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# Laser deposition of multiwalled titanium oxide microtubes

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***Abstract*. We propose approaches to producing micro- and nanostructured titanium oxide surfaces via exposure to cw laser radiation and repetitive laser pulses. By varying the experimental geometry (angle of incidence, substrate-target separation and other parameters), various structures can be obtained. Titanium oxide tubes grown in a nonuniform magnetic field are up to 1 μm in diameter and up to 500 μm in length. Such structures can be used in catalytic filtration and as multiwalled structures similar to superlattices.**

***Keywords***: *titanium oxide, titanium nitride, laser exposure, nanostructured surface.*

## 1. Introduction

Interest in titanium oxide stems from its unique catalytic properties, in particular from the fact that, on the surface of titanium oxide films, many toxic compounds can be decomposed to $CO_2$ and $H_2O$ by ultraviolet radiation [1]. Doping with Au, Fe and other atoms may alter the catalytic properties of titanium oxide films and membranes [2, 3]. Moreover, active interaction of gas molecules with pore walls in membranes may ensure both more effective gas purification and gas separation [4]. To enhance the effectiveness of titanium membranes, they should have as porous a structure as possible, with very long pores and a large specific surface area.

## 2. Basic experiments

One approach to producing porous structures with a large surface area is the synthesis of fractal structures [5, 6]. The formation of metal clusters in a laser-ablation plume has been addressed in a number of studies [7 – 9], which examined the synthesis of fractal filaments, clusters and multiwalled structures through laser ablation of metallic targets in buffer gases and discussed the principles behind the production of fractal structures when a plasma propagates in air [8].

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To produce titanium oxide structures, particles back-ejected from the surface of a titanium target in air [10] using a cw laser beam of moderate intensity (within $10^7$ W cm$^{-2}$) were deposited on a cold substrate. The surface structure of the titanium oxide deposit was examined on a Quanta 200 3D scanning electron microscope (SEM). We obtained isolated fractal filaments (Fig. 1a) and multiwalled structures (Fig. 1b), depending on the incident intensity, deposition time ($t \leqslant 10$ s) and the position of the substrate in the laser plume.

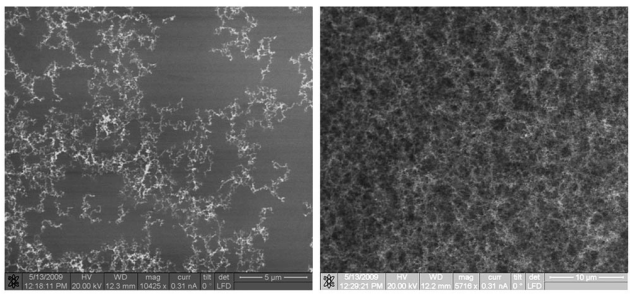

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**Figure 1.** SEM images of the surface of titanium oxide deposits: (a) fractal filaments obtained at an incident intensity of $10^5$ W cm$^{-2}$, ablation time of 5 s and substrate-target separation of 1.5 mm; (b) multifractal structure obtained at an incident intensity of $10^7$ W cm$^{-2}$, ablation time of 10 s and substrate-target separation of 1 mm.

At a given incident intensity, increasing the deposition time ($t \geqslant 20$ s) alters the nature of the structures forming in the deposit on the target surface (Fig. 2): we observe three-dimensional (3D) structures similar to fractal shells [7]. The titanium oxide microtubes forming on the sample surface are orientation-disordered. Such structures were also observed when titanium was annealed in a nitrogen atmosphere [11]. A number of reports (see, e.g., Refs [10, 12]) examined repetitive-pulse exposure as a more effective approach to the preparation of titanium oxides and nanostructured films.

In the next series of experiments, we used metallic targets and a $Q$-switched ytterbium laser with a pulse duration of 100 ns, average power of 10 W and pulse repetition rate of 40 kHz. The laser beam was scanned over the target surface at 1 mm s$^{-1}$, and the target-sample separation was 1.4 mm. The surface of the titanium oxide films thus produced is shown in Fig. 3.

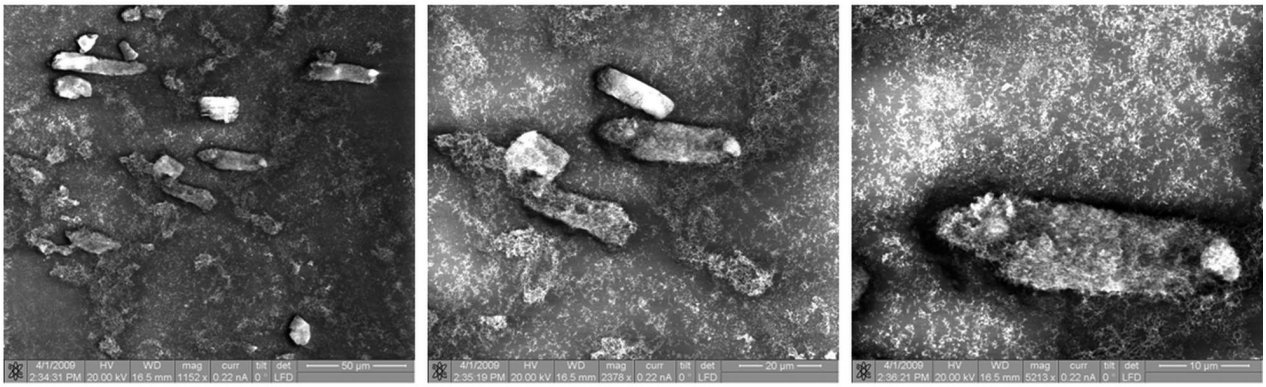

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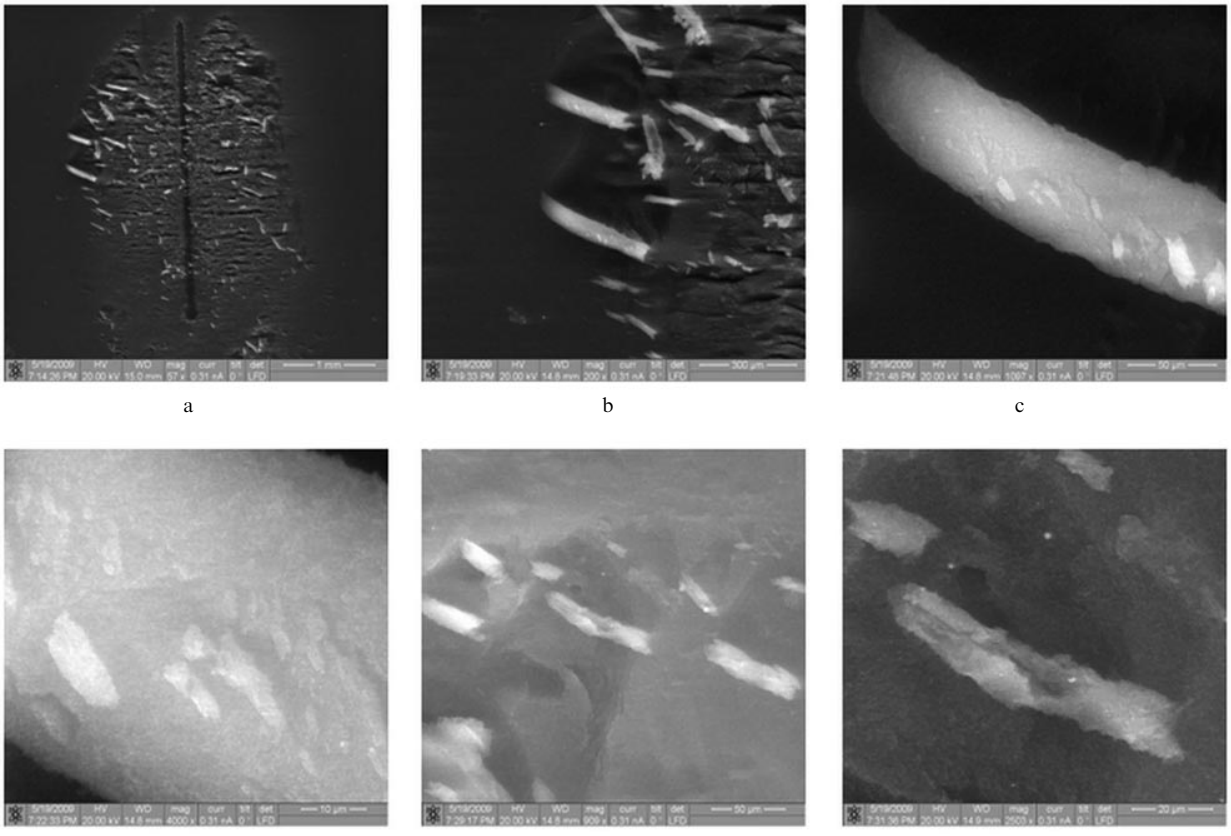
**Figure 2.** Surface of titanium oxide deposits with microtubes formed at an incident power of 14 W, laser beam diameter of 40 μm and exposure time of 25 s: (a) image taken 1 mm from the laser beam centre (at the left), (b) 2378×, (c) 5213×.

The structures obtained are identical to those produced by cw laser exposure, and the microtubes have reproducible parameters under particular experimental conditions. The number and length of tubes increase with decreasing laser pulse duration (Figs 3a, 3b): the average length increases from $\sim$ 20 to 100 μm in going from cw to nanosecond laser pulses, and the maximum length reaches 300 μm. The structure of the microtubes also experienced changes: short laser pulses produced 'scales' on their surface (Figs 3c, 3d), and some of the tubes were rolled incompletely. As seen in Figs 3e and 3f, the tubes are transparent and, hence, hollow. The appearance of the structures obtained suggests that the tubes result not only from bending of layers but also from subsequent self-assembly.

## 3. Self-assembly experiments

To study the feasibility of self-assembly, particles ejected from the target by laser ablation were deposited on a substrate in a weak nonuniform magnetic field of 90 Oe. In



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d e f

**Figure 3.** Titanium oxide films grown on the surface of a cold substrate by exposure to repetitive 100-ns laser pulses with an average power of 10 W: (a) deposited layer (the dark line is the laser beam path); (b) inhomogeneities to the right of the scan line; (c, d) portions of Fig. 3b at higher magnifications; (e) inhomogeneities to the left of the scan line; (f) magnified portion of Fig. 3e.

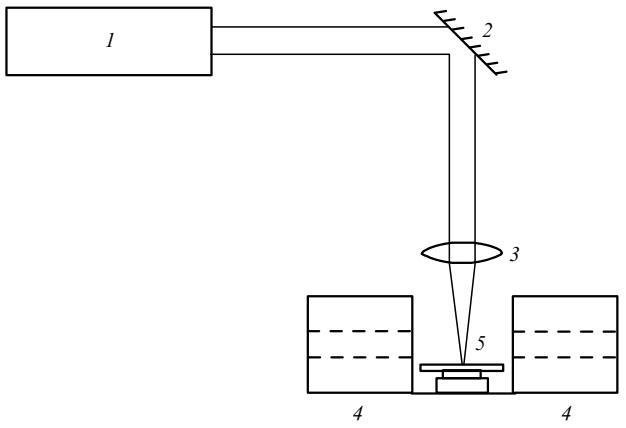


**Figure 4.** Experimental setup: (*1*) cw laser; (*2*) scanning mirror; (*3*) focusing lens; (*4*) magnets; (*5*) deposition unit (from top to bottom: quartz substrate, ceramic spacer, and titanium target).

a nonuniform magnetic field, magnetic dipoles move with an acceleration, which enables their selection. Since titanium is an anomalous paramagnetic material whose susceptibility increases considerably with temperature [13], the use of a magnetic field in a back ejection configuration with a cw laser allows one to control the growth of microtubes. To this end, two cylindrical magnets were incorporated into our experimental arrangement (Fig. 4).

The use of cw laser radiation was dictated by the necessity to maintain steady-state conditions in order to study the self-assembly process in greater detail. As a result, the following features of the process were revealed. When titanium oxide particles were deposited in a magnetic field at an incident power of 10 W, no titanium microtubes were formed on the substrate surface at exposures shorter than 10 s. At the same time, 24 h after the exposure we observed self-assembly of microtubes (Fig. 5).

The microtubes were translucent, as is typical of thin titanium oxide films [1]. The likely reason for the self-assembly of such structures 24 h after laser exposure is that the exposure produces single-domain nanostructures, leading to magnetisation vector rotation [14, 15]. Under the effect of the nonuniform magnetic field and the paramagnetic properties of titanium, the laser deposition process is accompanied by separation of different compounds and titanium oxide formation. The deposit has the form of 'web' and contains a sufficient amount of reactive titanium ions (cf. [16–20]). Thus, during the oxidation of titanium and formation of nanoparticles, reactive metal atoms persist even in relatively large nanoparticles (50–100 nm). In the deposited layer, consisting of orientation-disordered nanoparticles, the magnetic field has a topology atypical of bulk titanium. As a result, when reverting back to the paramagnetic state, the material undergoes self-ordering. Another mechanism of self-ordering is the magnetic-field-induced mechanical stress, which initiates the formation of microtubes. In either case, once formed the structures are no longer sensitive to the magnetic field (because their orientation remained unchanged in the external magnetic field). At the same time, such structures can be removed from the sample surface by mechanical means, e.g., with adhesive tape (Fig. 6).

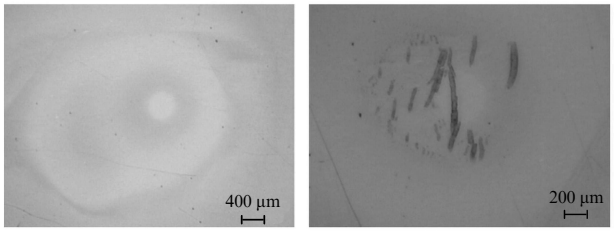


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**Figure 5.** Optical micrographs of the substrate surface (a) immediately and (b) 24 h after laser deposition in a nonuniform magnetic field.

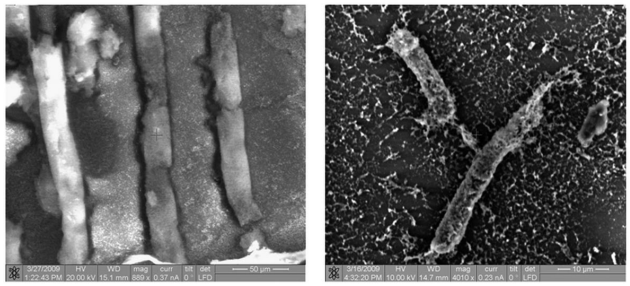

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**Figure 7.** Structure of layers deposited in 20 s at an incident power of (a) 10 and (b) 20 W.

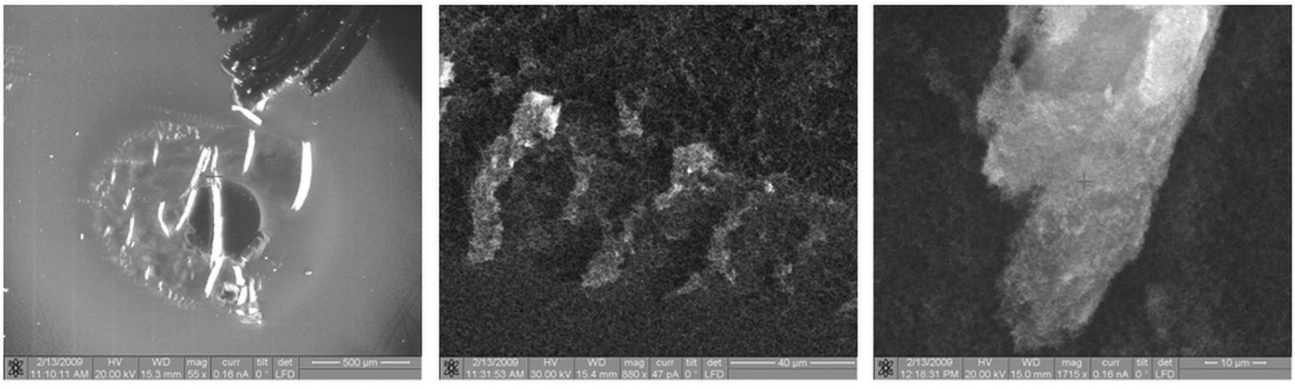

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**Figure 6.** SEM images of a deposited layer after self-assembly: (a) deposited film with traces of adhesive tape in the top right corner; (b) deposited layer with partially formed microtubes; (c) end of a microtube.

With increasing exposure time, microtubes begin to form during the deposition process. By raising the incident power, various structures can be obtained (Fig. 7).

## 4. Controlled growth of microtubes

Reducing the exposure time to 5 s, we were able to reproducibly obtain microtubes similar to those in Fig. 7b (Fig. 8). This process can be thought of as consisting of the following steps: the formation of initial structures (Fig. 8a) and the development of an initial filamentary structure (Fig. 8b) under the effect of the applied magnetic field and the associated mechanical stress. The filamentary structure rolls up the material around it and transforms into a microtube. As a result, the microtubes are surrounded by loose material.

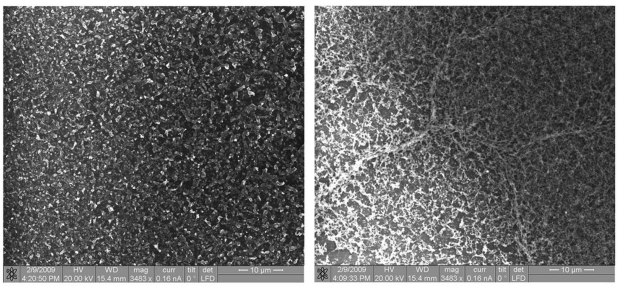

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**Figure 8.** (a) Structure of microtubes in the early stage of growth and (b) initial filamentary structure.

Starting at a certain incident power, the deposit contains nitrogen, which points to the formation of titanium nitride along with titanium oxide. The process begins at 700 °C [21] (Fig. 9) and leads to changes in the shape of the microtubes, which contain filaments of both titanium oxide and titanium nitride – materials differing in physical and chemical properties.

Scanning the surface of a titanium target with repetitive laser pulses in a nonuniform magnetic field, we obtained arrays of preferentially oriented microtubes (Fig. 10).

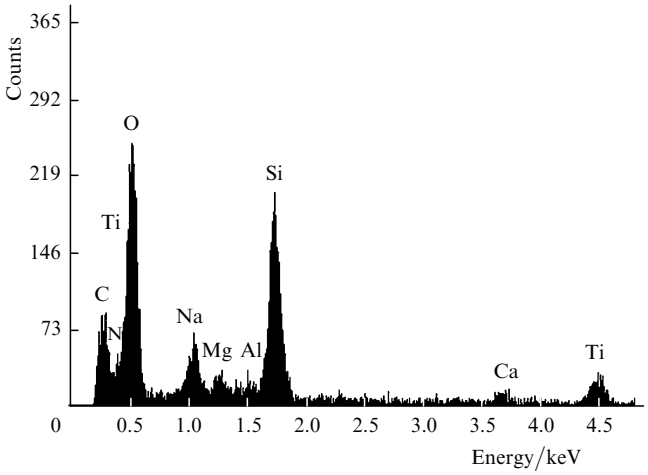


**Figure 9.** X-ray spectrum of a microtube produced by laser ablation of a titanium target.

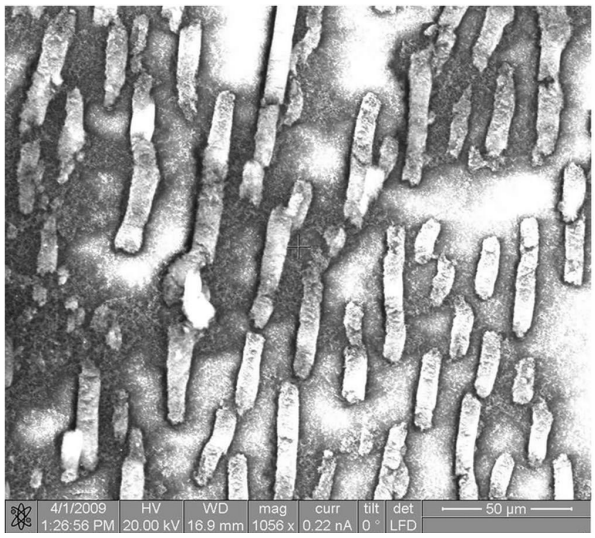


**Figure 10.** SEM image of the surface of a layer grown by laser ablation with 100-ns pulses at an average power of 10 W, beam scan speed of 1 mm $s^{-1}$ and pulse repetition rate of 60 kHz.

A 30-µm-diameter laser beam was scanned over the target surface in the direction of the structures formed, the magnetic field was perpendicular to the beam scan direction, and the total deposition time was 3 s. The structures formed by microtubes were similar to those in Fig. 7a. This means that the formation of 'chiral' microtubes in a magnetic field begins at a threshold mass of the deposit, at which the assembly process begins.

## 5. Conclusions

The present experiments demonstrate the formation of a new type of porous structure consisting of titanium oxides and nitrides. Such structures can be used in catalytic and membrane systems. The preparation of microtubes of mixed composition is of interest for microelectronic applications because the components of such microtubes differ drastically in electrical and thermal conductivity [22, 23]. The difference in characteristic length scale between such structures allows them to be used to design structures similar to superlattices in solids.

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