



Simulation of inhomogeneous pores filling in template electrodeposition of ordered metal nanowire arrays



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ABSTRACT

A model of inhomogeneous pores filling during electrodeposition of ordered metal nanowire arrays is developed. The model takes into consideration the ionic transfer both in the varying diffusion layer in the pores and in the diffusion layer above the template, which is determined by the external hydrodynamic conditions. The model takes into account the kinetics of electrochemical reaction (the Tafel equation) and the diffusion transfer of metal cations both in the pores and in the outer diffusion layer. In the quasi-steady-state approximation, two problems were considered. The problem for the case that the initial length of one pore differs from that of all other pores is solved analytically. The problem for the case that the initial lengths of all pores are different is solved numerically. The time dependences of unfilled pore length are obtained for various overpotentials and various initial distributions of pore length. It is found that the pores filling inhomogeneity increases with increasing overpotential.

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1. Introduction

The electrodeposition of metals and semiconductors in the pores of anodic aluminum oxide (AAO), which is used as the template, is one of the procedures applied for production of new materials by the electrochemical methods [1–26]. As a rule, the fabrication of the AAO templates involves several stages: (a) the formation of porous anodic oxide film on the aluminum substrate; (b) the separation of oxide films from metal substrate by the chemical dissolution of aluminum; (c) opening of the pore bottoms by chemical etching of alumina barrier layer; (d) the formation of thermally sputtered metal (copper, gold) layer on one side of porous oxide; the metal layer serves as the current lead in the metal deposition into the oxide film pores. The metal electrodeposition is performed under various (potentiostatic, galvanostatic, and pulse) electric modes. Fig. 1 shows a template prior to pores filling, at an intermediate stage of pores filling, and some pores filled with metal.

The porous AAO layer is commonly 50 μm thick, the pores are 40–50 nm in diameter (high aspect ratio pores), and the porosity is $\varepsilon = \pi k r^2 \approx 0.13$ (k is the number of pores per unit surface area of

specimen and r is the pore radius). The pores are spaced approximately 100 nm apart [5,19].

Based on the published works, we can recognize at least three main stages of pores filling with metal. (1) A stage of non-steady-state diffusion. When a potential is applied, the current increases abruptly and, then, decreases with time in accordance with the diffusion layer thickness increasing from zero to a certain value, which is determined by the conditions of the process. Here, the Cottrell equation is valid. (2) The main stage of pores filling with metal. At this stage, the current slightly varies with time. The duration of this stage (t_{fill}) is much longer than that of the first stage. (3) When the pores are filled up, the metal wires emerge from the template surface pores. The effective cathode surface area increases, the current steeply increases and, when the entire surface is coated with the metal film, it reaches a certain constant value.

It should be noted that the current and pores filling time t_{fill} depend on the overpotential of cathodic reaction [5,19,21]: The higher the overpotential up to the point where diffusion control takes over, the higher the current and shorter the time t_{fill} .

Earlier [22], within certain approximations, the analytical equations for calculating some characteristics of pores filling process were obtained: The variation of current with the time; the time required for pores filling (based on the experimental works [5,14], it was assumed that all pores are filled simultaneously) at various overpotentials; etc. The calculations were performed for the second stage of pores filling, because the first stage is relatively short and the third stage is beyond the pores filling process (the pores filling is completed at the second stage).

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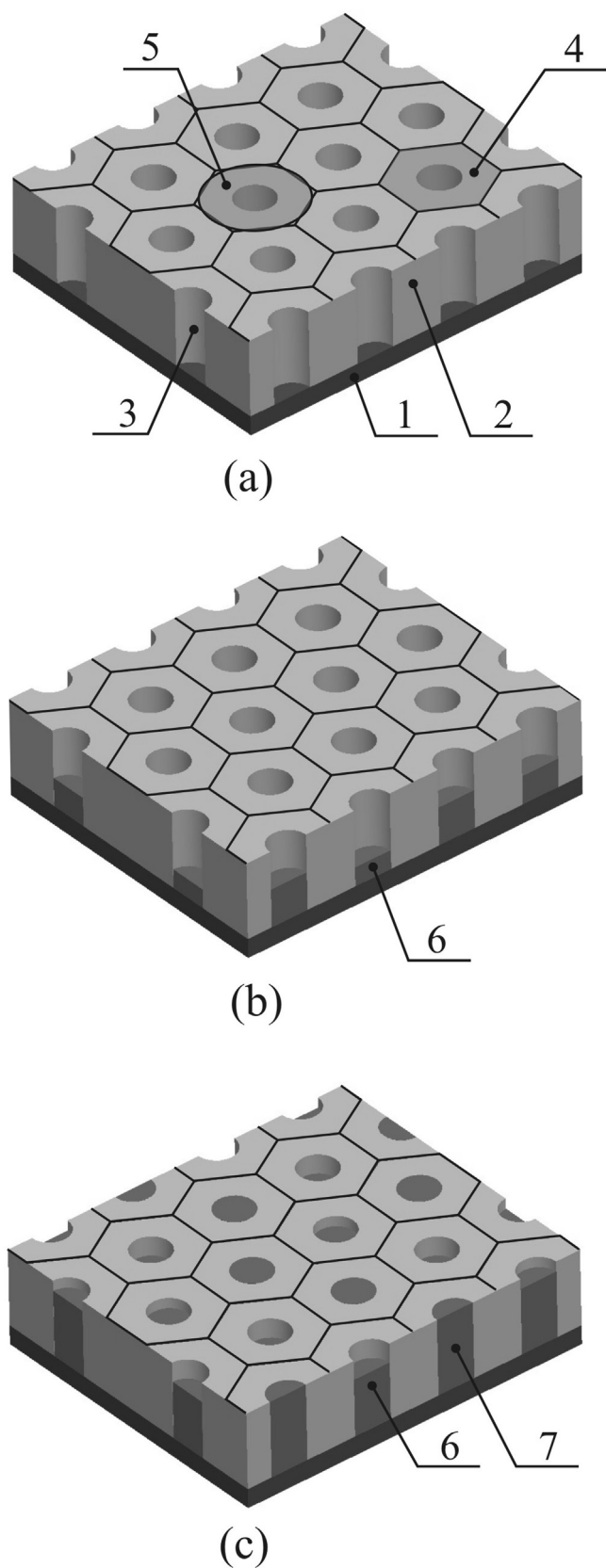


Fig. 1. A scheme of template metal electrodeposition into AAO. (a) The template prior to the metal deposition; (b) the template with partially filled pores; (c) the template with completely filled pores and with partially filled pores. (1) Conducting layer serves as the current lead, (2) template, (3) a pore, (4) template surface area corresponding to a single pore, (5) axisymmetric approximation of the template surface area corresponding to a single pore, (6) a nanowire that partly fills the pore, (7) a nanowire that completely fills a pore.

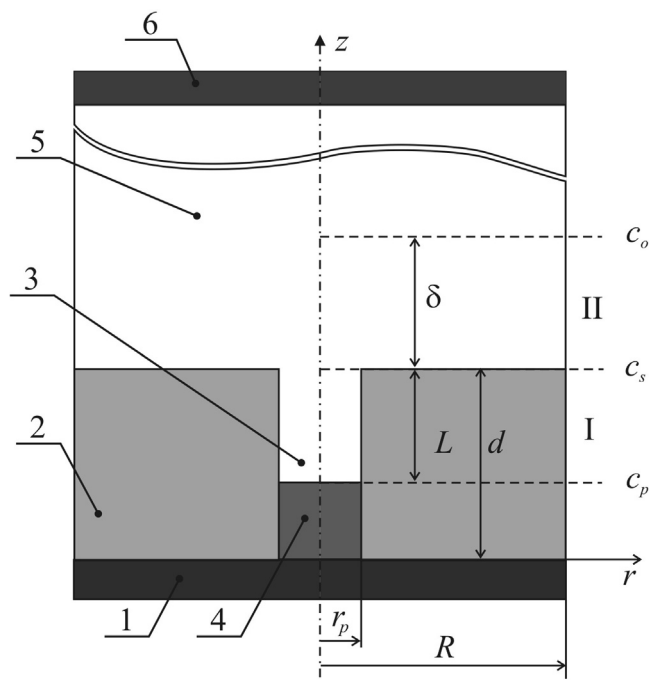


Fig. 2. A scheme for calculating the mass transfer in the metal deposition in a pore. (1) A conducting layer (current lead), (2) template, (3) a pore, (4) a pore portion filled with metal, (5) a space between the template and auxiliary electrode filled with the electrolyte, and (6) an auxiliary electrode (anode).

In [22], the transfer processes were considered both inside the pores (diffusion through the time-dependent unfilled pore part L) and in the outer diffusion layer (its thickness δ is prescribed by the hydrodynamic conditions in the electrochemical cell) (Fig. 2).

In [22], each hexagonal cell of AAO with a pore was approximated by a round cell. The use of axisymmetric approximation enables one to reduce a three-dimensional problem to two-dimensional one and, consequently, simplify the numerical solution. It was assumed that the metal deposition in the pores proceeds under mixed control and the process is characterized by equal initial pore lengths.

In several experimental works [5,19,21], it was shown that pores filling can proceed nonuniformly: When some pores were filled with metal to the entire length, other were filled only partially. According to [21], when 10–15% pores were filled completely, other pores were filled to approximately one-third. An increase in the overpotential of metal electrodeposition leads to an increase in a degree of pores filling inhomogeneity [5,19,21]. The inhomogeneity of deposition can be caused by a certain initial difference in the pore length, a delay of the onset of deposit growth in some pores as compared to other pores, or cessation of deposit growth in some pores, for example, due to the evolution of hydrogen bubbles. An increase in the overpotential has an ambiguous effect: It leads to an increase in a degree of pores filling inhomogeneity (a detrimental effect) and to an increase in the rate of deposit growth in the pores (a beneficial effect).

In this work, the effect of overpotential is studied theoretically. This can assist in choosing optimal conditions of the process in order to combine a sufficiently high productivity with an admissible degree of pores filling inhomogeneity.

In contrast to [22], here, it is assumed that the process is characterized by different initial pore lengths regardless of actual reason for the pores filling inhomogeneity. We will analyze the pores filling with metal under the potentiostatic conditions.

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