Model of the microscroll structure

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Abstract. In this paper, we propose a method for the formation of TiO2 microscrews due to the folding of thin layers in an external inhomogeneous magnetic field deposited on a glass substrate during laser ablation of a titanium target in the air. The models of the initial stages of the formation and structure of the microscrew are also proposed.

Introduction

Mechanisms for the formation of multilayer micro- and nanosciences through convolving nanosilicates were considered in [1-3]. It is assumed that the twisting of the micro and nanolayer is due to internal stresses arising due to the difference in forces applied to the upper and lower parts of the layer. And twisting of a layer usually does not end with one turn, but continues until the curvature of the tube provides an energy gain in the realization of such a process. [4]

Description of experimental studies on obtaining microscrolls

Today, nanocrystalline titanium dioxide (TiO2) has been the subject of many studies due to its unique operational and physical properties. One of the methods for producing layered microtubes of titanium oxide is the process of self-organization from a thin film obtained by laser ablation in air in an inhomogeneous magnetic field. To obtain a thin film of titanium oxides on a solid transparent substrate, a method of laser ablation of a titanium target in an air atmosphere was used. This method made it possible to form metastable phases of titanium oxide, due to the rapid cooling of matter from the melt.

During the action, a laser beam with a diameter of 30 μm scanned the surface, moving along a circle with a diameter of 3 mm in 30 μm steps. The exposure time at one point was 10 to 15 s, which allowed the formation of a deposited layer with a thickness in the range of 200 to 300 nm.

Under the influence of laser radiation (wavelength 1.06 μm, pulse duration 100 ns, pulse energy 1 μJ), partial melting of the target occurred with the formation of a vapor-gas jet directed toward the laser beam. In the process of action, a plasma-erosion torch was generated and propagated in the air atmosphere, which triggered the mechanism of formation of the oxide shell on the titanium particles. Collection of material on the collector substrate was carried out according to the scheme of direct deposition in the presence of an inhomogeneous magnetic field [5], created by two toroidal magnets with a field strength of 100 Oersteds. Due to laser action, nanoparticles are oriented along the lines of an inhomogeneous magnetic field (Fig. 1c), forming macroscopic magnetic domains, which generates mechanical stresses in the deposited layer.

When the critical voltage is reached, the thin layer breaks and the folding process begins (Fig. 1d), which results in the formation of titanium oxide microscrolls (Fig. 1b, e).
Fig. 1. Experimental scheme of sputtering of thin oxide layers of titanium by the method of laser ablation consisting of Ti-TiO shell particles: (a) laser exposure scheme; (b) SEM images of formed tubes with different spatial magnifications; (c) is a schematic representation of the process of folding of microtubes in the control of an inhomogeneous magnetic field: the orientation of the magnetic moments of the Ti-TiO shell particles on the substrate in the presence of a magnetic field; (d) misorientation of a single direction of magnetic moments, which is the initial phase of roll-up; (e) a tube profile showing a multilayered end face. Schematic representations are presented without scales.

A study was made of the composition and structure of the bonds of microscrolls of titanium oxide using an atomic force microscope Ntegra Spectra, combined with a prefix for Raman analysis.

It was found that folding the oxide film into microscrolls significantly changes the spectral characteristics of this coating - an additional maximum is formed in the wavelength range from 500 to 750 nm (with a film thickness variation from 200 to 300 nm). In this case, an increase in the film thickness shifts the position of the maximum in the long-wave region.

The investigated microtubules exhibit their layered nature when using a darkfield microscope with a 100x objective. Light scattering on the structure under study occurs non-uniformly, an uneven distribution of luminescence is observed inside the tube, which may be associated with a variation in the density and structure of the material.

**Model of the structure of the microscroll**
The initial stage in the formation of the microscroll structure is the appearance of a difference in the mechanical stresses in the nanolayer and, as a consequence, small oscillations. As such a model, we will consider a plate that performs small oscillations with respect to the equilibrium position. [6]

The biharmonic equation of small oscillations is used as a model equation.

In this connection, we consider the boundary value problem on the square domain $G = [0, 1] \times [0,1]$ for the inhomogeneous biharmonic equation in relative units:

$$\frac{\partial^4 \Psi(x,y,\tau)}{\partial \tau} + \frac{\partial^4 \Psi(x,y,\tau)}{\partial x^4} + 2 \frac{\partial^4 \Psi(x,y,\tau)}{\partial x^2 \partial y^2} + \frac{\partial^4 \Psi(x,y,\tau)}{\partial y^4} = -F(x,y), \quad (1)$$

$$\Psi(x, y, 0) = 0, \quad (2)$$

$$\Psi(0, y, \tau) = \Psi(1, y, \tau), \quad (3)$$

$$\frac{\partial \Psi(0, y, \tau)}{\partial x} = \frac{\partial \Psi(1, y, \tau)}{\partial x} = \frac{\partial \Psi(x,0,\tau)}{\partial y} = \frac{\partial \Psi(x,1,\tau)}{\partial y} = 0. \quad (4)$$

To construct a finite-difference analogue of partial derivatives of the fourth order, we use the second-order central difference operator, applied twice with respect to the corresponding variable [8]:

$$\left. \frac{\partial^4 \Psi(x,y,\tau)}{\partial x^4} \right|_{i,j} = \frac{\psi^k_{i+2,j} - 4\psi^k_{i+1,j} + 6\psi^k_{i,j} - 4\psi^k_{i-1,j} + \psi^k_{i-2,j}}{\Delta x^4} + O((\Delta x)^2), \quad (4)$$

$$\left. \frac{\partial^4 \Psi(x,y,\tau)}{\partial y^4} \right|_{i,j} = \frac{\psi^k_{i,j+2} - 4\psi^k_{i,j+1} + 6\psi^k_{i,j} - 4\psi^k_{i,j-1} + \psi^k_{i,j-2}}{\Delta y^4} + O((\Delta y)^2). \quad (5)$$

The approximation of the mixed derivative is defined using the five-point pattern of the second derivative [8] with respect to $x$ and $y$:

$$2 \left. \frac{\partial^4 \Psi(x,y,\tau)}{\partial x^2 \partial y^2} \right|_{i,j} = \frac{2}{144(\Delta x)^2(\Delta y)^2} \left( \begin{array}{c} \psi^k_{i+2,j+2} - 16\psi^k_{i+2,j+1} + 30\psi^k_{i+2,j} - 16\psi^k_{i+2,j-1} + \psi^k_{i+2,j-2} \\ \psi^k_{i+1,j+2} - 16\psi^k_{i+1,j+1} + 30\psi^k_{i+1,j} - 16\psi^k_{i+1,j-1} + \psi^k_{i+1,j-2} \\ \psi^k_{i,j+2} - 16\psi^k_{i,j+1} + 30\psi^k_{i,j} - 16\psi^k_{i,j-1} + \psi^k_{i,j-2} \\ \psi^k_{i-1,j+2} - 16\psi^k_{i-1,j+1} + 30\psi^k_{i-1,j} - 16\psi^k_{i-1,j-1} + \psi^k_{i-1,j-2} \\ \psi^k_{i-2,j+2} - 16\psi^k_{i-2,j+1} + 30\psi^k_{i-2,j} - 16\psi^k_{i-2,j-1} + \psi^k_{i-2,j-2} \end{array} \right) + O((\Delta x)^2(\Delta y)^2). \quad (6)$$

According to the above scheme, calculations were made of the deformation field of the plate under the action of the force $F = (x + y) \cdot t$. The value of the grid pitch was 0.1 relative units, the time step was 0.001 relative units. Figure 2 shows the calculation of the plate deformation field for a time interval $[0; 1]$. 


Fig. 2. The deformation field of the plate: a) the cross-section x, y at the beginning of the calculation b) the cross-section x, y at the end of the calculation c) the deformation field of the plate d) the level line of the plate strain field

It is evident from the calculations that the upper right corner of the plate experiences the maximum degree of deformation, from which the plate begins to roll into a scroll.

As a model describing the structure of the microscrew, a spiral was chosen. In the structure of a multilayer nanoscrew, a spiral forms around the selected center with a continuous change in radius. Each turn has an internal (rnutr) and external (router) radii, which eventually form the inner (Rinner) and external (Router) radii microscroll as a whole. When forming any turn with a change in radius from rinner to router there is one complete revolution of $2\pi$ (360°). Thus, the value of $\delta R$, which determines the change in radius when rotating by 1°, is calculated as:

$$\delta R = \frac{\Delta R}{2\pi} \quad (7)$$

It is known that the radius depends on the angle of rotation around the axis of the tube $\alpha$ during the transition from the node to the grid node during the calculation of the coordinates of the next atom:
\[ \alpha = 2 \arcsin \left( \frac{R_{\text{prev}}}{2R} \right) . \quad (8) \]

Thus, with the next turn, the rotation angle \( \alpha \) will change when the current radius \( R_{\text{cur}} \) changes. At the same time, the radius of the roll \( R_{\text{cur}} \) varies in proportion to the current twist angle of the entire spiral, which is found from the relationship:

\[ \varphi_{\text{cur}} = \varphi_{\text{prev}} + \alpha_{\text{cur}} , \quad (9) \]

where \( \varphi_{\text{prev}} \) is the twist angle obtained in the previous step, \( \alpha_{\text{cur}} \) is the angle from node to node (formula (8)) for the current value of the \( R_{\text{cur}} \) radius.

The process of obtaining coordinates is realized as follows. The coordinates of the atoms are calculated starting from the inner radius of the tube: \( R_{\text{cur}} = R_{\text{inner}} \), \( \varphi_{\text{cur}} = 0 \).

Then at each step:
1. the current value of the angle \( \alpha_{\text{cur}} \) is calculated, starting from \( R_{\text{cur}} \) according to the formula (7);
2. The radius is incremented: \( R_{\text{cur}} = R_{\text{prev}} + \delta R \cdot \varphi_{\text{cur}} \)
3. The new value of the twist angle of the whole \( \varphi_{\text{cur}} \) spiral is calculated by the formula (8);
4. For a given position along the axis of the tube, \( \varphi_{\text{cur}} \) and \( R_{\text{cur}} \), a transition is made from cylindrical to Cartesian coordinates. To translate coordinates from a cylindrical coordinate system to a Cartesian coordinate system, the axis of the tube is taken as the x-axis. Using known formulas for the transition between coordinate systems, it is easy to calculate the coordinates along the y and z axes. In this way:

\[ x = H; \quad y = R \cdot \sin (\alpha); \quad z = R \cdot \cos (\alpha); \]

As a result of calculating the position of each node, a set of coordinates of atoms in a cylindrical coordinate system is obtained: \( R \) is the radius of the microscroll, which is the same for each atom / node; \( \alpha \) - current angle of rotation around the axis; \( H \) (height) - position along the axis of the microscroll.

According to the coordinates \( (x, y, z) \) obtained at all stages of the folding (i.e., along the entire length of the nanotube), a three-dimensional distribution of atoms is constructed, which will be a model of a nanotube of the "scroll" type of given radius and length. [9]

For our case, to obtain models of rough microscrolls we modify the standard algorithm by introducing in the calculation formulas for the angle and the current radius the randomizing elements:

\[ \alpha = 2 \arcsin \left( \frac{R_{\text{cur}} + (-1)^{i} \cdot \text{rnd}}{2R} \right) \quad (10) \]

\[ R_{\text{cur}} = R_{\text{prev}} + (-1)^{i} \cdot (\delta R + \text{rnd} \cdot \varphi_{\text{cur}} , \quad (11) \]

where \( \text{rnd} \) is a uniformly distributed random variable describing the degree of randomization, \( I \) is the step number.

The directions of the turns of the microscroll were also randomized:

\[ \varphi_{\text{cur}} = \varphi_{\text{prev}} + (-1)^{i} \alpha_{\text{cur}} . \quad (12) \]

According to the above algorithm, calculations were carried out in relative units of profiles and cross sections of microbrushes and the dependence of the variation of the internal radius along the length of the microtubule.

At a small degree of randomization, microscrolls without self-intersections are obtained, visually similar to microtubes (Figure 3).
Fig. 3. Microscroll with small randomization a) Rinner = 1; Router = 1.01 frontal section b) Rinner = 1; Router = 1.01 three-dimensional view c) Rinner = 1; Router = 1.5 frontal section d) Rinner = 1; Router = 1.5 three-dimensional view

For a sufficiently large degree of randomization, highly roughened microscrolls are obtained (Figure 4)
A randomization of the angle of rotation was also carried out, which also made it possible to construct highly rough surfaces (Figure 5).

In addition, the case of reverse rotation of the turns was realized (Fig. 6). In this version, structures with self-intersections are modeled, which most closely reflect the structures of microscrolls obtained as a result of experiments.
Fig. 6. Microscrolls with reverse rotation of the turn $R_{\text{inner}} = 1; R_{\text{outer}} = 1.5$ a) a large number of turns a front section b) a large number of turns a lateral section c) a large number of turns a three-dimensional view d) fewer turns a front section e) fewer turns lateral section f) fewer turns three-dimensional view

As can be seen from the calculations, the degree of randomization and the direction of rotation have a strong influence on the formation of the microscroll, and the proposed approach allows one to simulate various forms of microscrolls.

Conclusion
The approaches and models proposed in the work allow qualitatively to model the structure and initial stages of the formation of microscrolls, as well as to evaluate the influence of model parameters on the structure of the obtained microscrolls.

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