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To cite this article: I Asenova *et al* 2014 *J. Phys.: Conf. Ser.* **559** 012008

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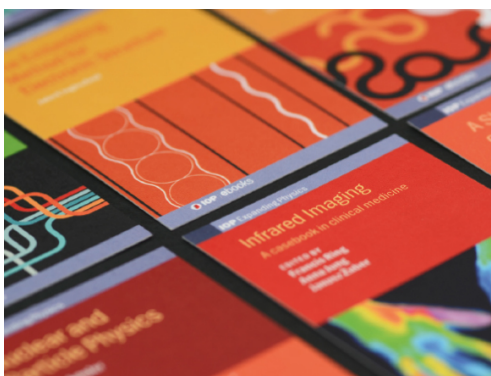
Incorporation of nitrogen into TiO$_2$ thin films during PVD processes

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Abstract. In this paper we investigate the possibility of incorporating nitrogen into amorphous, photocatalytic TiO$_2$ thin films, prepared at room temperature, during the growth process. The aim is to reduce the bandgap of the UV active thin films. Physical vapor deposition experiments employing a titanium vacuum arc with gas backfill ranging from pure oxygen to pure nitrogen, are carried out. The resulting films are characterized for chemical composition, phase composition, optical properties and hydrophilicity in order to determine a correlation between gas composition and thin film properties. The experimental results point that a visible change in the band structure of the deposited layers is achieved.

1. Introduction

Titanium dioxide is well known as a photoactive material [1, 2], either as a photocatalyst activated by UV irradiation or by reducing the surface energy under illumination thus exhibiting superhydrophilic [3], self-cleaning or anti-fogging surfaces. Except for powders, TiO$_2$ thin films can be produced using different ion assisted physical vapor deposition processes where either high temperature or increased ion energy is necessary to obtain an active phase [4]. Temperature sensitive substrates require low temperatures, ideally room temperature where an amorphous photoactive phase can be formed [5, 6]. Independent of the phase composition the band gap is always more than 3 eV (the exact value depending on the polymorph) necessitating UV-A radiation for activation. For increasing the reactivity of the thin films, especially indoors, a reduced band gap is desired. Doping with transition metals or with nitrogen has been reported in the literature [7, 8]. The latter dopant is, theoretically, readily accessible during the physical vapor deposition (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.

In this report we utilize a one-step physical vapor deposition (PVD) process for obtaining N-doped TiO$_2$ layers at room temperature, which maintains the usage of temperature sensitive substrates. The deposition is performed for a range of backfill gas composition (oxygen and nitrogen) in order to investigate the influence of the total pressure and nitrogen/oxygen ratio on the film properties. The resulting layers are subsequently investigated for correlation between their chemical composition, optical properties and hydrophilicity versus the gas composition. Secondary ion mass spectrometry

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(SIMS), scanning electron microscopy (SEM), Raman spectroscopy, UV absorption spectroscopy and contact angle measurement were carried out for films characterization.

2. Experiment

Silicon (100) and fused silica substrates were used for the investigations with fused silica necessary for the transmission measurements. No influence of the substrate on the phase composition was observed in previous work for pure TiO_2 [9]. The samples were positioned at distance of 39 cm from a d.c. cathodic arc with a pure titanium (99.99%) cathode, operating at 100 A. In order to increase the average kinetic energy of the Ti ions emitted from the arc, negative high voltage pulses of 3 kV with length of 30 μs at repetition rate of 3 kHz were applied to the substrate. All the experiments started at room temperature and no additional heating or cooling was employed. The deposition time for all samples was fixed to be 300 s with the substrate temperature at 50 °C or below after the deposition process. Oxygen and nitrogen in different composition ratios were used as a backfill gas with a flow rate ranging between 0 and 60 sccm. The obtained growth rate was around 0.85 nm/s, resulting in film thicknesses of approximately 250 – 280 nm. For comparison pure TiN and TiO_2 thin films were produced using the same deposition parameters. The pressure during the deposition process was always between 0.1 and 0.15 Pa.

Table 1. Oxygen and nitrogen flow rates for PVD thin films deposition.

| Sample No.	O_2 gas flow (sccm)	N_2 gas flow (sccm)
TiN	0	50
TiO_2	60	0
TiO30N30	30	30
TiO40N20	40	20
TiO50N10	50	10
TiO40N10	40	10
TiO45N5	45	5
TiO45N15	45	15
TiO40N5	40	5

The film thickness and deposition rate were derived from secondary ion mass spectrometry in a time-of-flight setup (TOF-SIMS) using 15 keV $^{69}Ga^+$ ions for analysis and 2 keV $^{133}Cs^+$ ions for sputtering, both incident at an angle of 45°. The sputter profiling was stopped right at the film-substrate interface to avoid the introduction of errors during the conversion of the time into a depth scale. Measuring the crater depth with an optical interferometer and assuming an identical sputter rate for the different layers leads to the determination of the film thickness. With the aid of the TiO_2 and TiN films produced in the same experiment, the nitrogen content in the layers was derived from the Cs_2N^+ secondary ion signal which showed the lowest matrix effect while still yielding enough signal intensity.

The film morphology was examined with scanning electron microscopy (SEM) using two different acceleration voltages of the electron beam (2 kV and 10 kV). The band gap was determined via ultraviolet (UV) absorption spectroscopy therefore identical layers were deposited on fused silica substrates. In order to investigate the hydrophilicity of the layers, water contact angle measurements were conducted before and after exposing the samples to irradiation for 3 hours. The irradiating UV-A light was generated from an actinic tube with a spectral range of 300 – 460 nm and a maximum at 365 nm, with an incident power density at the substrate position of 1 mW/cm^2. The ambient temperature and humidity were 21 ºC and 25% respectively. The contact angle measurements on the irradiated samples were conducted within three hours after the end of the illumination.

3. Results and discussion

As shown by previous studies on the subject [4, 9], titania films obtained via this procedure should be either amorphous or containing nanocrystallites smaller than 5 nm due to the rather low temperature and ion bombardment which is not sufficient for a complete crystallization. Accordingly, XRD and Raman measurements of the films containing an oxygen/nitrogen mixture yielded no information, indirectly confirming the amorphous or nanocrystaline nature.

In all the cases the film thickness was found to be similar (within the measurement error) which indicates a growth rate independent of either the ratio of the backfill gases or the total pressure [10]. Substoichiometric TiO_x is known to be very reactive and adsorbing a large amount of oxygen from the gas phase. Only when the oxygen supply is nearly depleted, i.e. the pressure is decreasing, a reduced oxygen content can be observed. In contrast, variations in the nitrogen gas flow lead to an immediate change in the Ti/N ratio for pure TiN thin films [11].
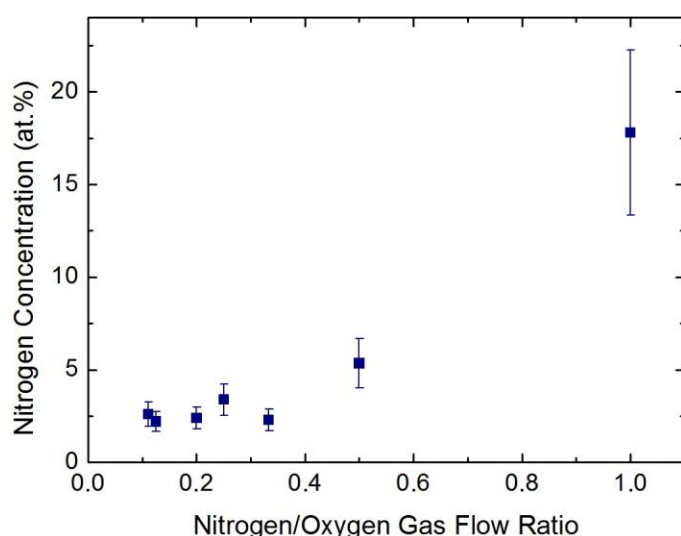

Figure 1. Amount of nitrogen incorporated in the layers versus the flow ratio of the backfill gases. The error bar from the assumed model is included.

The nitrogen concentration in the layers was extracted from the SIMS spectra using the procedure detailed in the experimental section. The results are plotted in figure 1. For all the samples grown with ratio of the backfill gases $N_2/O_2 < 0.3$ the amount of the incorporated nitrogen is the same within the error of calculation – about 3 at.%, if the linear concentration interpolation is valid. When the N_2/O_2 ratio in the gas phase exceeds 0.3, the nitrogen content in the films increases significantly – the sample with the highest amount of incorporated nitrogen of about 18 at.%, produced with an N_2/O_2 ratio of 1:1, implies a stoichiometry of this film corresponding to Ti_3O_2N or $(TiO_2)(TiN)$.

An alternative explanation with the nitrogen content inside the films being near zero for a nitrogen/oxygen gas flow of up to 0.25 cannot be ruled out from the experimental SIMS data as there is no alternative method for determining the nitrogen content for these rather thin films. However, using either interpretation, the competition between reactive oxygen and nearly inert nitrogen is skewing or delaying the nitrogen uptake towards a nitrogen poor regime (a N:O ratio of 1:2 in the gas leads to a N:O ratio of about 1:10 in the growing film). Alternatively, nitrogen radicals or plasma excitation are necessary to increase the nitrogen uptake [12].

The growth structure of the films has been investigated using cross-section examinations by SEM. The results for selected samples are presented in figure 2. All the layers are dense due to the energetic bombardment and the resulting surface mobility during the deposition process, and do not exhibit a porous, defect-rich structure. The viewgraphs of samples TiN and TiO30N30 reveal a distinct columnar morphology [13] with a column diameter of 20 – 30 nm, while the TiO_2 film exhibits less prominent columns of approximately the same width. However, the observed structures are

predominantly indicative of the fracture behavior and may not be representative of the film microstructure itself.
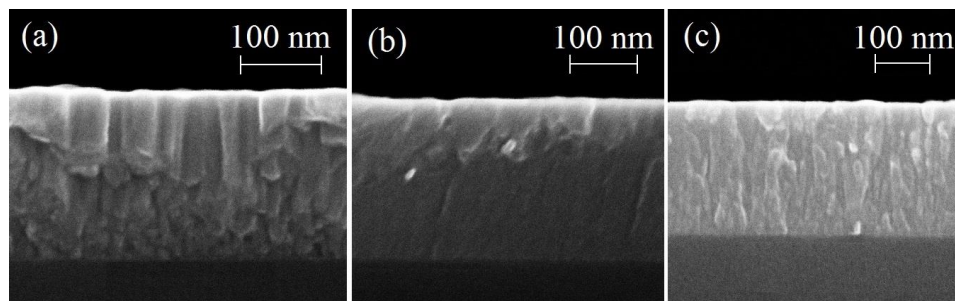

Figure 2. SEM cross-sectional viewgraphs of PVD films: (a) sample TiN; (b) sample TiO_2; (c) sample TiO30N30.

The surface viewgraphs of the same samples show minor droplet contamination from the arc deposition process which consists of metallic titanium, as depicted in figure 3. The lateral dimensions of the macrostructures – as shown in figure 4 – embedded in the layers are about 100 – 300 nm with the elliptical shape indicating a strong compressive biaxial stress within the films, again in agreement with the deposition process as described by general PVD models [14].
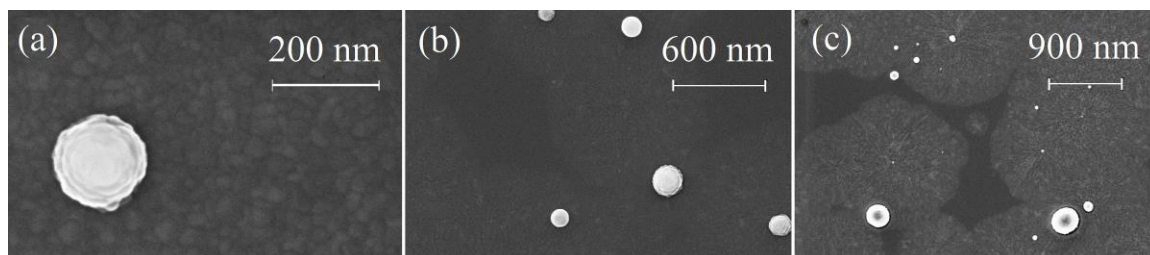
Figure 3. SEM surface topology viewgraphs of PVD films with macroparticles embedded in the film: (a) sample TiN; (b) sample TiO_2; (c) sample TiN30O30.
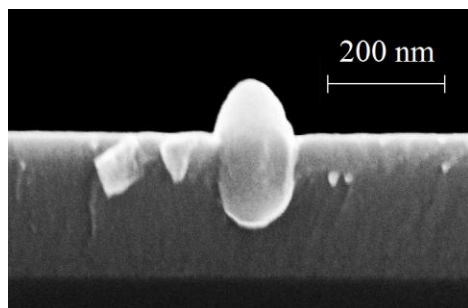
Figure 4. SEM image showing a cross-section of the sample TiO_2 with an embedded macroparticle.
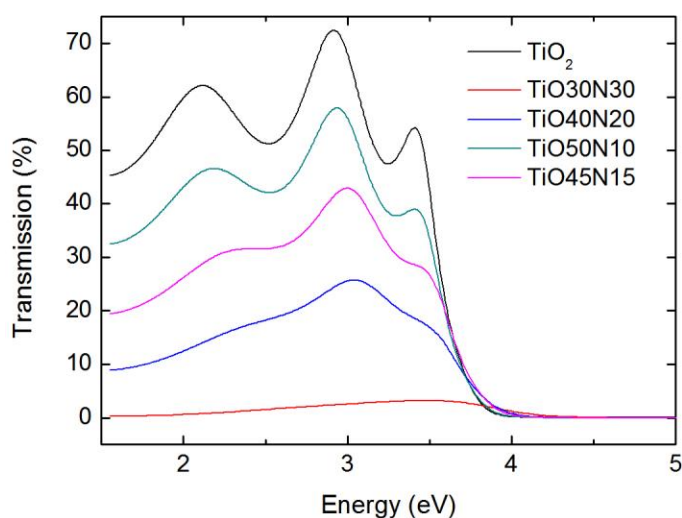
**Figure 5.** Transmission spectra for selected samples.

Optical properties of selected samples were investigated with UV absorption spectroscopy. The optical band gap E_g of the films was calculated using the Tauc plot formalism for amorphous samples. Here, linear regions for all the layers are observable, with the exception of samples TiN and TiO30N30. The corresponding transmission spectra used for preparing the Tauc plot are shown in figure 5, while the results, combining the values of E_g and nitrogen content, are systematized in table 2. The linear extrapolation of the relevant regions leads to values of $E_g \approx 3.2$ eV for most of the samples, slightly smaller than the optical gap for amorphous TiO_2 (this value for the pure titania film is in agreement with tabulated literature data). For the sample TiO40N20, a band gap narrowing down to $E_g \approx 3.0$ eV is observed. The samples produced with a lower nitrogen gas flow show a significant, smaller shift of the bandgap. In contrast, the coating TiO30N30 is already semimetallic, non-transparent in the optical region.

Table 2. Band gap E_g and nitrogen content of selected samples.

Sample No.	E_g (eV)	E_g (nm)	Nominal Nitrogen Content (at.%)
TiO_2	3.23	384	0
TiO50N10	3.21	386	2.4
TiO45N15	3.15	394	2.3
TiO40N20	3.07	404	5.3
TiO30N30	semimetallic	semimetallic	18

Assuming that the redshift in the band gap is due to the incorporation of nitrogen, a finite, non-zero nitrogen content is present for all samples produced with a nitrogen/oxygen gas mixture. Changes in the phase composition or morphology as the origin of the shift are unlikely. Apparently, a transition is occurring with a lower relative nitrogen uptake for a small nitrogen gas flow and a higher relative nitrogen uptake for higher nitrogen gas flow. The low nitrogen content region corresponds to films with a reduced band gap, while the high nitrogen content leads to semimetallic films.

No information about atomic positions of the nitrogen or influence of the gas flow is available at the present. For crystalline lattices, both interstitial and substitutional N doping of TiO_2 has been reported with the additional formation of detrimental oxygen vacancies [15]. However, the designation of interstitial or substitutional sites in amorphous thin films is not possible.
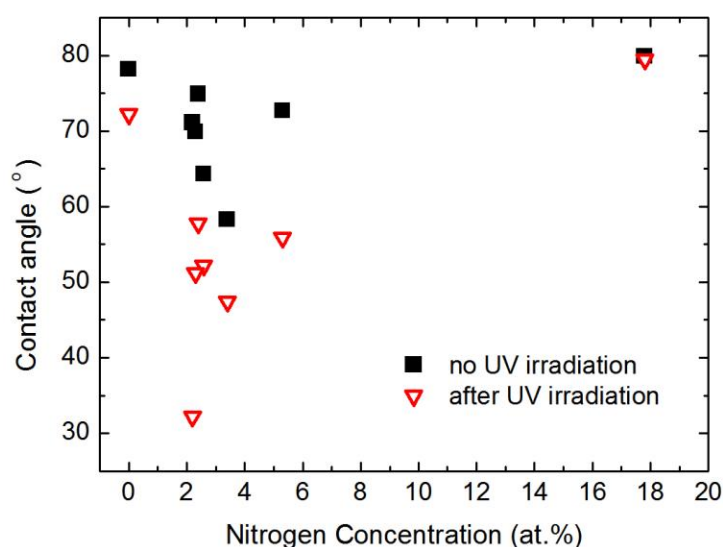
Figure 6. Contact angle of water before and after illumination as a function of the amount of incorporated nitrogen.

In order to test the photoactivity, i.e. the hydrophilicity of the layers, contact angle measurements were conducted before and after the samples being irradiated with UV-A light: the results are displayed in figure 6. With the exception of samples TiN and TiO30N30, which show no difference before and after the illumination, all the layers exhibit a tendency of contact angle reducing as the oxygen backfill decreases. This tendency is more prominent after irradiation, with a minimum found near 3 at.% nitrogen incorporation into the film. For higher contents, the contact angle increases again.

When interpreting these results, it has to be kept in mind that although the present deposition conditions lead to a significant reduction of the contact angle under illumination, the saturation level around 5° is not reached – the relative changes are for the present investigations more interesting than the absolute value. Furthermore, no influence of illumination at reduced energies or increased wavelengths has been investigated up to now.

4. Summary

Amorphous TiO_2:N layers were deposited at room temperature using a PVD method with pulse bias voltage and various backfill gas compositions. A correlation between the backfill gas composition and the nitrogen content and, furthermore, the band gap has been observed. Initially, for small nitrogen gas flows, a low nitrogen reactivity leads to a rather low relative nitrogen incorporation – which nevertheless results in a significant increase in the photoactivity, respective hydrophilicity. For higher gas flows, more nitrogen is incorporated (up to $(TiO_2)(TiN)$ in the present experiment) while the photoactivity under UV-A illumination is reduced again. For these irradiation conditions, only a very small amount of nitrogen incorporation and bandgap shift leads to optimized conditions. At the same time, amorphous or nanocrystalline structures have been observed which should not allow a distinction between interstitial or vacancy incorporation. Additional XPS measurement could be helpful for investigating the electronic structure.

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