



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



Alexey A. Noyan^a, Alexey P. Leontiev^b, Maxim V. Yakovlev^b, Ilya V. Roslyakov^{b,c}, Galina A. Tsirlina^{c,1}, Kirill S. Napolskii^{b,c,*}

^a Moscow Institute of Physics and Technology, 141700, Dolgoprudny, Russia

^b Department of Materials Science, Lomonosov Moscow State University, 119991, Moscow, Russia

^c Department of Chemistry, Lomonosov Moscow State University, 119991, Moscow, Russia

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.

© 2016 Elsevier Ltd. All rights reserved.

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

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

* Corresponding author at: Department of Materials Science, Lomonosov Moscow State University, 119991, Moscow, Russia.
Tel.: +7 495 9395248, fax: +7 495 9390998.

E-mail address: kirill@inorg.chem.msu.ru (K.S. Napolskii).

¹ ISE member.

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):

$$\frac{dL_s}{dt} = \frac{MD \left(C_m + \left(\frac{nF\rho C_0}{j_0 M} \right) \left(\frac{dL_s}{dt} \right) \exp\left(\frac{\alpha F \eta}{RT}\right) \right)}{\rho L_s} \quad (1)$$

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

$$\delta_k = \left(\frac{nFC_0 D}{j_0} \right) \exp\left(\frac{\alpha F \eta}{RT}\right) \quad (2)$$

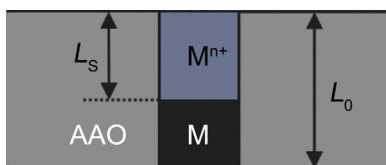


Fig. 1. Nanowire growth. L_0 is the membrane thickness, L_s is the length of unfilled part of the pore.

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

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

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 $K \rightarrow \infty$.

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 well-defined 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,

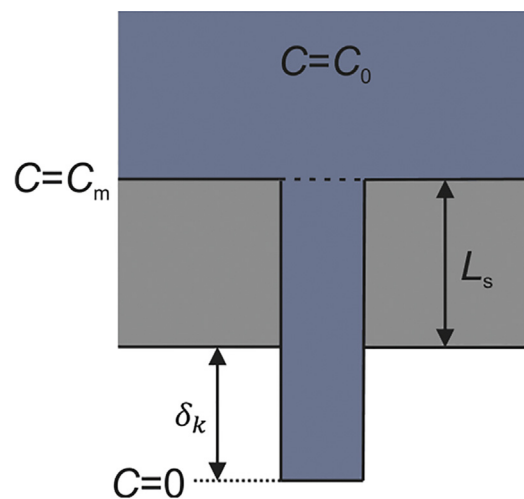


Fig. 2. Visualization of the equation (3). Kinetic length δ_k can be imagined as an additional pore length. L_s is the length of unfilled portion of the pore, C_0 is the concentration of metal ions in the bulk solution, C_m is the concentration of metal ions in the pore mouth.

Download English Version:

<https://daneshyari.com/en/article/4767605>

Download Persian Version:

<https://daneshyari.com/article/4767605>

[Daneshyari.com](https://daneshyari.com)