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Silicon dioxide coatings from dielectric barrier discharge in a two step process

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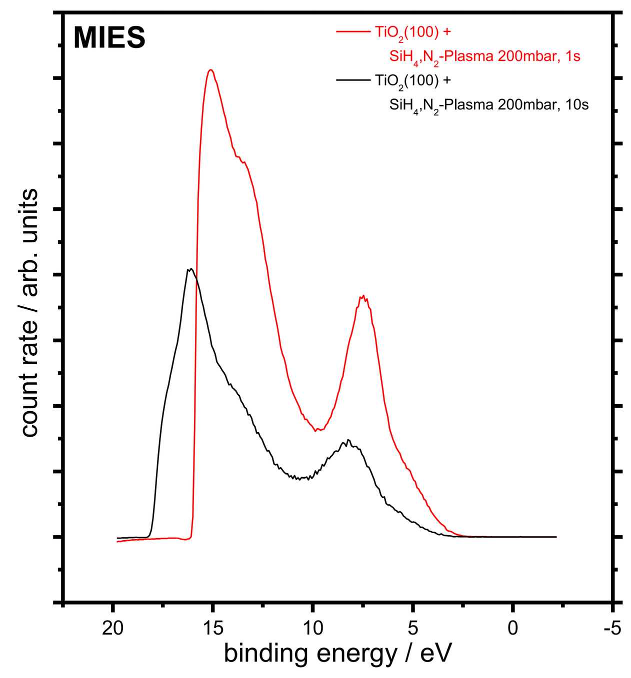
1. Introduction

The coating of the model substrate titanium dioxide with silicon dioxide has been investigated by means of X-ray Photoelectron Spectroscopy (XPS), Metastable Induced Electron Spectroscopy (MIES), Ultraviolet Photoelectron Spectroscopy (UPS) and Atomic Force Microscopy (AFM). The silicon was deposited using the gaseous precursor silane, which was diluted in 98.5% nitrogen for safer handling. The precipitation of the precursors before deposition through oxidation reactions was avoided by cutting the deposition process into two steps. In the first step, silicon was deposited in the form of silicon nitride. In the second step, the film was transformed into stoichiometric silicon dioxide by a second plasma treatment.

2. Experimental

For probing the surface of titanium dioxide we applied MIES and UPS using a hemispherical analyzer (VSW HA100) combined with a source for metastable helium atoms (mainly He*2^3S_1) and ultraviolet photons (HeI). Additional information for chemical analysis was obtained by XPS utilizing a commercial non-monochromatic X-ray source (Specs RQ20/38C).
The topography and roughness of the TiO_2 crystal, as well as the plasma treated samples were determined by AFM using a Veeco Dimension 3100 SPM. All measurements were performed in Tapping Mode with Al-coated silicon cantilevers (MicroMasch NSC15). The depiction, as well as the calculation of the root mean square roughness (RMS) was carried out with SPIP (Image Metrology A/S) according to ISO 4287/1.
The TiO_2 crystal was cleaned by Ar^+ ion sputtering (60 min.) and heating (750 °C, 30 min.). Afterwards the plasma treatment, a dielectric barrier discharge was performed in two steps. The process gas in the first step was a silane gas mixture (Linde Gas) consisting of 1.5% SiH_4 (99.999%) and 98.5% N_2 (99.9996%). The process gases in the second step were O_2 (Linde Gas, 99.995%) and atmospheric air.

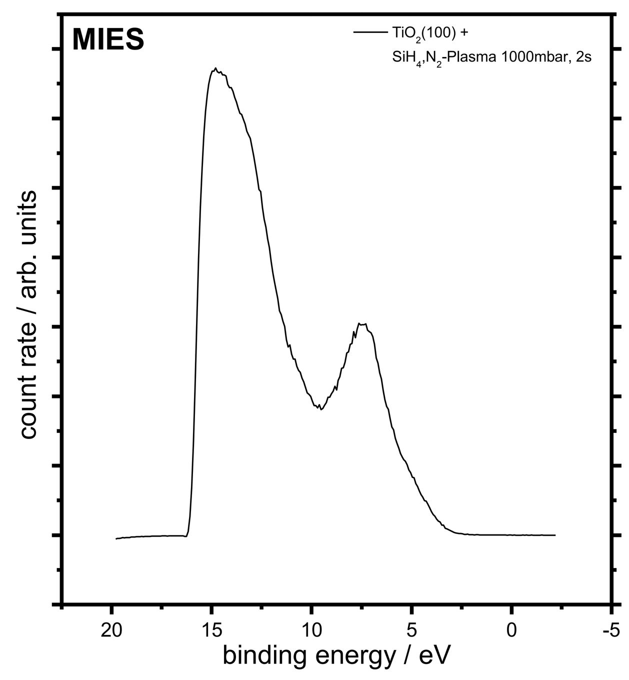
3. 200 mbar Silane/Nitrogen-Plasma

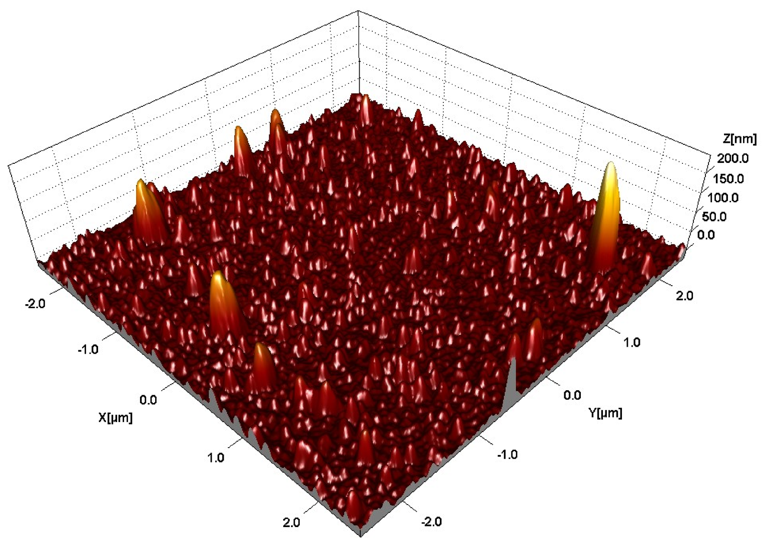


Stoichiometry	TiO_2(100)	SiH_4,N_2-Plasma 200 mbar 1s	SiH_4,N_2-Plasma 200 mbar 10s
Ti	27.3 %	14.8 %	0.0 %
O	72.7 %	41.4 %	0.0 %
C	0.0 %	12.6 %	0.0 %
N	0.0 %	8.4 %	29.6 %
Si	0.0 %	22.8 %	70.4 %
O / Ti	2.66	2.79	-
N / Ti	-	0.37	0.42
Layer	0.00 nm	1.80 nm	> 12 nm

closed layer of Si_3N
non-stoichiometric layer

4. 1000 mbar Silane/Nitrogen-Plasma



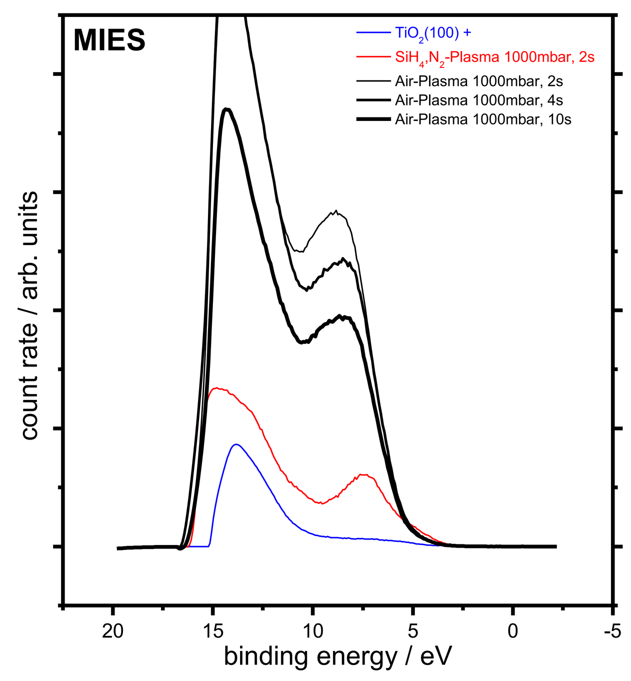


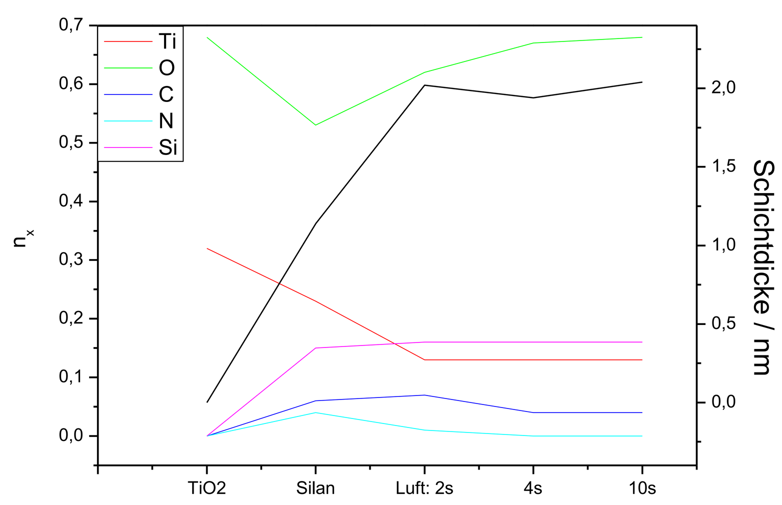
Stoichiometry	TiO_2(100)	SiH_4,N_2-Plasma 1000 mbar 2s
Ti	32.3 %	22.7 %
O	67.8 %	52.8 %
C	0.0 %	6.1 %
N	0.0 %	3.6 %
Si	0.0 %	14.9 %
O / Ti	2.10	2.32
N / Ti	-	0.24
Layer	0.00 nm	1.14 nm

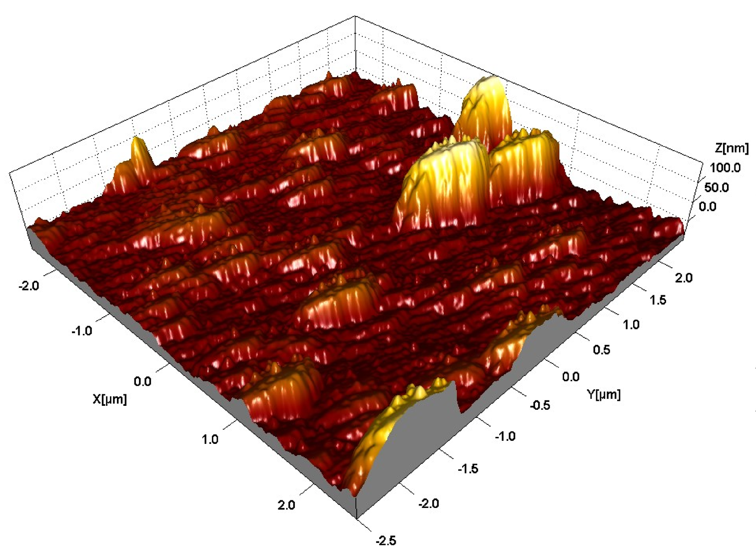
1.) **1000 mbar silane plasma treatment: formation of Si_3N-particles**

Avg. size of particles (w x l x h): 137 x 28 x 117 nm
352 x 195 x 213 nm, resp.
Avg. roughness: 9.53 nm
Rms roughness: 15.1 nm

5. Air-Plasma



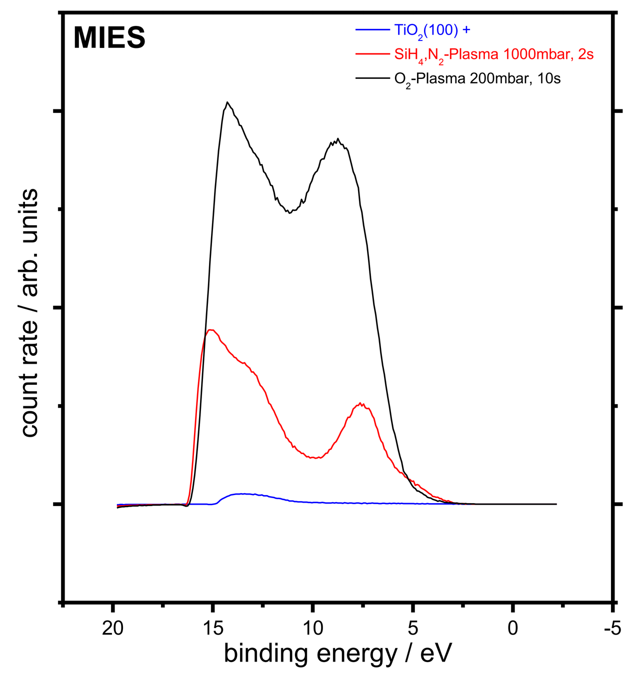


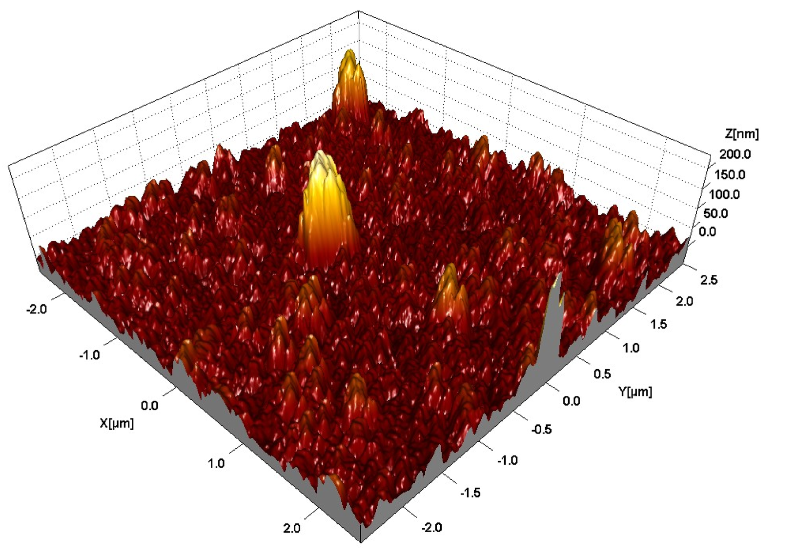


1.) 1000 mbar silane plasma treatment: formation of Si_3N-particles
2.) **1000 mbar air plasma treatment: agglomeration and transformation of Si_3N-particles**

Avg. size of particles (w x l x h): 626 x 891 x 156 nm
Avg. roughness: 11.0 nm
Rms roughness: 15.9 nm

6. 200 mbar Oxygen-Plasma



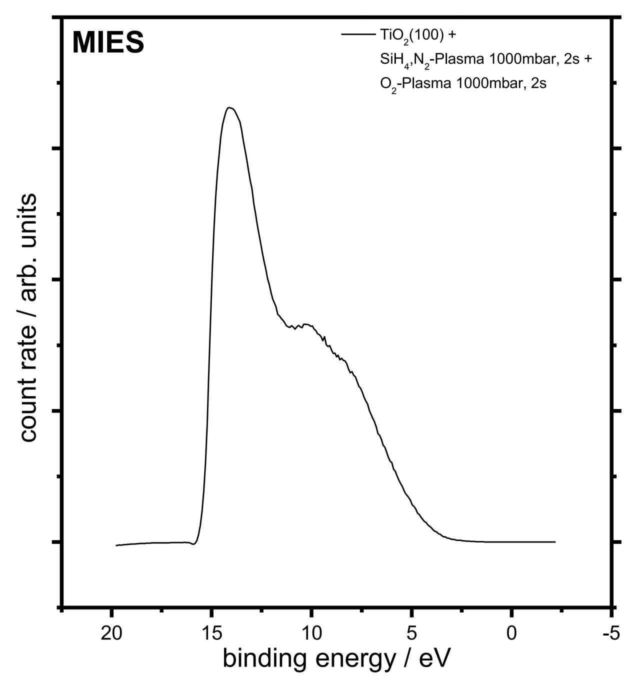


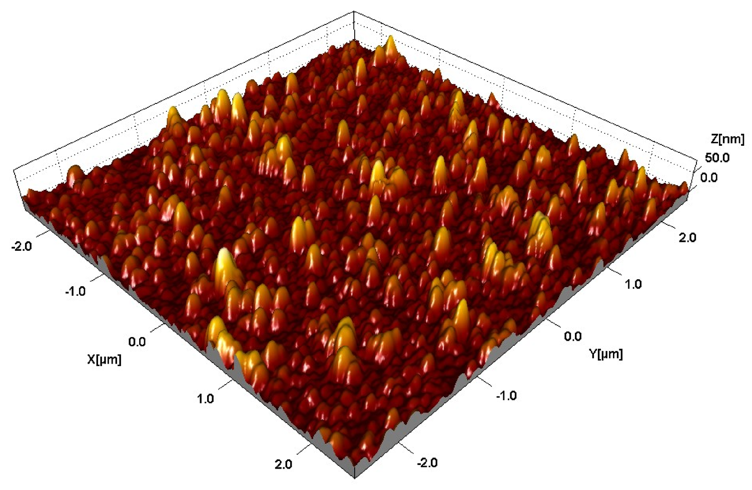
1.) 1000 mbar silane plasma treatment: formation of Si_3N-particles
2.) **200 mbar oxygen plasma treatment: transformation of Si_3N-particles, roughening of the surface**

Avg. size of particles (w x l x h): 665 x 704 x 206 nm
Avg. roughness: 16.4 nm
Rms roughness: 22.2 nm

Stoichiometry	TiO_2(100)	SiH_4,N_2-Plasma 1000 mbar 2s	O_2-Plasma 200 mbar 10s
Ti	25.5 %	9.2 %	6.8 %
O	74.5 %	30.6 %	65.7 %
C	0.0 %	12.2 %	2.4 %
N	0.0 %	12.7 %	2.2 %
Si	0.0 %	35.4 %	23.0 %
O / Ti	2.92	3.33	9.69
N / Ti	-	0.36	0.09
Layer	0.00 nm	3.22 nm	3.43 nm

7. 1000 mbar Oxygen-Plasma





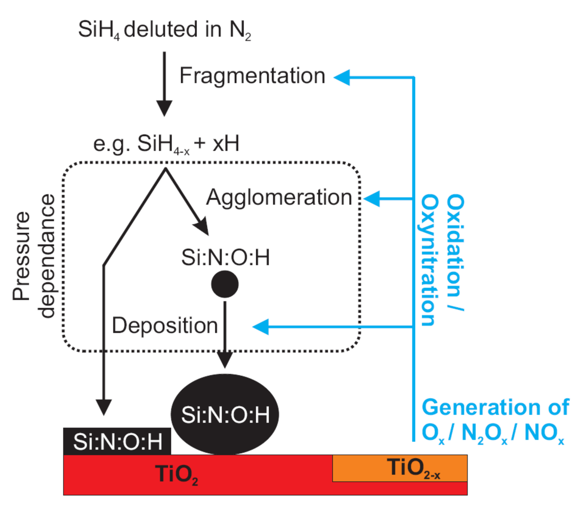
1.) 1000 mbar silane plasma treatment: formation of Si_3N-particles
2.) **1000 mbar oxygen plasma treatment: keeping Si_3N-particles at similar size**

Avg. size of particles (w x l x h): 176 x 215 x 52 nm
Avg. roughness: 9.70 nm
Rms roughness: 12.7 nm

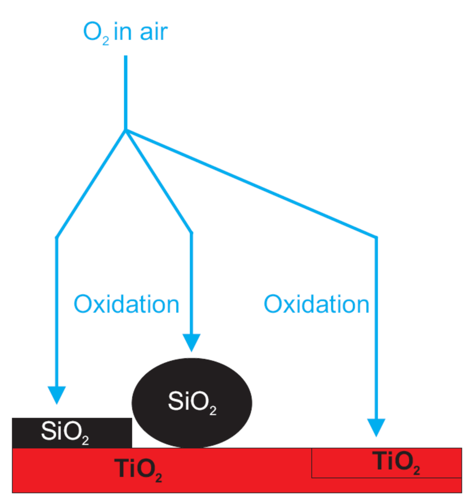
Stoichiometry	TiO_2(100)	SiH_4,N_2-Plasma 1000 mbar 2s	O_2-Plasma 1000 mbar 2s
Ti	33.3 %	21.3 %	20.3 %
O	66.7 %	53.3 %	60.5 %
C	0.0 %	13.4 %	8.7 %
N	0.0 %	2.6 %	2.0 %
Si	0.0 %	9.4 %	8.5 %
O / Ti	2.00	2.50	2.98
N / Ti	-	0.28	0.24
Layer	0.00 nm	1.01 nm	0.75 nm

8. Model

1.) Deposition step



2.) Transformation step



9. Literature

[1] P. Van Cappellen et. al., Geochim. Cosmochim. Acta 57, 3505-3518
[2] S. Dahle, L. Wegewitz, A. Weber, W. Maus-Friedrichs, International Conference on Plasma Surface Engineering (2012)

10. Acknowledgements

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Atom- und Molekülphysik an Oberflächen