Contents lists available at ScienceDirect





Electrochimica Acta

journal homepage: www.elsevier.com/locate/electacta

Electrochemical growth of nanowires in anodic alumina templates: the role of pore branching



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ARTICLE INFO

Article history: Received 10 November 2016 Received in revised form 23 December 2016 Accepted 23 December 2016 Available online 26 December 2016

Keywords: anodic alumina pore branching templated electrodeposition nanowire

ABSTRACT

A comparative study of electrochemical growth of nanowires in the anodic alumina templates with various degree of porous structure ordering is performed. Scanning electron microscopy and coulometric analysis are used for experimental evaluation of the average filling of pores with metal. The theoretical model of metal growth inside anodic alumina templates is proposed. The model takes into account the presence of branched channels in the real structure of anodic alumina and operates with completeness of template filling achieved at the moment when metal reaches the external surface of the oxide film. In case of the diffusion-controlled regime the strong dependence of the pore filling factor on the thickness of porous film and the degree of its structure ordering is predicted theoretically and observed experimentally. The influence of the nature of limiting current on the homogeneity and completeness of template filling is discussed.

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1. Introduction

One-dimensional (1D) nanostructures (e.g. nanotubes and nanowires) are of great interest owing to unique properties associated with their inherent shape anisotropy. 1D nanostructures can be easily prepared by templated electrodeposition, which combines the advantages of templated synthesis with versatility of electrochemical processing. For this purpose, porous matrices with long channels, e.g. track etched membranes and anodic aluminium oxide (AAO) films are commonly used. Both of these templates possess uniform cylindrical channels, which are aligned closely to the normal of the film surface in case of AAO [1,2] and can be substantially tilted about the normal in track-etched membranes [3]. In comparison to track-etched membranes, pore density in the structure of AAO films is more than an order of magnitude higher due to the assembly of the channels into the 2D hexagonal packing. Moreover, the use of different anodization conditions allows one to adjust the structural parameters of AAO (such as interpore distance

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 D_{int} , pore diameter D_p and film thickness L_0) in a wide range. In particular, D_{int} can be changed in controllable manner from 10 to 1000 nm, D_p can be varied from 5 to 500 nm, L_0 can exceed the hundreds of micrometres.

The combination of unique structure with high thermal, chemical and mechanical stability makes anodic alumina extremely attractive as templates for the synthesis of one-dimensional nanostructures [4–6]. The template-assisted approach has been successfully used for the synthesis of nanowires with constant or modulated composition [7–9], nanotubes [10,11], nanobelts [12], and nanorings [13] possessing the wide range of functional properties. The extraordinary magnetic behaviour of individual particles and their arrays [5,7], enhanced intensity of Raman spectra [14], and unusual electron transport properties [15] have been observed for nanowires obtained in AAO templates. Moreover, the prototypes of high technology devices based on AAO, such as field emission devices for X-ray instruments [16], flat panel displays [10], chemical and biological sensors [17,18], energy and memory storage devices [19–21] have been demonstrated.

Recently we have shown that the self-organization of AAO structure occurs via growth of domains with preferential in-plane orientation accompanied by the size reduction of other domains, which is similar to Ostwald ripening [22]. This process induces the unavoidable formation of branched and terminated channels. It is

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http://dx.doi.org/10.1016/j.electacta.2016.12.142 0013-4686/© 2016 Elsevier Ltd. All rights reserved.

worth noting that terminated channels cannot be filled during templated electrodeposition process. Obviously, these features of AAO structure negatively affect the transport efficiency of any species (e.g. ions, gas molecules, etc.) through AAO membranes [23]. Taking account of the extensive use of anodic aluminium oxide films as templates for the synthesis of various one-dimensional nanostructures, theoretical modelling and experimental study of the role of pore branching on the electrochemical growth of metal nanowires inside the AAO channels are of great interest. To the best of our knowledge, only a few theoretical works have been published on metal electrodeposition in one-dimensional channels of track-etched membranes [24–27] and AAO templates [23,28–33], whereas the influence of branched pores on the electrodeposition process has never been discussed.

Here we present the quantitative analysis of the impact of the defects (e.g. branched and terminated channels) in real structure of AAO porous films to electrochemical growth of nanowires in anodic alumina templates. The crucial characteristic of templated electrodeposition is a maximum achievable pore filling. Firstly, it determines the attainable length of nanowires and the replication accuracy of pore shape by embedded material. Secondly, the increase in pore filling leads to the enhancement of mass-sensitive properties of resulted nanocomposite, such as magnetization and capacity.

2. Theoretical part

We consider the model developed by Bograchev et al. [29–31] as the most suitable for the description of electrodeposition in straight pores. The numerical simulation implemented for typical geometric parameters of AAO porous structure (pore diameters and lengths) demonstrates that the issue can be reduced to 1D quasi-steady-state problem with varying pore length [29]. The authors obtained the following equation for the filling of single pore with metal M forming in the course of *n*-electron reduction of M^{n+} ion (Fig. 1):

$$\frac{dL_s}{dt} = -\frac{MD\left(C_m + \left(\frac{nF\rho C_0}{J_0 M}\right)\left(\frac{dL_s}{dt}\right)\exp\left(\frac{\alpha F\eta}{RT}\right)\right)}{\rho L_s}$$
(1)

where L_s is the length of unfilled part of the pore, D is the diffusion coefficient of metal ions, M is the molar weight of the metal, ρ is the metal density, n is the number of electrons involved in electrochemical reaction, j_0 is the exchange current density, α is the transfer coefficient, $\eta = E_d - E_{eq}$ is the overpotential, E_d is the deposition potential, E_{eq} is the equilibrium potential for M^{n+}/M redox system, R is the gas constant, T is the absolute temperature, F is the Faraday constant, C_m is the concentration of metal ions in the pore mouth, C_0 is the concentration of metal ions in the bulk solution.

Bograchev et al. [29] suggested to denote the quantity dependent on the kinetics of electron transfer as

$$\delta_k = \left(\frac{nFC_0D}{j_0}\right) \exp\left(\frac{\alpha F\eta}{RT}\right) \tag{2}$$



Fig. 1. Nanowire growth. L_0 is the membrane thickness, L_s is the length of unfilled part of the pore.

and to present Eq. (1) as follows [30]:

$$\frac{dL_s}{dt} = -\frac{MD \quad C_m}{\rho \quad (L_s + \delta_k)} \tag{3}$$

where δ_k has the dimension of length and can be tentatively presented as an additional pore length. This interpretation is also true for branched pores. In the present paper we designate δ_k as "kinetic length". Also we use the dimensionless parameter $K = \delta_k/L_0$ (where L_0 is AAO membrane thickness) treated as "relative kinetic length" (Fig. 2). For purely diffusion control of electrochemical reaction K=0, whereas for purely kinetic control $K \to \infty$.

To calculate the time dependence of current, additional assumptions about outer diffusion were used in [29–31]. In present work we propose only one assumption concerning outer diffusion, namely that C_m has the same value near all pore mouths at any fixed time, but can change with time. This assumption is enough to calculate the final length distribution of nanowires and filling factor of pores by the metal.

When Choi et al. [34], Napolskii et al. [22], Petukhov et al. [35], and Kasi et al. [36] observed pore branching on cross-sectional scanning electron microscopy (SEM) images of AAO membranes, they assumed that all branches have the same direction, and a pore can divide into two branches during anodization, but pores never merge. Hence, pore densities at two opposite sides of AAO membrane (top and bottom) are not equal. In the theoretical model we consider the growth starting (i) either from the top, or (ii) from the bottom of AAO membrane. In experiment, (i) or (ii) can be arranged by forming the conductive layer on top or bottom side of AAO porous film.

Many observations have been also reported concerning welldefined growth front of nanowires inside AAO membrane when some other wires already reached the outer surface. We consider this 'internal' growth front as the second front and demonstrate below that it originates just from pores branching.

2.1. Working electrode located at the bottom of an AAO membrane

If conductive layer (working electrode) is deposited on the bottom of an AAO template the branches are directed upside down, and nanowires are merging while growing. In general,



Fig. 2. Visualization of the equation (3). Kinetic length δ_k can be imagined as an additional pore length. L_s is the length of unfilled portion of the pore, C_0 is the concentration of metal ions in the bulk solution, C_m is the concentration of metal ions in the pore mouth.



Fig. 3. Branched pore and straight pore in case when a conductive layer is deposited on the bottom of an AAO membrane. Nanowires in branched pores are growing more slowly than nanowires in straight pores. H_0 is the distance between the bottom of membrane and the bifurcation point of the pore, L_0 is the AAO membrane thickness, *h* is the final length of nanowire in the branched pore.

nanowires in branched pores are growing more slowly than nanowires in straight pores because of more severe diffusion limitations. In our model we consider only straight pores and branches with a single bifurcation. The rate of nanowires growth in branches with several bifurcations is much slower, and there is a little chance to observe these wires at the cross-section of a nanocomposite.

Nanowires forming in straight pores reach the surface of AAO membrane earlier, and then the growth in branched pores stops due to its screening. Final length of nanowires (h) in branched pore depends on the distance H_0 between the bottom of membrane and the bifurcation point of the pore (Fig. 3).

An equation for length h is obtained in appendix (A1) as a piecewise function of H_0 :

$$\text{If } \frac{H_0}{L_0} \le \frac{1+2K}{3}, \frac{h}{L_0} = (1+K) - \sqrt{1+K^2 - \left(1-\frac{H_0}{L_0}\right)^2 - \left(\frac{H_0}{L_0}\right)^2}$$

$$\mathrm{lf}\frac{H_0}{L_0} > \frac{1+2K}{3}, \frac{h}{L_0} = \left(2 - \frac{H_0}{L_0} + K\right) - \sqrt{\left(2 - \frac{H_0}{L_0} + K\right)^2 - (1+2K)}$$
(4)

The obtained function $h(H_0)$ (4) contains relative kinetic length K as a parameter. From distance H_0 distribution of pores in the membrane, one can obtain final nanowire length (h) distribution, using the function (4).

The length distributions of nanowires were numerically calculated for the case when pores are uniformly distributed over H_0 in the interval (0, L_0), for different *K*, as shown in Fig. 4.

The distribution has sharp maximum which emerges because h (H_0) function has a minimum. Near the point of the minimum the derivative is small.

In appendix (A2) the equations for the position of nanowire distribution maximum h_{max} depending on parameter *K* are obtained:

$$If K < 0.25, \frac{h_{max}}{L_0} = \frac{1 + 2K}{3}$$

If
$$K \ge 0.25, \frac{h_{max}}{L_0} = (1+K) - \sqrt{0.5 + K^2}$$
 (5)

It is worth noting that the obtained solution does not depend on pore distribution over H_0 if this distribution is a smooth function. Fig. 5 shows the plot of $\frac{\hbar_{max}}{L_0}(K)$ function (5). The maximum of the nanowire length distribution is expected to be observed on cross-sectional SEM image of membrane as growth front of nanowires behind straight nanowires that have reached the surface of the membrane.

It can be clearly seen that the relative height of the second growth front undergoes the changes only for K below 2.5, and lies in the range of 90–100% of template thickness at higher K values.



Fig. 4. (a) Functions $h(H_0)$, plotted according to the equation (4) for different relative kinetic lengths *K*: K = 0 (diffusion control), K = 0.3, K = 0.8 (mixed control). (b) Nanowire final length distributions, calculated for pores uniformly distributed over H_0 in the interval (0, L_0), for different relative kinetic lengths *K*. Number of nanowires within 2.5% interval of membrane thickness is expressed as percentage of the total number of branched nanowires.

1



Fig. 5. Nanowire length distribution maximum h_{max} depending on relative kinetic length *K* according to equation (5). This maximum is expected to be observed on cross-section of the membrane as the second growth front of nanowires. Graph for *K* from 0 to 1 is shown in inset.

The former interval looks narrow in *K* scale, but in terms of overvoltage it corresponds to semi-infinitive range of deposition potentials.

2.2. Working electrode located at the top side of an AAO membrane

If conductive layer (working electrode) is deposited on the top of an AAO template the branches are directed upwards, and nanowires are branching while growing. Nanowires in branched pores are growing faster than nanowires in straight pores because of the diffusion limitations. Fig. 6 shows a branched nanowire, overrunning straight one.

The model takes into account multiple pore branching, which occurs only at the domain boundaries (Fig. 6a), whereas pore branching inside the domains is not considered. This assumption is credible because bifurcations occur on moving domain boundary [22,34].

We assume that bifurcations are located at equal distances. Fig. 6a shows the most rapid way for nanowire in a branch to reach the surface of a membrane. When the first nanowires reach the top side of the membrane, they screen neighbouring pores causing other nanowires to stop the growth.

With the aim to get an analytical solution of the problem, we obtained an approximate equation for diffusion flow through the branch of *N* pores (Appendix A3):

$$I_N = I_1 \sqrt{N} \tag{6}$$

where I_1 is the flow through a straight pore with the same length as the branch. This equation gives us solutions lying within 5% error from exact solutions for $N \ge 1$.

Using (6), we obtained an approximate equation for the height of straight nanowires h_0 at the moment when the first branched nanowire reaches the top of the membrane (Appendix A4):

$$\frac{h_0}{L_0} = (1+K) - \sqrt{1+K^2 - \frac{4}{3\sqrt{N}}}$$
(7)

where *N* is the number of bifurcations in the branch. It is assumed that N >> 1.

The equation for *N* is:

$$\frac{4}{3\sqrt{N}} = 2(1+K)\frac{h_0}{L_0} - \left(\frac{h_0}{L_0}\right)^2 - 2K$$
(8)

If *K* = 0, i.e. in the case of diffusion-controlled regime, equations (7) and (8) are simplified:

$$\frac{h_0}{L_0} = 1 - \sqrt{1 - \frac{4}{3\sqrt{N}}} \tag{9}$$

$$\frac{4}{3\sqrt{N}} = 2\frac{h_0}{L_0} - \left(\frac{h_0}{L_0}\right)^2$$
(10)

Low filling factors of a membrane are expected when a conductive layer, serving as a working electrode, is deposited on the top side of an AAO membrane with only a few nanowires reaching the surface.

3. Experimental part

High-purity aluminium foils (0.5 mm thick, 99.999%) were used for the preparation of the AAO templates. Before anodization Al was annealed at 150 °C for 12 hours and after that at 550 °C for 24 hours for removing mechanical stress and forming coarse grain structure of the foil. Then aluminium plates 40 mm in diameter



Fig. 6. (a) Sketch of the filling of straight and branched pores by metal when working electrode is deposited on the top of an AAO membrane. L_0 is the membrane thickness, *N* is the number of pores in the branch, h_0 is the final height of nanowires in a straight pore at the moment when the metal in branched channel reaches the top surface of template. (b) SEM image of the branched nanowire, overrunning the growth front of metal, in Cu/AAO nanocomposite with Au current collector sputtered on the top side of an AAO membrane (see experimental details below).

were sanded by SiC abrasive papers (Smirdex) and mechanically polished by 3 μ m diamond suspension DiaDuo-2 (Struers) and colloidal silica suspension OP-S (Struers). In order to obtain the foils with a mirror-like surface, electropolishing of the pretreated aluminium in a solution containing 13 M H₃PO₄ (IREA 2000, 85%) and 1.85 M CrO₃ (Vekton, 99.7%) at 80 °C in an impulse mode was used. 40 impulses for 3 s were imposed at an anodic current density of 0.4 A cm⁻². Finally, aluminium was cleaned in deionized water and dried in airflow at room temperature.

Anodization was carried out in two-electrode electrochemical bath in 0.3 M oxalic acid (99.5%, Chimmed) at constant applied potential difference of 40 V using DC power supply N8741A (Agilent). Polished Al foil was used as an anode and Al ring served as a cathode. The cathode surface area was several times higher than that of the anode; the distance between electrodes was 30 cm. The electrolyte was intensively agitated by overhead stirrer RW 20 digital (IKA) and its temperature was kept equal to 0 °C using thermostat Unistat Tango (Huber). Large volume of electrochemical bath (20 litres) allowed us to control the temperature of electrolyte precisely. The thickness of AAO films was controlled coulometrically. Two series of AAO films with the thickness from 30 to 90 µm were used as templates. In order to obtain AAO films with high degree of pore ordering, two-step anodization technique was applied, whereas one-step anodization was performed for the preparation of AAO with higher quantity of branched channels in their structure.

In case of two-step anodization 45 μ m thick sacrificial alumina layer, formed during first anodization step, was selectively dissolved in an aqueous solution containing 0.5 M H₃PO₄ and 0.2 M CrO₃ at 70 °C for 30 min. The second anodic oxidation of Al in 0.3 M oxalic acid at 40 V leads to the formation of AAO with 2D hexagonal arrangement of pores.

Aluminium was selectively dissolved in 4 M solution of Br_2 in methanol to obtain freestanding oxide films. Then barrier oxide layer was removed by chemical etching in 3 M H_3PO_4 solution at room temperature with the electrochemical detection of pore opening moment [37]. The diameter of channels in AAO was

widened by etching of porous films in 0.5 M H_3PO_4 solution at 60 $^\circ C$ for 3 min.

In order to illustrate the role of pore ordering in AAO templated electrodeposition process, the electrochemical growth of copper nanowires in AAO membranes was carried out. Electrodeposition was performed in a three-electrode cell from a solution containing 0.1 M CuSO₄ and 0.1 M H₂SO₄ (pH = 1.08) in potentiostatic mode using PGSTAT100N (Autolab). Thin Au layer (ca. 200 nm thick) was deposited by magnetron sputtering (Q150T ES, Quorum Technologies) onto one side of the AAO template to serve as current collector. Pt wire ring with diameter of ca. 2 cm was used as a counter electrode. Saturated (KCl) Ag/(AgCl) electrode connected with the cell via Luggin capillary served as the reference electrode. Deposition potentials -0.4 V and -0.2 V were chosen using cyclic voltammetry. During electrodeposition the electrolyte was constantly agitated by magnetic stirrer (IKA big squid) with the rate of 400 rpm.

Current-time transients registered by PGSTAT100N (Autolab) during metal electrodeposition were used for the characterization of the growth process of Cu nanowires inside AAO porous films. To calculate the average pore filling factor achieved at the moment when metal reaches external surface of a template, the volume of electrodeposited metal was estimated by the Faraday's law with account for current efficiency. Electrodeposition charge was found by the numerical integration of current-time transient. SEM images of the AAO membranes and Cu/AAO nanocomposites were collected using field-emission scanning electron microscopes Supra 50 VP (LEO) and NVision 40 (Carl Zeiss). Before SEM analysis, 5 nm thick layer of gold was sputtered onto surface of the samples by magnetron sputtering.

4. Results and discussion

Structure parameters of AAO templates were calculated by statistical analyses of the SEM images of the top and the bottom of porous oxide films (Fig. 7). All AAO templates possess nearly equal interpore distance of 102 ± 5 nm and pore diameter of 49 ± 3 nm,



Fig. 7. SEM images of anodic alumina films. (a) Top and (b) bottom of the AAO membrane after the first anodization step; (c) top and (d) bottom of the AAO template obtained by two-step anodization process. The bottom views were recorded after removal of the barrier layer by chemical etching. Insets in panels (b) and (d) display schematic cross-section of alumina films obtained by one- and two-step anodization, respectively.



Fig. 8. Cyclic voltammogramms of porous electrode, based on $45 \,\mu$ m thick AAO with ordered porous structure, in an aerated solution containing 0.1 M CuSO₄ and 0.1 M H₂SO₄. Potential scan rate is 50 mV s⁻¹. Experiments were performed under various rate of electrolyte agitation: without stirring (blue), 100 rpm (orange), 200 rpm (yellow), 300 rpm (violet), 400 rpm (green). The currents were normalized on geometric area of the sample (0.2 cm²).

corresponding to the porosity of ca. 20%. At the beginning of first anodization step pores nucleate stochastically on the smooth surface of the electropolished aluminium substrate (Fig. 7a). The pores self-organize during first oxidation step and, thus the twodimensional hexagonal honeycomb-like porous structure can be seen on the bottom of the AAO template (Fig. 7b). Self-organization process is accompanied by the branching of pores followed by the formation of terminated channels (inset in Fig. 7b) [22]. It should be noted that the terminated pores cannot be opened by any etching procedures applied usually for barrier layer removal. If the duration of anodization is long enough, only the top part of oxide film is disordered, whereas the bottom part of AAO possesses ordered structure with low concentration of branched and terminated channels (inset in Fig. 7b). In case of two-step anodization the second oxidation step begins on pre-patterned metal surface obtained after the selective dissolution of sacrificial alumina layer. This allows us to obtain porous films with ordered structure over all the thickness of AAO (Fig. 7c,d).

Obviously, the presence of terminated channels decreases maximum achievable filling of AAO by the metal, whereas the impact of branched channels on electrodeposition process depends on the nature of the limiting step of electrochemical reaction. The growth rate of the nanowires in branched pores under diffusion control may be substantially different from that in straight pores. On the contrary, under kinetic control the rate of metal growth does not depend on the number of branches.

To determine the potential regions of various regimes of metal electrodeposition, cyclic voltammetry was used (Fig. 8). The experiments were carried out in an electrolyte containing 0.1 M CuSO₄ and 0.1 M H₂SO₄. The working electrode consisted of 45 μ m thick AAO template with gold sputtered to the bottom of oxide film.

The current of Cu electrocrystallization does not depend on the rate of electrolyte agitation, manifesting the kinetic regime of deposition, when electrode potential is positive. On the contrary, at E < -0.3 V, the limiting diffusion current is observed, which increases significantly with stirring. Intermediate potential region corresponds to mixed reaction control. Unfortunately, electrodeposition under purely kinetic control results in too slow metal growth rate, and can be complicated by gradual increase in pore diameter during long electrodeposition process due to dissolution of AAO in acidic solution. This is why to check the effect of regime, two deposition potentials $E_d = -0.4$ (diffusion control) and -0.2 V (mixed control) were chosen for further experiments. It is worth noting, that the onset of hydrogen evolution appears to drift to more negative potentials with electrolyte agitation rate. This feature can result from the Ohmic drop contribution, as the currents are high enough.

Fig. 9 shows cross-sectional SEM images of Cu/AAO nanocomposites based on 60 μ m thick AAO templates obtained by oneand two-step anodization. A conductive layer serving as working electrode was sputtered on the bottom of porous film, hence branches were directed upside down. Cu nanowires were deposited under diffusion ($E_d = -0.4$ V, Fig. 9a and c) and mixed ($E_d = -0.2$ V, Fig. 9b and d) growth control. All depositions were stopped after sharp current increase, which indicates that significant number of nanowires reached the outer surface of the membrane [38].

SEM images shown in Fig. 9 were recorded using secondary electrons with high acceleration voltage of 20 kV. This regime allows us to obtain the images with atomic-number contrast: the brighter the region on cross-section, the higher the quantity of pores filled by the metal. We should stress that the decrease in



Fig. 9. Cross-sectional SEM images of Cu/AAO nanocomposites based on $60 \,\mu$ m thick AAO templates obtained by one- (a,b) and two-step (c,d) anodization. Cu electrodeposition was performed at $-0.4 \,V(a,c)$ and $-0.2 \,V(b,d)$. Gold was sputtered on the bottom of AAO porous film, hence branches were directed upside down. The place of working electrode (WE) is shown by arrow.



Fig. 10. Current-time transients for Cu electrodeposition at $E_d = -0.4$ V in AAO membranes with different thickness and degree of pore ordering. Gold was sputtered on the bottom of AAO templates. Samples are denoted as XstepY, where X is the number of anodization steps (1 or 2), Y is the thickness (in μ m) of AAO layer formed at the first or second anodization step, respectively.

overpotential leads to the increase in the number of wires which reach the AAO outer surface. As a consequence, after deposition in mixed regime the surface of the samples was covered by continuous layer of electrodeposited Cu (Fig. 9b,d), whereas under diffusion control only individual semispherical caps were observed. The longest wires which approached the outer surface are formed in non-branched channels when the working electrode is located at the AAO bottom. Contrary, when deposition starts from the opposite side of membrane (working electrode located at the top, Fig. 6b), the 'fastest' wires are formed in branched pores. For the latter case, h/L_0 ratio depends both on *K* and *N*, and in future Eq. (9) can be probably used for diagnostics of branching.

Although the metal started growth on external surface of nanocomposite, high degree of pore filling with copper is observed only in near bottom parts of Cu/AAO nanocomposites obtained at $E_d = -0.4 \text{ V}$ (Fig. 9a,c). Equal thickness of this bright layer throughout the sample cross-section testifies that the nanowires grow with close rates. It is worth noting that these nanowires form the second growth front. First growth front is formed by a small portion of wires which reached the top surface of AAO template, and is not visible. Cu/AAO nanocomposites obtained at $E_d = -0.2 \text{ V}$ possess similar morphology with two clearly visible growth fronts of metal nanowires.

The existence of two growth fronts can not be explained with the use of a deposition model considering only straight pores in porous template. Thus, although the second growth front of metal nanowires in AAO template was often observed [33,38–40], none of existing theoretical models can describe this kind of morphology.

The theoretical model presented above (see Theoretical part) refers to the existence of two growth fronts with branched pores. Nanowires in straight pores reach the surface of AAO membrane faster, and, thus, form the first growth front. Metal nanostructures in branched channels with one bifurcation form the second growth front (see Fig. 4 and 9). According to SEM analysis, the average pore filling and the ratio of final length of nanowires in branched pores to the template thickness (h/L_0) are higher in the case of mixed control as compared to diffusion-controlled regime of electrode-position (Fig. 9). This experimental observation is in good agreement with the suggested theoretical model (Fig. 5).

We should stress that several assumptions are used in the suggested theoretical model. Firstly, the nucleation is considered as instantaneous for all overpotentials. Actually, progressive nucleation may take place at lower overpotentials ($E_d = -0.2$ V). If so, the length dispersion of nanowires in growth front should increase. Indeed, the length dispersion of the nanowires forming the first and the second growth fronts, is higher in case of mixed control electrodeposition (compare Fig. 9c and d). Secondly, the model considers branched pores with only one bifurcation. Actually, the pore branches with several bifurcations exist. They may form additional growth fronts of metal nanowires.

To observe the influence of the degree of pore ordering on completeness and homogeneity of the pore filling with metal. Cu electrodeposition under diffusion control was performed. According to the theoretical model, diffusion-controlled electrodeposition should reveal the most pronounced effect of pore branching on metal electrocrystallization. For this purpose, AAO porous films with the thickness from 30 to 90 µm obtained by one- and twostep anodization were used as the templates. Current-time transients of template-assisted copper electrodeposition at E_d = -0.4 V are shown in Fig. 10. During Cu deposition in AAO pores, the current density is constantly increasing. It is caused by the increase in concentration gradient of electroactive species with reduction of the length of the unfilled pore regions (see Eq. (3)). It is worth noting that current-time transients recorded for AAO templates of the same thickness, but with different structure ordering (obtained by one- and two-step anodization) are almost similar. Current density is systematically higher for AAO films obtained by two-step anodization, probably due to a lower number of terminated and branched pores in their structure. By the way, this difference



Fig. 11. Cross-sectional SEM images of Cu/AAO nanocomposites based on $30-90 \,\mu\text{m}$ thick AAO templates obtained by two-step anodization. Cu electrodeposition was performed at $-0.4 \,\text{V}$ using a solution containing 0.1 M CuSO₄ and 0.1 M H₂SO₄. Gold was sputtered on the bottom of AAO porous films; hence branches were directed upside down. The place of working electrode (WE) is shown by arrow.



Fig. 12. h/L_0 ratios for Cu/AAO nanocomposites with different thickness and degree of pore ordering. Cu electrodeposition was performed at -0.4 V from electrolyte containing 0.1 M CuSO₄ and 0.1 M H₂SO₄. Gold was sputtered on the bottom of AAO templates. Experimental data are fitted using Eq. (5) – solid line. Dash lines show 95% confidence bounds.

diminishes for the thick templates, in which the layer with disordered porous structure, formed at the beginning of the first anodization, plays a minor role. When in some pores Cu nanowires reach the outer surface of the template, the electroactive surface area enlarges, which results in the steep increase in current density (Fig. 10).

Cross-sectional SEM images for $30-90 \,\mu$ m thick Cu/AAO nanocomposites based on porous films obtained by two-step anodization are shown in Fig. 11. It can be clearly seen that the relative height of the second growth front (h/L_0) decreases with template thickness. This behaviour can be explained by the increase in diffusion current contribution to the total current with the increase in template thickness. According to the theoretical model, the ratio h/L_0 falls down to 1/3 when electrodeposition passes from mixed control to diffusion-controlled regime (Fig. 5). According to experimental data, h/L_0 varies from 26% (90 μ m membrane, obtained by one-step anodization) to 55% (30 μ m membrane, formed by two-step anodization), which is in line with the suggested model.

The template thickness-dependence of h/L_0 ratios is summarized in Fig. 12. Experimental data are fitted using Eq. (5). Since the kinetic length δ_k is constant, function (5) may be considered as the function of L_0 . Obtained value of δ_k is $5 \pm 4 \mu$ within 95% confidence bounds. Monotonic decrease in h/L_0 with template thickness can be clearly seen for both types of AAO templates obtained by one- and two-step anodization. Moreover, h/L_0 ratio is the same within an error for the AAO with ordered and disordered porous structure. It agrees well with the theory: the ratio depends only on parameter *K*, where *K* is a function of membrane thickness and overpotential, but does not depend on the number of branched pores.

On the other hand, average filling of AAO can be estimated coulometrically from the charge spent for Cu electrodeposition at the stage of the metal growth inside AAO matrix, as the ratio of metal volume to the pore volume. The quantity of electrodeposited Cu was calculated taking account of 90% current efficiency at $E_d = -0.4$ V. For 60 µm thick templates average pore filling rises substantially with increase of pore ordering (38% versus 49% in case of AAO prepared by one- and two-step anodization, respectively). The observed difference in pore filling decreases with template thickness because the defects of porous structure

(e.g. terminated channels and pore branches) concentrate upon the top part of AAO obtained by one-stage anodization. The average filling of the thickest templates (90 μ m) is nearly the same (equal to 30% within an error) for the AAO with ordered and disordered porous structure.

5. Conclusions

The theoretical model of metal growth inside the pores of anodic alumina films, which takes into account the features of the real structure of AAO templates (e.g. terminated and branched channels), has been developed. The model explains the existence of two growth fronts, which are usually experimentally observed on cross-section view of metal/AAO nanocomposites at the moment when nanowires reach the external surface of the template.

According to the model, the microstructure of metal/AAO composites depends on the choice of the AAO side on which a conductive layer should be sputtered. In AAO membranes, pores branch, but never merge, hence two cases should be considered:

- If a conductive layer was sputtered on the bottom of an AAO membrane, all branches are directed upside down, and nanowires are merging while growing. In this case, nanowires in straight pores reach the surface of AAO template firstly, and branches with one bifurcation form the second growth front behind them.
- 2) If a conductive layer was sputtered on the top of an AAO membrane, all branches are directed upwards, and nanowires are branching while growing. In this case, nanowires with the greatest number of bifurcations reach the surface firstly, and straight pores form the second growth front behind them.

The theoretical predictions were proved by experiments on templated electrodeposition of Cu in anodic alumina obtained at 40 V in 0.3 M oxalic acid electrolyte. Two growth fronts and branched pores overrunning straight ones were observed on crosssectional SEM images. Experiments on templated Cu electrodeposition showed that height of the second growth front decreases with membrane thickness, and increases with decrease in overpotential. These observations are in good agreement with the theoretical model. High filling of AAO templates can be reached by electrodeposition of required substance under kinetic control in thin porous films with ordered porous structure.

Acknowledgments

This work was supported by Russian Science Foundation (grant number 14-13-00809). The authors are grateful to Andrei A. Eliseev (Lomonosov Moscow State University) for fruitful discussions. We thank Alexander E. Baranchikov and Vladimir K. Ivanov (Kurnakov Institute of General and Inorganic Chemistry) for providing the opportunity to investigate the samples by scanning electron microscopy. We appreciate the help of Ekaterina A. Chernova with proof-reading of the manuscript.

Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.electacta.2016. 12.142.

References

 I.V. Roslyakov, A.A. Eliseev, E.V. Yakovenko, A.V. Zabelin, K.S. Napolskii, Longitudinal pore alignment in anodic alumina films grown on polycrystalline metal substrates, J. Appl. Crystallogr. 46 (2013) 1705.

- [2] I.V. Roslyakov, D.S. Koshkodaev, A.A. Eliseev, D. Hermida-Merino, A.V. Petukhov, K.S. Napolskii, Crystallography-induced correlations in pore ordering of anodic alumina films, J. Phys. Chem. C 120 (2016) 19698.
- [3] A. Vlad, V.-A. Antohe, J.M. Martinez-Huerta, E. Ferain, J.-F. Gohy, L. Piraux, Three-dimensional interconnected Ni core – NiO shell nanowire networks for lithium microbattery architectures, J. Mater. Chem. A 4 (2016) 1603.
- [4] Y.N. Xia, P.D. Yang, Y.G. Sun, Y.Y. Wu, B. Mayers, B. Gates, Y.D. Yin, F. Kim, Y.Q. Yan, One-dimensional nanostructures: synthesis, characterization, and applications, Adv. Mater. 15 (2003) 353.
- [5] L. Sun, Y. Hao, C.L. Chien, P.C. Searson, Tuning the properties of magnetic nanowires, IBM J. Res. Dev. 49 (2005) 79.
- [6] M.R. Lukatskaya, L.A. Trusov, A.A. Eliseev, A.V. Lukashin, M. Jansen, P.E. Kazin, K. S. Napolskii, Controlled way to prepare quasi-1D nanostructures with complex chemical composition in porous anodic alumina, Chem. Commun. 47 (2011) 2396.
- [7] K.S. Napolskii, A.A. Eliseev, N.V. Yesin, A.V. Lukashin, Y.D. Tretyakov, N.A. Grigorieva, S.V. Grigoriev, H. Eckerlebe, Ordered arrays of Ni magnetic nanowires: Synthesis and investigation, Physica E. 37 (2007) 178.
- [8] Y.K. Su, D.H. Qin, H.L. Zhang, H. Li, H.L. Li, Microstructure and magnetic properties of bamboo-like CoPt/Pt multilayered nanowire arrays, Chem. Phys. Lett. 388 (2004) 406.
- [9] Y. Piao, H. Lim, J.Y. Chang, W.Y. Lee, H. Kim, Nanostructured materials prepared by use of ordered porous alumina membranes, Electrochim. Acta 50 (2005) 2997.
- [10] J.S. Lee, G.H. Gu, H. Kim, K.S. Jeong, J. Bae, J.S. Suh, Growth of carbon nanotubes on anodic aluminum oxide templates: fabrication of a tube-in-tube and linearly joined tube, Chem. Mater. 13 (2001) 2387.
- [11] H.Q. Cao, L.D. Wang, Y. Qiu, Q.Z. Wu, G.Z. Wang, L. Zhang, X.W. Liu, Generation and growth mechanism of metal (Fe Co, Ni) nanotube arrays, Chemphyschem 7 (2006) 1500.
- [12] C.T. Lin, T.H. Chen, T.S. Chin, C.Y. Lee, H.T. Chiu, Quasi two-dimensional carbon nanobelts synthesized using a template method, Carbon 46 (2008) 741.
- [13] S. Wang, G.J. Yu, J.L. Gong, D.Z. Zhu, H.H. Xia, Large-area uniform nanodot arrays embedded in porous anodic alumina, Nanotechnology 18 (2007) 4.
- [14] V.G. Stoleru, E. Towe, Plasmon resonant Au nanospheres and nanorods in anodic alumina matrix, Microelectron. Eng. 81 (2005) 358.
- [15] Y. Zhang, L. Li, G.H. Li, L.D. Zhang, Electrical transport properties of singlecrystal antimony nanowire arrays, Phys. Rev. B 73 (2006) 3.
- [16] O. Yilmazoglu, R. Joshi, A. Popp, D. Pavlidis, J.J. Schneider, Pronounced field emission from vertically aligned carbon nanotube blocks and bundles, J. Vac. Sci. Technol. B 29 (2011) 5.
- [17] H. Feng, J.W. Elam, J.A. Libera, M.J. Pellin, P.C. Stair, Oxidative dehydrogenation of cyclohexane over alumina-supported vanadium oxide nanoliths, J. Catal. 269 (2010) 421.
- [18] S.J. Li, J. Li, K. Wang, C. Wang, J.J. Xu, H.Y. Chen, X.H. Xia, Q. Huo, A nanochannel array-based electrochemical device for quantitative label-free DNA analysis, ACS Nano 4 (2010) 6417.
- [19] P. Banerjee, L. Perez, L. Henn-Lecordier, S.B. Lee, G.W. Rubloff, Nanotubular metal-insulator-metal capacitor arrays for energy storage, Nat. Nanotechnol. 4 (2009) 292.
- [20] K. Nielsch, R.B. Wehrspohn, J. Barthel, J. Kirschner, U. Gosele, S.F. Fischer, H. Kronmuller, Hexagonally ordered 100 nm period nickel nanowire arrays, Appl. Phys. Lett. 79 (2001) 1360.
- [21] C.L. Xu, H. Li, G.Y. Zhao, H.L. Li, Electrodeposition and magnetic properties of Ni nanowire arrays on anodic aluminum oxide/Ti/Si substrate, Appl. Surf. Sci. 253 (2006) 1399.
- [22] K.S. Napolskii, I.V. Roslyakov, A.A. Eliseev, D.V. Byelov, A.V. Petukhov, N.A. Grigoryeva, W.G. Bouwman, A.V. Lukashin, A.P. Chumakov, S.V. Grigoriev, The

kinetics and mechanism of long-range pore ordering in anodic films on aluminum, J. Phys. Chem. C 115 (2011) 23726.

- [23] D.I. Petukhov, K.S. Napolskii, M.V. Berekchiyan, A.G. Lebedev, A.A. Eliseev, Comparative study of structure and permeability of porous oxide films on aluminum obtained by single- and two-step anodization, ACS Appl. Mater. Interfaces 5 (2013) 7819.
- [24] S. Valizadeh, J.M. George, P. Leisner, L. Hultman, Electrochemical deposition of Co nanowire arrays; quantitative consideration of concentration profiles, Electrochim. Acta 47 (2001) 865.
- [25] I.U. Schuchert, M.E.T. Molares, D. Dobrev, J. Vetter, R. Neumann, M. Martin, Electrochemical copper deposition in etched ion track membranes: experimental results and a qualitative kinetic model, J. Electrochem. Soc. 150 (2003) C189.
- [26] L. Philippe, N. Kacem, J. Michler, Electrochemical deposition of metals inside high aspect ratio nanoelectrode array: analytical current expression and multidimensional kinetic model for cobalt nanostructure synthesis, J. Phys. Chem. C 111 (2007) 5229.
- [27] S. Blanco, R. Vargas, J. Mostany, C. Borrás, B. Scharifker, Modeling the growth of nanowire arrays in porous membrane templates, J. Electrochem. Soc. 161 (2014) E3341.
- [28] A. Ghahremaninezhad, A. Dolati, Diffusion-controlled growth model for electrodeposited cobalt nanowires in highly ordered aluminum oxide membrane, ECS Trans. 28 (2010) 13.
- [29] D.A. Bograchev, V.M. Volgin, A.D. Davydov, Simple model of mass transfer in template synthesis of metal ordered nanowire arrays, Electrochim. Acta 96 (2013) 1.
- [30] D.A. Bograchev, V.M. Volgin, A.D. Davydov, Simulation of inhomogeneous pores filling in template electrodeposition of ordered metal nanowire arrays, Electrochim. Acta 112 (2013) 279.
- [31] D.A. Bograchev, V.M. Volgin, A.D. Davydov, Modeling of metal electrodeposition in the pores of anodic aluminum oxide, Russ J. Electrochem. 51 (2015) 799.
- [32] M.C. Lopes, C.P.d. Oliveira, E.C. Pereira, Computational modeling of the template-assisted deposition of nanowires, Electrochim. Acta 53 (2008) 4359.
- [33] S. Shin, T.T. Al-Housseiny, B.S. Kim, H.H. Cho, H.A. Stone, The race of nanowires: morphological instabilities and a control strategy, Nano Lett. 14 (2014) 4395.
- [34] Y.C. Choi, S.D. Bu, Nanopore domain growth behavior by nanopore changes near domain boundaries in porous anodic alumina, J. Nanosci. Nanotechno. 11 (2011) 1346.
- [35] D.I. Petukhov, K.S. Napolskii, A.A. Eliseev, Permeability of anodic alumina membranes with branched channels, Nanotechnology 23 (2012) 1.
- [36] A.K. Kasi, J.K. Kasi, N. Afzulpurkar, M.M. Hasan, B. Mahaisavariya, Bending and branching of anodic aluminum oxide nanochannels and their applications, J. Vac. Sci. Technol. B 30 (2012) 031805.
- [37] M. Lillo, D. Losic, Pore opening detection for controlled dissolution of barrier oxide layer and fabrication of nanoporous alumina with through-hole morphology, J. Membrane Sci. 327 (2009) 11.
- [38] K.S. Napolskii, I.V. Roslyakov, A.A. Eliseev, D.I. Petukhov, A.V. Lukashin, S.F. Chen, C.P. Liu, G.A. Tsirlina, Tuning the microstructure and functional properties of metal nanowire arrays via deposition potential, Electrochim. Acta 56 (2011) 2378.
- [39] R. Inguanta, S. Piazza, C. Sunseri, Influence of electrodeposition techniques on Ni nanostructures, Electrochim. Acta 53 (2008) 5766.
- [40] B.R. Tzaneva, A.I. Naydenov, S.Z. Todorova, V.H. Videkov, V.S. Milusheva, P.K. Stefanov, Cobalt electrodeposition in nanoporous anodic aluminium oxide for application as catalyst for methane combustion, Electrochim. Acta 191 (2016) 192.