Proceedings of the III National Conference on Nanotechnology *NANO 2009*

Characterization of Transparent and Nanocrystalline TiO_2:Nd Thin Films Prepared by Magnetron Sputtering

J. Domaradzki*, D. Wojcieszak, E. Prociow and D. Kaczmarek

Faculty of Microsystem Electronics and Photonics, Wrocław University of Technology, Wrocław, Poland

In this work structural and optical properties of TiO_2 thin films doped with different amount of Nd have been outlined. The result have shown that by quantity of Nd amount in the film dense nanocrystalline or amorphous thin films were obtained.

PACS numbers: 61.82.Rx, 68.55.−a, 68.60.−p, 68.60.Dv, 78.20.−e

1. Introduction

Thin films based on oxides are widely applied as different coatings, like for example protective against harsh environment, decorative, hard coatings, etc. Also doping of pure oxides with some selected elements enables to extend their applications by changing their different properties (for example mechanical, optical). In recent two decades particularly thin films with so-called nanocrystalline structure (i.e. polycrystalline composed of crystallites lower than 100 nm in mean size) are extensively investigated. Scientific reports have proved that such thin films have definitely different properties from the bulk ones [1].

Nowadays, particularly thin films based on TiO_2 are highly advisable from application point of view. Particularly TiO_2-anatase is highly advisable form of TiO_2 for application reasons, like for example sensor films [2], photocatalytic coatings [3], hydrophilic coatings [4], etc. However, also TiO_2-rutile due to its high thermal stability is applied in, for example, high-temperature sensor devices [5] or thermal resistant protective coatings [6]. Titanium dioxide, except of its own advantages is applied as a matrix for different dopant as well. Particularly, elements from the rare earth (RE) group, like e.g. Eu, Nd or Er, are often applied as structural and optical modifiers [7]. In the present paper influence of Nd dopant on the structural and optical properties of nanocrystalline TiO_2 thin films has been discussed.

2. Sample preparation

The magnetron sputtering process was used for thin films manufacturing. Process was conducted in reactive oxygen atmosphere (10^{-1} Pa). The Nd dopant was alloyed to the TiO_2 matrix during the thin film deposition process from mosaic Ti–Nd target. Thin films were deposited on Si (100) and SiO_2 substrates. Manufactured samples were also additionally post-process annealed by 2 h at 1070 K in an ambient air. The energy disperse spectroscopy results have shown that in two sets of prepared thin films was 0.84 at.% and 8.51 at.% of Nd, respectively.

3. Result and discussion

The thin films structure was examined with the aid of X-ray diffraction (XRD) method. DRON-2 powder diffractometer was used in order to perform the measurements. In Table I the XRD results of as-deposited and annealed at 1070 K TiO_2:Nd (0.84 and 8.51 at.%) thin films have been collected.

Our previous work [10] have shown that the magnetron sputtering process allowed to obtain nanocrystalline TiO_2 matrix, which had thermodynamically stabile rutile form. The XRD results (Table I) have shown that doping with Nd caused distinct changes of the properties of examined thin films. Directly after deposition amorphous behavior was obtained. The additional post-process annealing at 1070 K caused recrystallization of the examined thin films. The TiO_2 doped with 8.51% at. Nd had nanocrystalline (average crystallites size was 12 nm) rutile form after annealing, while the thin films doped with 0.84 at.% of Nd had the anatase crystallites of 6 nm in average size. The structure of both annealed TiO_2:Nd thin films was compressive (the anatase was more compressed than the rutile). The compression stress was determined on the basis of percentage change of the interplanar distance value (Δd).

Atomic force microscope (AFM), which was working in contact mode, was used to determine the surface diversification and roughness of prepared thin films. In Fig. 1 the AFM images of as-deposited and annealed TiO_2:Nd thin films have been presented. Parameters and the roughness obtained based on the AFM images, have been collected in Table II. Similar to XRD the AFM results have shown that annealed TiO_2:Nd (0.84 and 8.51 at.%) thin films were nanocrystalline. Although from XRD patterns amorphous nature was determined for as-deposited samples, the AFM measurements have shown that very small crystallites, which came into construction of grains, can be observed.

* corresponding author; e-mail: jaroslaw.domaradzki@pwr.wroc.pl

TABLE I

The XRD results of as-deposited and annealed at 1070 K TiO_2:Nd thin films, deposited on Si (100).

Thin films on Si (100)	TiO_2:Nd (0.84% at.)		TiO_2:Nd (8.51% at.)	
	as-deposited	annealed at 1070 K	as-deposited	annealed at 1070 K
phase	amorphous	anatase	amorphous	rutile
average crystallites size D [nm]	–	6.0	–	12
interplanar distance d [nm]	–	0.3499 $d_{PDF} = 0.3520$ [8]	–	0.3240 $d_{PDF} = 0.3470$ [9]
Δd [%]	–	−0.59	–	−0.22
type of stress	–	compression	–	compression

d_{PDF} — standard interplanar distance [8, 9], $\Delta d = [(d - d_{PDF})/d_{PDF} \times 100\%]$

TABLE II

Parameters of TiO_2:Nd thin films obtained from AFM images, deposited on Si (100) substrates.

TiO_2:Nd thin film	Amount of Nd [at.%]	Parameters	
		RMS [nm]	average number of grains per 1 μm^2 area
as-deposited	0.84	2.74	1750
annealed at 1070 K		2.85	825
as-deposited	8.51	0.29	–
annealed at 1070 K		4.19	650

Diversification of the thin films surface was determined on the basis of roughness analysis. The root mean square (RMS) value was used to specify the roughness. The results (Fig. 1c, Table II) have shown that surface of as-deposited TiO_2:Nd (8.51 at.%) thin film, which was amorphous according to XRD results, was very smooth (RMS = 0.29 nm). However, as-deposited TiO_2 doped with 0.84 at.% of Nd, which also was amorphous according to XRD results, had nanocrystalline grains (Fig. 1a, Table II). The roughness determined from image 2a was RMS = 2.74 nm.

Additional post-process annealing at 1070 K, performed on TiO_2:Nd (0.84 and 8.51 at.%) thin films, caused considerable increase of diversification of the surface (increase in RMS values). Recrystallization of the TiO_2:Nd (8.51 at.%) structure into the rutile by additional annealing, was accompanied by increase in RMS value from 0.29 up to 4.29 nm (Fig. 1, Table II). The average number of grains per 1 μm^2 area was 650 after annealing. Similarly, in case of TiO_2:Nd (0.84 at.%) thin film, RMS value had changed only in small range — from 2.74 nm up to 2.85 nm, whereas additional annealing caused increase of grain sizes and thus the average number of grains per 1 μm^2 area decrease at about 50% (from 1750 down to 825), as compared to as-deposited thin film.

Optical transmission method was used to determine optical properties of examined thin films. In Fig. 2, the optical transmission characteristics of as-deposited and annealed TiO_2:Nd (0.84 and 8.51 at.%) thin films, deposited on SiO_2 substrates, have been presented. Optical results (Fig. 2) have shown that 10-fold increase in the amount of the Nd dopant in TiO_2 from 0.84 up to 8.51 at.% did not caused a considerable decrease in transparency level. Increased Nd amount in TiO_2 shifted a bit the position of the absorption edge into the longer wavelength range from 315 up to 319 nm. Similar red-shift could be observed after additional post-process annealing in case of the both examined samples. The strongest effect of the annealing process could be observed for the TiO_2:Nd (0.84 at.%) thin films. After annealing the slope of the $T(\lambda)$ characteristic is lower. Refraction index, calculated on the basis of recorded curves for all examined samples was about 2.3.

Thickness of the prepared thin films, as calculated using well known envelope method, was about 500 nm and 130 nm for TiO_2:8.51 at.% Nd and TiO_2:0.84 at.% Nd thin films, respectively.

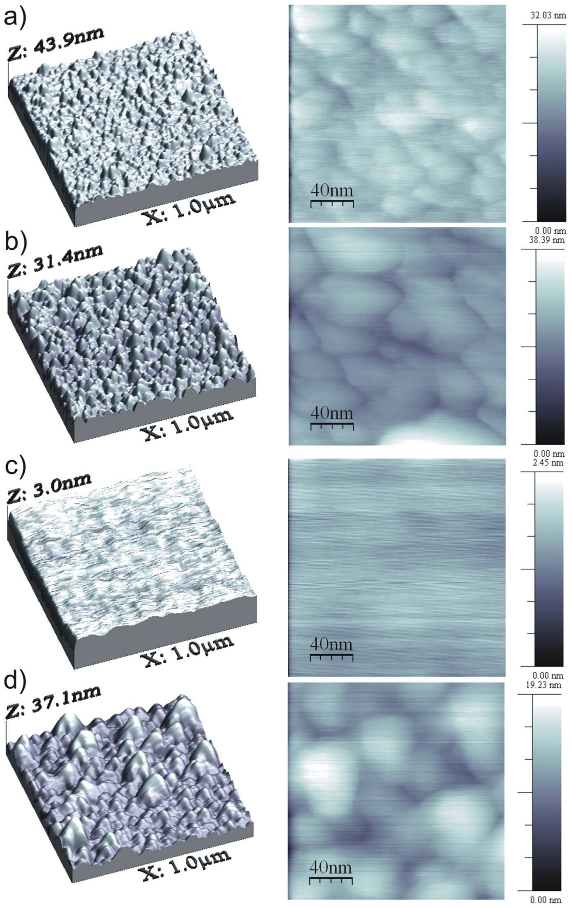

Fig. 1. The AFM images of TiO_2 thin films doped with Nd at the amount of 0.84 at.%: (a) as-deposited and (b) annealed at 1070 K and 8.51 at.%; (c) as-deposited and (d) annealed at 1070 K.

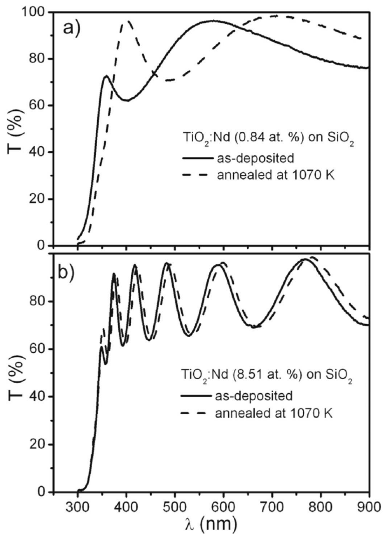

Fig. 2. Optical transmission characteristics of as-deposited and annealed TiO_2:Nd: (a) 0.84 at.% Nd and (b) 8.51 at.% Nd thin films, deposited on SiO_2 substrates.

4. Conclusions

Neodymium, as a dopant, allows to obtain high nanocrystalline and transparent thin films. By changing the amount of Nd and, or by post-process annealing, the structure of TiO_2:Nd thin films can been modified. Nanocrystalline rutile or especially thermal stable (in 1070 K) anatase have high meaning from applications point of view. However, Nd dopant also enable to obtain homogeneous structure, with minor level of diversification of the surface. For this reasons application of TiO_2:Nd thin films can be used especially for hydrophilic or protective coatings. Optical investigations have shown that examinated TiO_2:Nd thin films had high transparency (about 80%), even after additional annealing.

Acknowledgments

This work was financed from the sources granted by the NCBiR in the years 2008–2010 as a development research project no. N R02 0019 04.

References

[1] K. Okimura, *Surf. Coat. Technol.* **135**, 286 (2001).

[2] G. Korotcenkov, *Mater. Sci. Eng. B* **139**, 1 (2007).

[3] A.I. Martınez, D.R. Acosta, G. Cedillo, *Thin Solid Films* **490**, 118 (2005).

[4] L. Sirghi, T. Aoki, Y. Hatanaka, *Thin Solid Films* **422**, 55 (2002).

[5] L. Zheng, M. Xu, T. Xu, *Sensors Actuators B* **66**, 28 (2000).

[6] Z. Niu, X. Jia, W. Zhang, W. Chen, K.Y. Qian, *Appl. Surf. Sci.* **252**, 2259 (2006).

[7] R. Weingartner, O. Erlenbach, A. Winnacker, A. Welte, I. Brauer, H. Mendel, H.P. Strunk, C.T.M. Ribeiro, A.R. Zanatta, *Opt. Mater.* **28**, 790 (2006).

[8] Powder Diffraction File, Joint Committee on Powder Diffraction Standards ASTM Philadelphia PA, 1967, Card 21-1272.

[9] Powder Diffraction File, Joint Committee on Powder Diffraction Standards ASTM Philadelphia PA, 1967, Card 21-1276.

[10] D. Kaczmarek, J. Domaradzki, D. Wojcieszak, R. Wasilewski, A. Borkowska, E.L. Prociów, A. Ciszewski, *Appl. Surf. Sci.* **254**, 4303 (2008).