Metamaterials based on titanium dioxide rolls

A Osipov¹, V Samyshkin¹, I Skryabin¹, I Chestnov²,³,¹, A Istratov¹,
S Kutrovskaya²,³,¹

¹Vladimir State University named after A. G. and N. G. Stoletovs, Gorkii St. 87, 600000, Vladimir, Russia
²Westlake University, 18 Shilongshan Road, Hangzhou 310024, Zhejiang Province, China
³Institute of Natural Sciences, Westlake Institute for Advanced Study, 18 Shilongshan Road, Hangzhou 310024, Zhejiang Province, China

E-mail: osipov@vlsu.ru

Abstract. Titan dioxide is a widespread material used for a plenty of industrial applications. Nowadays it especially attracts a scientific attention due to the new forms such as nanostructured materials and nanocomposites with controlled morphological, physical, chemical and optical properties.

1. Introduction

Nanostructured titanium dioxide, which has high chemical and thermal stability with impure electron structure levels in material, which are made by determined doping type is a unique stuff for the creation of new functional materials (which may be used in catalysis, sensing, photocatalysis and photovoltaics) on its basis. The special interest is paid to titan dioxide due to the creation of photocatalyst on its basis also. Such kind of photocatalysts are very effective in visible range of the electromagnetic spectra. Moreover, titan dioxide can be used for the creation of the device components for the effective conversion of solar energy to electric one (solar batteries and Graetzel cells [1])

In this work we present the multilayer TiO₂ microtubes by self-organization from thin films synthesized by laser ablation in air. We show that the absorption spectra of the synthesized microtubes are strongly sensitive to the thickness of the film. This observation certifies of the layered structure of the self-organized microwires. It is promising for applications in three-dimensional metamaterials based on TiO₂.

2. The method of formation of the multilayer microtubes

We have used the laser ablation method for the synthesis of metastable forms of titanium oxides. Thin films of titanium oxide have been deposited on a solid transparent substrate due to the fast cooling of a melted phase created by laser ablation of a titanium target in air [3]. A 30 µm laser beam has been used to scan the surface of a target by moving over circles with a diameter of 3 mm. Scanning has been realised with steps of 30 µm and each spot has been illuminated during 10 to 15 seconds in order to deposit a layer of thickness from 200 to 300 nm, respectively.
Figure 1. The schema of TiO2 tubes formation. (a) The method of laser deposition TiO₂ nano-particles (b) dark-filed images of the resulting microtubes; (c,d) the schematic of the self-induced formation of microwires; (e) shows the SEM image of the profile of the microtube: its multilayer structure is apparent; (f) is the schematic of the resulting microtube (out of the scale).

The self-assembly of microtubes is triggered by the external magnetic field (see the schematic in Fig. 1c, d). Titanium is an anomalous paramagnetic material whose magnetic susceptibility increases with the temperature increase [4]. The deposited nanoparticles possess metallic nuclei that form macroscopic magnetic domains oriented by the external magnetic field [5], as figure 1(c) shows. Domain walls are subject to mechanical strain that competes with a weak adhesion of the thin film of titanium oxide to the surface.

Once a critical strain value is achieved, the film breaks, and the attraction of magnetic nanoparticles leads to its rolling, as figure 1(d) schematically shows. Finally, multilayer microtubes of titanium oxide are formed as the scanning electron microscopy (SEM) images certify (see figures 1(b, e)). An idealised schematic image of the resulting microtube is shown in figure 1(f).

3. The microscopy and optical studies
The measured absorption spectra show the typical features of the titanium oxide (see inset to Fig. 2(a)). However, rolling of the films of oxide into microtubes significantly affects the spectra. Namely, a supplementary peak forms at the wavelength from 500 to 750 nm that corresponds to the film widths of 200 and 300 nm respectively. The increase of the thickness of the film leads to the red shift of the absorption peak. Figure 2(b) shows that the red-shift of absorption depends on the thickness of the film linearly. This dependence certifies of the multilayer structure of the studied microtubes. The reduction of the transmission coefficient at a given wavelength \( \lambda \) may be interpreted as an effect of multiple scattering of light from the layers of TiO₂ characterised by the optical thickness of \( d \times n_{\text{eff}} = \lambda \).

We extract the effective refractive index from the slope of the straight line fitting the experimental points in Figure 2b. The best fit yields \( n_{\text{eff}} \approx 2.5 \). A significant broadening of the observed absorption resonances may be attributed to the inhomogeneity of the initial thin film that contains a variety of titanium oxide phases.
Figure 2. Optical properties of the titanium dioxide tubes. (a) shows the optical absorption spectra of microtubes formed from the films of various thicknesses. The inset shows the spectra of microtubes obtained from the films of 200 and 300 nm widths; (b) shows the dependence of the wavelength of light that corresponds to the maximum of absorption on the thickness of the film. (c) shows the modelling results for the absorption spectra. It is assumed that all light that is not transmitted is absorbed. The spectra are calculated for three mean values of the thin film width \( d_2 \). Dashed lines show the spectra calculated within the approximation of a spatially homogeneous film that has the same thickness everywhere in the place. In contrast, solid lines are obtained assuming the inhomogeneous film whose width is described be a Poissonian distribution. The calculated spectra are averaged over 100 numerical experiments for every wavelength. Vertical dotted lines denote the peak positions.

The studied microtubes reveal their multi-layer nature also in the images obtained with use of the dark-field microscope with a 100x objective (Fig. 1(b)). Note that the total area of the sample corresponding to this image is 50x50 µm. The intensity of light scattering by the studied structure is inhomogeneous in space. Namely, inside the microtubes we observe a non-uniform distribution of the signal that may be attributed to the fluctuations of the density and variations of the structure of the tube. It is important to note that the parts of film that are not self-assembled to microtubes give zero contribution to the dark-field microscope signal. The observed high intensity image is characteristic of a multilayer metamaterial that provides a non-linear optical response to the incident light field.

In order to interpret the correlations between the spectral position of the maximum and the width of the film we have calculated the absorption spectra of a model planar structure containing the alternating layers of titanium oxide and air. This toy-model appears to capture the essential features of the optical response of multilayer microtubes. We take into account the fluctuations of the width of the thin film in the calculation. Namely, we assume that the film has an average width \( d_2 \) and it is characterised by the width fluctuations of a magnitude \( d_1 \), that is comparable with the characteristic size of deposited nanoparticles (up to 100 nm). We argue that due to these fluctuations empty spaces
must remain between neighbouring layers of TiO$_2$ in the course of formation of the multilayer microtubes. We have assumed the Poissonian distribution of the width of the i-th layer $d_2(i)$ with a mean value $d_2$ and the variance $d_1$. The transfer matrix method has been employed for this calculation [6]. As a refractive index of semiconductor layers we have used one of the amorphous TiO$_2$ in the rutile phase [7]. The refractive index of the empty spaces has been taken equal to 1. We took advantage of the fact that the characteristic widths of studied microtubes are of the order of units of micrometers, while the thickness of the initial film is an order of magnitude smaller. Having this in mind, we have assumed a model structure comprising 10 layers. The resulting absorption spectra are shown in Fig. 2(c).

In the limiting case of the constant widths of all layers we obtain a sharp photonic bandgap characterised by zero transmission (dashed lines in Fig. 2(c)). Variation of the layer thicknesses results in the smearing of the photonic gap and the increase of transmission. The best qualitative agreement between the toy model calculation and the experiment is achieved at the mean optical thickness of semiconductor layers $d_2 n_{TiO_2}$ matching the wavelength of light. The deviations between the model results and the data is mostly caused by the geometry factor: the studied microtubes have a different geometry from the planar model structure, obviously.

4. Conclusion

Optical metamaterials based on the titanium dioxide find multiple applications in various areas of photonics. The enhancement of the plasmonic resonance has been observed in multilayer structures of TiO$_2$ that is highly promising for the realization of a new generation of solar cells. This work presents the experimental method for realization of multilayer microtubes based on titanium oxide and reports on the strong dependence of the optical absorption spectra of these microtubes on the width of the thin films used to fabricate the tubes. We can control the thickness of the films in the framework of the laser ablation process we developed that provides us with an efficient tool of control on the optical properties of the resulting metamaterial. As the next stage, we are going to embed metallic nanoparticles inside the microtubes in order to attempt realization of an ideal wideband absorber.

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