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Variation of the Wettability of Cluster-Assembled TiO₂ Films under the Action of Annealing and Ultraviolet Irradiation

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We have studied the mechanism of the wettability variation of a special class of nanostructured coatings: cluster-assembled TiO₂ thin films (of 200 nm to 1 μm in thickness) under the action of high-temperature annealing and ultraviolet irradiation. Our results show that annealing of TiO₂ films in air (800 °C, 3 h) significantly decreases the contact angle from 83° even to zero because of the changes in structure (anatase-to-rutile phase transformation), surface chemistry (change of state Ti⁴⁺ → Ti³⁺) and surface morphology (recrystallization). Irreversible structure and morphology changes prevent the recovering of contact angles to their initial values with time. The same change in the TiO₂ contact angle due to the ultraviolet irradiation (wave-length is 365 nm, 7 h) is attributed to a radical change in the surface chemistry only. As opposite to the annealed coatings, the UV-irradiated ones restore their hydrophobic properties after being held in the dark for about 2 weeks. It was shown that the wettability of nanostructured films can be efficiently controlled using the different surface treatments, such as annealing and ultraviolet irradiation.

Key words: nanoscale materials, wettability control, annealing, ultraviolet irradiation.

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Introduction

Nanostructured coatings with controlled wettability are of interest for many applications, such as biocompatible coatings for medical implants, chemical and biosensors, high-capacity condensers in electrochemistry. In particular, nanostructured titanium dioxide (ns-TiO₂) has been commonly used for the production of photoelectrochemical cells, optical filters, chemical sensors and systems with enhanced catalytic activity [1]. Thin TiO₂ coatings are applied as automobile side view mirrors, window films, exterior tiles, highway road wall panels, as potential substances for solar energy conversion and environmental purification [2]. For these applications the film wettability plays a key role. The study of the chemical and morphological factors that influence on the wettability of solid films is very important in view of the production of surfaces with tailored properties and functions [3]. In previous papers [4-6] we have found that to tune the wettability of carbon materials, surface chemical treatments, such as the hydrogenation/oxidation of diamond polycrystalline films [4], or changes in composition by doping of metal-fullerene films [5, 6] may be used. In [7] we pointed out the critical influence of morphological parameters such

as surface roughness and pattern on the wetting properties of cluster-assembled carbon thin films. From these results it should be possible to control the wettability simply by controlling the surface morphology at a nanometric and micrometric scale, rather than by changing the chemical state of the surface. At last in [8] we have found that the wettability of nanostructured cluster-assembled titanium dioxide (ns-TiO₂) films can be controlled using surface treatment as annealing.

In the present work the comparative study of the effect of the annealing and ultraviolet irradiation on wettability as well as structure, surface morphology and chemical state of (ns-TiO₂) films had been performed. TiO₂ coatings were annealed in air in the temperature range from 100 to 800 °C with holding time of 3 hours at each temperature. For UV irradiation treatment (7 hours), we used the 365 nm wave-length radiation. X-ray photoelectron spectroscopy (XPS), Raman spectroscopy, atomic force microscopy (AFM) and contact angle measurements were used to evaluate of the solid surface properties. The contact angle measurements [3-10] is the most popular at present as a rather simple in experimental realization yet informative method. The method is extremely sensitive to the peculiarities of the structure and chemical state of the film surface.

I. Experiment

1. Obtaining of cluster-assembled TiO₂ films

The nanostructured TiO₂ thin films were produced using of supersonic cluster beam deposition technique (SCBD) allows the high-rate synthesis of cluster-assembled films with hierarchical organisation and properties controlled by mass and energy distribution of the clusters prior to deposition on Si substrate. The film deposition procedures have been described in detail in [1]. The cluster beam was generated in the microplasma source via ablation of titanium target by confined He plasma. The ejected particles condense to form clusters, which consequently expand through a nozzle into high vacuum to form the supersonic beam directed to the substrate. Typically a log-normal cluster mass distribution is obtained ranging from few tens of atoms per cluster up to several thousand, with an average size of 950 atoms/cluster. Beams depleted from large clusters (diameter ~ 2 nm) can be obtained by using an aerodynamical filter. As the kinetic energy of the clusters is below 0.4 eV, no fragmentation occurs upon impact on the surface.

2. Structure and morphology analysis

Micro Raman spectra were recorded at Laboratory of Nanocrystal Materials, Milan University, Italy. Micro Raman measurements have been carried out by a triple grating Jobin-Yvon T64000 spectrometer, equipped with a Nd: YAG laser (532 nm), and a microscope Olympus BX40. The surface morphology, roughness and thickness of the films have been determined by atomic force microscopy (Digital Instruments, Nanoscope IIIA). The film thickness varied from from 200 nm to 1 μm while the r.m.s. roughness was in the range of 3.4 –83 nm. AFM surface topographies illustrate that the roughness R increases with the film thickness. The films show a granular morphology, the smallest grains typical size being a few tens nanometres (the result of a cluster aggregation process).

3. Wetting measurements

The wettability of TiO₂ films with double-distilled water has been examined by the sessile-drop method [11]. The drop of 0.5-1 mm diameter was released from a tip of syringe on a sample surface. The advancing contact angles on the left and on the right of each drop were measured at 20 ± 1°C with an experimental system that includes a device for reading and analysis of the drop optical image. The accuracy of the contact angle measurements was within ±2°. We study wettability of the TiO₂ film surface after ultraviolet irradiation at λ = 365 nm for 7 hours and high-temperature annealing at a temperature of 800°C for 3 hours in air, and then after their storage in dark for 3 months.

II. Results and discussion

1. Wettability peculiarities of nanostructured TiO₂

film:effect of annealing

Investigation of the wettability of ns-TiO₂ films has shown, that as-deposited film has hydrophobic properties (fig. 1, curve 1). Besides, a clearly monotone dependence of the contact angle on the film thickness has been found. The variation of film thickness (and roughness, respectively) along the sample leads to an increase in the contact angle from 66 to 83° because the water contact angle strongly depended on roughness of the surface [7]. The unannealed ns-TiO₂ coatings exhibited the high stability to oxidation: the contact angles did not change after being held in the dark for 3 months (fig. 1, curve 2). Annealing the TiO₂ film in air (800°C, 3 h) decreases the

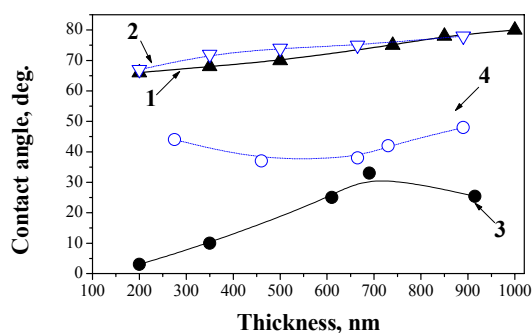


Fig. 1. Variation of the wettability of TiO₂ films caused by annealing: 1 – freshly prepared film; 2 – after storage in the dark for 3 months; 3 – annealed at 800 °C during 4 hours; 4 – after storage in the dark for 3 months after annealing.

contact angle from 83° even to zero (fig. 1, curve 3). The dependence of the contact angle on the film thickness has been observed too: when a water drop touches the thinnest region of the film, it spreads instantaneously ($\theta = 0^\circ$); then the contact angle increases from 0 to 34° with the thickness. When the annealed sample was stored in the dark for 3 months the θ value increased slowly (40–50°) with the storage time (fig. 1, curve 4). After annealing the irreversible structure and surface morphology changes prevent the recovering of contact angles to their initial values.

To explain the variation in wettability (see fig. 1) we used different surface analysis. We supposed, that the change in the wettability was attributed to a radical change in the surface chemistry and the structure due to the annealing. This is confirmed by the Raman spectroscopy, AFM and XPS data. Really, according to XPS data (fig. 2) at high temperature annealing the $Ti^{4+} \rightarrow Ti^{3+}$ transformation takes place. Chemical state of Ti was determined by the energetic position of Ti2p XPS spectra. Then the $Ti^{3+}(H_2O)_6$ complex forms easily, since Ti^{3+} is essentially more reactive than Ti^{4+} [12]. This causes the film better wettability with water and high hydrophilicity. Micro Raman spectra (fig. 3) of the heat-treated TiO₂ sample show the evolution of the TiO₂ phases. They indicate that only anatase peak 513 cm⁻¹ [13] is in the Raman spectra of as-deposited TiO₂ sample (see fig.

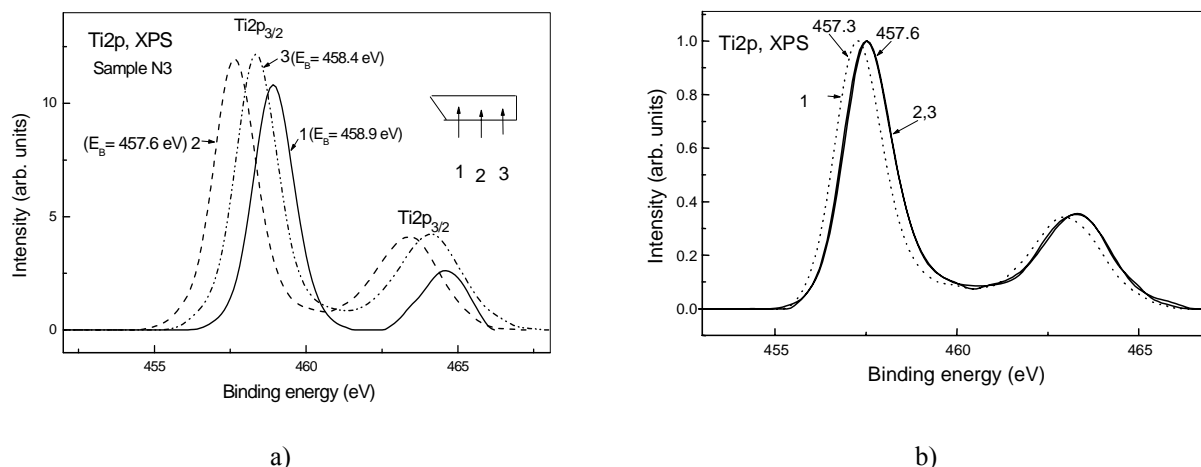


Fig. 2. Variation in the surface chemistry of the ns-TiO₂ film caused by annealing: (a) – XPS spectra of as-deposited TiO₂ films (1 – Ti⁴⁺ state; 2 – Ti³⁺ state; 3 – Ti⁴⁺ state). The sample thickness increases along the samples from point 1 to point 3; (b) – XPS spectra of annealed TiO₂ sample (we can see only Ti³⁺ state). Ti⁴⁺ → Ti³⁺ transformation due to annealing of TiO₂ film has been found.

3 a), whereas four peaks at 143, 239, 447 and 612 cm⁻¹ that revealed rutile phases [13] are observed after annealing (see fig. 3 b). The phase transformation anatase-to-rutile takes place upon annealing above 750 °C [13], which leads to changes in the surface chemistry and morphology of the sample. Really, an essential decrease of the wetting angle of the TiO₂ film

recovery of the wetting properties of the TiO₂ film after its storage in the dark is connected with the reversible surface chemical state changes only, which is attributed to the air oxygen substitution for chemisorbed OH-groups [14]. This process proceeds quicker for the thin region of the sample.

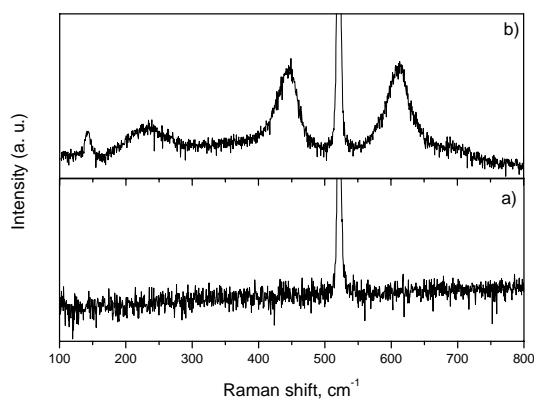


Fig. 3. Raman spectrum of nanostructured TiO₂ films before (a) and after (b) post deposition annealing.

after its annealing is supported the surface rearrangement, which affects on wettability too. AFM images presented at fig. 4 show the change in the surface topography of the analyzed sample caused by annealing. The AFM image (fig. 4 b) shows well-oriented crystalline structure for annealed sample. After the ns-TiO₂ sample was stored in dark for 3 months, the contact angle increased slowly (fig.1, curve 4) due to reverse transformation Ti⁴⁺ → Ti³⁺ which was occurred, presumably. But irreversible structure and morphology changes prevent the recovering of contact angles to their initial values (fig. 1, curve 1). An a partial gradual

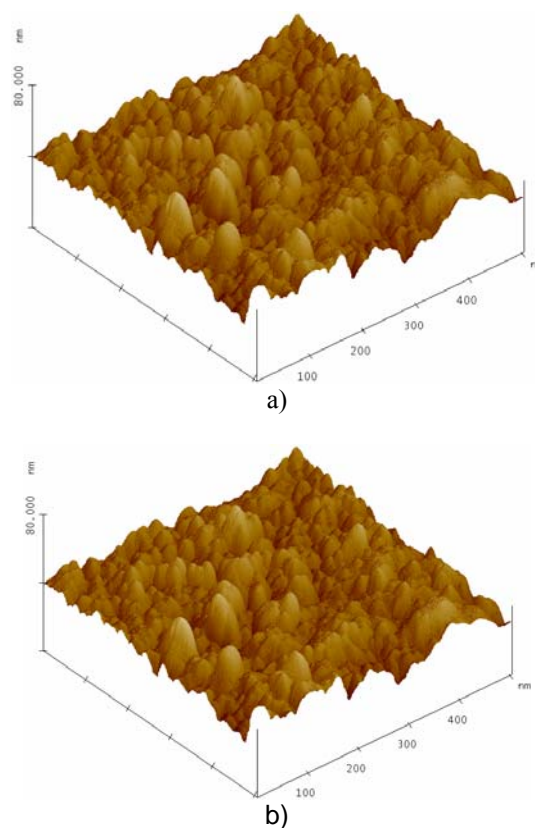


Fig. 4. Variation of the surface topography of ns-TiO₂ film caused by annealing: (a) – as-deposited film; (b) – annealed at 800°C during 3 hours.

2. Wettability peculiarities of nanostructured TiO₂ film: effect of uv-irradiation

The UV illumination causes the same change of hydrophobic-hydrophilic properties (fig. 5), but it might be attributable to a radical change in the surface chemistry only, without the phase transformation. Raman spectra (not shown here) did not show any changes after the UV irradiation of TiO₂. According to [12] the created Ti³⁺ defect sites are healed by the UV illumination via the adsorption of the hydroxyls of dissociated water that coexist additionally with the adsorbed molecular water. Adsorption of dissociated water on the surface and appearance of the active OH- groups improve the wettability [14]. An essential increase of the water contact angle of the TiO₂ film after its storage in the dark is attributed to the air oxygen substitution for chemisorbed OH-groups. So, as opposed to the annealed coatings, the UV-illuminated coatings completely restore their hydrophobic properties after being held in the dark for about 2-5 h due to gradual water desorption. The observed hydrophobic-hydrophilic conversion due to the UV irradiation is a repeated process, because only a reversible surface chemical change takes place. The process of the TiO₂ surface wettability conversion can be repeated at subsequent film irradiations (fig. 5).

III. Conclusions

1. The wettability of the ns-TiO₂ film significantly increases after annealing in air (800°C, 3 h) and UV irradiation ($\lambda = 365$ nm; 7 h): the θ value reduces from 83° to 34° for thick (1 μ m) films and even to zero angle for thin (200 nm) films.
2. The annealing influence is assumed to be, in a part, due to the phase transformation anatase-to-rutile in nanophase TiO₂ according to Raman spectra, surface

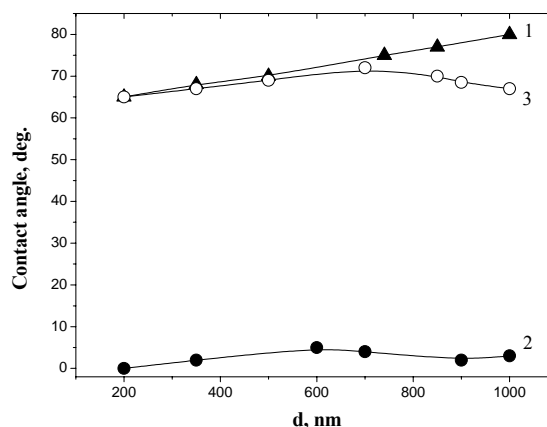


Fig. 5. Variation of the wettability of TiO₂ films caused by UV irradiation: 1 – freshly prepared film; 2 – irradiated by UV ($\lambda = 365$ nm) during 7 hours; 3 – after storage in the dark for 3 months after irradiation.

morphology modification as evidenced by AFM images, and by the surface chemistry changes (Ti⁴⁺ → Ti³⁺) as revealed by XPS.

3. The observed hydrophobic-hydrophilic conversion, induced by UV-irradiation, can be understood in terms of TiO₂ surface chemistry changes only (adsorption of the hydroxyls and then the air oxygen substitution for chemisorbed OH-groups after storage in the dark).

4. As the surface state can be controlled by the different surface treatments (high-temperature annealing or UV-irradiation), the possibility is open to vary the wettability of a broad class of cluster-assembled coatings.

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Зміни змочування кластерних плівок TiO_2 при відпалі та ультрафіолетовому опроміненні

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В роботі вивчалися механізми зміни змочуваності тонких плівок (200 нм – 1 мкм) нанокластерного діоксиду титану під дією термовідпалу та ультрафіолетового опромінення. Встановлено, що відпал TiO_2 на повітрі (800°, 3 год) істотно зменшує (від 83° до нульового значення) кут змочування плівок дистильованою водою. Це відбувається внаслідок зміни структури (фазове перетворення анафаз-рутіл), хімії (зміна стану $\text{Ti}^{4+} \rightarrow \text{Ti}^{3+}$) та морфології (рекристалізація) поверхні плівки. Безповоротні зміни структури та морфології поверхні при відпалі перешкоджають відновленню з часом значень кутів змочування до вихідних. Змочуваність плівок TiO_2 можна також ефективно змінювати шляхом ультрафіолетового опромінення ($\lambda = 365$ нм, 7 год) але за іншим механізмом, за рахунок оборотніх змін тільки хімічного стану поверхні. Тому, на відміну від відпалу, кути змочування опромінених плівок при витримці в темряві швидко повністю відновлюються. Показана можливість спрямованого керування змочуваністю нанокластерних плівок, що є важливим для їх багатьох застосувань.