PROPERTIES OF TIO₂ THIN FILMS PRODUCED BY IBSD

Altin Gjevori[*], Luan Kola[**]

[*]*Polytechnic University of Tirana, Bulevardi "Dëshmorët e Kombit", Sheshi "Nënë Tereza" 4, 1019 Tirana, Albania*
[**]*University of Elbasan, Rruga Ismail Zyma, 3001 Elbasan, Albania*
Corresponding Author: altingjevori@yahoo.com

Abstract

Titanium dioxide (TiO_2) belongs to the family of transition metal oxides. Among the semiconductors, TiO_2 (E_g = 3.2eV) has proven to be the most suitable for widespread environmental applications, since it is biologically and chemically inert; it is stable with respect to photocorrosion and chemical corrosion. TiO_2 can be prepared in the form of powder, crystals, or thin films. While powders are frequently utilized, thin films prepared by PVD processes, are also under investigation.

In this work we have utilized Ion Beam Sputter Deposition for obtaining TiO_2 thin films. The deposition is performed in an existing experimental setup previously used for investigations on Ag and Ge thin film PVD processes where the influence of the sputtered and reflected particles and their accompanying energy flux on the grain size, surface morphology and conductivity have been measured. By adjusting the geometry between incident ion beam, sputter target and substrate, independently from the primary ion energy and species, a controlled deposition of samples is possible.

Keywords: *TiO_2, IBSD, ESMS, Sputtering geometry, Film thickness*

INTRODUCTION

Titanium dioxide is well known as a photoactive material to be activated under UV irradiation [1,2] and employed either as a photocatalyst or exhibiting superhydrophilic behavior after reducing the surface energy under illumination for self-cleaning or anti-fogging surfaces [3]. Alternative to powders, TiO_2 can be produced as thin films using chemical sol-gel processes operating at air or physical vapour deposition (PVD) processes where either high temperature or increased ion energy is necessary to obtain a photoactive phase [4]. Even coating of membranes is possible using a more complex process [5]. There, temperature sensitive substrates require low temperatures, ideally near room temperature where an amorphous photoactive phase can be formed under certain conditions [6,7].

Independent of the phase composition the band gap is always more than 3 eV (the exact value depending on the polymorph), thus necessitating UV-A radiation for activation. For increasing the reactivity of the thin films under solar illumination, a reduced band gap is desired. Doping with transition metals or with nitrogen has been reported in the literature [8,9]. The latter dopant is – theoretically – readily accessible during PVD processes. However, the incorporation of nitrogen into the growing film, in contrast to ion implantation into TiO_2 thin films or selective oxidation of TiN, is a much more complex process which is presently not completely understood [10]. Alternatively, TiO_2 nanotubes with a reduced band gap [11], visible-light-active N-doped TiO_2 nanorods by hydrothermal treatment [12] or hydrazine doping of brookite nanorods at 200 °C for 18 h have been proposed recently [13]. Despite the large amount of published work, even the photoactivity of pure TiO_2 thin films are still controversially discussed.

In this project we will utilize an energetic one-step PVD process for obtaining TiO_2 layers, which should allow the usage of temperature sensitive substrates. The deposition will be performed in an existing experimental setup previously used for investigations on Ag and Ge thin film PVD processes where the influence of the sputtered and reflected particles and their

1

accompanying energy flux on the grain size, surface morphology and conductivity have been measured. By adjusting the geometry between incident ion beam, sputter target and substrate, independently from the primary ion energy and species, a controlled deposition of samples is possible.

MATERIAL AND METHODS

The samples are produced by using Ion Beam Sputter Deposition. Figure 1 shows a schematic sketch of the IBSD setup inside the deposition chamber. It consists of a broad beam ion source, a target holder and a substrate holder. The ion beam source and the target holder are placed on rotary tables, which have their centre of rotation at the centre of the target surface plane. Additionally, an energy-selective mass spectrometer can be used to measure the energy distribution of sputtered target ions and backscattered primary ions. The deposition chamber is of rectangular shape with a dimension of $1 \times 1 \times 0.7$ m^3. The chamber is pumped by a 2200 l/s turbo molecular pump to a base pressure of 2×10^{-6} mbar. The working pressure during sputtering is about 5×10^{-5} mbar. The ion beam source is of radio-frequency (RF) type with a three-grid multi-aperture extraction system with an open diameter of 16 mm. The process gases were Ar or Xe with a volumetric flow rate of 3.5 sccm or 1.1 sccm, respectively. The RF power was set to 70 W for all experiments resulting in a total ion current of about 7 mA. The distance between the exit plane of the ion beam source and the target centre is about 0.15 m, i.e. it is much smaller than mean free path length of the primary ions (Ar: 1.28 m; Xe:0.72 m). The substrate holder is of semi-circular shape with a radius of curvature of 0.15 m. The holder is segmented such that substrates up to 15×15 mm^2 can be placed at different polar emission angles in steps of 10∘. One set of TiO$_2$ films was grown under variation of ion energy, ion species and ion incidence angle on unheated Si (100) substrate with a size of about 12×12 mm^2. A poly-crystalline Ti target with a purity of 99.99% was used. The deposition was done in oxygen atmosphere with an oxygen volumetric flow rate of 2 sccm. The resulting oxygen partial pressure was about 1.5×10^{-5} mbar.

Figure 1. Sketch of the IBSD experimental setup

RESULTS AND DISCUSIONS
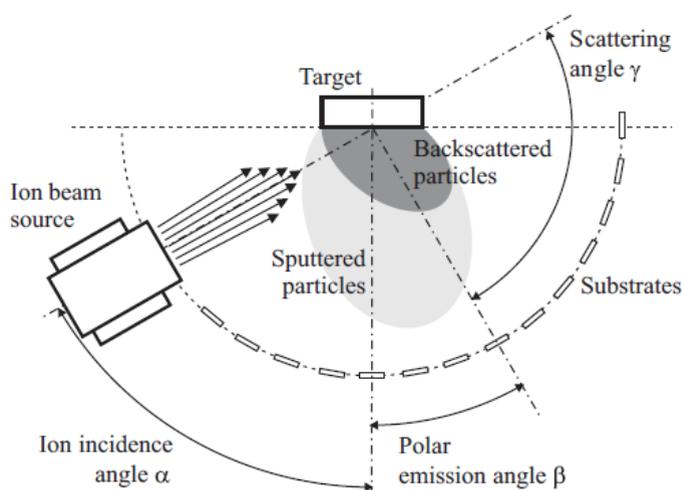
An ESMS Balzers Quadstar PPM 422 was used for measuring the mass distribution of secondary ions and the energy distribution of individual ion species. The mass ranges from 1 up to 512 amu with a resolution of 1 amu. The energy range is from 0 up to 500 eV with a resolution of 0.5 eV. Different combinations of incidence angle α and emission angle β can be realized by rotating the target and/or the ion source. The minimal detectable emission angle is limited by the geometrical dimensions of the ESMS and the ion source. An incidence angle of 0°, 30°, and 60° results in a minimal emission angle of 60^0, 30^0, and 0^0, respectively. The energy distribution of sputtered (Ti, TiO, and O), backscattered (Ar and Xe), and O_2 ions was measured at emission angles in steps of 10° for primary ion energies of 0.5, 1.0, and 1.5 keV and incidence angles of 0°, 30°, and 60°. The measured energy distributions were smoothed by the method of moving average with an average over 50 adjacent data points.
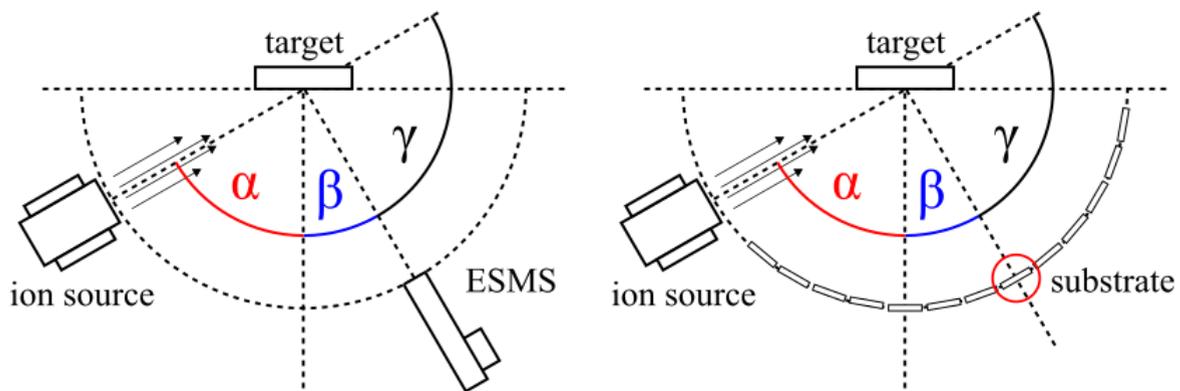

Figure 2. Setup for deposition and ESMS measurements with same geometry (Ti target + 2 sccm O_2)

We observe that predominant secondary ion species are: O^+ (16 amu), O_2^+ (32 amu), Ar^+ (40 amu), Ti^{+s} (48 amu) and TiO^+ (64 amu). Energy distributions of O^+, Ar^+, Ti^+, and TiO^+ broaden with increasing emission angle β (decreasing scattering angle γ). The same behavior is observed for simulated energy distributions using SRIM.
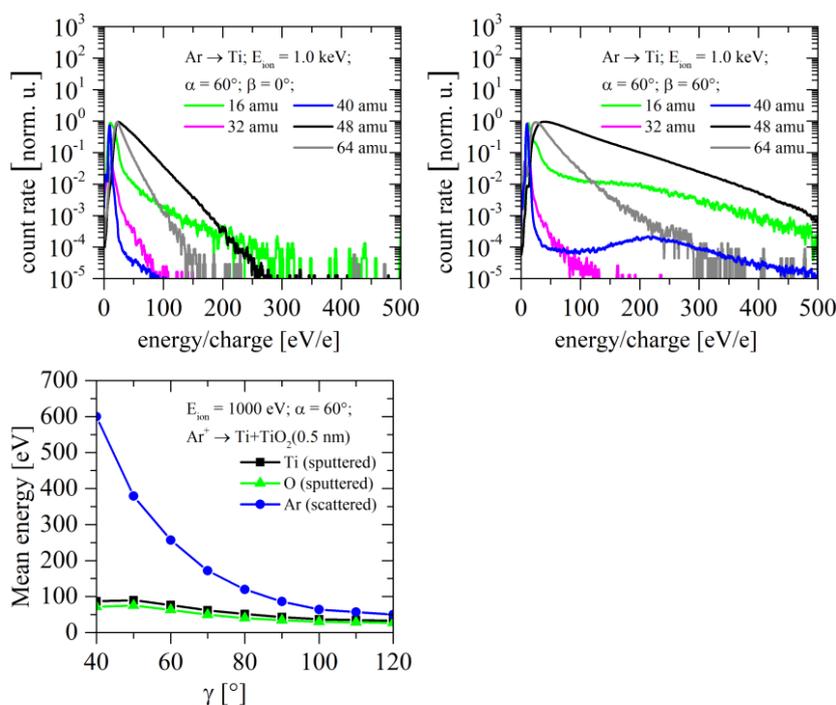
Figure 3. Measured energy distributions of Ti ions sputtered from a polycrystalline Ti target under Ar ion bombardment with steady oxygen flow

The influence of the sputtering geometry on the energy of the secondary particles are depicted in Fig. 3. Spectroscopic ellipsometry measurements are used for determining the film thickness as function of position (cf. Fig. 4). Additionally, there is actually a slight increase in absorption at 532 nm after the implantation.
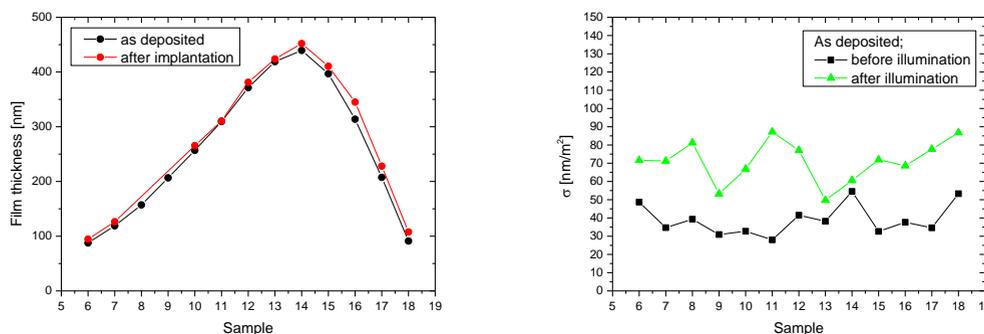

Figure 4. Film thickness and Surface energy as estimated by ellipsometry and CAM

BIBLIOGRAPHY

[1]   W. Hofmeister, E. Tillmanns, W.H. Bauer, Refinement of barium tetratitanate, BaTi4O9, and hexabarium 17-titanate, Ba6Ti17O40, Acta Crystallogr. C 40 (1984) 1510–1512.

[2]   A. Fujishima, K. Honda, Electrochemical photolysis of water at a semiconductor electrode, Nature 238 (1972) 37–38.

[3] R. Wang, K. Hashimoto, A. Fujishima, M. Chikuni, E. Kojima, A. Kitamura, M. Shimohigoshi, T. Watanabe, Light-induced amphiphilic surfaces, Nature 388 (1997) 431–432.

[4] P. Löbl, M. Huppertz, D. Mergel, Nucleation and growth in TiO2 films prepared by sputtering and evaporation, Thin Solid Films 251 (1994) 72–79.

[5] K. Fischer, M. Kühnert, R. Gläser, A. Schulze, Photocatalytic degradation and toxicity evaluation of diclofenac by nanotubular titaniumdioxide–PES membrane in a static and continuous setup, RSC Adv. 5 (2015) 16340–16348.

[6] J.M. Schneider, S. Rohde, W.D. Sproul, A.Matthews, Recent developments in plasma assisted physical vapour deposition, J. Phys. D. Appl. Phys. 33 (2000) R173–R186.

[7] D. Manova, A. Gjevori, F. Haberkorn, J. Lutz, S. Dimitrov, J.W. Gerlach, E. Valcheva, S. Mändl, Formation of hydrophilic and photocatalytically active TiO2 thin films by plasma based ion implantation and deposition, Phys. Status Solidi A 206 (2009) 71–77.

[8] T. Morikawa, R. Asahi, T. Ohwaki, K. Aoki, Y. Taga, Band-gap narrowing of titanium dioxide by nitrogen doping, Jpn. J. Appl. Phys. 40 (2001) L561–L563.

[9] D.H. Lee, Y.S. Cho,W.I. Yi, T.S. Kim, J.K. Lee, H. Jin Jung, Metalorganic chemical vapor deposition of TiO2:N anatase thin film on Si substrate, Appl. Phys. Lett. 66 (1995) 815–816.

[10] I. Asenova, D. Manova, S. Mändl, Incorporation of nitrogen into TiO2 thin films during PVD processes, J. Phys. Conf. Ser. 559 (2014), 012008.

[11] B. Choudhury, S. Bayan, A. Choudhury, P. Chakraborty, Narrowing of band gap and effective charge carrier separation in oxygen deficient TiO2 nanotubes with improved visible light photocatalytic activity, J. Colloid Interface Sci. 465 (2016) 1–10.

[12] S. Abu Bakar, G. Byzynski, C. Ribeiro, Synergistic effect on the photocatalytic activity of N-doped TiO2 nanorods synthesised by novel route with exposed (110) facet, J. Alloys Compd. 666 (2016) 38–49.

[13] J. Pan, S.P. Jiang, Synthesis of nitrogen doped faceted titaniumdioxide in pure brookite phase with enhanced visible light photoactivity, J. Colloid Interface Sci. 469 (2016) 25–30.