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Estimation of local and long-range ordering of the structure of TiO_2 nanotubes

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Abstract: We present a study of the scanning electron microscopy images of the TiO_2 nanotube array. The initial and modified samples were examined before and after annealing. It has been found that the annealing of the modified and unmodified samples results in different degrees of the local ordering. The nanotubular coverings were modified by Pt nanoparticles formed by the H_2PtCl_6 solutions infiltration for change of their electro- and photo-catalytic properties estimated by measuring the photoelectric currents. The influence of the morphology and ordering degree of the nanotubular coverings on the manifestation of their functional properties has been studied. A two-dimensional Fourier transform was applied for obtaining information on the occurrence of periodicities in the ordering of nanotubes. Correlation analysis was performed to find out the invisible regularities and periodicities in the structure of the nanotube arrays. The analysis of the photoactivity of the samples was also carried out.

Keywords: nanotubes, titanium dioxide, ordered structure

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Материалы конференции
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Оценка локального и дальнего упорядочения массива нанотрубок диоксида титана

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Аннотация. В работе проведено исследование изображений сканирующей электронной микроскопии массива нанотрубок диоксида титана. Изучались исходные и модифицированные образцы до и после отжига. Обнаружено, что отжиг образцов приводит к различным степеням локального упорядочения. Исследовано влияние морфологии и степени упорядочения нанотубулярных покрытий на проявление их функциональных свойств.

Ключевые слова: нанотрубки, диоксид титана, упорядоченная структура

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Introduction

Nanostructured and microstructured materials, whose principally new physical properties result from the developed surface and quantum-size effects, constitute the group of promising objects for advanced materials science. In the last decade, adsorption, optical, electrical, catalytic, and photocatalytic properties of TiO_2 have attracted a special interest of researchers [1–3]. Self-organization of titanium dioxide can be attained by its anodization in acids (for instance, sulfuric or phosphoric), most often, in fluorine-containing electrolytes, since dissolution proceeds there through formation of fluoride complexes. Anodic oxidation of titanium in a fluorine-containing electrolyte enables one to obtain nanostructured coatings consisting of TiO_2 nanotubes, whose parameters can be controlled varying the oxidation conditions [4–9].

Materials and Methods

Anodic oxidation of titanium was performed in a two-electrode electrochemical cell using a B5-49 direct current source. Pt served as an auxiliary electrode, the Ti plate was a working electrode. To obtain the nanotubular structure of titanium anodes, an aqueous solution of $NH_4F{\cdot}HF$ with addition of Na_2SO_4 and complexing agents was used. Thereafter, for the sake of properties modification, the obtained Ti/TiO_2(nano) systems were held in an aqueous solution of H_2PtCl_6 of the concentration $3{\cdot}10^{-2}$ mol·l^{-1} for 1 h, dried, and annealed in a muffle furnace at 500 °C for 4 h (Table 1). The surface structure was investigated on a Hitachi S-5500 scanning electron microscope (SEM) (Hitachi, Japan).

Table 1

Modification Condition

Sample	H_2PtCl_6 concentration, M	Anneal time, h
No. 1	–	–
No. 2	–	4
No. 3	$3{\cdot}10^{-2}$	–
No. 4	$3{\cdot}10^{-2}$	4

The photocurrent generated by the sample under the action of the UV radiation was measured to determine the photoactivity of titanium dioxide. The measurements were carried out using the DUV-35W Labino UV xenon lamp with the spectrum within the range of 315–400 nm with the peak at 365 nm. The current was recorded using the AUTOLAB POSTAT-302N potentiostat with PC-controlled data acquisition.

Results and Discussion

Nanotubes with well-defined boundaries of a regular form are observed in the SEM-image of Sample 1 (Fig. 1, *a*, *b*).

A sufficiently great number of boundaries approximates the shape of convex polygons with well-defined directions of sides. The average diameter of nanotubes is approximately 100 nm. Some defects of the surface can be also seen in the sample. Considering the local configurations of nanotubes, it can be observed that they are sufficiently similar in nature to the ‘plate’ structure. Because the boundaries of nanotubes often have marked sides, the nanotubes ‘contact’ each other along these sides. Therefore, different types of local ordering arise. Sometimes, one can also observe the near correct configurations in the shape of square, rectangle and, less frequently, hexagon.

Fig. 1, *c*, *d* show that the boundaries of nanotubes become blurred and widen after annealing. Although the structure deteriorates and becomes generally more uneven, the short-range local order in the relative positioning of nanotubes is preserved. The same stable configurations in the shape of square, rectangle and hexagon can be seen (Fig. 1, *c*).

Let us consider the SEM-image of Sample 3 modified by Pt (Fig. 1, *e*, *f*). A large quantity of platinum nanoparticles can be observed; their size mainly is in the order of 10 nm but can also reach 30 nm. We used the X-ray photoelectron spectroscopy method to confirm that Pt nanoparticles on the surface of nanotubes correspond to the non-oxidized and oxidized states.

The nanotubes, in contrast to Sample 1, have no individual boundaries. Neighboring nanotubes are separated by common and, at the same time, sufficiently wide boundaries (walls), whose thickness can reach 20–50 nm. The inner diameters of nanotubes are commensurate with the wall thickness and predominantly equal 50–60 nm. It can be said that the structure of the nanotube array is completely stochastically uniform, including only rare 'pieces' of regular local configurations of nanotubes.

After annealing, the common structure of the nanotube array acquires a sharpness (Fig. 1, *e*). The boundaries of nanotubes become essentially thinner and, in this case, the inner diameter of nanotubes increases automatically. The image is more contrasted compared to Sample 3, which

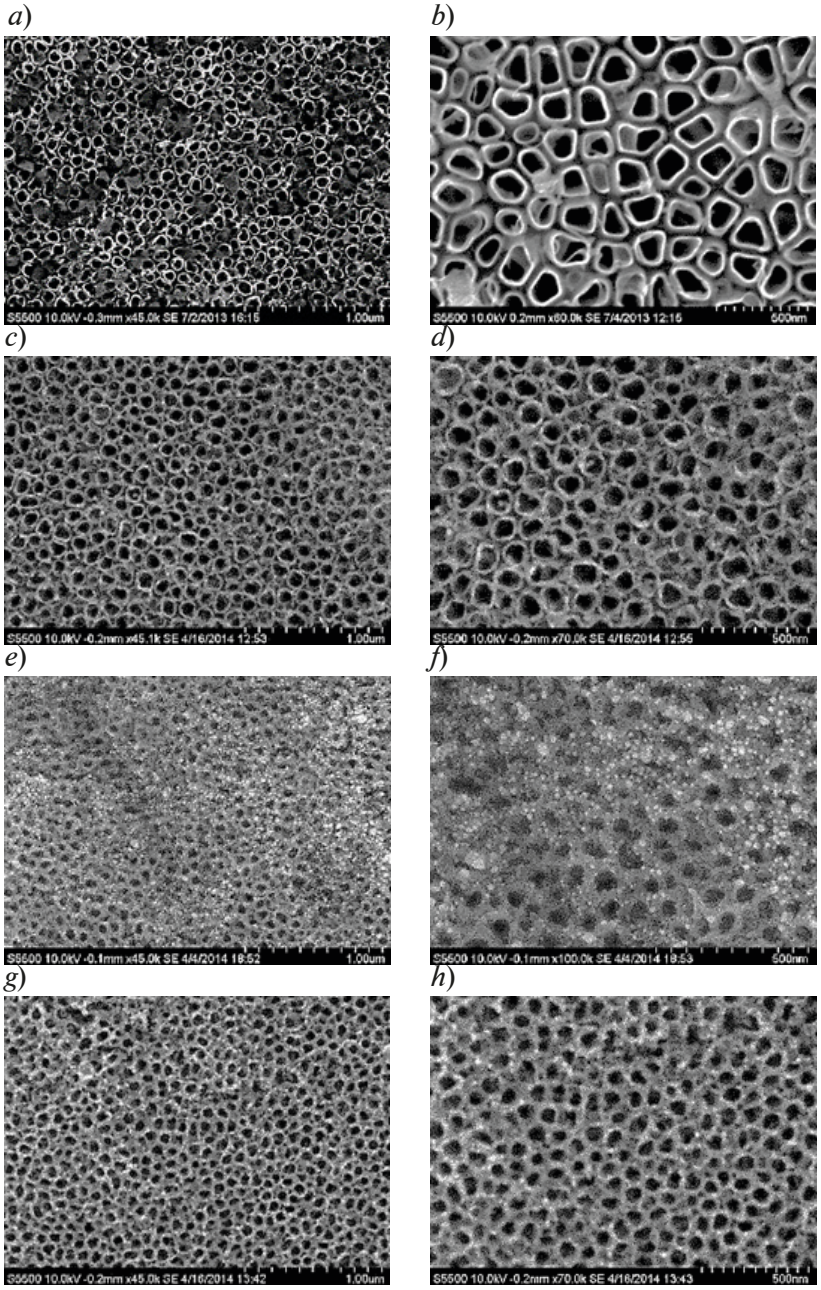

Fig. 1. SEM images of electrode surface: Sample 1 (*a*, *b*); Sample 2 (*c*, *d*); Sample 3 (*e*, *f*); Sample 4 (*g*, *h*).

is to say that the nanotubes become deeper or open. The observed quantity of the platinum nanoparticles decreases essentially compared to Sample 3.

Because the walls of nanotubes become thinner after annealing, this suggests local ordering. Considering the fact that the average diameter of nanotubes changes weakly and the sections of nanotubes are tightly packed on the image plane, the hexagon should be the predominant configuration. The character of the Fourier spectrum may provide evidence to confirm this circumstance.

The two-dimensional Fourier transform [10] allows to reveal the periodicities and regularities in the structure of the object observed in the process of visual analysis. Fig. 2 shows the respective two-dimensional spectra for the SEM-images of the samples considered.

Contrary to expectations, the SEM-images are characterized by roughly the same topology differing only in detail. In all images, the halo responsible for the short-range ordering is present. Such halo is characteristic of the 'amorphous' order where the structural elements have the order only within the limits of the first coordination sphere.

The halo for Sample 1 is poorly expressed in spite of the sharp edges of nanotubes in the SEM-image. There is no pronounced periodicity in all directions, which stipulates the weak intensity of the halo. The presence of the low-frequency region in the spectrum can be identified with the defects of nanotubes structure within the SEM-image. Judging from Sample 1, we can draw the preliminary conclusion that the Fourier spectrum in this case does not reflect the well-defined boundaries of separate nanotubes.

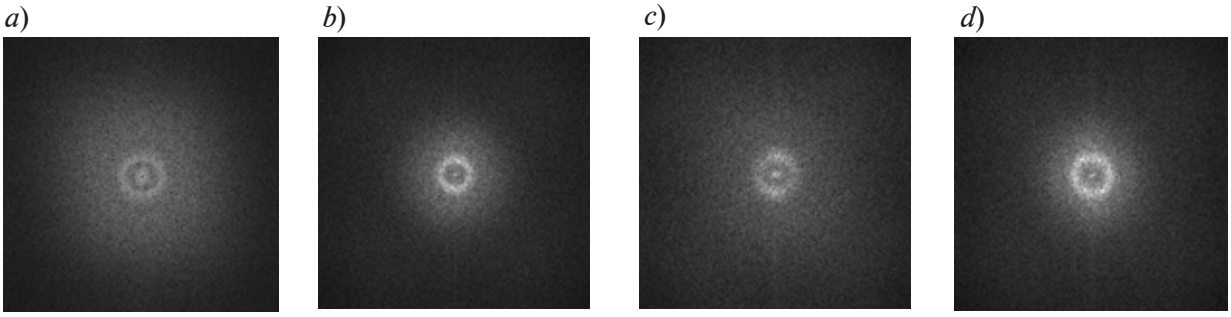

Fig. 2. Fourier spectra of SEM-images: Sample 1 (*a*); Sample 2 (*b*); Sample 3 (*c*); Sample 4 (*d*).

In Spectrum 2, the halo is shown brighter than in Spectrum 1. Such change is due to the fact that the boundaries of nanotubes 'become blurred' under annealing, at the same time the hollows of nanotubes take on a more identical shape. Such 'averaging' of nanotube configurations leads to the fact that the structure within the SEM-image becomes more uniform and isotropic. The uniformity of the structure elements (in the absence of well-defined local configurations) results in the pronounced halo. The low-frequency components in Spectrum 2 (as well as in Spectra 3, 4) are practically non-existent which shows a decrease in the number of defects in the structure of the array of nanotubes.

Modifying the sample with platinum worsens visually the structure of the array of nanotubes. The existence of halo in Spectrum 3 can be related to the fact that the nanoparticles Pt do not cover the nanotubes but lie predominantly at their boundaries. Thereby, the structure is for the most part preserved.

The SEM-image of Sample 4 is similar enough to the image of Sample 2 and differs only in the fact that the boundaries of nanotubes form a solid continuous 'grid'. In the present case, even more significant 'averaging' is observed which touches on the boundaries of nanotubes also. The halo in Spectrum 4 begins to acquire a hexagonal shape with the intensity maxima in its corners. This spectrum coincides with the expectable one.

Next, we turn to correlation analysis which allows to additionally find out the hidden regularities and periodicities in the structure of the nanotube arrays. We use the one-dimensional autocorrelation function (ACF) under the vertical direction of the SEM-image [11].

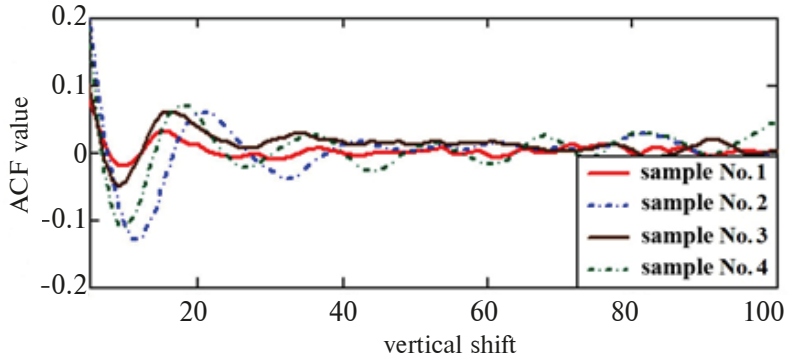

Fig. 3. Fragments of ACF for the SEM-images

It has been established that ACFs do not have overly large differences (Fig. 3). At the same time, the value of the range of the first side maximum allows to obtain the additional information about the ordering. The relative range of the first side maximum for ACFs *1*, *2*, *3* and *4* was 5.3%, 18.8%, 11.2% and 18.2% respectively. Over the first 1–2 periods, ACFs *1* and *3* as well as ACFs *2* and *4* are similar to one another. As seen from Fig. 3 (as well as from presented quantitative evaluations), ACFs *1* and *3* fall within the group of less structured ones. ACFs *2* and *4*, which are characterized by a practically similar value of the first side maximum, are more pronounced. In this case, the same as for analysis of the Fourier spectra, the 'averaging' of the nanotube structure under annealing influences the ACF ordering.

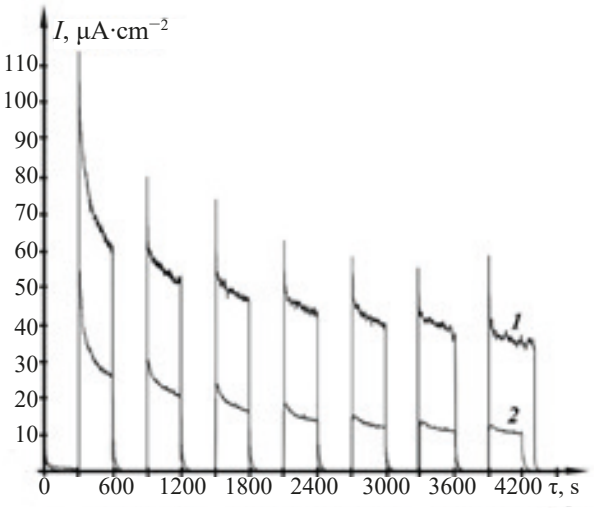

Fig. 4. Impulses of photoinduced current for TiO_2 nanotubes: Sample 4 (*1*); Sample 1 (*2*).

The photoactivity of nanotubular covers of titanium dioxide was also examined. Fig. 4 shows that the sample modified with platinum and exposed additionally to heat treatment has the characteristic values of photocurrents which are 2–3 times as large compared with the non-modified sample.

We can argue that the values of the detected photocurrent change over time from 60–110 mA·cm^{-2} (the first UV-irradiation) to 40–60 mA·cm^{-2} (the final UV-irradiation) for the modified sample. The photocurrent density of the non-modified sample also demonstrates a tendency to reduction with increase of the UV-exposition time, in this case, the values change from 26–54 mA·cm^{-2} to 10–12 mA·cm^{-2}.

Conclusion

In this paper, we have carried out analysis of the ordering indicators of the nanotube arrays both as an independent objective and in connection with the functional properties. The titanium dioxide nanotubes obtained using the aqueous solution of NH_4F·HF with added Na_2SO_4 and complexing agents (Sample 1) have a sufficiently well-defined structure, sections appearing to be shaped as roundish convex polygons as well as boundaries individual for each nanotube. Visually, the local order can be characterized as the most pronounced. Moreover, Sample 1 does not exhibit meaningful ordering at the level of the Fourier-spectra and ACF due to defects of structure.

Modification with Pt (Sample 3) results in changing the character of the nanotube structure and 'coarseness', 'adhesion' of the boundaries of nanotubes with disturbance of geometry as well as appearance of large number of the platinum nanoparticles predominantly at the boundaries of nanotubes. Visually, the given sample is the least ordered.

Annealing of these samples leads to different results. For the unmodified sample, the shape of the nanotube sections became less delineated (Sample 1 → Sample 2). The SEM-image became 'blurred' and local ordering was less pronounced. Conversely, the annealing of the modified sample

(Sample 3 → Sample 4) has resulted in thinning of nanotube boundaries and manifestation of this structure because it has no well-defied structure in the initial state. Therefore, the short-range order of Sample 4 was best manifested in the local configurations of nanotubes, even though not so sharply as in Sample 2. Visually, Samples 2 and 4 are similar enough. According to the Fourier-spectra shapes and behavior of ACFs, they demonstrate homogeneity of the structure and pronounced periodicity.

Morphology of TiO_2 covers was analyzed to determine the elemental composition at different points. It has been established that the elemental composition of covers at different points (inwardly, at the boundary of nanotubes) differs by the ratio of Ti:O with micro-impurities of other elements. Analysis of photoactivity of the samples was also carried out. It has been established that the samples modified with Pt under the UV-irradiation demonstrate the photocurrent values which are 2–3 times higher than non-modified ones.

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