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Influence of nanocrystalline structure and composition on hardness of thin films based on TiO_2

Research Article

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Abstract: In this work, the influence of Tb-doping on structure, and especially hardness of nanocrystalline TiO_2 thin films, has been described. Thin films were formed by a high-energy reactive magnetron sputtering process in a pure oxygen atmosphere. Undoped TiO_2-matrix and TiO_2:Tb (2 at. % and 2.6 at. %) thin films, had rutile structure with crystallite sizes below 10 nm. The high-energy process produces nanocrystalline, homogenous films with a dense and close packed structure, that were confirmed by X-ray diffraction patterns and micrographs from a scanning electron microscope. Investigation of thin film hardness was performed with the aid of a nanoindentation technique. Results of measurements have shown that the hardness of all manufactured nanocrystalline films is above 10 GPa. In the case of undoped TiO_2 matrix, the highest hardness value was obtained (14.3 GPa), while doping with terbium results in hardness decreasing down to 12.7 GPa and 10.8 GPa for TiO_2:(2 at. % Tb) and TiO_2:(2.6 at. % Tb) thin films, respectively. Incorporation of terbium into TiO_2-matrix also allows modification of the elastic properties of the films.

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Keywords: hardness • TiO_2 • thin film • terbium • nanocrystalline

1. Introduction

Application areas of nanocrystalline materials are increasing nowadays due to the new properties the structure allows in comparison with standard coatings. Presently, thin films are being applied as different hydrophilic [1] or hydrophobic coatings [2], optical filters [3], antireflection coatings [4], or protective films [5]. The possible application of manufactured films in commercially accessible products depends on the durability of produced coatings, which in turn, is considerably dependent on their hardness [6]. The newest examples in the literature, describe nanocrystalline films as having a higher hardness value when compared to standard coatings [7].

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In this work, analysis of structural properties of transparent and nanocrystalline TiO_2 thin films doped with Tb, and comparisons of their hardness, have been outlined. Titanium dioxide is a well known material, which has a lot of applications in the coating industry. It exists in three different forms – brookite, anatase, and rutile, but only anatase and rutile are useful from a technological point of view. Anatase is a thermodynamically non-stable form of TiO_2, which has high sensitivity for different external factors [8, 9], and high photocatalytic activity [8, 10]. Rutile is a thermodynamically stable form which can be obtained after annealing the anatase above 750°C. It has lower sensitivity and photocatalytic activity as-compared to anatase, but, it is a temperature stable form. It has a denser structure and higher resistance to environmental hazards than anatase [8, 10, 11].

Properties of TiO_2 thin films can be modified by a change of deposition process parameters, or by doping with different elements e.g. lanthanides [12–14]. Thin films described in this work have been formed by using a high energy reactive magnetron sputtering process [14, 15]. In previous works, authors have revealed that the high energy sputtering process gives opportunity to manufacture nanocrystalline, homogenous, and dense packed films [14]. In the case of undoped TiO_2-matrix, directly after deposition nanocrystalline rutile structure was observed. Incorporation of terbium atoms into the rutile matrix, results in densification of the structure and an increase of photocatalytic properties, as described earlier by authors [14]. In this work, the hardness of transparent TiO_2 thin films doped with different amounts of Tb, was described. The hardness of all manufactured thin films was above 10 GPa which is much higher in comparison to soda-lime glass (5 GPa) [16], allowing it to be used for self-cleaning and antireflection coatings.

2. Experimental

Nanocrystalline thin films were manufactured by a high-energy reactive magnetron sputtering process (HE RMS) [12–15]. It is well known that the initial growth of the structure is dependent on the energy of condensing particles at the place of the thin film formation. For the TiO_2-rutile structure, higher energy per nucleus during deposition must be delivered. The HE RMS process is a so called 'hot target' type, where some modifications were introduced. First, an enhancement of target temperature close to its melting point was applied [15, 17]. The collisions of additional 'hot' electrons, thermo-emitted from the target, with neutral oxygen atoms at its outer boundary, allow an increase of plasma density. To avoid overheating the target, the power was applied in pulses by a magnetron power supply working in the unipolar mode with pulses of 165 kHz sinusoidal, and 1.6 kHz, grouped together. Additionally, deposition was carried out under low oxygen pressure (0.1 Pa) using pure Ti and mosaic Ti-Tb targets. The main advantage of low pressure is a longer mean free path that allows oxygen ions to bombard the surface with higher energy. An additional advantage is the absence of the argon ions, and elimination of collisions which cause variations in the paths of sputtered material particles on their way between the target and the substrate. Thanks to that, the energy of the process was increased from tens (for conventional magnetron sputtering) to hundreds of eV. In the HE RMS method, an increase in the energy of ions that sputter the target and impart sufficient energy to the nucleus from the oxygen ions reaching the substrate, allow a nucleation of TiO_2 thin films, in the rutile form, directly during deposition.

For hardness measurements, undoped TiO_2, TiO_2:(2 at. % Tb) and TiO_2:(2.6 at. % Tb) thin films have been selected. The amount of Tb-dopant in the nanocrystalline matrix was determined by energy dispersive spectroscopy.

Structural investigation was performed with the aid of an X-ray diffraction (XRD) method. Measurements were performed by a Dron-2 powder diffractometer. The parameters of thin film structures were recorded with the aid of RTG software. Based on XRD patterns, average crystallites of size D were estimated in accordance with the Scherrer formula. Analysis of structural properties was extended by measurements of hardness (H) and elastic modulus (E). For measurements, a Hysitron nanoindenter with Triboscope head was used. Thin films were measured at room temperature and in ambient air. For nanoindentation, a 2 mN force was used, which was equivalent to the physical thickness of examined films. Presented values of hardness and elastic modulus were averaged from 10 tests for each sample.

High optical quality, mirror-like facets, of the examined nanocrystalline films on silicon substrates were obtained by precise scribing with a diamond tip, followed by a cleaving process. Furthermore, a sample cross-section was examined with a Hitachi S-4700 scanning electron microscope (SEM) tool, working in ultra high resolution mode. No additional sputtering of a thin conductive layer, e.g. 20 nm of Au/Pd film, was provided before the SEM observations. A high contrast of SEM micrographs was achieved, which may be caused by antistatic properties related to nanocrystalline TiO_2 films [18]. Based on SEM images, analysis of thin film structures and determination of their physical thickness were carried out.

3. Results and discussion

Structural investigation has shown that all examined thin films had nanocrystalline TiO_2-rutile structure. Doping with terbium results in the decreasing of crystallite sizes, D, from 8.7 to 6.6 nm for undoped TiO_2 and Tb doped films, respectively. Thanks to the application of the high energy sputtering process, directly after deposition nanocrystalline films with TiO_2-rutile structure were obtained [14]. Moreover, incorporation of Tb-dopant into TiO_2 results in densification of the rutile structure. In Table 1, structural parameters of manufactured thin films with their thicknesses have been collected. Thickness of thin films was determined based on optical transmission and reflection measurements. Received results were confirmed by analysis of SEM cross-section images. Thickness of pure TiO_2 matrix was 377 nm, while for nanocrystalline films doped with 2 at. % and 2.6 at. % of Tb the thickness was 522 nm and 582 nm, respectively. In Fig. 1, SEM cross-section images of TiO_2 thin films doped with different amounts of Tb have been presented. Images have confirmed that all examined thin films were nanocrystalline and homogenous with dense packed grains. It can also be seen that all films have column structure. Decrease of column sizes was observed based on recorded images due to incorporation of Tb-dopant into TiO_2-rutile matrix. This confirms densification of TiO_2-rutile structure by Tb-doping, the observation based on results of X-ray diffraction and atomic force microscopy [14].

Table 1. Structural parameters of TiO_2 thin films doped with Tb.

Thin film	Amount of Tb dopant (at. %)	Phase	Crystallites size D (nm)	Thickness (nm)
TiO_2	-	rutile	8.7	377
TiO_2:Tb	2		6.6	522
	2.6		6.6	585

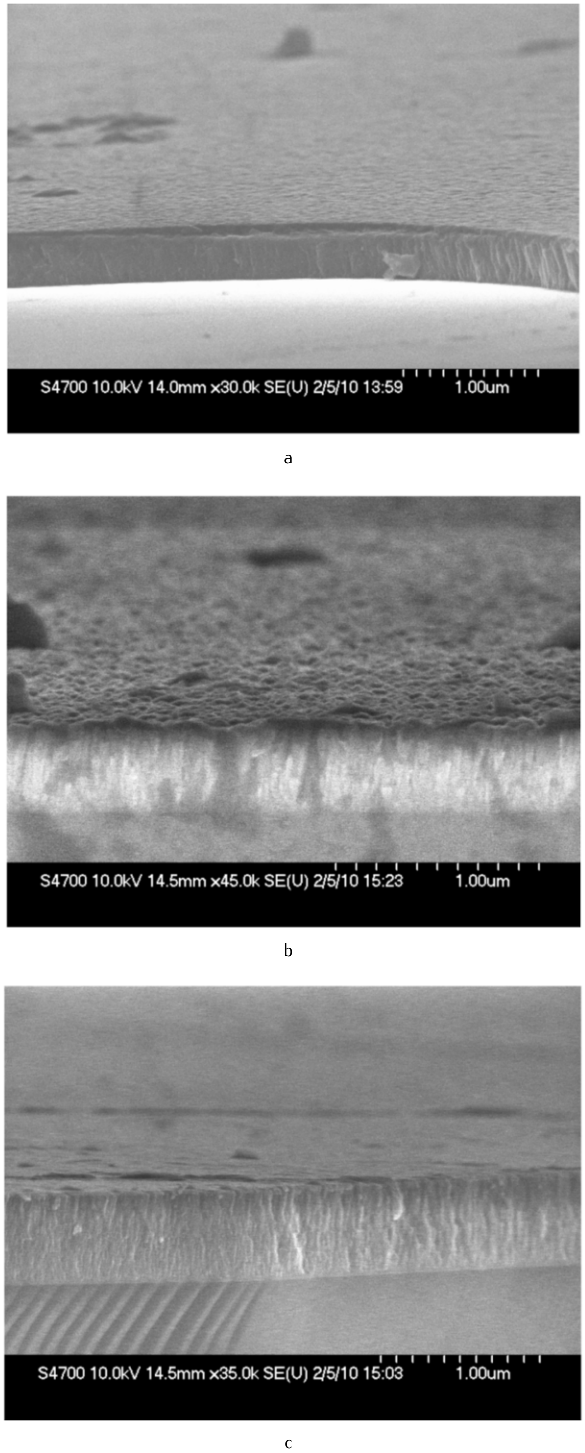

Figure 1. SEM micrographs of a) TiO_2, b) TiO_2:Tb (2 at. %) and c) TiO_2:Tb (2.6 at. %) nanocrystalline thin films as-deposited on Si (100) substrates.

In Figs. 2 and 3, the influence of Tb-dopant quantity on hardness and elastic modulus of as deposited nanocrystalline TiO_2 thin films, have been presented, respectively. Nanoindentation has shown that all manufactured nanocrystalline films had high hardness. The hardness of undoped TiO_2 with rutile structure was the highest (H = 14.3 GPa) when compared to thin films doped with terbium. Incorporation of 2 at. % of Tb-dopant into TiO_2-rutile matrix during sputtering, results in a 15% decrease of hardness (down to 12.7 GPa). Increase in quantity of terbium dopant, up to 2.6 at. %, gives a 30% decrease of hardness value (H = 10.8 GPa) as compared to undoped TiO_2. In the case of elastic properties, received values were higher as compared to standard TiO_2 coatings. Elastic modulus E, similar to hardness, was dependent on the amount of terbium in the matrix. Doping with 2 at. % of Tb results in 5% decrease of elastic modulus from 167.3 GPa down to 160.3 GPa, while increase of Tb dopant up to 2.6 at. % gives an effective increase of elastic modulus up to 175.9 GPa. It is 10% higher as compared to undoped TiO_2. For measurements at 2 mN, maximum force was used, which was equivalent to the measurements being executed without influence on the substrate, because contact depth was lower than 10% of the film thickness. Results of all measurements have shown that the contact depth was higher for the films with lower hardness. Parameters obtained from nanoindentation of thin films have been collected in Table 2.

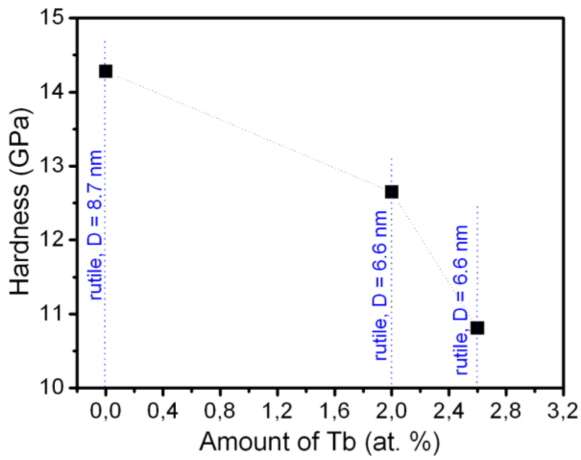

Figure 2. Influence of Tb-dopant amount on hardness of nanocrystalline TiO_2 thin films.

Table 2. Nanoindentation results of TiO_2 thin films doped with Tb.

Thin film	Amount of Tb dopant (at. %)	Phase	Maximum force F_m (mN)	Contact depth CD (nm)	Elastic modulus E (GPa)	Hardness H (GPa)
TiO_2	-	rutile	2	25.3	167.3	14.3
TiO_2:Tb	2			29.8	160.3	12.7
	2.6			35.6	175.9	10.8

The results of nanoindentation have shown that the hardness of all manufactured films was much higher compared to soda-lime glass (~ 5 GPa) [16], and higher than for bulk coarse grained TiO_2 (~ 10 GPa) [19]. Moreover, received values of hardness were above typical literature values for

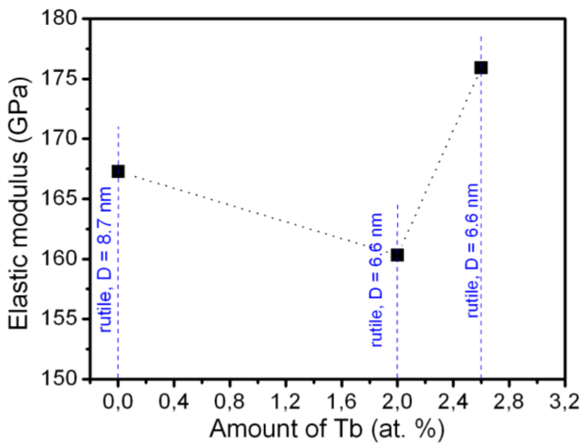

Figure 3. Influence of Tb-dopant amount on elastic modulus of nanocrystalline TiO_2 thin films.

Si (~ 11 GPa) [6] and SiO_2 (~ 7.9 GPa) [20]. Thus, the applications of all manufactured films as self-cleaning and antireflection coatings are of interest.

Our results of hardness measurements for TiO_2 films as deposited in a standard sputtering process and having the anatase structure, have shown that the hardness of the film, directly after deposition, was about 3 GPa. Even after additional annealing at 800°C, which results in recrystalization of the anatase into the rutile structure [21], hardness of the film was only about 8 GPa. This confirms that the higher hardness value of the film was caused by an increase of the film nanocrystallinity. Higher density values of the films are related to the enhanced energy of the HE RMS process delivered to the thin film formation location.

Lower hardness of TiO_2:Tb thin films as-compared to undoped TiO_2 may be due to the fact that the disproportionate size of Tb^{3+} and Ti^{4+} makes replacement of titanium in the TiO_2 lattice unlikely and thus the Tb^{3+} ions are mainly located at the surroundings of the TiO_2 nanocrystals. Therefore, TiO_2 nanocrystals in TiO_2:Tb thin films are spaced further from each other and the planes of an easy slip can be formed.

4. Conclusions

In this work, hardness of nanocrystalline TiO_2 thin films doped with Tb in comparison with their structural properties has been discussed. Application of a high-energy magnetron sputtering process results in nanocrystalline rutile structure with crystallite size below 10 nm. Doping with Tb generates 25% smaller rutile crystallites as compared to the undoped matrix. Investigations performed with the aid of a nanoindentation technique have revealed that hardness of all manufactured films was above 10 GPa as compared to standard TiO_2 films. In the case of undoped TiO_2-matrix, the highest value of hardness was recorded (14.3 GPa), while doping with Tb results in a decrease of hardness. Results of our work have shown that nanocrystalline thin films have a hardness above the typical level for SiO_2 or bulk coarse grained TiO_2. A change of thin film composition generates modifications to their hardness and elastic properties. Presented results confirm that nanocrystalline thin films based on TiO_2, due to their high transparency in the visible light range, may be more competitive for the coating industry than standard coatings.

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