm in the depth of the pore to 60 nm in the upper part). The disjunctive growth of the crystals is retained in the volume of a compact (as a whole) PdCu film above SiO_2.

The experimentally observed columnar morphology of growth corresponds to the Thornton band diagram [27], for vacuum ion-plasma condensates. The morphology of the sediment is formed under conditions of limited mobility of adatoms, the material is received by the ballistic mechanism. It causes the effect of shading of the condensate volume and the development of porosity. Activation of surface diffusion causes the formation of a fibrous microstructure of the film with indistinctly cut, highly disperse grains. With an increase in the thickness of the condensate, the evolutionary growth of grains is realized, the crystallites acquire a columnar shape, and intercrystallite boundaries are formed. Under MS conditions, the argon pressure leads to a decrease in the effective T_s at the moment of creation of the film, it reduces the intensity of the condensation-stimulated processes in the buildup layer. The later action of plasma components (electromagnetic radiation, electron bombardment) increases the effective T_s and activates the surface diffusion of adatoms. Therefore, as the thickness of the ion-plasma condensates increases, the gradient character of growth morphology and microstructure of the film is realized in the following sequence: compact isotropic; fibrous porous; columnar loose; columnar compact.

In figure 3 for comparison the crystal structure and the phase composition of the PdCu ion-plasma condensate fragments of electron diffraction patterns and TEM images of the structure of the cross FIB section of crystallites in the region of the growth front of the film above SiO_2 and inside the pore are given.

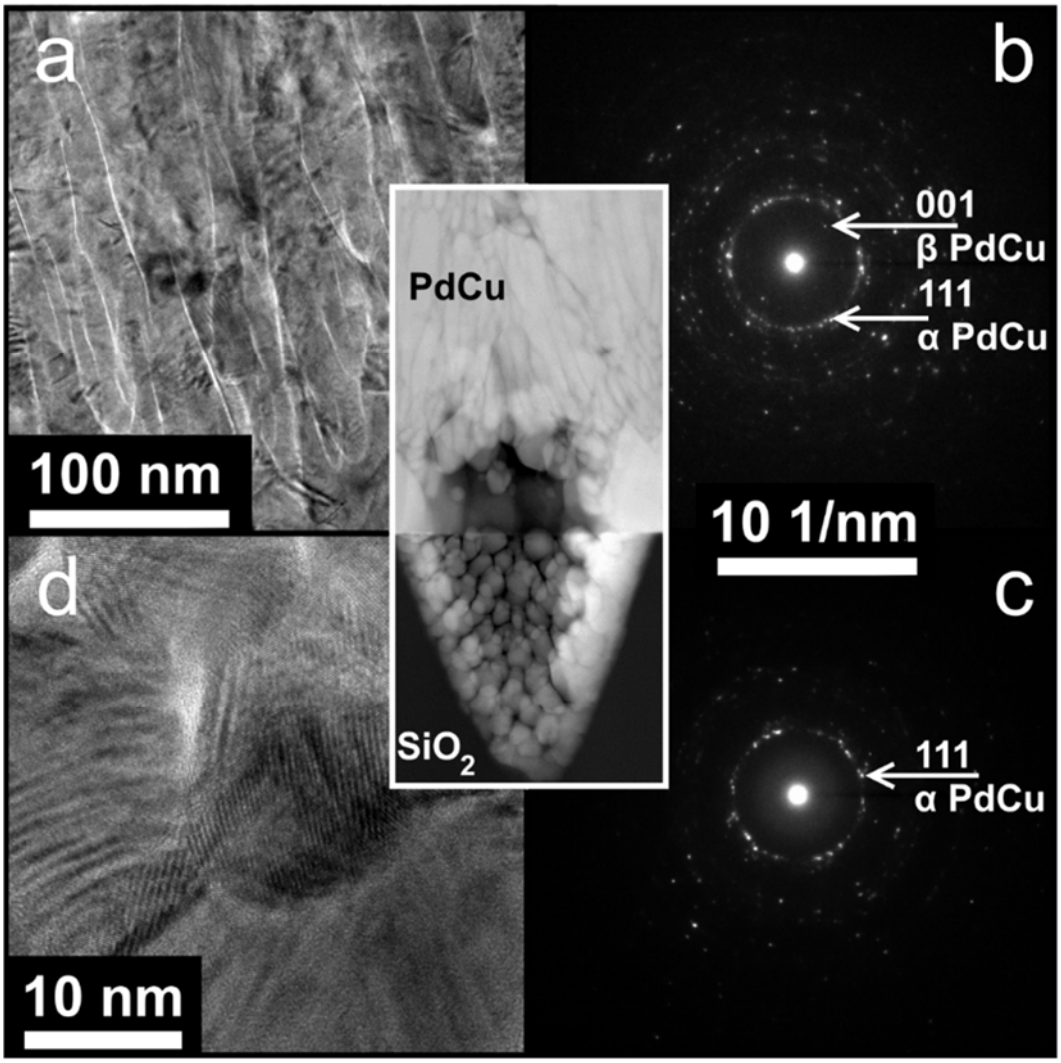

*Fig. 3 Fragments of the SAED (b, c) and TEM image of the structure (a, d) cross FIB section of PdCu crystallites in the region remote from the interphase boundary with SiO_2 (c, d) and inside the pore (a, b). Sample type **II**.*

From the electronogram (fig. 3b, c) it follows that for MS PdCu and condensation in vacuum on SiO_2 substrates (T_s = 670 K) two-phase films are formed: primitive cubic lattice (type CsCl) of ordered solid solution (β phase, a = 0.298 nm) and disorder Solid solution (fcc lattice, α phase, a = 0.379 nm). The reflections of the ordered and disordered phases observed on the electronogram show the parallelism of the fcc plane system of the α phase lattice and the primitive cubic phase β: {111} α ‖ {110} β, it gives grounds for assuming the realization of the orientation relation of the equivalent Nishiyama-Wasserman relation, which is realized for fcc and bcc lattices under microtwinning and phase transitions in austenitic steels according to the deformation mechanism of Bein. However, since this orientation relationship is not located in the sectioned FIB plane, additional conclusions about the equivalence of orientation are necessary for further investigation. According to EDX, the elemental composition of the ion-plasma condensate corresponds to the composition of the sputtered

target. The two-phase composition of PdCu is formed in the region of the entire film, excluding the interior pore volumes of SiO_2. Inside the pores, as follows from fig. 3d, ion-plasma condensate monophasic - fcc lattice of a disordered solid solution. The crystal structure inside and outside the pore also has significant differences: outside the pore (fig. 3a), the α and β phases elongated in the direction of growth of the anisotropic grains with a low density (3×1011 m^{-2}) of twins (characteristic of fcc crystals disordered solid solution PdCu), moire contrast is caused by the superposition of crystal lattices of adjacent grains; and inside the pore (fig. 3d) - isotropic, defect-free grains of α phase are characterized by a high proportion of intercrystalline boundaries and extinction contrast, since their dimensions are smaller than the thickness of the FIB section. Thus, the growth of the ion-plasma condensate outside the pore is characterized by a significant activation of volume diffusion and recrystallization processes, the formation of a compact film with a well-developed grain boundary structure (including the boundaries of twins), organization in the direction of the arrival of the material of a gradient columnar structure (anisotropic crystallites with crystallographic faceting), the ordering of the crystal lattice by the type of CsCl. Inside the pore, the main regularity of growth morphology is a highly dispersed isotropic nanocrystalline structure, the formation of globular α phase crystallites and a system of slit-like, globular nanopores.

Al_2O_3/PdCu system. Fig. 4 shows a SEM image of the fracture of a PdCu film on the surface of a porous alumina and a TEM image of a cross FIB section of Al_2O_3/PdCu. The small diameter of the open pores of Al_2O_3 and the increase in the thickness of the ion-plasma condensate lead to the appearance of macrotension that can tear off the growing layer (fig. 4a). The morphology of the film at the boundary with the substrate and at the surface shows a globular character of the surface relief; the dimensions of the globules of the film and the pores of the substrate are similar, it explains the shallow penetration of the material into the substrate. The mechanical destruction of the Al_2O_3/PdCu heterosystem occurs along the interphase boundary, due to the weak physicochemical interaction of the ion-plasma condensate and the substrate.

The image of the FIB section (fig. 4b) indicates the formation of individual clusters of the PdCu alloy elemental composition (in the EDX data) close to the composition of the sputtered target in the pores of the oxide. From a comparison of the fracture and section of the ion-plasma condensate (see figs 4a and 4b), it follows that as the film thickness grows, the globular crystallites combine and form a columnar structure that contains a large fraction of intergranular boundaries and a complex porous system. The lower layer of the film (~ 200 nm) is the lightest, that in the Z-contrast registration mode, either an increased content of a heavy element or a lower porosity in comparison with the rest of the film.

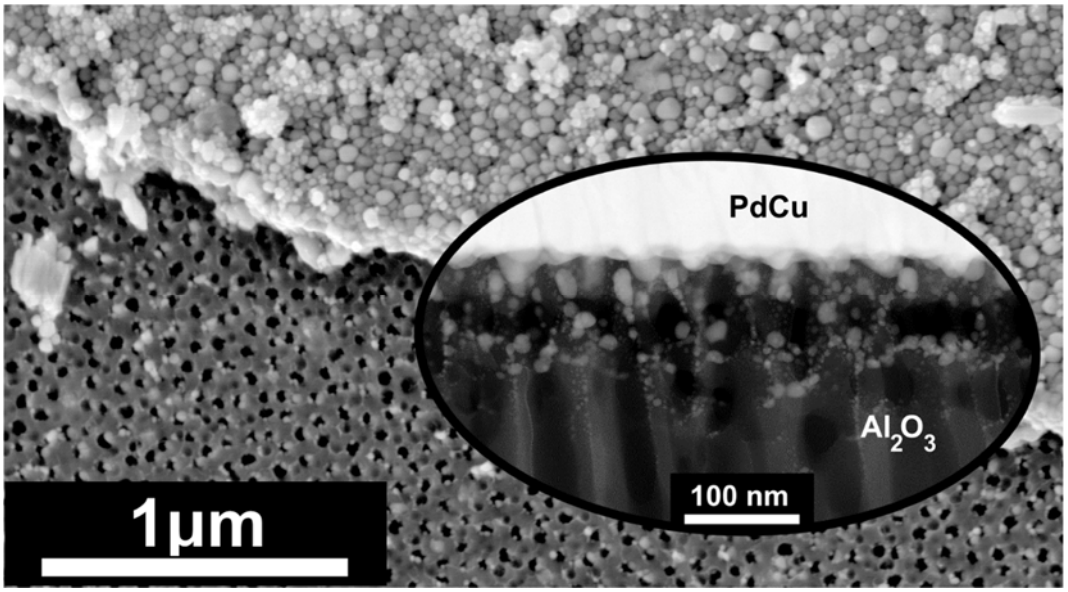

Fig. 4 SEM image of the fracture of the PdCu film on the surface of porous alumina (a) and the TEM image (in the Z-contrast recording mode) of the cross FIB section of the Al_2O_3/PdCu (b).

Since the content of palladium with a film thickness (according to EDX) fluctuates insignificantly, only the ultimate compactness (nonsense) of the lower layer – the "pedestal" of the condensate in comparison with the upper layer. The penetration of the condensed material into the pores of Al_2O_3 (diameter 80 nm) of the substrate does not exceed 200 nm, i.e. filling of open pores occurs (in the given conditions) by discrete clusters (size from 4 to 25 nm) to a depth of 2-3 pore diameters.

Fig. 5 shows fragments of electronograms and TEM images of the cross FIB section Al_2O_3/PdCu. From the electronograms (fig. 5a) it follows that for MS PdCu and condensation in vacuum on the substrates of porous Al_2O_3 (T_s = 670K), as in the case of type II samples, two-phase (α + β) solid solution (PdCu) films are formed, individual crystallites are mutually oriented with; {111} α || {110} β, but most of them have an arbitrary mutual orientation, i.e. the ratios of Nishiyama-Wasserman, Kurdyumov-Zaks and Groeninger-Troyano were not revealed. Outside the pore, the crystalline structure of the condensate is characterized by a growth texture – anisotropic grains of α and β phases with low density (3×10^{11} m^{-2}) twins with a clear grain-boundary structure (including boundaries of twins) of anisotropic faceted crystallites.

The elemental composition of the condensate corresponds to the composition of the sputtered target. The two-phase composition of PdCu is formed in the region of the entire film, excluding the clusters located in the volume of the Al_2O_3 pores. Inside the pores, as follows from fig. 5d, the clusters crystallize exclusively in the fcc lattice of the disordered solid solution.

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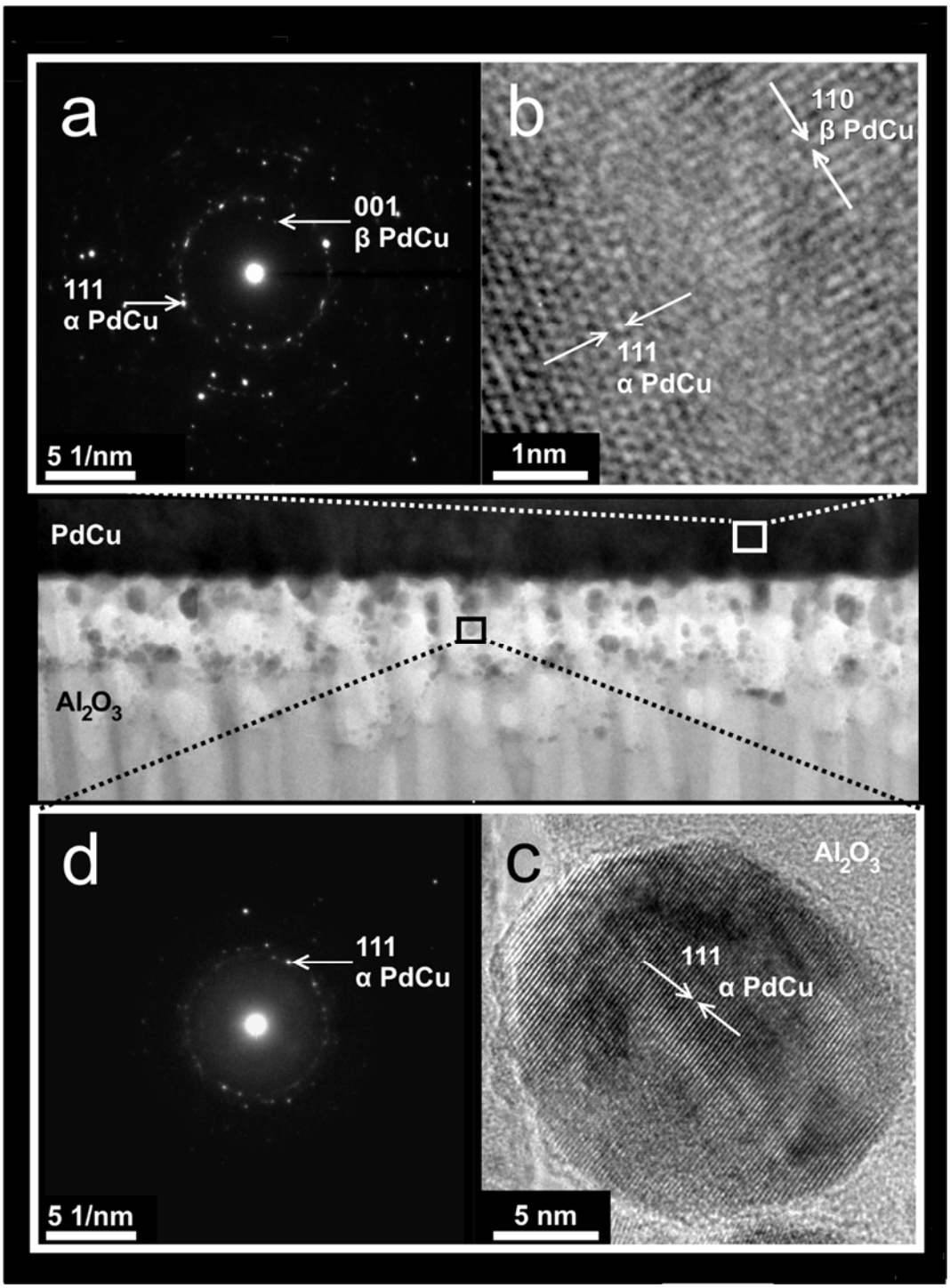

Fig. 5 Fragments of the SAED (a, d) and TEM image (phase contrast) cross FIB section of Al_2O_3/PdCu from the region of the PdCu film remote from the interphase boundary with the substrate (b) and inside the pore (c).

Figure 5b illustrates the direct resolution of the crystallographic (111) planes of α and (110) β phases of a two-phase film of a solid solution of PdCu (far from a porous substrate). The grains of an ordered and disordered solid solution are arbitrarily oriented, for this reason, there may be no coherent boundary and the grains are separated by an amorphous interlayer ~ 2 nm thick.

PdCu clusters in a porous oxide matrix (fig. 5c) with a lateral size of more than 4 nm already form a contrast of direct resolution of crystalline planes, having a size larger than 15 nm acquire a facet, and larger than 50 nm form internal boundaries and obtain an extinction contrast caused by variable thickness.

In mathematical modeling of the initial stage of condensation overgrowing of pores in alumina, the authors of [28] predict: for silver and gold uniform pore coating with subsidence; for iron - overgrowing islets and forming a nanostructure inside the pore; for palladium atoms – film subsidence over the pore and the preservation of a non-overgrowing hole. A significant discrepancy with the experiment is due to the short counting time, however, the experimental results for the PdCu ion-plasma condensate indicate a nanostructuring of the condensate inside the pore diameter from 60 to 450 nm, both for Al_2O_3 and SiO_2.

Conclusion

Growth morphology and structure of PdCu ion-plasma condensate in the pores of SiO_2 and Al_2O_3 amorphous matrices were studied. It was established that for heterosystems synthesized by MS PdCu alloy and vacuum condensation on the surface of SiO_2 and Al_2O_3 with open porosity, the main regularities of structure formation and features of the morphology of SiO_2/PdCu and Al_2O_3/PdCu are:

- the free film has a two-phase composition (ordered and disordered phases of a solid solution of PdCu); the closed volume of the pore (SiO_2 and Al_2O_3) excludes the synthesis of the ordered phase;

- a highly dispersed isotropic nanocrystalline structure of globular α-phase crystallites and a system of slit-like, globular nanopores is formed inside the pore of SiO_2 with a diameter 300 and 450 nm to the entire depth;

- pores of Al_2O_3 (diameter 80 nm) fill discrete clusters (from 4 to 25 nm) of disordered solid solution to a depth of 2-3 pore diameters.

Based on established regularities, the following model for the formation of the PdCu ion-plasma condensate was suggested. At the stage of film formation, on the interphase boundary with the substrate, the morphology of the compact nanocrystalline layer - "pedestal" is realized. With a weak physico-chemical interaction of the condensate with the substrate, nanocrystals form a fibrous and then columnar structure with a high proportion of interior pores. In the conditions of the ballistic arrival mechanism and limited mobility of adatoms, the effect of shading of the condensate volume and the formation of pores appear. Under MS conditions, the presence of the working gas reduces the effective T_s and the intensity of the condensation-stimulated processes at the stage of film nucleation. The energy components of the plasma increase the effective T_s and activate the surface diffusion of adatoms. These competing processes contribute to form the parameters of the morphology and microstructure of the film along the thickness of the gradient layer. With increasing thickness of the

condensate, the evolutionary growth of grains is realized, the crystallites take on a columnar shape, intercrystallite boundaries are formed.

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