Densification of TiO$_2$ structure in High Energy magnetron sputtering process by Nd-doping

D Kaczmarek, D Wojcieszak, J Domaradzki and E Prociow

Faculty of Microsystem Electronics and Photonics, Wroclaw University of Technology, ul. Z. Janiszewskiego 11/17, 50-372 Wroclaw, Poland

E-mail: damian.wojcieszak@pwr.wroc.pl

Abstract. The nanocrystalline materials nowadays have a very wide range of applications. This is directly connected with new properties, that the nanocrystalline structure allows to obtain, as compared to standard materials. Applications like, for example, protective, photocatalytic or antireflection coatings are only a part of nanocrystalline materials applications. In this work, studies of the TiO$_2$ thin films doped with Nd, deposited by High Energy magnetron sputtering process are presented. The structural properties were determined using the X-Ray Diffraction (XRD) method. The amount of Nd was determined by the Energy Dispersive Spectroscopy. The Surface topography and density of grains packing, which is the range of structure densification, were determined based on the Atomic Force Microscopy (AFM). The XRD results showed that, after doping of stable TiO$_2$ – rutile matrix with 0.84 at. % of Nd, too, an amorphous structure was obtained. However AFM studies showed that the structure of films was nanocrystalline with grains size below 10 nm. The Nd-doping caused a high densification of matrix structure. An occurrence of crystalline phases on XRD patterns was revealed only after an additional post-process annealing at 1070K. However, contrary to the expectations, only the thermodynamically non-stable TiO$_2$ – anatase form was observed. This fact testifies to the temperature stabilization of TiO$_2$ – anatase structure by Nd-dopant.

1. Introduction

Materials which have a highly nanocrystalline structure allow to accrue new and unique properties which are advisable from the point of view of applications [1-3]. Particularly thin films based on metal oxides, such as TiO$_2$, VO$_2$, or SnO$_2$, are at present at the center of interest of material engineering studies [4]. Especially TiO$_2$ is a material which allows to obtain advisable structural properties that directly determine optical, electrical and chemical properties. Modifications of TiO$_2$ structure are nowadays customized by doping or by changing the fabrication parameters [5, 6]. The doping of TiO$_2$ matrix especially by rare earth elements (RE), such as Tb, Eu or Nd, allows to obtain thin films, which are hydrophilic or hydrophobic [7], have a high transparency range [5, 6] and good photocatalytic [2] or photoluminescence properties [8]. Thin films with crystallite sizes lower than 30 nm have different properties than standard materials [5, 6]. High nanocrystalline densification of thin films structure gives opportunity to obtain advisable properties [9]. The structure densification by Nd doping allows to obtain a highly nanocrystalline anatase. The anatase, which particularly is stable at 1070 K, could be very advisable from a point of view for sensors or in photocatalysis applications.
2. Experimental details
Thin films were deposited on silicon substrates by the High Energy magnetron sputtering process [4, 5, 10]. In this process particles were sputtered from the mosaic Ti-Nd target in oxygen reactive plasma. The oxygen pressure was kept at $10^{-1}$ Pa. The amplitude of unipolar voltage pulses was increased up to 1800 V. Reduction of the physical contact between the target and cooled magnetron, compared to the standard sputtering process, caused an increase in temperature of sputtered target. This allowed to enhance the energy of sputtered particles. As-deposited TiO$_2$:Nd thin films were also additionally annealed at 1070 K in the ambient air.

The thickness of the TiO$_2$ and the TiO$_2$:Nd (0.84 at. %) thin films was about 500 nm and about 130 nm, respectively.

Structural properties of thin films were examined by X-Ray diffraction, using the DRON-2 powder diffractometer with Fe-filtered Co $K_{\alpha}$ radiation. The XRD results allowed to determine the phase, average crystallite size and interplanar distance.

The amount of Nd was determined by the Energy Dispersive Spectroscopy (EDS). The EDS spectra were obtained by the scanning electron microscope equipped with EDS attachment (Hitachi S-4700N, Noran Vantage).

Surface diversification was carried out on the basis of Atomic Force Microscopy results. For the measurements, the Veeco Pico Force microscope which was working in the contact mode (in the ambient air) was used. The samples were examined in the same conditions (one after another), with the aid of the same tip. The humidity of the ambient air was lower than 30 % and it does not have a significant influence on the topography of the examined samples. The AFM images were processed by using WSxM software ver. 4.0. [11]. The software enables to perform the roughness analysis and to estimate the dimension of the grains from the cross-section of the AFM images.

3. Results
Structural properties which were determined on the basis of the XRD measurements, have shown that after deposition of pure TiO$_2$ matrix, a thermodynamically stable rutile form was obtained (table 1) [5]. The average crystallite size of pure matrix was 7.8 nm. However, after doping with Nd at the amount of 0.84 at. %, an amorphous thin film after deposition was obtained. The EDS results have shown that the Nd amount in TiO$_2$ matrix was about 0.84 at. % (figure 1).

Table 1. XRD results of TiO$_2$ and TiO$_2$:Nd thin films on Si (100).

| Thin film on Si (100) | TiO$_2$       | TiO$_2$:Nd     | TiO$_2$:Nd     |
|----------------------|---------------|---------------|---------------|
| as-deposited          | as-deposited  | annealed at 1070 K |
| Amount of Nd (at. %) | -             | 0.84          | 0.84          |
| Phase                | rutile        | amorphous     | anatase       |
| Average crystallite size D (nm) | 7.8       | -             | 6.0           |
| Interplanar distance $d$ (nm) | 0.3255  | -             | 0.3499        |
| $d_{PDF}$ = 0.3247 [12] | $d_{PDF}$ = 0.3520 [13] |
| $\Delta d$ (%)       | +0.25         | -             | -0.59         |
| Type of stress       | tension       | compression   |               |
Moreover, the XRD results confirm that after the additional post-process annealing at 1070 K, the TiO$_2$ – anatase form was obtained (table 1). No separate phases from Nd were recorded. The results also show that the Nd-doping of TiO$_2$ caused 20 % decrease of an average crystallite size. Nevertheless, the AFM results have shown that as-deposited TiO$_2$:Nd thin film has the nanocrystalline structure, which is observed on the images. This fact testifies to high densification of nanocrystalline structure. The crystallite sizes in the examined as-deposited TiO$_2$:Nd thin film were smaller than sizes which the XRD method allowed to be measured. Although the AFM method allowed to qualitatively and quantitatively determine the properties of the nanocrystalline thin films, the XRD and AFM results cannot be directly compared to each other, which follows from the different measurement methods. The AFM image testifies to a high nanocrystallinity of the examined as-deposited TiO$_2$:Nd thin film. In the case of the XRD measurements of nanocrystalline thin films the information about the average crystallite size is received. While on the basis of the AFM images the grain sizes can be determined. The grains visible on the images could be composed of few crystallites. In the effect this make comparison of XRD and AFM results impossible.

The surface diversification, which was determined on the basis of roughness analysis (figure 3), has shown that Nd-doping caused increase in the degree of the thin film homogeneity. The RMS parameter (root mean square) [11], which defines surface diversification was higher in the case of pure TiO$_2$. The Nd-doping caused about 50 % decrease of the RMS value (table 2, figure 3). This testifies to the increase of surface homogenity by Nd-doping, compared to pure TiO$_2$.

### Table 2. XRD results of TiO$_2$ and TiO$_2$:Nd thin films on Si (100).

| Thin film on Si (100) | TiO$_2$ as-deposited | TiO$_2$:Nd as-deposited | TiO$_2$:Nd annealed at 1070 K |
|----------------------|----------------------|-------------------------|-----------------------------|
| Amount of Nd (at. %) | -                    | 0.84                    | 0.84                        |
| RMS (nm)             | 4.16                 | 2.33                    | 2.36                        |
| FWHM (nm)            | 7.46                 | 4.16                    | 5.22                        |
| Average number of grains on area 1 (µm$^2$) | 500 | 1500 | 1150 |
However, the FWHM value of thin film roughness, which accurately allows to show the thin film diversification, indicates that the fabricated thin films have a higher degree of surface diversification than that shown by the RMS parameter (table 2, figure 3.4). Also, the average number of grains on the 1 µm² area of the surface testifies that Nd caused a high structure densification. The number of grains increased about 3-times after Nd-doping of TiO₂ matrix (table 2). Moreover, AFM studies have shown that the post-process additional annealing at 1070 K does not meaningfully change the surface diversification (figure 2, table 2). The values of RMS parameters of TiO₂:Nd as-deposited and annealed thin films are almost the same, however the FWHM values show that additional annealing caused minor diversification, which is connected with grain size increase due to annealing (table 2). This was also reflected in the 25 % decrease of the average number of grains on the 1µm² area after additional annealing of TiO₂:Nd thin film.

**Figure 2.** AFM images of as-deposited TiO₂ (a) and TiO₂:Nd (0.84 at. %) as-deposited (b) and annealed at 1070K (c) thin films.
4. Conclusions
Preparation of titanium dioxide thin films by the High Energy magnetron sputtering process [10], allowed to obtain new and unique properties by Nd-doping. The neodymium dopant caused high densification of the structure, which is very advisable from the point of view of applications [1-4, 7, 8]. The XRD and AFM results have shown that the Nd doping, at the amount of 0.84 at. %, allows to change the matrix structure – from the rutile to the anatase during the deposition process. Change of structure properties by Nd caused also densification and homogeneity of thin films. The results have also shown that the structure of the fabricated TiO$_2$:Nd thin films is stable in consequence of Nd-doping.
5. Acknowledgement
This work was financed from the sources for science development in the years 2007-2009 as a research project No NN515 4401 33.
Authors would like to thank R. Wasielewski from the Institute of Experimental Physics, University of Wroclaw, Poland for his help in providing experimental data from AFM.

References
[1] Niu Z, Jia X, Zhang W, Chen W and Qian K 2006 Reactive sputtering TiO$_2$ films for surface coating of poly(dimethylsiloxane) *Applied Surface Science* **252** pp 2259-2264
[2] Choi W 2006 Pure and modified TiO$_2$ photocatalysts and their environmental applications *Catalysis Surveys from Asia* **10** pp 16-28
[3] Zhang J-Y, Boyd I W, O’Sullivan B J, Hurley P K, Kelly P V and Senator J-P 2002 Nanocrystalline TiO$_2$ films studied by optical, XRD and FTIR spectroscopy *Journal of Non-Crystalline Solids* **303** pp 134-138
[4] Ganduglia-Pirovano M V, Hofmann A and Sauer J 2007 Oxygen vacancies in transition metal and rare earth oxides: Current state of understanding and remaining challenges *Surface Science Reports* **62** pp 219-270
[5] Wasielewski R, Domaradzki J, Wojcieszak D, Kaczmarek D, Borkowska A, Prociów E L and Ciszewski A 2008 Surface characterization of TiO$_2$ thin films obtained by high energy reactive magnetron sputtering *Applied Surface Science* **254** pp 4396-4400
[6] Kaczmarek D, Domaradzki J, Wojcieszak D, Wasielewski R, Borkowska A, Prociów E L and Ciszewski A 2008 Structural investigations of TiO$_2$:Tb thin films by X-ray diffraction and atomic force microscopy *Applied Surface Science* **254** pp 4303-4307
[7] Wu K-R, Wang J-J, Liu W-C, Chen Z-S and Wu J-K 2006 Deposition of graded TiO$_2$ films featured both hydrophobic and photo-induced hydrophilic properties *Applied Surface Science* **252** pp 5829-5838
[8] Podhorodecki A, Nyk M, Misiewicz J and Strek W 2007 Optical investigation of the emission lines for Eu$^{3+}$ and Tb$^{3+}$ ions in the GaN powder host *Journal of Luminescence* **126** pp 219-224
[9] Okimura K 2001 Low temperature growth of rutile TiO$_2$ films in modified rf magnetron sputtering *Surface and Coatings Technology* **135** pp 286-290
[10] Prociow E L, Domaradzki J, Kaczmarek D and Berlicki T 2007 Polish patent No P382163
[11] Horcas I, Fernandez R, Gomez-Rodriguez J M, Colcherlo J, Gomez-Herrero J and Baro A M 2007 *Review of Scientific Instruments* **78** 013705
[12] Powder Diffraction File 1967 Joint Committee on Powder Diffraction Standards ASTM Philadelphia PA Card 21-1272
[13] Powder Diffraction File 1967 Joint Committee on Powder Diffraction Standards ASTM Philadelphia PA Card 21-1276