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## Modeling of formation of nanostructured metal surfaces by electrodeposition through a monolayer colloidal crystal mask

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### Abstract

Electrochemical deposition is a feasible and well-controlled method for the formation of various micro- and nanostructures. A rich variety of periodical nanostructures of functional materials with multi-shaped and tunable morphologies can be fabricated by the electrochemical deposition, in particular, using monolayer colloidal crystal (MCC) mask. A mathematical model of the mass-transfer processes and deposit surface evolution during the metal electrodeposition through MCC mask is presented. The mathematical model involves the equations for the potential and deposit surface evolution. The problem was solved numerically by the boundary element method, and the "Level Set" method. The numerical experiments were used to study the effect of parameters, which characterize the mask geometry and the process conditions, on the initial distribution of current density over the deposit surface and the variation of current density distribution in the course of the deposition.

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### 1. Introduction

The understanding of surface phenomena at a micro- and nanometer scale, has played a fundamental role in the many fields, such as: electronics, energy, optics, tribology, biology, biomimetics, etc. [1]. The manufacturing of features on the nanometer scale is challenging, and has been the subject of intensive research and development [2]. The relationships between the technologies for structuring surfaces, their functional properties (improved adhesion, superhydrophobicity, antireflection and other optical properties, generation and preservation of energy, hard and tough surfaces, efficient heat transfer, antibiofouling, changing color, and self-healing) and the applications exploiting the surface functionality are a common denominator of the research carried out in the last years [3].

The template-based methods occupy a prominent place among various methods of production of nanostructures and nanostructured materials [4]. These methods enable one to fabricate the desired material in the pores of nanoporous template.

### Nomenclature

$d_{sp}$	diameter of spherical particles
$h$	height of unit cell
$H$	dimensionless height of unit cell
$i_0$	applied current density
$k$	number of computational point
$n$	number of time step
$\mathbf{N}$	unit vector of outer normal to surface
$R$	dimensionless radius of spherical particles
$t$	time
$x, y, z$	coordinates
$X, Y, Z$	dimensionless coordinates
$z_c$	function, which describes deposit surface
$Z_c$	dimensionless function, which describes deposit surface
$\varepsilon_V$	volumetric electrochemical equivalent
$\eta$	current efficiency
$\tau$	dimensionless time
$\Delta \tau$	dimensionless time step
$\varphi$	potential

$\chi$	conductivity of electrolyte solution
$\Phi$	dimensionless potential
C	subscript, which denotes deposit surface
U	subscript, which denotes outer boundary of unit cell
I	subscript, which denotes side surfaces of unit cell and surface of spherical particle

Various methods can be used for the template-based synthesis of nanoporous structures: the chemical polymerization, sol-gel deposition, chemical vapor deposition and also the electrochemical and electroless deposition and electrochemical dissolution [5].

The template-based electrochemical methods of synthesis of nanostructures and nanomaterials have several important advantages: a high extent of pore filling, a possibility to obtain the materials of various types, the absence of considerable internal stresses, easy control, a possibility to vary the physicochemical properties and composition of the deposit. For example, the electrochemical methods enable one to produce heterogeneous nanostructured materials for the electrochemical power sources, fuel cells, and catalyst for various purposes [6].

Solid templates of polycarbonate track membranes or nanoporous aluminum oxide with linear pores 50-200 nm in diameter and 10-50  $\mu\text{m}$  in depth are used most commonly [7]. They are used to produce the 1D structures of various materials: the metal nanowire arrays [8], the nanowires of various metal compounds [9]. Using the developed technologies, the electrochemical deposition of metals, alloys, and various chemical compounds in the pores of these templates is performed in order to fabricate modern miniature devices of magnetic memory, optoelectronics, sensors, power sources, supercapacitors, catalysts, and various electronic devices. The deposition of iron, nickel, or cobalt for fabrication of unique one-dimensional magnetic structures and also copper, ZnO, Ag<sub>7</sub>Te<sub>4</sub>, Co-Sb, MnO<sub>2</sub>, Cu<sub>3</sub>Se<sub>2</sub>, Bi, Pt-Pb, Fe-Pt, Ni-Pt, Co-Pt, Si, LaMnO<sub>3+ $\delta$</sub> , etc. are examples. Solis templates are also used to produce bimetal and composite nanowires, which exhibit unique properties. For example, the electrodeposition at an electrode potential varying with time is used to fabricate the nanowires consisting of alternating copper and cobalt layers, where the effect of giant magnetic resonance is observed [7]. This method is also used to produce the structures of core-shell type and segmented metal-polymer composites [10].

Among other template structures, the templates consisting of regularly arranged monodispersed spherical particles are of most interest. They are used to produce composite materials, photon crystals, the structures with highly developed surface, for example, metal foams, for modification of surface properties, etc.

Colloidal crystals, which are formed by orderly arranged monodispersed spherical particles, are used as the templates for production of nano-ordered structures of metals, semiconductors, inorganic oxides, polymers, etc. [11]. In general case, the production of nano-ordered structures by using the colloidal crystal mask involves three stages:

- (1) self-assembling of mask on the substrate surface;
- (2) filling the pores between the template spherical

particles;

(3) removal of template by chemical or thermal etching. (In some cases, for example, in the production of photonic crystals, the template is not removed.)

The 3D (multilayer) [12] and 2D (monolayer) [13] colloidal crystals are used as the masks. The MCC masks can be close-packed [14] or consist of regularly arranged non-close-packed particles [15].

The electrochemical deposition through a colloidal crystal mask enables one to produce high-density metal deposits, which exhibit no considerable shrinkage when the template is removed [16]. In addition, the deposits of various metals with prescribed structure can be produced, and the thickness and properties of deposited layer can be controlled accurately [17]. The application of a layer of metal or alloy, which acts as a catalyst for a chemical reaction, is the most important application of the process. An example is the application of a layer of relatively expensive platinum catalyst with developed (rough) surface onto a plane substrate of inexpensive material, such as iron.

To our knowledge, the electrodeposition through a colloidal crystal mask was investigated theoretically by the numerical simulation using the finite element method only in few works [18, 19].

In these papers the Laplace's equation in a unit cell with triangular cross-section for the face-centered cubic colloidal crystal was solved numerically. The process of pore filling and the variation of the mass-transfer conditions with increasing deposit thickness were not considered.

Here, we perform the numerical simulation of mass-transfer processes during the metal electrodeposition through a MCC mask with regard for the variation of deposited layer thickness with the time.

## 2. Statement of problem and basic equations

Figure 1 gives a scheme of metal electrodeposition with the use of monolayer colloidal crystal mask. Taking into account the arrangement of particles in the mask, a unit cell with a regular hexagonal cross-section is used (Fig. 2a). A plane, which is far removed from the mask, so that the distribution of the current density over this plane can be considered as uniform, is taken to be the outer (upper) boundary of a unit cell. The surface of growing metal deposit is taken to be the lower boundary of unit cell. The unit cell can be replaced by the axisymmetric one with no considerable error (Fig. 2b).

The Laplace equation for the electric field potential in the electrolyte solution (1) and the equation of deposit surface evolution (2) are used as the mathematical model:

$$\frac{\partial^2 \varphi}{\partial x^2} + \frac{\partial^2 \varphi}{\partial y^2} + \frac{\partial^2 \varphi}{\partial z^2} = 0 \quad (1)$$

$$\frac{\partial z_c}{\partial t} = -\eta \varepsilon_v \chi \frac{\partial \varphi}{\partial N} \sqrt{1 + \left(\frac{\partial z_c}{\partial x}\right)^2 + \left(\frac{\partial z_c}{\partial y}\right)^2} \quad (2)$$

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