

**INFLUENCE OF ION DOPING ON PHOTOACTIVITY OF TiO<sub>2</sub> THIN FILMS BY  
MEPIII&D**

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**ABSTRACT**

TiO<sub>2</sub> is widely used, either as a powder or as thin films, with different preparation methods reported in the literature, including magnetron sputter deposition and metal arc deposition. In this report, TiO<sub>2</sub> thin films are formed by inserting an auxiliary rf plasma source in an experimental setup for depositing thin films with a cathodic vacuum arc and high voltage pulses, i.e. metal plasma immersion ion implantation & deposition (MePIII&D).

The photoactivity of TiO<sub>2</sub> thin films was examined by contact angle measurements (CAM) after exposing the samples to UV light, generated from an actinic tube with a spectral range of 300 nm – 460 nm with the maximum at 365 nm, at an intensity of 1 mW/cm<sup>2</sup>, for up to 3 hours. As the contact angle of two liquids against the thin films was measured, it was possible to calculate the surface energy before and after illumination with UV light. From the samples produced we have selected 4 pairs, one promising to be photoactive and the other not at all for each pair. Then, the above listed amorphous samples are doped with carbon and nitrogen, using an Ion Implanter IMC-200. The aim was to reduce the band gap of the UV active TiO<sub>2</sub> thin films as well as to investigate the effect of implantation on non photoactive TiO<sub>2</sub> thin films. No systematic differences were found before illumination, however a strong effect was found after doping and illumination on all samples.

**Keywords:** *TiO<sub>2</sub>, MePIIID, Ion doping, CAM, Surface energy*

**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<sub>2</sub> 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].

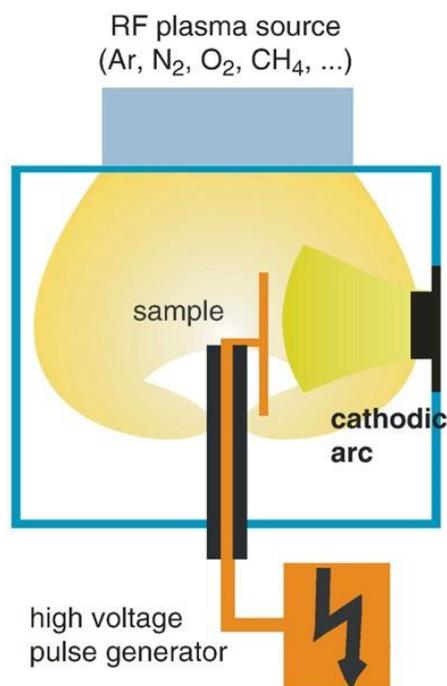
Independent of the phase composition the band gap is always more than 3 eV (the exact value depending on the polymorph), thus necessitating UV-A radiation for activation. For increasing the reactivity of the thin films under solar illumination, a reduced band gap is desired. Doping with transition metals 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<sub>2</sub> thin films or selective oxidation of TiN, is a much more complex process which is presently not completely understood [10]. Alternatively, TiO<sub>2</sub> nanotubes with a reduced band gap [11], visible-light-active N-doped TiO<sub>2</sub> 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<sub>2</sub> thin films are still controversially discussed.

In this work, TiO<sub>2</sub> thin films are formed by inserting an auxiliary rf plasma source in an experimental setup for depositing thin films with a cathodic vacuum arc and high voltage pulses, i.e. metal plasma immersion ion implantation & deposition (MePIII&D). Conventional ion implantation is employed to implant either carbon or nitrogen ions below the surface for bandgap engineering.

The resulting thin films are subsequently investigated for photoactive properties. The aim was to find the effect of ion doping on the photoactivity.

### MATERIAL AND METHODS

The TiO<sub>2</sub> thin films are produced by Metal Plasma Immersion Ion Implantation and Deposition. A d.c. cathodic arc with a pure titanium (99.99%) cathode, running at 100 A was employed to generate Ti ions. An oxygen supply of 45 to 70 sccm was used to establish a working pressure between 0.03 and 0.3 Pa. Converting the nominal Ti ion current from the cathode of about 10 A at an average charge state of 2.1 into a particle flux and comparing this value with the oxygen flow, a O/Ti ratio of roughly 2.5:1 to 3.5:1 is established in the gas phase (assuming a homogeneous distribution within the vacuum chamber, which is definitely not true for the Ti flux). Silicon (100) coupons were used as substrate material, mounted at a fixed distance of 39 cm from the cathode.



**Figure 1:** Schematic of the MePBIID deposition system with auxiliary plasma source.

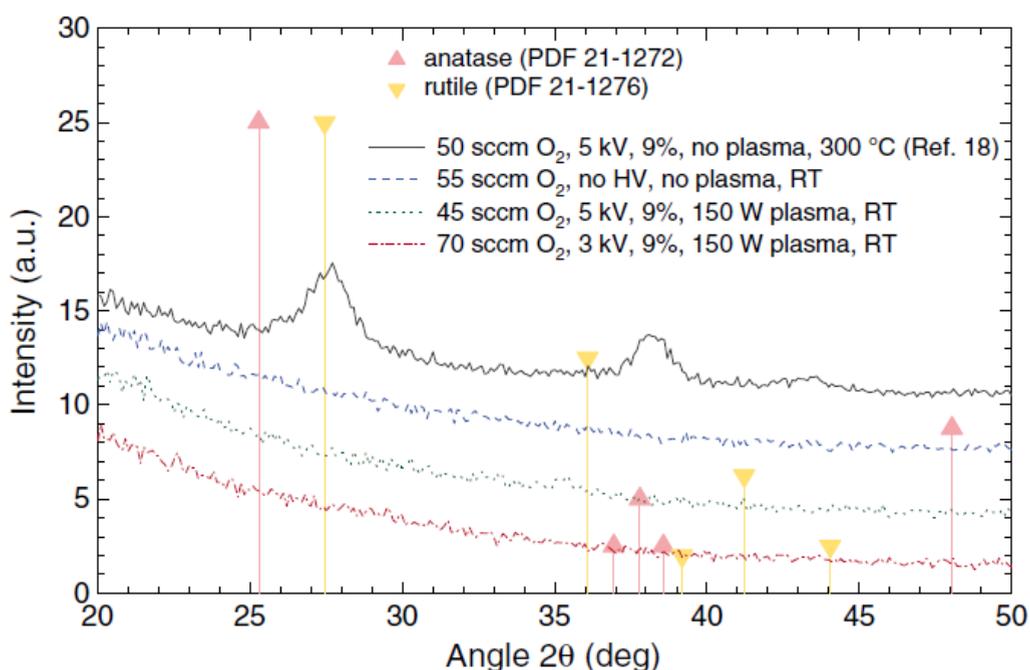
No additional heating system was installed, thus the temperature of the substrates was always starting at room temperature (RT), rising to 50 °C or less at the end of the experiment. The nominal kinetic energies of 10–50 eV for Ti ions emanating from the d.c. arc were enhanced by negative high voltage pulses between 1 and 5 kV with a length of 30 μs at repetition rate of 1–3 kHz (duty cycle 3–9%). Furthermore, a 40.68 MHz rf plasma source was selectively employed

at a fixed power of 150 W to create a background oxygen plasma. Without arc, an oxygen plasma density of  $6 \times 10^9 \text{ cm}^{-3}$  at an electron temperature of 1 eV was measured by a Langmuir probe. The utilized geometry with the substrates facing towards the arc is depicted in Figure 1. A total deposition time of 5 min was used for all samples.

The film morphology was investigated with scanning electron microscopy (SEM) and Atomic Force Microscopy (AFM). X-ray diffraction measurements were performed in  $\theta/2\theta$ -geometry.

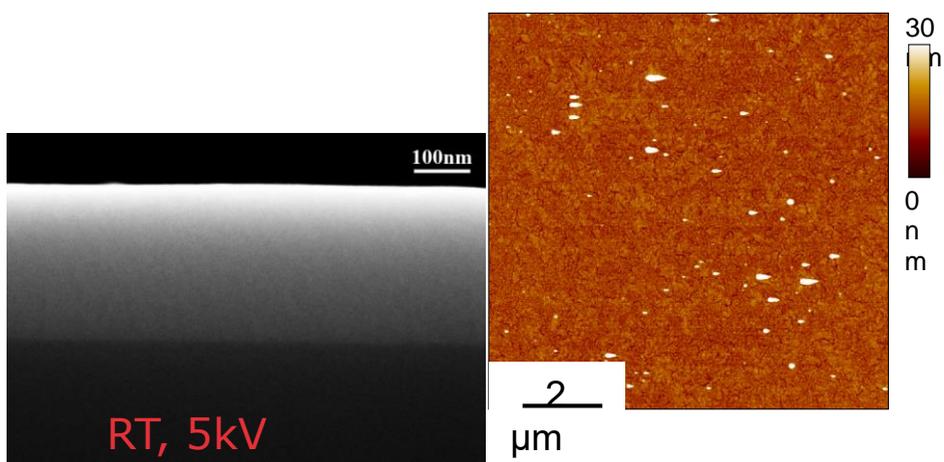
## RESULTS AND DISCUSSION

As shown in Figure. 2, no crystalline anatase or rutile phases could be detected at RT for the pulse voltage range from 0 to 5 kV, independent of gas flow and plasma activation, indicating either an amorphous structure or nanocrystallites with a size of less than 5 nm.



**Figure 2:** XRD spectra of samples produced at RT with different ion bombardment parameters and auxiliary oxygen plasma on or off. Additionally, results from deposition at 300 °C are shown for comparison. The expected peak positions according to the powder diffraction files for anatase and rutile are indicated. The spectra are shifted vertically for clarity.

Similar results are obtained for the film morphology when investigating thin film cross-sections with SEM. No contrast is visible for a film deposited at room temperature with 5 kV pulse voltage. AFM results confirm the SEM results on the morphology, both depicted in Figure 3.



**Figure 3:** SEM and AFM viewgraphs of the sample produced at RT with 5kV high voltage pulses and auxiliary oxygen plasma on.

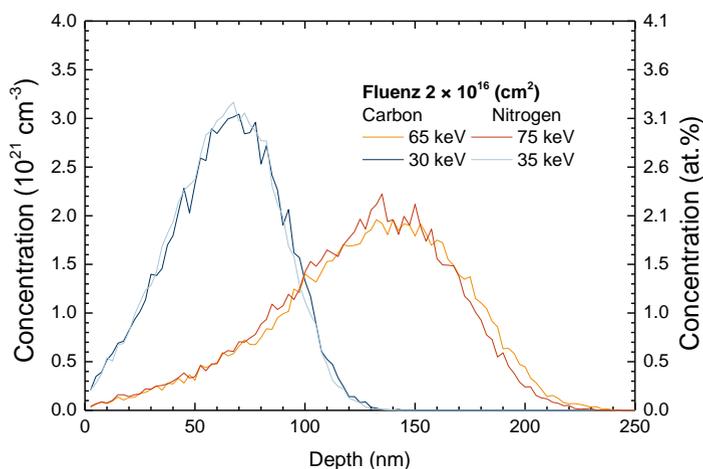
Contact angle measurements on TiO<sub>2</sub> samples were performed using a Krüss Contact Angle measuring system G2 and the results are obtained from the software DSA II (Drop shape analysis II). In dynamic CAM mode two different liquids are used, deionised water and ethylene glycol, employing manual drop position on the surface with 2 – 4 drops (because of high wettability of the samples surface after UV-irradiation). From each liquid a start-volume 3 μl and end-volume 4 μl, 10 successive snapshots for each drop were taken.

No of Pairs	Sample ID	Substrate	Flow Rate (O <sub>2</sub> )	Time	HV	Pulse Length	Repetition Rate	RF Plasma	Distance from axis	Photoactive
1	9020	Si	55sccm	5min	0kV	30μs	3kHz	150W/1%	20cm	42.3 (No)
	9021	Si	55sccm	5min	5kV	30μs	3kHz	150W/1%	20cm	82.9 (Yes)
2	9022	Si	55sccm	5min	3kV	30μs	3kHz	150W/1%	20cm	112.2 (Yes)
	9024	Si	55sccm	5min	5kV	30μs	3kHz	150W/1%	10cm	40.6 (No)
3	9025	Si	55sccm	5min	3kV	30μs	3kHz	150W/1%	10cm	95.2 (Yes)
	9027	Si	55sccm	5min	0kV	30μs	3kHz	150W/1%	10cm	40.3 (No)
4	9029	Si	55sccm	5min	3kV	30μs	3kHz	150W/1%	0cm	73.6 (Yes)
	9030	Si	55sccm	5min	1kV	30μs	3kHz	150W/1%	0cm	47.5 (No)
Substrate holder diameter Φ=7.8cm (9020-9031)										

**Table 1.** Selected Sample list from photoactivity results

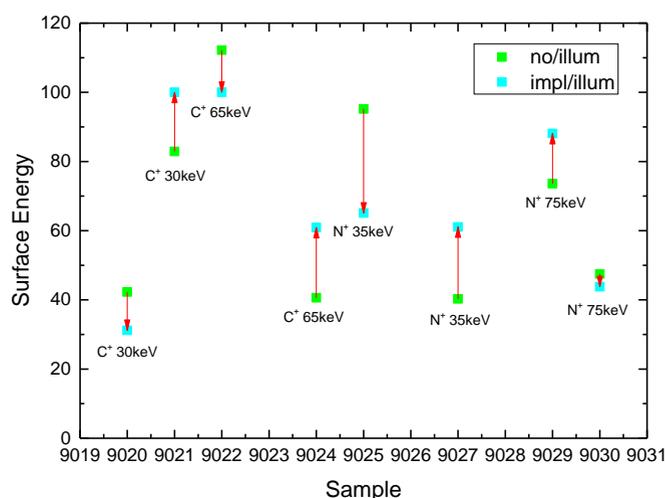
The surface energy was derived from contact angle measurements employing water and ethylene glycol with the data analysis according to the Owens-Wendt method. The samples were exposed to UV-A light, generated from an actinic tube with a spectral range of 300 – 460 nm and the maximum intensity at 365 nm, with an irradiation power intensity of 1 mW/cm<sup>2</sup>, for 3 hours. The ambient temperature and humidity was 21 °C and 25%, respectively.

From the samples produced we have selected 4 pairs, one promising to be photoactive and the other not at all for each pair. The samples parameters and photoactivity characteristics are depicted in the table 1.



**Figure 4.** Concentration profiles of Carbon and Nitrogen

Then, the above listed amorphous samples are doped with carbon and nitrogen, using an Ion Implanter IMC-200. The aim was to reduce the band gap of the UV active TiO<sub>2</sub> thin films as well as to investigate the effect of implantation on non photoactive TiO<sub>2</sub> thin films.



**Figure 5.** Surface energy of selected samples after implantation with/without UV-illumination

The following implantation parameters have been used: energies for C<sup>+</sup> ions 30 keV and 65 keV, for N<sup>+</sup> ions 35 keV and 75 keV, average implantation time 35 min and total fluence of 2

$\times 10^{16} \text{ cm}^{-2}$ . The concentration profiles of carbon and nitrogen as calculated by SRIM are shown in Fig. 4.

After implantation the samples are illuminated with UV light for 3 hours and the surface energy is derived from contact angle measurements. The results from contact angle measurements are presented in the Figure 5. We observe an increase of surface energy from some samples after implantation, but on some of them no change or decrease of surface energy can be seen from this graph.

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