

Sebastian Dahle<sup>1,2</sup>, Alfred Weber<sup>3</sup>, Wolfgang Viöl<sup>2</sup> and Wolfgang Maus-Friedrichs<sup>1,4\*</sup>

<sup>1</sup> Institut für Energieforschung und Physikalische Technologien, TU Clausthal, Leibnizstraße 4, Clausthal - Zellerfeld, D - 38678, Germany

<sup>2</sup> Hochschule für Angewandte Wissenschaft und Kunst, Fakultät für Naturwissenschaften und Technik, Von-Ossietzky-Straße 99, 37085 Göttingen, Germany

<sup>3</sup> Institut für Mechanische Verfahrenstechnik, TU Clausthal, Leibnizstr. 19, 38678 Clausthal-Zellerfeld, Germany

<sup>4</sup> Clausthaler Zentrum für Materialtechnik, TU Clausthal, Leibnizstr. 4, 38678 Clausthal-Zellerfeld, Germany



## 1. Introduction

Titanium dioxide nano particles are used commonly in various applications due to their high catalytic activity. Many of these applications require subsequent treatments after the deposition of the TiO<sub>2</sub> particles. Some of these include thermal processing at high temperatures, e.g. roof tiles. During such procedures the nano particles transform from the catalytical highly active anatase structure to the substantially less active rutile structure. This structural change has been found to be significantly retarded when coating the TiO<sub>2</sub> nano particles with a closed film of SiO<sub>2</sub>. During the thermal treatment, these films break open, revealing the underlying TiO<sub>2</sub>. Thus, the film thickness has to be appropriate for the designated treatment subsequent to the nano particle deposition.

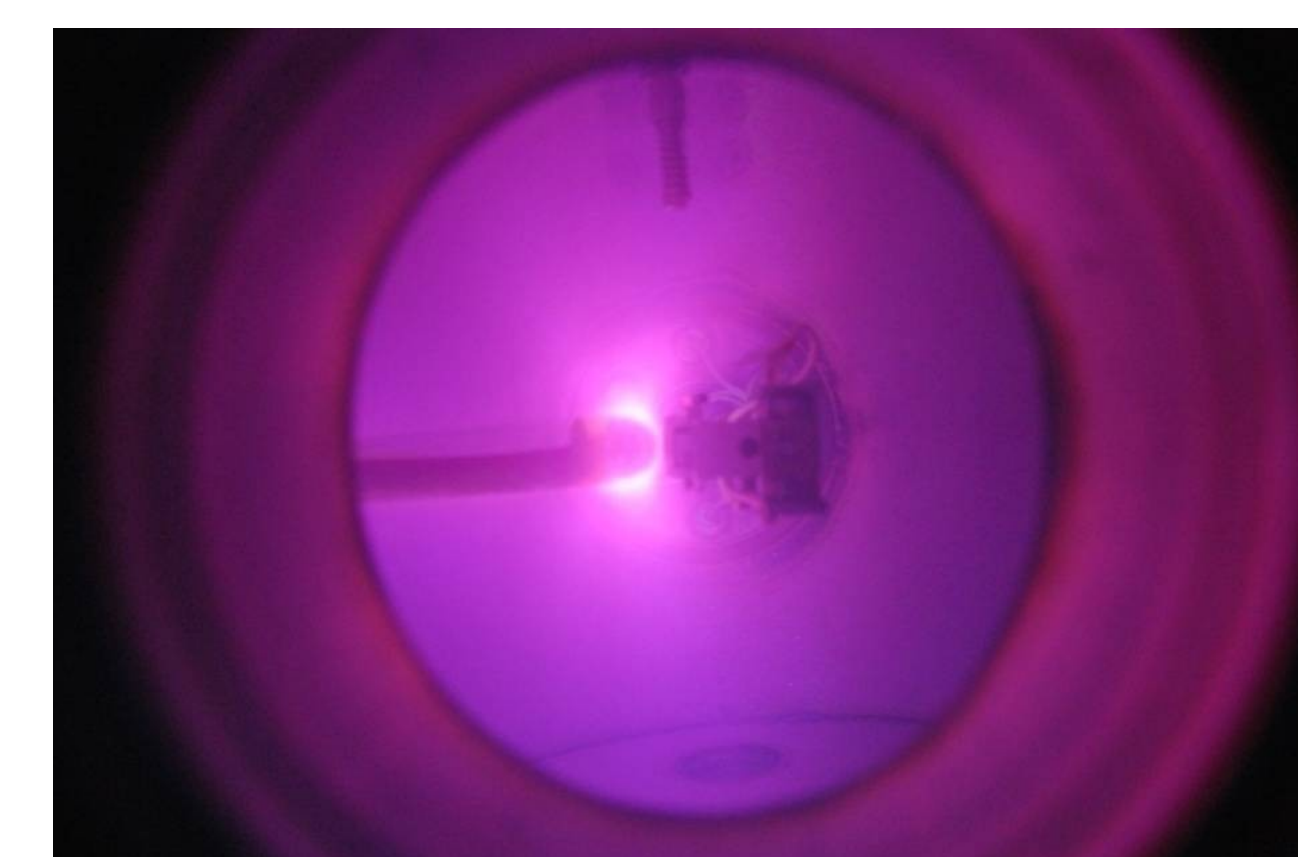
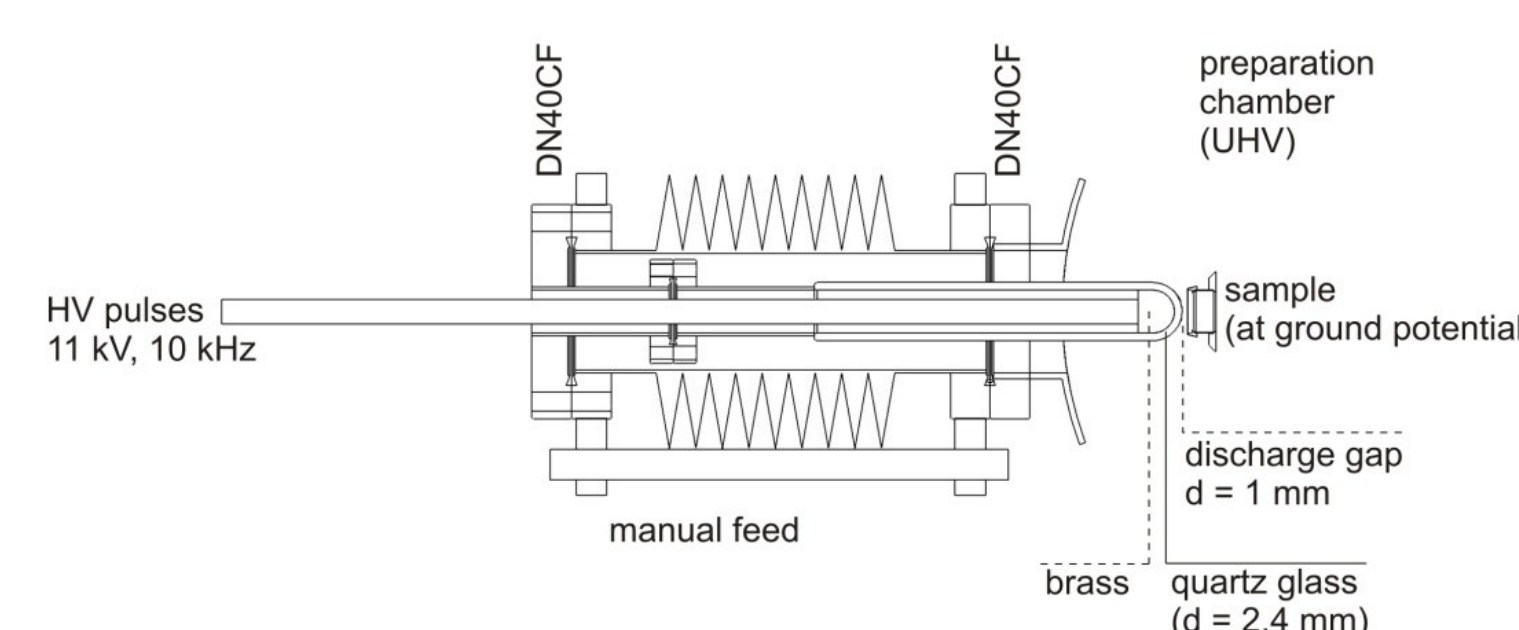
In this study, we present an approach of SiO<sub>2</sub> film deposition out of silan gas. For technical implementations, test gas containing about 1.5% silan in 98.5% nitrogen is preferred over pure silan, since much less precautions are needed. Closed films produced by dielectric barrier discharges in such mixtures of gases consist of mainly non-stoichiometric silicon nitride. The conversion of this silicon nitride layer to silicon dioxide is shown to be largely possible by subsequent plasma treatment in different atmospheres such as pure O<sub>2</sub>, as well as in environmental air.

All studies have been carried out in an ultra high vacuum apparatus, while the plasma treatments have been carried out at atmospheric pressure. During the investigations we employed metastable induced electron spectroscopy, ultraviolet photoelectron spectroscopy, X-ray photoelectron spectroscopy and atomic force microscopy.

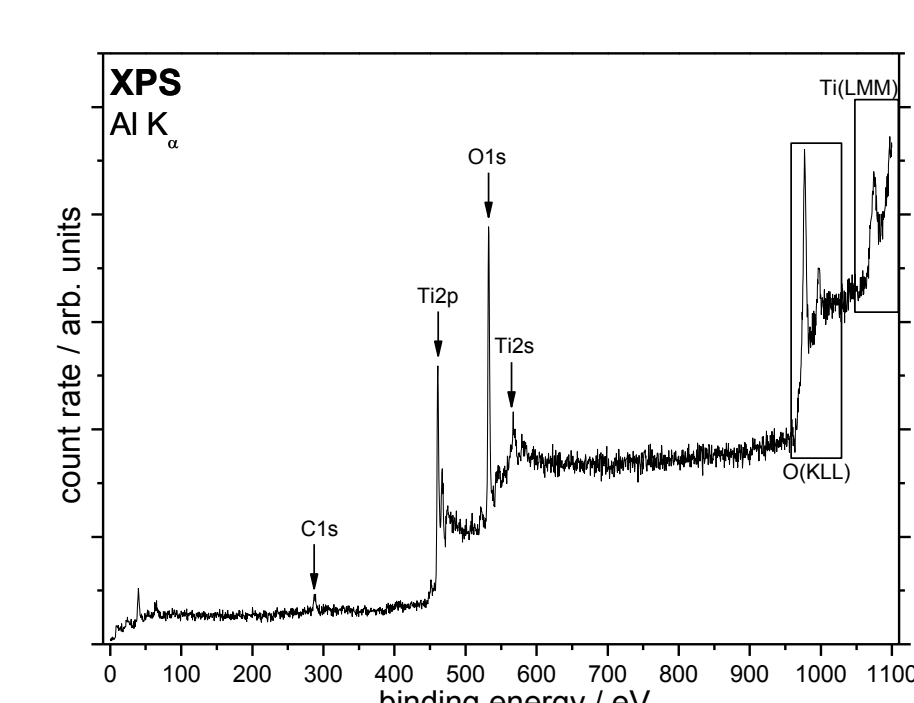
## 2. Experimental

For probing the surface density of states (SDOS) we applied MIES and UPS using a hemispherical analyzer (VSW HA100) combined with a source for metastable helium atoms (mainly He\*2<sup>3</sup>S<sub>1</sub>) and ultraviolet photons (HeI). Additional information for chemical analysis was obtained by XPS utilizing a commercial non-monochromatic X-ray source (Specs RQ20/38C) using Al K $\alpha$  at a photon energy of 1486.6 eV. Fit curves were gained using OriginPro 7G with the Peak Fitting Module. A Veeco Dimension 3100 SPM is employed for tapping mode AFM with silicon cantilevers (NSC15 with Al backside coating from Micromasch).

Plasma treatments have been carried out employing alternating high voltage pulses with a peak voltage of 11 kV, a pulse duration of 0.6  $\mu$ s and a pulse repetition rate of 10 kHz. The used process gases were O<sub>2</sub> (Linde Gas, 99.995%), N<sub>2</sub> (Linde Gas, >99.8%), atmospheric air and a silane gas mixture (Linde Gas) consisting of 1.5% SiH<sub>4</sub> (99.999%) and 98.5% N<sub>2</sub> (99.9996%).

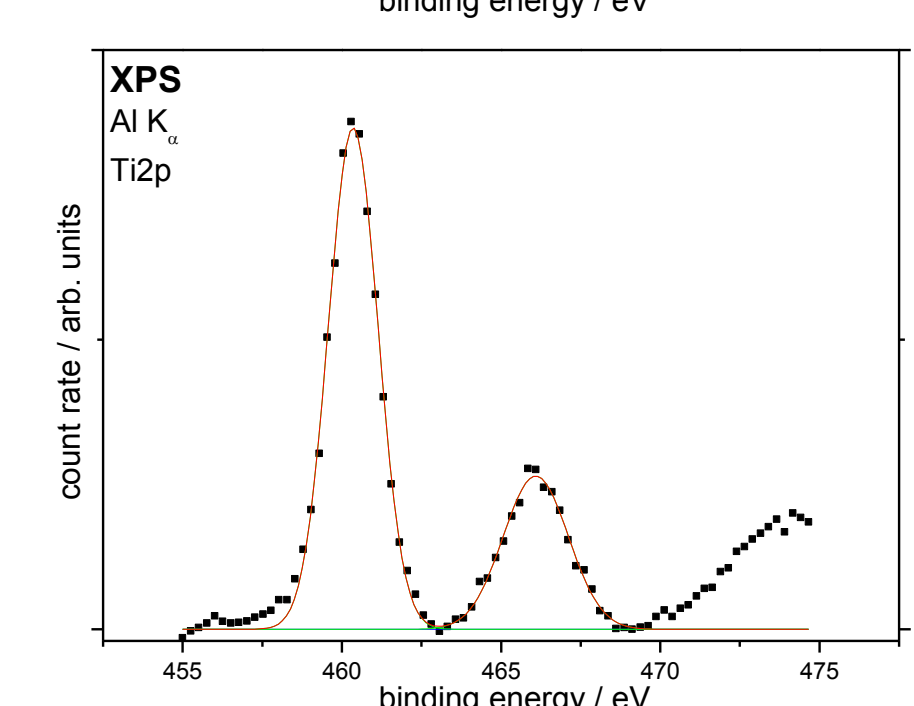
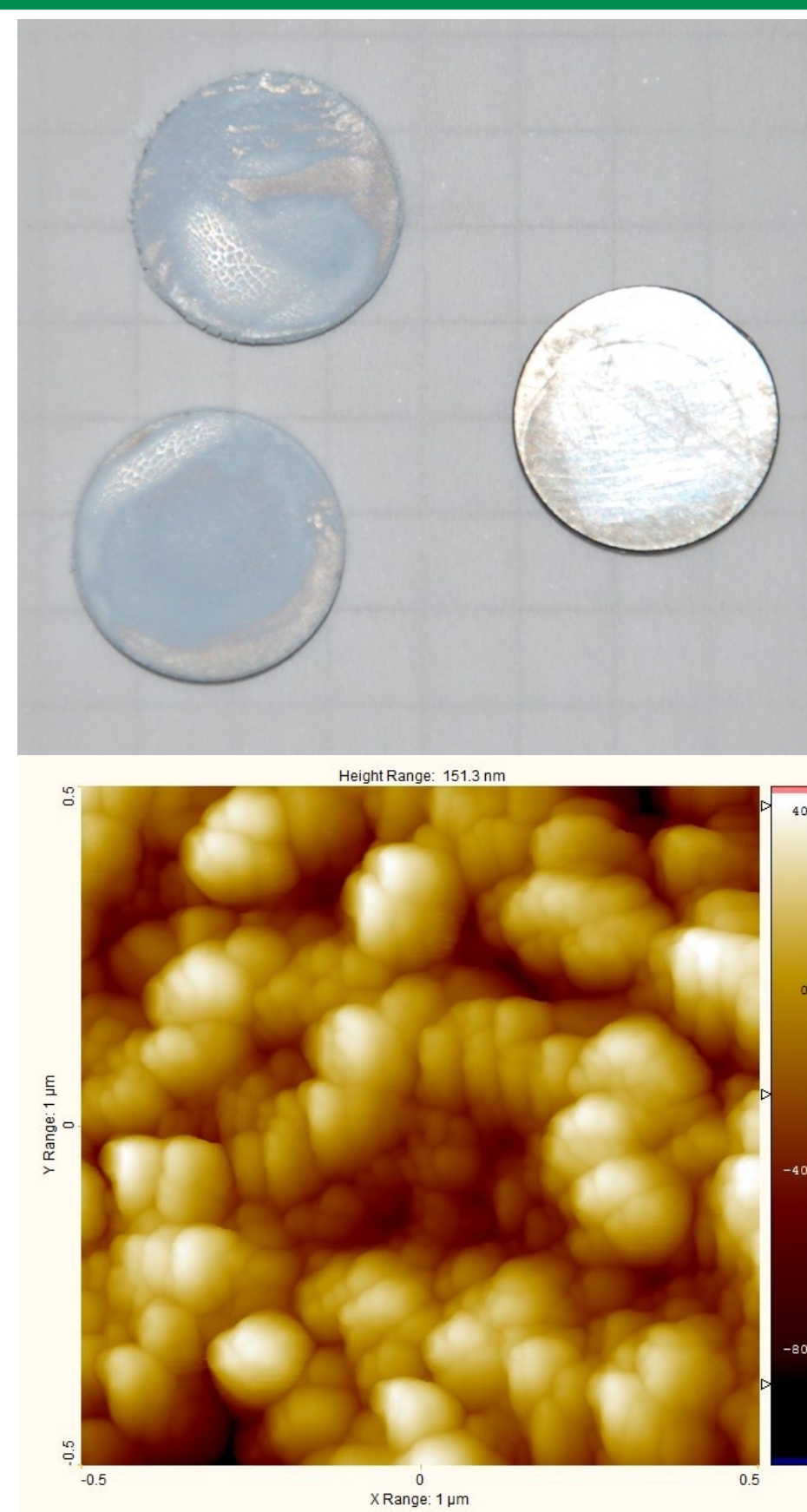


## 3. Sample preparation



**Stoichiometry:**  
C 15.4%  
Ti 23.4%  
O 61.2%

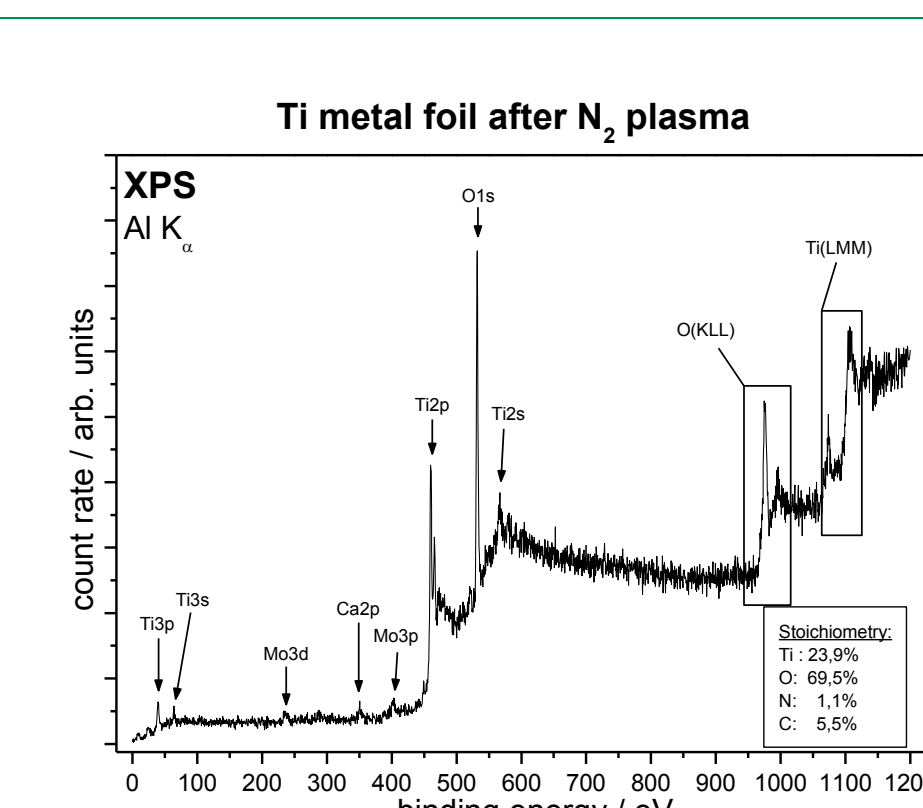
- Stoichiometric TiO<sub>2</sub> particles
- Adsorbents at the surface from air



TiO<sub>2</sub> nanoparticles :  
Degussa P25  
(d<sub>50</sub> ~ 21 nm, >99.5%)

Drop-coating onto molybdenum washer suspended in ethanol

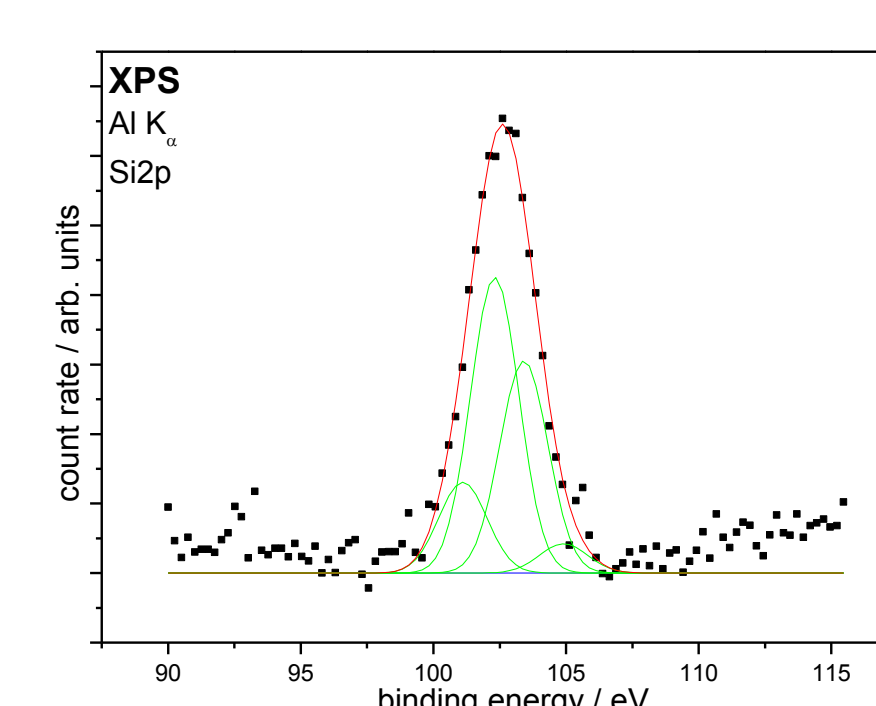
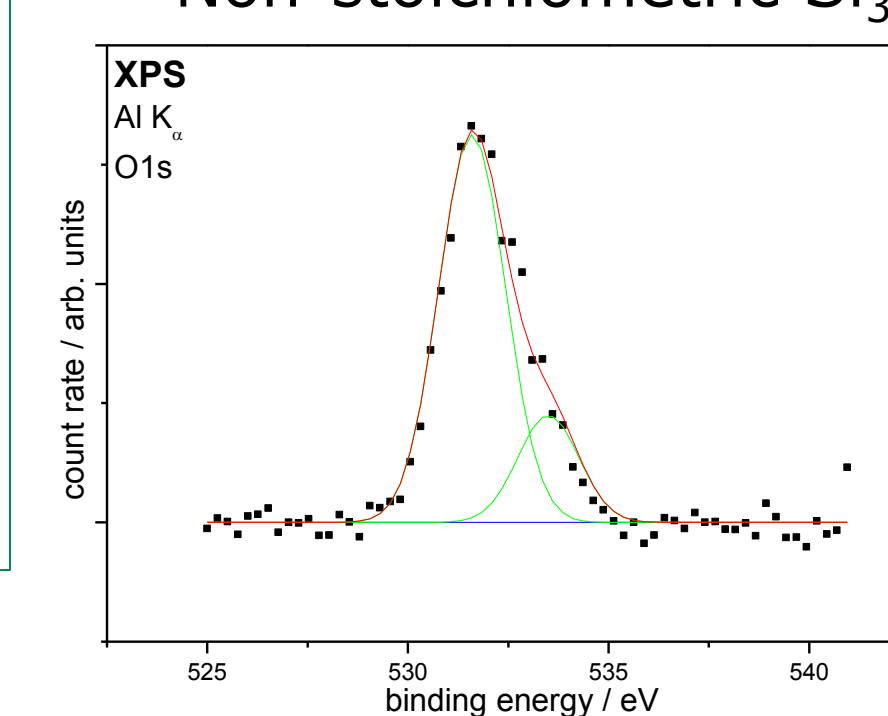
## 4. SiH<sub>4</sub>/N<sub>2</sub> plasma treatment (1<sup>st</sup> step)



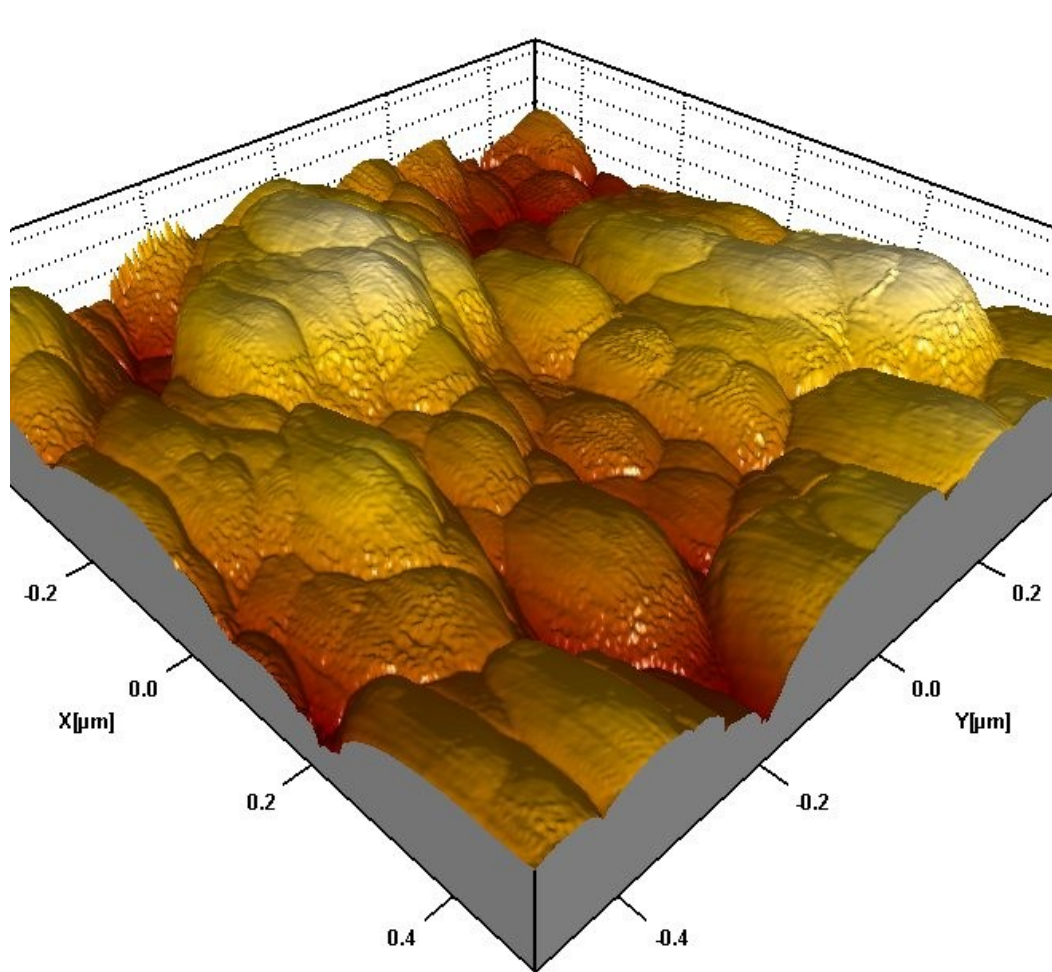
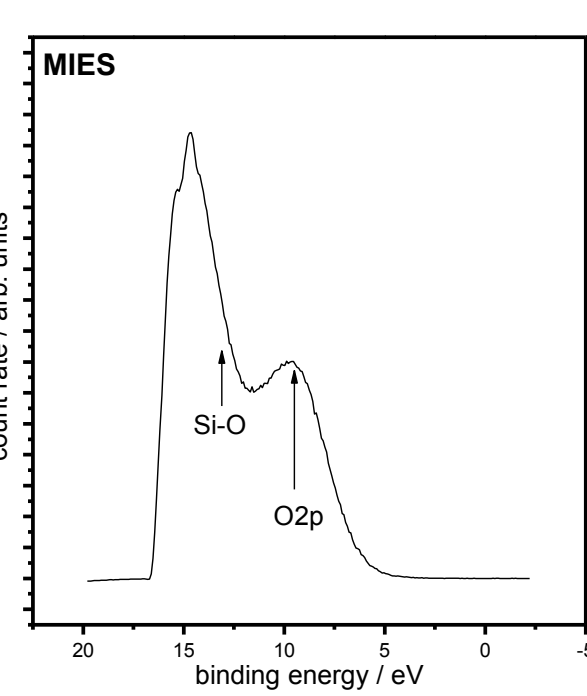
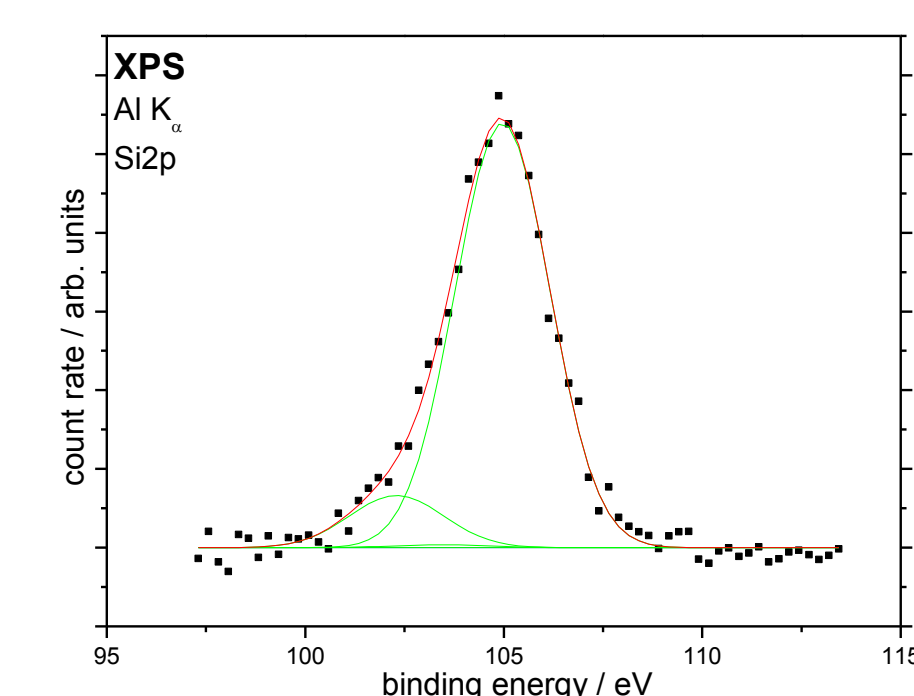
**Stoichiometry:**  
C 5.9%  
N 20.1%  
Ti 6.0%  
Si 46.5%  
O 20.6%

- Carbon reduction
- Ti<sub>2</sub>O<sub>3</sub> defects at particle surfaces
- Non-stoichiometric Si<sub>3</sub>N cover layer

- Plasma treatment in dry N<sub>2</sub> mainly leads to oxidation
- Energy transfer N<sub>2</sub>\* → O<sub>2</sub>\* [1,2,3,4] responsible for high efficiency of oxidation?



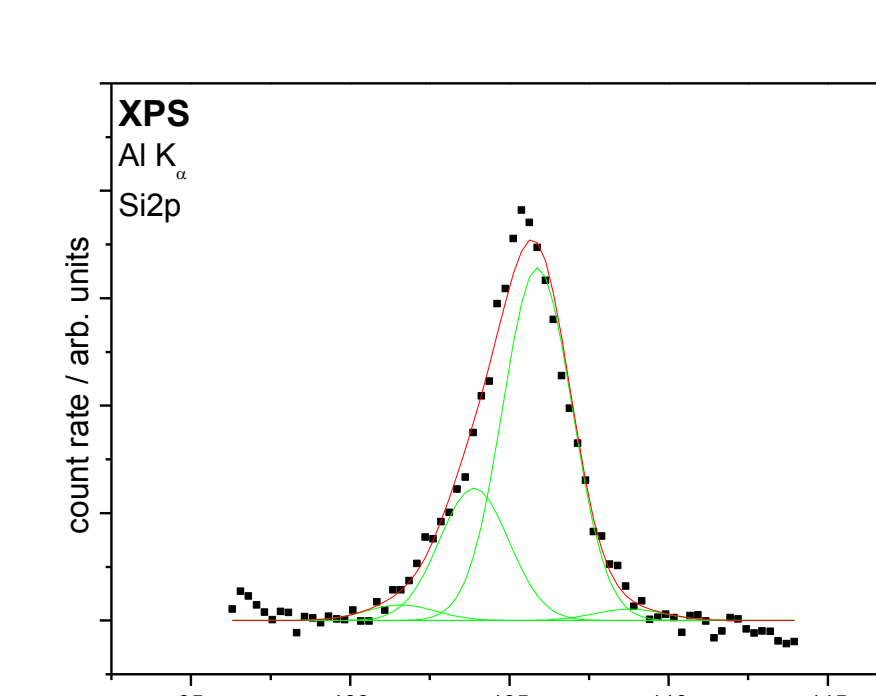
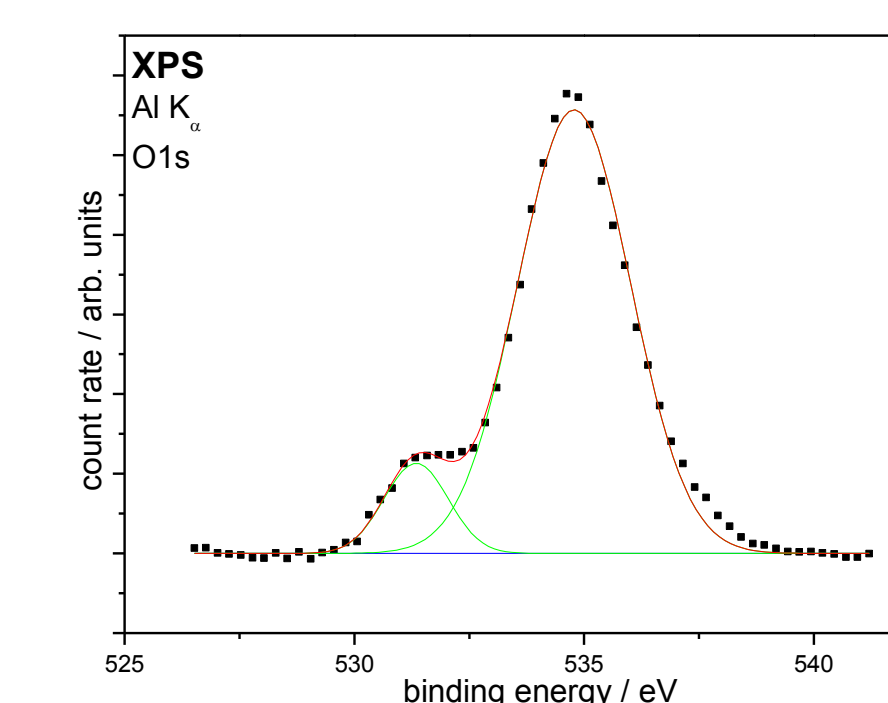
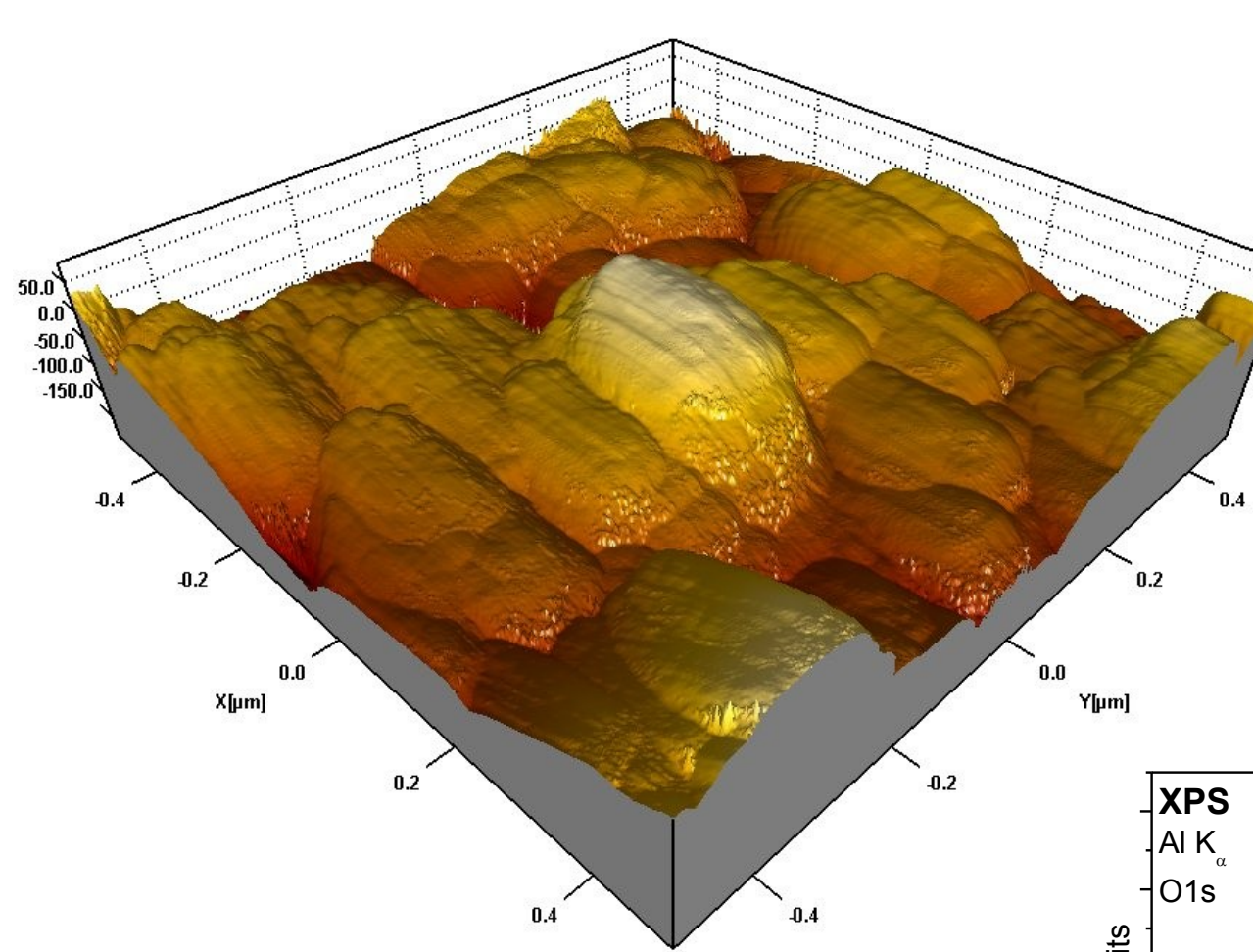
## 5a. O<sub>2</sub> plasma treatment (2<sup>nd</sup> step)



**Stoichiometry:**  
C 0.0%  
N 5.0%  
Ti 5.7%  
Si 23.7%  
O 65.7%

- Complete removal of carbon
- Severe reduction of nitrogen
- Healing of interfacial Ti<sub>2</sub>O<sub>3</sub> defects
- Transformation of cover layer into substoichiometric SiO<sub>2</sub>

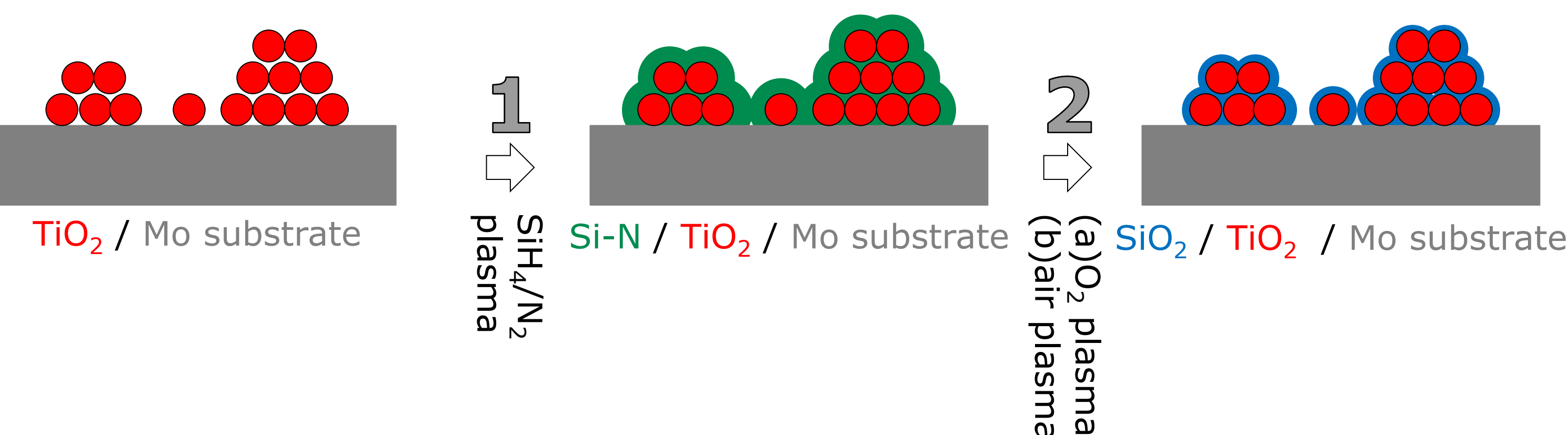
## 5b. Air plasma treatment (2<sup>nd</sup> step)



**Stoichiometry:**  
C 2.3%  
N 3.0%  
Ti 3.0%  
Si 27.8%  
O 63.9%

- Further removal of carbon
- Severe reduction of nitrogen
- Healing of interfacial Ti<sub>2</sub>O<sub>3</sub> defects
- Transformation of cover layer into substoichiometric SiO<sub>2</sub>

## 5. Discussion



See also: S. Dahle, L. Wegewitz, A. Weber, W. Maus-Friedrichs, International Conference on Plasma Surface Engineering (2012)

## 6. Literature

[1] F. J. Trompeter, PHD thesis at the RWTH Aachen, 2001.  
[2] B. M. Penetrante, M. C. Hsiao, J. N. Bardsley, B. T. Merritt, G. W. Vogtlin, A. Kuthi, C. P. Burkhart, J. R. Bayless, Plasma Sources Sci. Technol. **6** (1997) 251-259.  
[3] N. L. Aleksandrov, E. M. Bazelyan, I. V. Kochetov, N. A. Dyatko, J. Phys. D: Appl. Phys. **30** (1997) 1616-1624.  
[4] L. G. Piper, G. E. Caledonia, J. P. Kennealy, J. Chem. Phys. **74** (1981) 2888-2895.

\*Email: w.maus-friedrichs@pe.tu-clausthal.de

## 7. Acknowledgements

We thankfully acknowledge the technical assistance of Lienhard Wegewitz and Dana Schulte genannt Berthold, the provision of the atomic force microscope by the group of Professor W. Daum (Institut für Energieforschung und Physikalische Technologien, TU Clausthal) and the financial support of the Deutsche Forschungsgemeinschaft (DFG) under Project Nos. MA 1893/18-1 and VI 359/9-1.

