

Modelling the growth of porous alumina matrix for creating hyperbolic media

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Abstract. Porous aluminum oxide is a regular self-assembled structure. During anodization it is possible to control nano-parameters of the structure using macroscopic parameters of anodization. Porous alumina films can be used as a template for the creation of hyperbolic media. In this work we consider the anodization process, our model takes into account the influence of layers of aluminum and electrolyte on the rate of growth of aluminum oxide, as well as the effect of surface diffusion. As a result of our model we obtain the minimum distance between centers of alumina pores in the beginning of anodizing process. We also present the results obtained by numerical modelling of hyperbolic media based on porous alumina film.

1. Introduction

Currently, the development of nanotechnology and metamaterials requires the ability to obtain regular self-assembled structures with different parameters [1-2]. One such structure is porous alumina film, which is a self-organizing structure that consists of hexagonally packed cylindrical pores (Figure 1). Artificially on the surface of the aluminum may be built a thick layer of porous aluminum oxide film. During anodization it is possible to control nano-parameters of the structure (such as diameter of pores and distance between them) using macroscopic parameters of anodization (pH of electrolyte, anodizing voltage, temperature, anodization time). Highly ordered pores may be obtained using two-stage anodization process, proposed in 1995 by Masuda et al. [3]. Pore size can vary from 2 to 350 nm and the distance between pores from 5 to 50 nm.

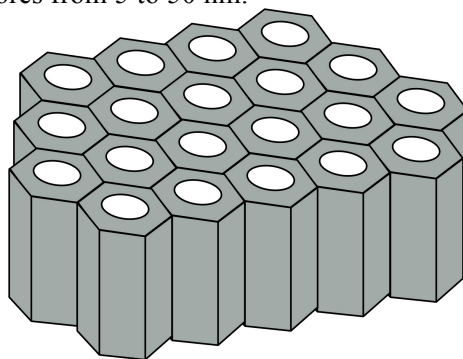


Figure 1. Hexagonal packing of the porous AAO



Anodizing is carried out in a vessel with electrolyte (aqueous solution of acid: oxalic, phosphoric acid; chromium, etc.), where are placed anode (aluminum) and cathode (inert conductive material), which are respectively connected to the positive and negative power supply output (Figure 2).

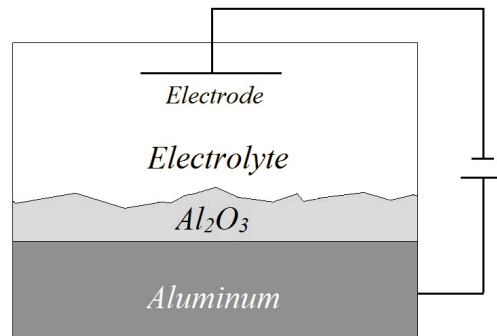


Figure 2. Anodizing process

On the surface of the aluminum grows thin dense alumina film – barrier layer. Barrier layer grows due to the migration of aluminum ions towards oxygen ions. The thickness of this barrier layer (0.01 – 0.1 nm) does not change throughout the process as it dissolves at the outer side exposed to the electrolyte [4].

The nucleation of pores occurs in the centers of inhomogeneities of aluminum surface, the oxide dissolves more intense the higher the inhomogeneity of the field. The thicker the structure, the more uneven grows the pore walls.

2. Model

In this paper we describe an analytical model of the growth of anodic alumina. We consider the motion of the interfaces between the electrolyte- Al_2O_3 (dissolution) and between the Al_2O_3 -aluminum (oxidation) (Figure 2).

In each of the areas under consideration Laplace equation for the electric potential is solved. The process of growth of porous alumina is described by the theory of small perturbations. In zero approximation boundaries are considered flat and the speed of their movement proportional to the current density at these boundaries. The first approximation takes into account the small perturbations of the interface, which lead to small changes in the potentials and currents at these boundaries. The evolution of small perturbations of the interface is defined as a perturbation of the current density at the borders, and the process of surface diffusion.

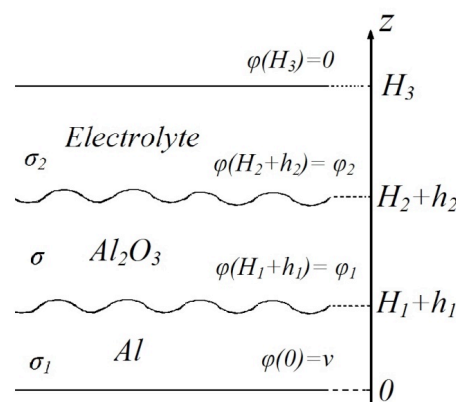


Figure 3. Inhomogeneous film with rough boundaries.

Using conditions of continuity of the current density at both interfaces we obtain the system of equations relating the potential disturbance on the interfaces:

$$\begin{cases} \left(-\sigma_2 sh(kH) - \sigma ch(kH) \right) \hat{\varphi}_{2\bar{k}} + \sigma \hat{\varphi}_{1\bar{k}} = \beta e^{kH} - \alpha \\ -\sigma \hat{\varphi}_{2\bar{k}} + \left(\sigma_1 sh(kH) + \sigma ch(kH) \right) \hat{\varphi}_{1\bar{k}} = \beta - \alpha e^{kH} \end{cases} \quad (1)$$

where $\alpha = (v/\vartheta) h_{1\bar{k}}$, $\beta = (v/\vartheta) h_{2\bar{k}}$. $\hat{\varphi}_{\bar{k}}$ - the Fourier transform of the potential disturbance to the coordinates x, y , $\varphi = \varphi_{(z)}^0 + \hat{\varphi}$, $\varphi_{(z)}^0$ - stationary potential for the homogeneous problem, $\hat{\varphi}$ - potential oscillations, ϕ_1 - electrostatic potential of the aluminum layer on Al-Al₂O₃ interface, ϕ_2 - electrostatic potential of the aluminum layer on electrolyte-Al₂O₃ interface, σ_1 - conductivity of the aluminum, σ - conductivity of aluminum oxide, σ_2 - conductivity of the electrolyte, $\vartheta = \left(H/\sigma + H_1/\sigma_1 + (H_3 - H_2)/\sigma_2 \right)$, v - anodization voltage, H - thickness of aluminum oxide, $H_1 + h_1$ - thickness of the aluminum layer, $H_3 - (H_2 + h_2)$ - thickness of electrolyte, $h_{1\bar{k}} = \int_{-\infty}^{\infty} \exp[-ik_y y] \int_{-\infty}^{\infty} \exp[-ik_x x] h_1 dx dy$, $h_{2\bar{k}} = \int_{-\infty}^{\infty} \exp[-ik_y y] \int_{-\infty}^{\infty} \exp[-ik_x x] h_2 dx dy$.

We considered the solutions of the system (1) for different values of kH .

The rate of change of small perturbations of the boundaries Al-Al₂O₃ and Al₂O₃-electrolyte without the influence of surface diffusion is proportional to the perturbation of the current density at these interfaces $dh/dt = a\sigma d\varphi/dz$. Since the conductivity of the electrolyte and alumina is small compared with aluminum we see that the perturbation on the interface of Al₂O₃-electrolyte increases indefinitely with time.

The rate of change of small perturbations of the interfaces Al-Al₂O₃ and Al₂O₃-electrolyte with the influence of surface diffusion is described by the relation $\frac{\partial h}{\partial t} = V + D\Delta^2 h$, where D - is the surface diffusion coefficient.

For Al-Al₂O₃ interface we get the wavelength corresponding to the limit of stability:

$$\lambda_1 = 2\pi \sqrt[3]{a_1 v / \vartheta D_1}. \quad (2)$$

All perturbations of this interface with wavelength $\lambda > \lambda_1$ are unstable.

For Al₂O₃-electrolyte interface we get the wavelength corresponding to the limit of stability:

$$\lambda_2 = 2\pi \sqrt[3]{a_1 v / \vartheta D_2}. \quad (3)$$

All perturbations of this interface with wavelength $\lambda > \lambda_2$ are unstable.

We assume that surface diffusion coefficient D_2 on the Al₂O₃-electrolyte interface is larger than the same coefficient on D_1 the Al-Al₂O₃ interface. According to (2), (3), the correspondent critical wavelength satisfies of inequality $\lambda_2 < \lambda_1$. Therefore, for perturbations with wavelength λ in interval $\lambda_2 < \lambda < \lambda_1$ the upper boundary of alumina layer is unstable and bottom boundary is stable. The perturbations of upper boundary in this interval of wavelength are the source of porous formation. For wavelength $\lambda > \lambda_1$ the bottom boundary of alumina is unstable. The evolution of perturbations in this wavelength region determines the irregularities of porous structure.

3. Numerical investigation of hyperbolic material based on porous alumina template

We conducted numerical experiments using CST Microwave Studio. A model of an ordered system of silver nanorods with 10 nm in diameter was created.

Numerical experiments were conducted at a frequency of radiation 750 THz corresponding to the wavelength of 400 nm. The value of the dielectric constant of alumina 1.3365 for the selected frequency was specified in tabular form in accordance with the database of the company SOPRA SA [5].

In the first numerical experiment the dipole radiator was placed in the center of the medium, and the distribution of the magnetic field emitted by electromagnetic waves was detected; the result of this series is shown in Figure 4a. In the second series the medium was radiated by the dipole source and the refraction of light was observed, results of the second experiment are illustrated in Figure 4b.

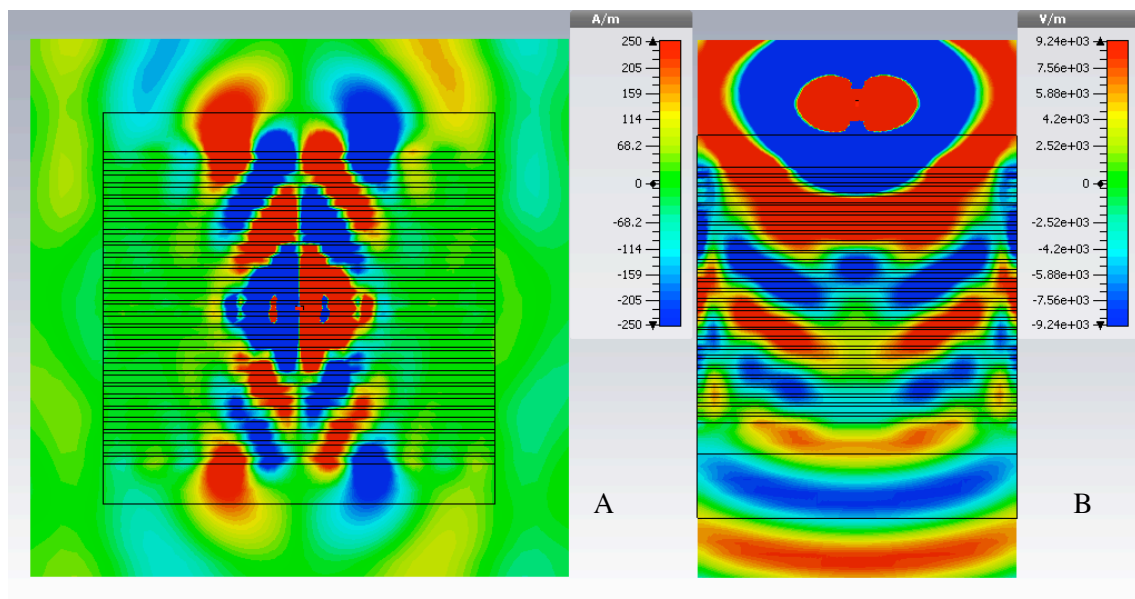


Figure 4. Spatial distribution of the intensity of magnetic field (a) and the electric field (b) of the radiation of a dipole placed in the composite material with silver rods with the 10 nm radiuses placed in porous alumina.

From the Figure 4a it is seen that in the present nanocomposite with the 10 nm rods the spatial distribution of the dipole radiation is characteristic to a hyperbolic media [6].

Figure 4b shows that the silver rods with a radius of 10 nm grown in porous alumina plate begin to act as a collecting lens, indicating a negative refraction and hence the occurrence of hyperbolic environment.

4. Conclusion

As a result of the developed model we obtained the minimum distance $2\pi\sqrt[3]{a_1kv/\partial D_2}$ between centres of aluminum oxide pores in the beginning of anodizing process. The irregularities of porous structure have wavelength $\lambda > 2\pi\sqrt[3]{a_1kv/\partial D_1}$.

The dependence of distance between centers of inhomogenities on anodizing voltage is shown in Figure 5. It follows that the bigger the anodizing voltage, the less smooth the surface should be at the beginning of anodization process.

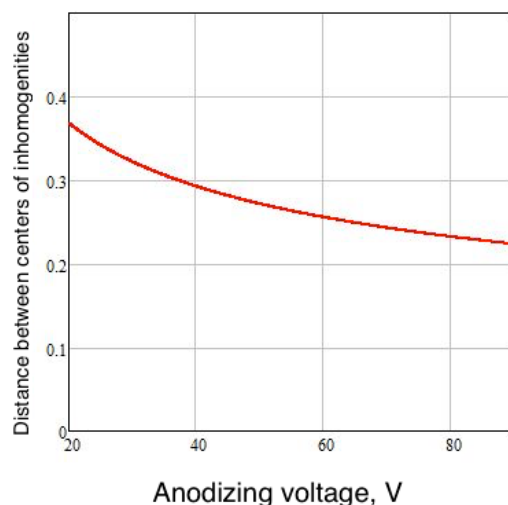


Figure 5. Dependence of distance between centers of inhomogeneities on anodizing voltage

A numerical model of a hyperbolic media grown in a porous alumina template with the pore diameter of 10 nm was created. This model shows that silver rods grown in porous alumina matrix with pore diameter of 10 nm begin to act as a collecting lens at the radiation wavelength of 400 nm, indicating a negative refraction and hence the occurrence of hyperbolic environment.

Acknowledgments

This work was financially supported by the Government of Russian Federation, Grant 074-U01.

References

- [1] Limonov A G 2010 *Matem. Mod.* **22** 97–108
- [2] Petukhov D I, Napolskii K S and Eliseev A A 2012 *Nanotechnology* **23** 335601
- [3] Masuda H, Fukuda K 1995 *Science*, **268**(9) 1466-8
- [4] Patermarakis G 2009 *Journal of Electroanalytical Chemistry* **635** 39–50
- [5] Sopra S A dispersion database: <http://www.sspectra.com/sopra.html>
- [6] Simovski C R, Belov P A, Atrashchenko A V, Kivshar Yu S 2012 *Advanced Materials* **24** 4229–48