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Effect of substrate type on nanostructured titania sol–gel coatings for sensors applications

Ljubica M. Nikolić*, Ljijana Radonjić, Vladimir V. Srdić

Department of Materials Engineering, Faculty of Technology, University of Novi Sad, Bul. Cara Lazara 1,
21000 Novi Sad, Serbia and Montenegro

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Abstract

Titania coatings were obtained by the sol–gel method, starting from stable and transparent titania sol. Thin titania coatings were deposited onto different substrates: quartz glass, single crystal quartz (1 0 1), single crystal Si(1 0 0) and alumina. Effect of substrate type and heat treatment conditions on important characteristics determining the sensing properties were studied. Nanostructured titania coatings with grain size up to 50 nm and thickness less than 1 μm were obtained on all substrates, but their phase composition depends on substrate type. The slightly orientation of titania coatings as well as the interactions between titania coating and alumina and silicon single crystal were observed.

Keywords: A. Films; A. Sol–gel processes; D. TiO_2; E. Sensors; E. Substrates

1. Introduction

Semiconducting metal oxide gas sensors, based on thin In_2O_3, SnO_2, CdO or TiO_2 coatings, have been extensively investigated due to their broad application in very important areas such as different manufacturing process control, monitoring of toxic and combustible gases, manufacturing safety, etc. [1,2]. New opportunities in sensor technology have been opened recently by development of nanosized metal oxide coatings, as their sensing properties are considerably improved compared to the coarse-grained structures [3]. Nanocrystalline titanias with excellent properties (electrical, dielectrical, optical, etc.), are very promising materials for gas sensing arrays. Titania has three polymorphs: brookite (orthorhombic), anatase and rutile (both tetragonal). Since rutile is the most stable phase, previous fundamental as well as applied researches were centered on this titania phase and the electronic properties of anatase were previously ignored. However, for many applications, anatase displays even more interesting properties and performances, quite different from rutile phase. Thus, Tang et al. [4] were shown that anatase thin coatings at relatively low temperatures ($350\ ^\circ C < T < 400\ ^\circ C$) have better sensing properties to some gases than rutile. It is also shown [5] that composite mixtures of anatase (exhibiting n-type semiconducting properties) and rutile (exhibiting p-type semiconducting properties) behave as a percolating system, with n-type behavior for samples containing less than 75% rutile and p-type behavior for pure rutile, which is also very interesting from the application point of view. Now it is well known that the sensing properties (sensitivity, response time) of titania coatings depend on titania crystalline phase type, their structural characteristics (such as average grain size) and coating thickness. These are the reasons why many researches [6,7] attempted to control the anatase → rutile transition and to understand the relationship between the coating microstructure and sensing properties. The properties of titania coating sensors could be controlled by doping (which modifies the carrier concentration and mobility) and microstructural changes, but also with selecting the appropriate substrate as it could have strong influence on coating microstructure. It is important to note that even many researches groups were used different substrates, such

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* Corresponding author. Fax: +381 21 450 413.
E-mail address: ljunik@uns.ns.ac.yu (L.M. Nikolić).

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are: alumina [8,9], silicon single crystal [10,11], various type of glass [12–15] etc., there is no systematic investigation of their effect on the structure of obtained titania coating.

The aim of this study is to investigate effect of substrate type and heating conditions on the nanostructured titania coating suitable for sensing arrays. This investigation was undertaken in order to elucidate effects of substrate type on: (a) phase transformations of nanostructured titania coatings, (b) interactions between titania coating and substrates and (c) formation of oriented titania coatings.

2. Experimental

Titania coatings were obtained by sol–gel method, started from stable and transparent titania sols. These sols were prepared from titanium-butoxide ($Ti(OC_4H_9)_4$ from Fluka, Switzerland) as raw material, isobutanol as a solvent and diethanolamine (DEA) as chelating agent. As titanium-alkoxide is very reactive in water solution, chelating agent DEA was used to control the degree of hydrolysis and subsequent polycondenstion reactions [16] and provide coatings of high quality. Titania sol was prepared by slowly adding water/isobutanol solution to the mixture of titanium-alkoxide, isobutanol and DEA, under vigorous stirring, according to the procedure proposed in earlier work [16]. The final molar ratio of starting materials in the titania sol was $Ti(OC_4H_9)_4$:H_2O:isobutanol:DEA = 1:2:5:1 and pH value about 6. The titania sol for coatings was deposited by dip coating technique on various substrates (quartz glass, quartz (1 0 1) single crystal, silicon (1 0 0) single crystal and polycrystalline α-alumina) with withdrawal speed of 0.02 cm/s. Before coating, all substrates were carefully cleaned on specific way, depending on substrate type. Titania gel coatings, obtained on this way, were subjected to heat treatment at 500 °C for 10 min. This procedure was repeated five times and after that, all samples were heat treated at temperatures between 510 and 700 °C for different times.

Titania coatings were characterized by X-ray diffraction, measured with a Siemens D 5000 instrument using Ni filtered Cu Kα radiation. The XRD data were recorded with a step size of 0.05 ° and a collection mode of 8 s/step. The rutile mass fraction, X_R (as well as anatase), was estimated from following expression [17]:

$$X_R = \frac{1}{1 + 1.26\frac{I_A}{I_R}} \tag{1}$$

where I_A and I_R are relative intensities of the anatase (1 0 1) peak at 2θ = 25.4° and the rutile (1 1 0) peak at 27.5°, respectively. The average grain size of anatase and rutile in titania coatings was estimated from the broadening of characteristic X-ray peaks by Scherrer's formula [18]:

$$d = \frac{0.94\lambda}{\beta\cos\theta} \tag{2}$$

where d is crystallite size; λ, wavelength of X-ray radiation; θ, diffraction angle and β, line width at half maximum height, after subtraction of instrumental broadening. The surface, cross section, structure and average grain size of the coatings were performed using scanning electron microscope (JEOL 6460LV) and high-resolution scanning electron microscope, HRSEM (Philips XS 30).

3. Results and disscusions

3.1. Nanostructure of titania coating

HRSEM micrographs of titania coating on different substrates heat treated at 560 °C, for 7 h are shown in Fig. 1. Micrographs of the sample cross sections indicate that all coatings have well adherence to the substrate, uniform thickness less than 1 μm and fine grain structure with grain size less than 50 nm. The grain size distributions in titania coatings are obtained from HRSEM micrographs (Fig. 2), showing (Table 1) that grain sizes are in range from 15 to 25 nm in coatings heat treated at 560 °C and from 25 to 45 nm in samples heat treated at 660 °C. The average grain sizes estimated by the XRD line broadening, also given in Table 1, are very close to the values obtained from HRSEM micrographs.

3.2. Phase transformation of titania coatings

X-ray diffraction was used for crystal phase identification and estimation of anatase-to-rutile ratio and the average

Table 1
The average grain size (d_a: anatase, d_r: rutile) estimated from XRD data and HRSEM micrographs (d); and mass fractions of anatase (X_a) in titania coatings on various substrates after different heat treatment

Sample notation	Heat treatment conditions							
	560 °C for 7 h				660 °C for 5 h			
	d_a (nm)	d_r (nm)	d_{SEM} (nm)	X_a (mass%)	d_a (nm)	d_r (nm)	d_{SEM} (nm)	X_a (mass%)
TDKS	18		20	100	24	45	45	67
TDKM	17		22	~90	24	41	40	66
TDSM	27	41	30	52		41	40	0
TDA	25		25	93	29	40	35	32

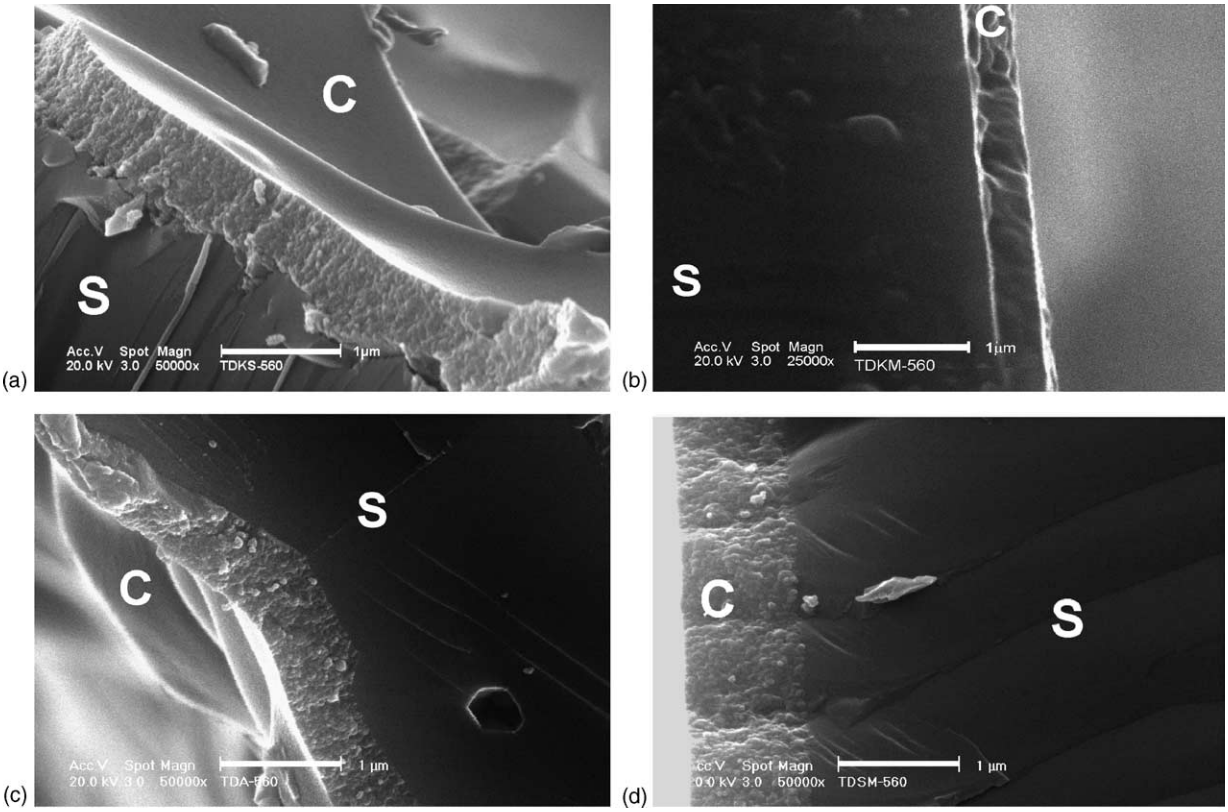

Fig. 1. HRSEM micrographs of titania coating after heat treatment at 560 °C, for 7 h on different substrates: (a) quartz glass, (b) single crystal quartz, (c) alumina and (d) single crystal silicon (C: coating, S: substrate) (bar = 1 μm).

grain size. In the case of titania coatings on crystalline substrates, especially on alumina, crystal phase identification was quite difficult due to overlapping of the anatase, rutile and substrate diffraction peaks (Fig. 3). Fig. 3a shows that the titania coating on quartz glass (TDKS) after heating at 560 °C for 7 h is single phase anatase. However, the titania coatings on alumina (TDA) and quartz single crystal (TDKM) besides peaks of anatase, consist of slightly peaks of rutile phase, Fig. 3b and d. The titania coating on the silicon single crystal (TDSM) consists of anatase and rutile too, but characteristic peak from rutile is stronger than those from anatase, Fig. 3c. By increasing the temperature of heat treatment to 660 °C for 5 h, it is apparently that on all substrates anatase transforms to rutile, Fig. 3. The titania coatings on quartz glass, quartz single crystal and on alumina, consist of mixture of anatase and rutile phases, while the titania coating on the single crystal Si is pure rutile. According to the XRD results (Fig. 3) and the fractions of rutile and anatase, estimated from XRD (Table 1), it is obvious that the phase transformation rate of titania coatings depend on the substrate type. The phase transformation rate of noncrystalline titania is the lowest on quartz glass and quartz single crystal, higher on alumina and the highest on silicon single crystal. The observed differences could be due to substrate structure effects (as substrate surface offers sites for heterogeneous nucleation) and mismatch of thermal

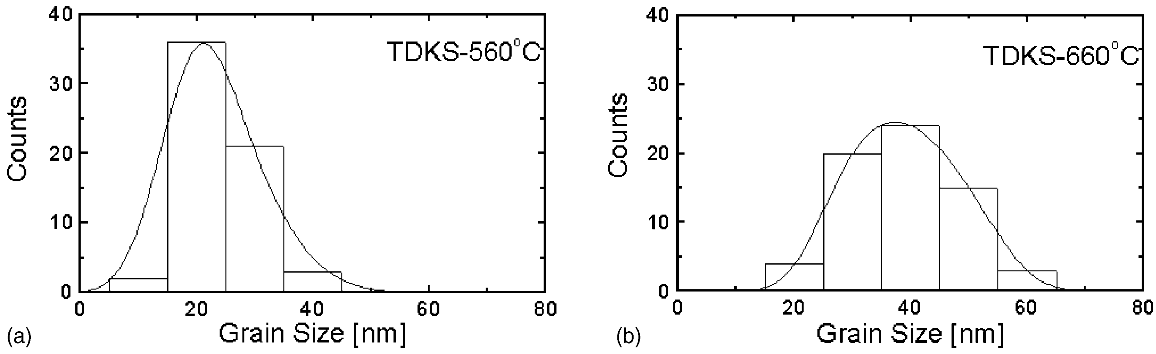

Fig. 2. Grain size distribution in anatase coating on quartz glass after heat treatment at: (a) 560 °C, for 7 h and (b) 660 °C, for 5 h.

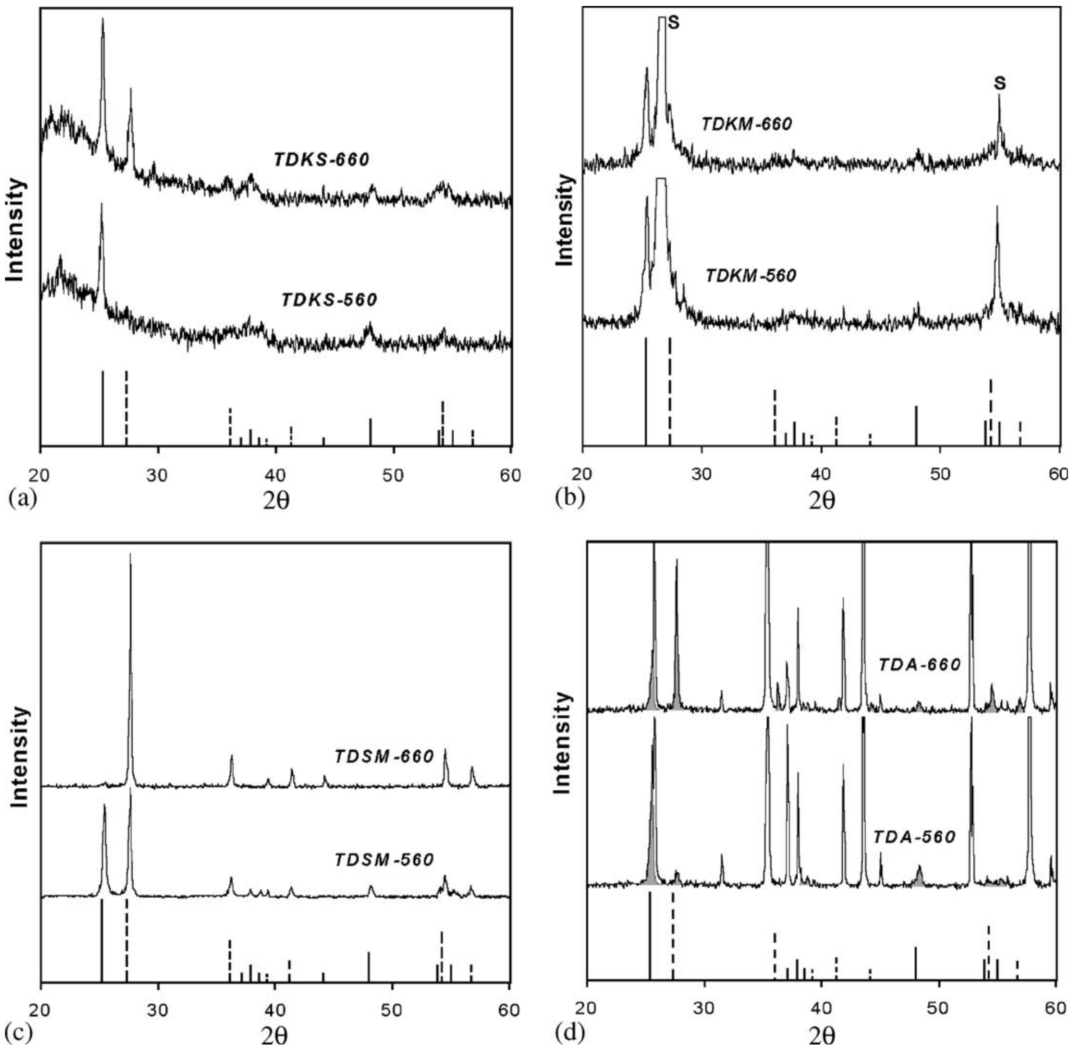

Fig. 3. XRD results of titania coatings after heat treatment at 560 °C for 7 h and 660 °C for 5 h on: (a) quartz glass, TDKS, (b) single crystal quartz, TDKM, (c) single crystal Si TDSM, and (d) alumina, TDA, (S: substrate; solid and dash vertical lines represent data from JCPDS cards no. 21-1272 for anatase and no. 21-1276 for rutile, respectively).

expansion coefficients (CTE) between titania coating and substrate [19,20], since coatings on all substrates were obtained under the same conditions.

3.3. The interaction of titania coating and substrates

Two kinds of interactions: one between titania coatings and alumina substrate and the other between titania coatings and single crystal Si with (1 0 0) orientation have been observed. In the case of the titania coating on alumina it is important to note that the alumina substrate has polyphase nature, since its XRD pattern consists of characteristic α-alumina and spinel ($MgAl_2O_4$) peaks [21] and probably has glass phase on alumina grain boundaries [22]. In Fig. 4 two very narrow ranges of diffraction angles, 2θ between 25 and 26° and 36 and 39°, are presented. The alumina diffraction peaks (designated by A: α-alumina and SP: spinel) are shifting towards higher diffraction angles, after coating,

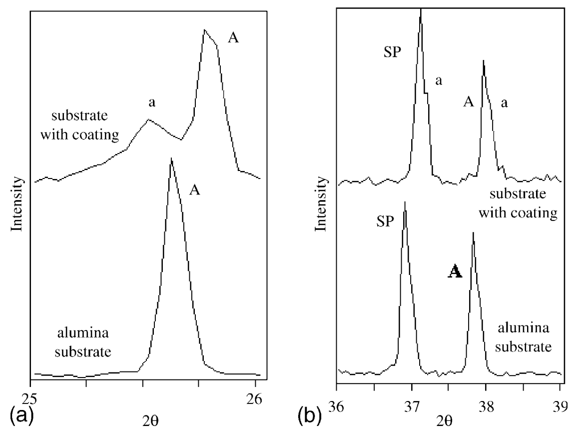

Fig. 4. XRD results of alumina substrate without coating and with titania coating, after heat treatment at 560 °C for 7 h, for range of diffraction angles 2θ: (a) 25–26° and (b) 36–39° (A: alumina, SP: spinel, a: anatase).

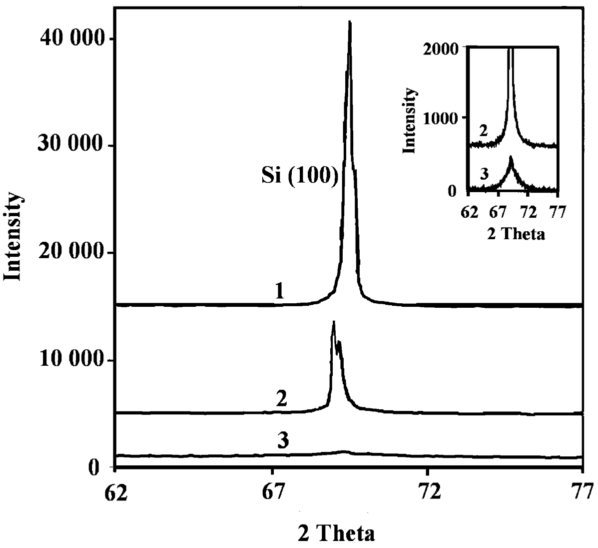

Fig. 5. Diffraction peak of single crystal Si(1 0 0). Pattern 1: without coating; pattern 2: with titania coating after heat treated at 560 °C for 7 h; and pattern 3: with titania coating after heat treated at 660 °C for 5 h.

in respect to the pure alumina substrate, indicating compression stress on coated alumina surface. In addition, anatase diffraction peaks appear at higher diffraction angles than in the corresponding JCPDS card (no. 21-1272), what means that compression stress is present in anatase coating, too.

X-ray diffraction also indicates interaction between titania coating and single crystal Si(1 0 0). As it is obvious from Fig. 5, characteristic peak of single crystal Si(1 0 0), at 2θ about 69.5° (pattern 1) decreases in intensity after deposition of titania coating and heating at 560 °C for 7 h. In the same time diffraction peak of the single crystal Si is splitting and shifting to the smaller diffraction angles. Increasing the heat treatment temperature to 660 °C for 5 h leads to further rapid decreasing of the peak intensity, Fig. 5. Mechanism of this interaction between titania coating and single crystal silicon is not clear, but there are several possible explanations. The most probably explanation is described below. Titania coating was obtained by heat treatment of gel-coating, which was prepared from very reactive titania sol. During heat treatment of the gel-coating under atmospheric conditions, oxygen diffuses through coating to the substrate surface and with the substrate atoms a thin silica interfacial interlayer is formed. In addition, as titania is soluble in silica (up to 11.5%) [23], it is expected that Ti^{4+} ions could replace Si^{4+} ions in silica tetrahedron. The difference in ion radii of Ti^{4+} (0.68 nm) and Si^{4+} (0.41 nm) leads to the silica network distortion and appearance of tensile stress on the substrate surface.

3.4. The orientation of titania coatings

The position and intensities of the diffraction peaks from titania coatings and the powder diffraction peaks (according to the JCPDS cards no. 21-1272 for anatase and no. 21-1276 for rutile) are compared. In all coatings anatase (1 0 1) or/and rutile (1 1 0) reflection is the most intense peak (Fig. 3), with a relative intensity higher than the corresponding one for the powder with randomly oriented crystallites (JCPDS card). The degree of orientation was estimated using the Lotgering orientation factor, f, which is defined as [10,24]:

$$f = \frac{P - P_0}{1 - P_0} \qquad (3)$$

The values of P and P_0 were calculated as the ratio of intensity of the anatase (1 0 1) (or rutile (1 1 0)) peak to the sum of intensities of all anatase (or rutile) peaks corresponding to measured XRD (value P) and JCPDS card (value P_0). Orientation of titania coating is very expressed on the single crystal silicon. Anatase is oriented along [1 0 1] direction with the orientation factor of 0.4 (Table 2) in the coating heat treated at 560 °C. After increasing heat treatment temperature to 660 °C, Fig. 3c, on the same substrate, anatase is completely transformed to rutile with significant orientation along the [1 1 0] direction with orientation factor f = 0.5. Orientation is also visible on other substrates (Fig. 3 and Table 2). It is well known [20] that the orientation of the crystalline coating can result from the similarity between the structure of the substrate and that of the crystal phase in the coating. However, the orientation could appear also in the case when the surface structure of substrate forces the growth of the nuclei with the specific orientation, whereas prevent nucleation of other orientations. The orientation of anatase in [1 0 1] direction and rutile in [1 1 0] direction is already mentioned in literature [25,26], and is explained with fact that the crystal plane with the lowest Gibbs free energy will grow preferentially.

Table 2
The values of orientation factor, f, of anatase and rutile in titania coatings on all studied substrates, after the same heat treatment

Sample notation	Heat treatment conditions			
	560 °C for 7 h		660 °C for 5 h	
	f anatase [1 0 1]	f rutile [1 1 0]	f anatase [1 0 1]	f rutile [1 1 0]
TDKS	0.1	–	0.3	0.3
TDKM	0.4	–[a]	0.4	–[a]
TDSM	0.4	0.4	–	0.5
TDA	0.4	–[a]	0.2	0.4

[a] Due to very low peak intensities results are unreliable.

4. Conclusions

Titania coatings on different substrates (quartz glass, quartz single crystal, silicon single crystal and alumina) were obtained by sol–gel method, started from stable and transparent titania sol. All coatings have well adherence to the substrate, uniform thickness less than 1 μm and fine grain structure with grain size less than 50 nm. It is shown that the transformation of noncrystalline titania coating to anatase and its stability depend on substrate type. The phase transformation rate of noncrystalline titania is the lowest on quartz glass and single crystal quartz, higher on alumina and the highest on single crystal silicon. The orientation of titania coatings as well as the interactions between titania coating and alumina and silicon single crystal were observed.

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