ATOM PHYSICS AND PHYSICS OF CLUSTERS AND NANOSTRUCTURES

Conference materials
UDC 538.911+546.82+544.6+544.478
DOI: https://doi.org/10.18721/JPM.184.115

Fabrication of TiO_2 nanopillar arrays and their structural evolution

L.S. Volkova [1, 2] ✉, T.S. Grishin [1], 2, A.A. Dudin [1], Yu.V. Nazarkina [2],
S.V. Dubkov [2], D.G. Gromov [2], S.A. Gavrilov [2]

[1] Institute of Nanotechnology of Microelectronics RAS, Moscow, Russia;
[2] National Research University of Electronic Technology, Zelenograd, Moscow, Russia
✉ lidiya.volkova.96@mail.ru

Abstract. We report the fabrication and structural study of TiO_2 nanopillar arrays produced by two-step anodization of Al/TiN bilayer (1000 nm/250 nm). The as-prepared nanopillars are amorphous; their structural evolution was investigated upon air annealing in the 300–800 °C range. Annealing at 300 °C initiates crystallization, at 500 °C predominantly nanocrystalline anatase is formed, while at 800 °C grain growth and coexistence of anatase and rutile are observed. The array morphology (diameter ~20 nm, pitch ~50 nm, height ~150 nm) remains intact even after high-temperature treatment. These results indicate that ~500 °C is an optimal annealing condition to obtain pure anatase while preserving the nanostructured geometry, which is important for photocatalytic applications and for using TiO_2 nanopillar arrays as platforms for hybrid SERS-substrates.

Keywords: TiO_2 nanopillars, anodization, photocatalysis, anatase, rutile

Funding: This research was funded by the Russian Science Foundation (Project No. 24-19-00610), https://rscf.ru/project/24-19-00610. The samples were obtained in the laboratory "Photonic Sensorics and Plasmonic Materials" of the National Research University MIET under State Assignment FSMR-2024–0012.

Citation: Volkova L.S., Grishin T.S., Dudin A.A., Nazarkina Yu.V., Dubkov S.V., Gromov D.G., Gavrilov S.A., Fabrication of TiO_2 nanopillar arrays and their structural evolution, St. Petersburg State Polytechnical University Journal. Physics and Mathematics. 18 (4.1) (2025) 93–98. DOI: https://doi.org/10.18721/JPM.184.115

Материалы конференции
УДК 538.911+546.82+544.6+544.478
DOI: https://doi.org/10.18721/JPM.184.115

Формирование массивов наностолбиков TiO_2 и их структурная эволюция

Л.С. Волкова [1, 2] ✉, Т.С. Гришин [1, 2], А.А. Дудин [1], Ю.В. Назаркина [2],
С.В. Дубков [2], Д.Г. Громов [2], С.А. Гаврилов [2]

[1] Институт нанотехнологий микроэлектроники РАН, Москва, Россия;
[2] Национальный исследовательский университет «МИЭТ», г. Зеленоград, Москва, Россия
✉ lidiya.volkova.96@mail.ru

Аннотация. Представлены изготовление и структурное исследование массивов наностолбиков TiO_2, полученных методом двухстадийного анодирования двухслойной

структуры Al/TiN (1000 нм/250 нм). В исходном состоянии наностолбики аморфны. Отжиг при 300 °C инициирует кристаллизацию; при 500 °C формируется преимущественно нанокристаллический анатаз; при 800 °C наблюдаются рост зерен и сосуществование анатаза и рутила. Морфология массива (диаметр ~20 нм, шаг ~50 нм, высота ~150 нм) сохраняется даже после высокотемпературной обработки без спекания столбиков. Показано, что ~500 °C является оптимальным режимом получения анатаза при сохранении наноструктурированной геометрии, что важно для фотокаталитических приложений и использования массивов наностолбиков TiO_2 как платформ для гибридных SERS-подложек.

Ключевые слова: наностолбики TiO_2, анодирование, фотокатализ, анатаз, рутил

Финансирование: Исследование выполнено при финансовой поддержке Российского научного фонда (проект № 24-19-00610), https://rscf.ru/project/24-19-00610. Образцы получены в НИЛ ФСПМ НИУ «МИЭТ» по государственному заданию FSMR-2024–0012.

Ссылка при цитировании: Волкова Л.С., Гришин Т.С., Дудин А.А., Назаркина Ю.В., Дубков С.В., Громов Д.Г., Гаврилов С.А. Формирование массивов наностолбиков TiO_2 и их структурная эволюция // Научно-технические ведомости СПбГПУ. Физико-математические науки. 2025. Т. 18. № 4.1. С. 93–98. DOI: https://doi.org/10.18721/JPM.184.115

Introduction

Titanium dioxide (TiO_2) is a popular functional material in nanotechnology due to its excellent photocatalytic properties [1–3], chemical stability, and bioinertness [4, 5]. It is widely used for photocatalytic decomposition of organic pollutants, water and air purification [6], as well as in solar energy devices [7] and sensors [8]. The photocatalytic activity of TiO_2 essentially depends on its phase state and surface morphology. Amorphous TiO_2 is known to have much lower photocatalytic activity compared to crystalline forms due to rapid recombination of charge carriers [9]. Anatase (metastable tetragonal phase of TiO_2 with a bandgap width of ~3.2 eV) usually exhibits higher photocatalytic efficiency than rutile (stable tetragonal phase with a bandgap width of ~3.0 eV) due to slower recombination of photogenerated electron-hole pairs [10]. Rutile, in turn, possessing a narrower band gap, has an absorption spectrum extended into the visible region, but the high rate of charge recombination reduces the efficiency of rutile-only photocatalysts [11]. On the other hand, a combination of phases (e.g., anatase-rutile mixed structure) can improve the total photocatalytic activity by broadening the spectral response [12]. Therefore, the control of the phase composition of TiO_2 is a key factor in the development of high-performance photocatalytic systems.

To date, many approaches to obtain nanostructured TiO_2 [13] have been proposed, ranging from sol-gel technologies [14] and hydrothermal synthesis [15] to anodic oxidation [16–18]. Among them, the anodization of massive titanium is particularly prominent, which allows the formation of highly ordered arrays of TiO_2 nanotubes directly on the metal surface [19]. Classical anodization of Ti leads to the formation of an array of densely packed hollow nanotubes. In recent years, the approach of anodizing thin films of Ti or TiN through a sacrificial Al layer has been developed, which allows to obtain arrays of vertically oriented TiO_2 nanopillars [20] separated by a certain distance. By varying the anodization modes and heat treatment conditions, it is possible to vary the geometry of such an array as well as the phase composition of TiO_2. Thus, the combined anodization of Al/TiN layers opens possibilities for the synthesis of ordered 3D nanostructured TiO_2 substrates with controlled morphology and phase state. In this work, two step anodic synthesis of TiO nanopillar arrays on Al/TiN substrate was realized and their morphology and structural evolution during thermal annealing in the range of 300–800 °C were investigated.

Materials and Methods

TiO_2 nanopillar arrays were fabricated by two-step anodization of a silicon substrate with Al/TiN/SiO_2 layers (1000 nm/250 nm/300 nm). The anodization procedure followed the scheme described in [21]. In the first step, the Al layer was anodized in a 5% H_2SO_4 electrolyte at a constant current of $I_1 = 0.07$ mA and voltage $U_1 = 30$ V for $t_1 = 2.5$ min. During this stage, a layer of nanoporous anodic aluminum oxide (AAO) was formed and subsequently removed by chemical etching in a $CrO_3 + H_2SO_4$ solution. As a result, a quasi-ordered hexagonal array of dimples was formed on the surface of the remaining Al.

In the second step, the anodization of the Al layer was carried out in the same electrolyte, starting from $U_1 = 30$ V with a voltage ramp of 1 V every 5 s up to $U_2 = 115$ V, followed by a constant-voltage anodization for $t_2 = 5$ min. At this stage, the anodic oxidation front reached the TiN layer through the thin AAO barrier layer, initiating localized oxidation of TiN at the pore bottoms and leading to the formation of vertically oriented TiO_2 nanopillars confined by the pore geometry. The remaining porous AAO was removed by a second etching in $CrO_3 + H_2SO_4$ solution for 10 min, after which the samples were rinsed with deionized water and air-dried.

To investigate the phase evolution of the fabricated TiO_2 nanopillars, the samples were annealed in air for 60 min at 300 °C, 500 °C, and 800 °C. Annealing was performed in a muffle furnace with a heating rate of ~5 °C/min. After annealing, the samples were allowed to cool naturally to room temperature together with the furnace.

The morphology of the obtained nanostructures was examined using a dual-beam scanning electron microscope (SEM) Helios G4 CX (TFS, USA). The internal structure and phase composition of the nanopillars were studied with a transmission electron microscope (TEM) JEM-2100 Plus (JEOL, Japan). For TEM analysis, thin cross-sectional lamellae of the arrays were prepared using a focused ion beam (FIB). To protect the region of interest from unwanted ion-beam damage, the samples were pre-coated with a thin amorphous carbon layer.

Results and Discussion

Fig. 1 shows typical SEM images of the fabricated TiO_2 nanopillar arrays. The top-view image (Fig. 1, *a*) confirms the regularity of the structure: the nanopillars form an ordered hexagonal array with a pitch of ~50 nm. SEM images with 52° tilt (Fig. 1, *b*) demonstrate that the nanopillars are approximately 150 nm in height. The pillars have slightly conical shape; some of them are bended at the base, but their tips are predominantly oriented perpendicular to the substrate. The nanopillar diameter at the base is ~20 nm, tapering to ~10 nm toward the top.

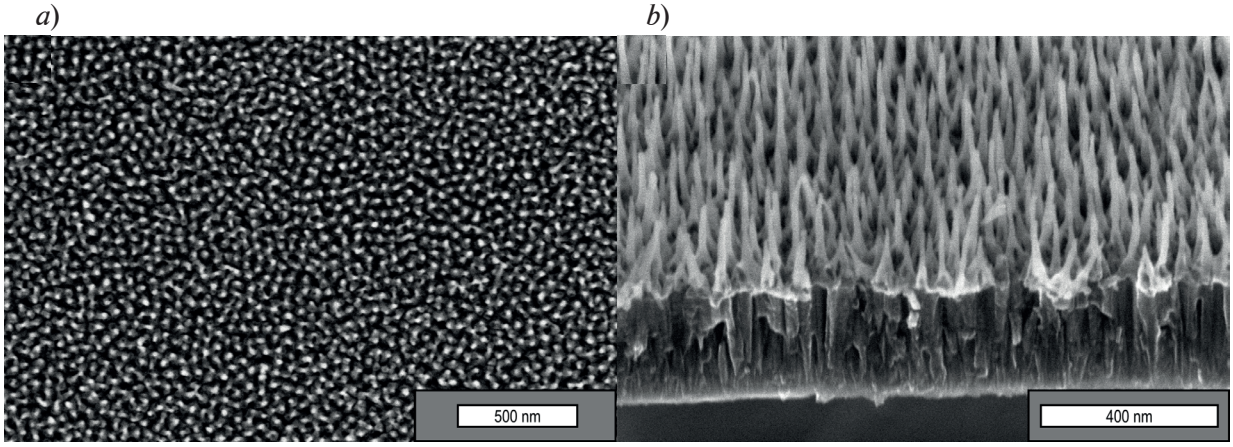

Fig. 1. SEM images of the formed array of TiO_2 nanopillars: top view (*a*), 52° view (*b*)

The nanopillars are firmly anchored to a thin continuous underlayer formed as a result of TiN anodization. This layer provides mechanical stability of the array and prevents delamination from the substrate. Thus, the two-step anodization method enabled the formation of vertically oriented TiO_2 nanopillar arrays with reproducible geometric parameters (diameter, height, and pitch), robustly fixed to the substrate. No residual Al or porous AAO fragments are observed on the surface, which confirms the completeness of the anodization and subsequent etching process.

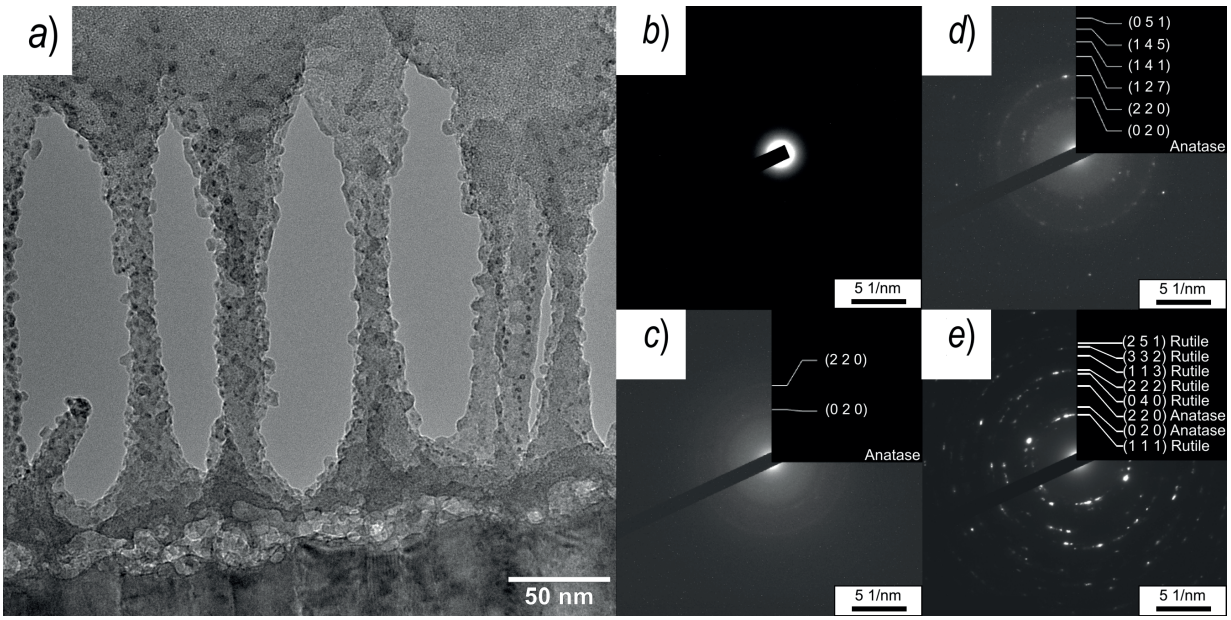

Fig. 2. TEM image of a cross-sectional view of TiO_2 nanopillars array before annealing. The nanopillars are coated with amorphous carbon, which was sputtered to protect the array from undesirable effects of the ion beam (*a*). Electron diffraction patterns obtained from unannealed (*b*), annealed at 300 °C (*c*), 500 °C (*d*), 800 °C (*e*) nanopillars

Despite their well-defined morphology, the nanopillars are amorphous immediately after anodization, as confirmed by TEM observations (Fig. 2, *a*): HRTEM images do not reveal ordered atomic planes typical of crystalline structures, and the selected area electron diffraction (SAED) pattern shows only an amorphous halo and a bright central spot corresponding to the direct beam (Fig. 2, *b*). The absence of distinct diffraction rings indicates the lack of crystalline grains of appreciable size. The high intensity of the central spot with a very weak amorphous background is explained by the fact that the electron beam passes mainly through empty space between the pillars (due to the low material filling of the selected area), so the fraction of electrons scattered by the structure is small.

Low-temperature annealing at 300 °C initiates the onset of TiO_2 crystallization, although the overall degree of crystallinity remains low. After annealing at 300 °C, the nanopillars are still predominantly amorphous; however, the SAED pattern exhibits the first signs of ordering: weak diffraction rings are observed (Fig. 2, *c*), most likely corresponding to anatase reflections. Due to the small number of reflections and low intensity of the rings, definite phase identification is not possible. It is likely that at 300 °C nanocrystallites with a size of only a few nanometers begin to form within the nanopillars.

Significant structural changes occur after annealing the nanopillars at 500 °C (Fig. 2, *d*). Direct observation of nanocrystallites in HRTEM images is complicated by the carbon coating; nevertheless, the SAED patterns clearly indicate the presence of anatase. Compared to the 300 °C sample, the amorphous halo in the 500 °C diffraction pattern is substantially weakened, and the diffraction rings have “spotty” appearance. Such “spotty” ring appearance may indicate crystallite growth and a modest orientation spread; however, this interpretation could not be confirmed by HRTEM because direct lattice imaging was limited by the carbon coating on the FIB-prepared lamella.

During annealing at 800 °C, the most pronounced changes in the phase composition of TiO_2 occur. The SAED pattern of the sample annealed at 800 °C (Fig. 2, *e*) is characterized by the appearance of well-defined diffraction rings of significantly higher intensity, with distinct spot reflections, indicating an increased degree of crystallinity. The measured interplanar spacings suggest the coexistence of both anatase and rutile phases. Thus, at 800 °C the onset of the anatase-to-rutile phase transition is observed, which is consistent with literature data on the stability ranges of TiO_2 polymorphs [22]. It should be emphasized that the nanopillar morphology is preserved after crystallization.

Conclusion

Two-step anodization of the Al/TiN structure (1000 nm/250 nm) enables the formation of quasi-ordered arrays of vertically aligned TiO_2 nanopillars with a diameter of about 20 nm and a height of ~150 nm. In the as-prepared state, the nanopillars are amorphous. Annealing at 300 °C initiates their crystallization, while annealing at 500 °C results in crystallization into the anatase phase, with preservation of the nanostructured morphology. High-temperature treatment at 800 °C leads to grain growth and the coexistence of anatase and rutile phases, while the original nanopillar morphology is retained.

Crystallization of TiO_2 into the anatase phase at ~500 °C is important for achieving high photocatalytic activity under UV irradiation. This annealing temperature can be considered optimal for realizing UV-induced photocatalytic self-cleaning of the surface. In addition, TiO_2 nanopillars can serve as a 3D-scaffold for plasmonic nanoparticles [23], opening the possibility of creating hybrid SERS substrates that combine Raman signal enhancement with photocatalytic surface self-cleaning [24].

REFERENCES

1. **Armaković S.J., Savanović M.M., Armaković S.,** Titanium Dioxide as the Most Used Photocatalyst for Water Purification: An Overview, Catalysts. MDPI AG. 13 (1) (2022) 26.

2. **Jain A., Vaya D.,** Photocatalytic activity of TiO_2 nanomaterial, J. Chil. Chem. Soc. SciELO Agencia Nacional de Investigacion y Desarrollo (ANID).62 (4) (2017) 3683–3690.

3. **Ali I., et al.,** Recent advances in syntheses, properties and applications of TiO_2 nanostructures, RSC Adv. Royal Society of Chemistry (RSC). 8 (53) (2018) 30125–30147.

4. **Racovita A.D.,** Titanium Dioxide: Structure, Impact, and Toxicity, IJERPH. MDPI AG. 19 (9) (2022) 5681.

5. **Rempel A.A., et al.,** Titanium dioxide nanotubes: synthesis, structure, properties and applications, Russ. Chem. Rev. 90 (11) (2021). 1397–1414.

6. **Muscetta M., Russo D.,** Photocatalytic Applications in Wastewater and Air Treatment: A Patent Review (2010–2020), Catalysts. MDPI AG. 11 (7) (2021) 834.

7. **Gnida P., et al.,** Impact of TiO_2 Nanostructures on Dye-Sensitized Solar Cells Performance, Materials. MDPI AG. 14 (7) (2021). 1633.

8. **Ramanavicius S., Jagminas A., Ramanavicius A.,** Gas Sensors Based on Titanium Oxides (Review), Coatings. MDPI AG. 12 (5) (2022). 699.

9. **Kéri O., et al.,** Photocatalytic Crystalline and Amorphous TiO_2 Nanotubes Prepared by Electrospinning and Atomic Layer Deposition, Molecules. MDPI AG. 26 (19) (2021) 5917.

10. **Luttrell T., et al.,** Why is anatase a better photocatalyst than rutile - Model studies on epitaxial TiO_2 films, Sci Rep. Springer Science and Business Media LLC. 4 (1) (2014).

11. **Sachs M., et al.,** Evaluation of Surface State Mediated Charge Recombination in Anatase and Rutile TiO_2, J. Phys. Chem. Lett. American Chemical Society (ACS). 7 (19) (2016) 3742–3746.

12. **Ishigaki T., et al.,** Enhanced visible-light photocatalytic activity of anatase-rutile mixed-phase nano-size powder given by high-temperature heat treatment, R. Soc. open sci. The Royal Society. 7 (1) (2020) 191539.

13. **Zuo F., et al.,** Titanium Dioxide Nanomaterials: Progress in Synthesis and Application in Drug Delivery, Pharmaceutics. MDPI AG. 16 (9) (2024) 1214.

14. **Calabrese C., et al.,** Novel Sol-Gel Synthesis of TiO_2 Spherical Porous Nanoparticles Assemblies with Photocatalytic Activity, Nanomaterials. MDPI AG. 13 (13) (2023) 1928.

15. **Nassar M., et al.,** Efficient One-Pot Hydrothermal Synthesis of TiO_2 Nanostructures for Reactive Black 5 Dye Removal: Experimental and Theoretical Insights, Processes. MDPI AG. 12 (12) (2024) 2786.

16. **Savchuk T.P., et al.,** Synthesis and investigation of multifunctional TiO_2 photocatalysts modified by metal nanoparticles, Catalysis Communications. Elsevier BV. 187 (2024) 106907.

17. **Gavrilin I., et al.,** Differences in the local structure and composition of anodic TiO_2 nanotubes annealed in vacuum and air, Applied Surface Science. Elsevier BV. 516 (2020) 146120.

18. **Szaniawska-Białas E., et al.,** Recent Advances in Preparation, Modification, and Application of Free-Standing and Flow-Through Anodic TiO_2 Nanotube Membranes, Molecules. MDPI AG. 29 (23) (2024) 5638.

19. **Cao W., Chen K., Xue D.,** Highly Ordered TiO_2 Nanotube Arrays with Engineered Electrochemical Energy Storage Performances, Materials. MDPI AG. 14 (3) (2021) 510.

20. **Sjöström T., Fox N., Su B.,** Through-mask anodization of titania dot- and pillar-like nanostructures on bulk Ti substrates using a nanoporous anodic alumina mask, Nanotechnology. IOP Publishing. 20 (13) (2009) 135305.

21. **Chen P.-L., et al.,** Self-organized titanium oxide nanodot arrays by electrochemical anodization, Applied Physics Letters. AIP Publishing. 82 (17) (2003) 2796–2798.

22. **Hanaor D.A.H., Sorrell C.C.,** Review of the anatase to rutile phase transformation, J Mater Sci. Springer Science and Business Media LLC. 46 (4) (2010) 855–874.

23. **Grishin T.S., et al.,** Evolution of morphological parameters in self-assembled Ag nanoparticle arrays for high-performance SERS, Optical Materials. Elsevier BV. 167 (2025) 117260.

24. **Wu H.-Y., et al.,** Highly Sensitive, Robust, and Recyclable TiO_2/AgNP Substrate for SERS Detection, Molecules. MDPI AG. 27 (19) (2022) 6755.

THE AUTHORS

VOLKOVA Lidiya S.
lidiya.volkova.96@mail.ru
ORCID: 0000-0003-4860-0585

DUBKOV Sergey V.
sv.dubkov@gmail.com
ORCID: 0000-0003-1507-8807

GRISHIN Timofey S.
grishin.t@outlook.com
ORCID: 0000-0001-6261-5316

GROMOV Dmitry G.
gromadima@gmail.com
ORCID: 0000-0002-4563-9831

DUDIN Alexander A.
dudin.aa@outlook.com
ORCID: 0000-0001-7617-8815

GAVRILOV Sergey A.
rector@miet.ru
ORCID: 0000-0002-2967-272X

NAZARKINA Yulia V.
engvel@mail.ru
ORCID: 0000-0002-5200-9299

Received 15.09.2025. Approved after reviewing 17.11.2025. Accepted 17.11.2025.