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The plasma treatment of Titanium in Oxygen, Nitrogen and Air studied with X-ray Photoelectron Spectroscopy

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René Gustus[1], Sebastian Dahle[1], Wolfgang Maus-Friedrichs[1,2]

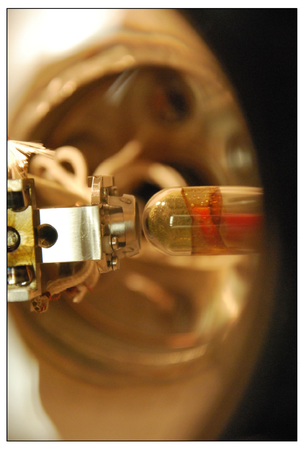
[1] *Institut für Physik und Physikalische Technologien, Technische Universität Clausthal, Leibnizstraße 4, 38678 Clausthal-Zellerfeld, Germany*
[2] *Clausthaler Zentrum für Materialtechnik, Technische Universität Clausthal, Leibnizstraße 4, 38678 Clausthal-Zellerfeld, Germany*

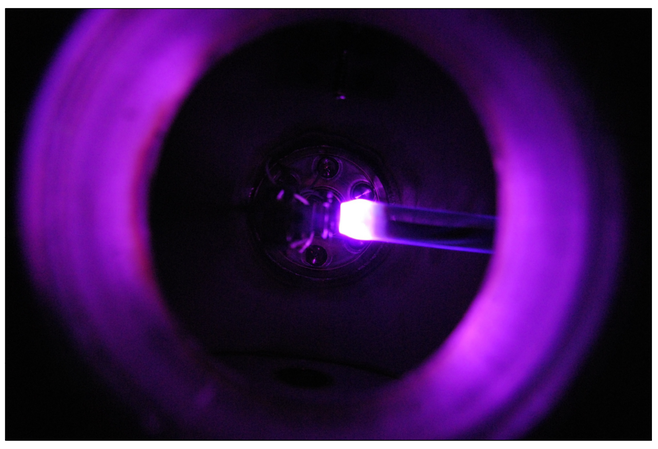
Introduction

Titanium and its alloys attain much attention due to their high corrosion resistance, light weight, biocompalibility, and photocatalytic properties in the case of TiO_2 [1] and are therefore widely used in several applications for example in aerospace, automobile industry, medicine and microelectronics [2]. Likewise there is still a large interest to improve the mechanical and tribological properties as well as to extend the fabrication techniques and the field of implementation. In this regard plasma treatment is a commonly used procedure for surface modifications like etching, surface cleaning and hardening. The choice of the applied covergas depends on the desired functionalization. Nitrogen rich gases for example are reported for nitriding and to produce high hardnes surface films [3], oxygen to form titanium oxid layers [4]. This work deals with the plasma treatment of Titanium in Oxygen, Nitrogen and Air by a dielectric barrier discharge (DBD). The advanteges of DBD compared to other techniques are the moderate operating temperature and pressure. To investigate the chemical reactions and species which were formed, X-Ray Photoelectron Spectroscopy (XPS) is used.

Experimental

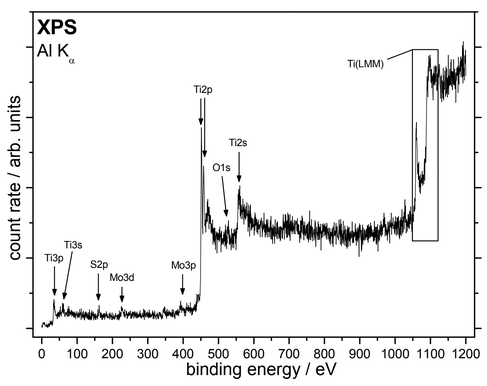
All measurements were carried out in an ultra-high vacuum system with a base-pressure of $5x10^{-11}$ hPa combined with a self-contained preparation-chamber equipped with the electrode for the dielectric barrier discharge. As substrate material a Titanium foil (Alfa Aesar, 99.99+%) of 1x1 cm is used. The surface of the substrate is investigated by XPS using a commercial non-monochromatic X-Ray source (Specs RQ20/38C) and a hemispherical analyzer (VSW HA 100). To remove raw impurities the Ti sample is cleaned with Ethanol in an ultrasonic bath. After transferring it in the UHV system and just before each plasma-treatment, the substrate is sputtered and heated up to 1100°C to get an impurity-free surface. The discharge is performed in different atmospheres by backfilling the preparation-chamber via a gas inlet system with Oxygen (200 hPa), Nitrogen (200 hPa) and Air (1000 hPa) respectively and is sparked by high voltage pulses (11 kV, 10 kHz, 0.6 µs).

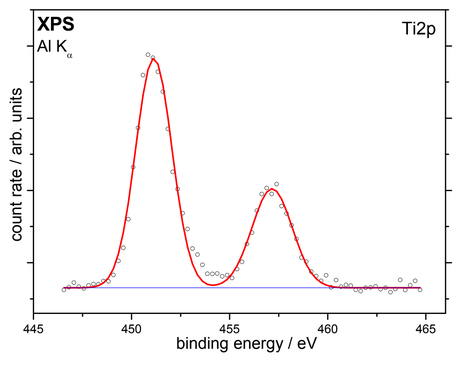




View into the preparation–chamber with the substrate in front of the plasma-electrode. The figure on the right hand side shows the same assembly while the discharge is running.

Clean Ti-foil

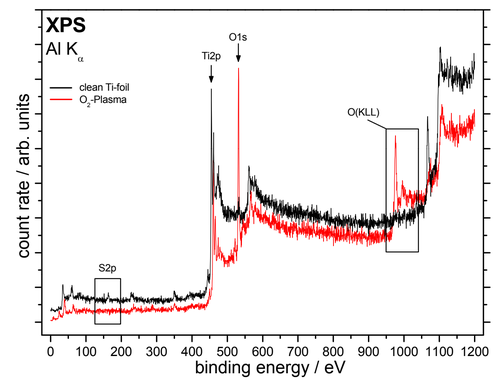


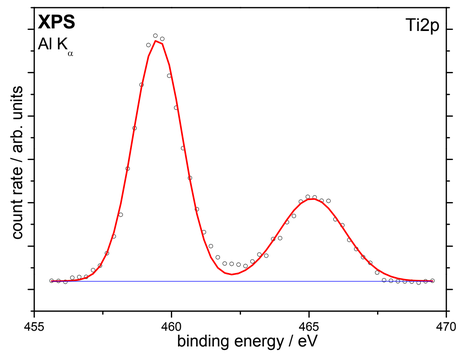


Stoichiometry:
Ti: 81% S: 9%
O: 10% C: <1%

- after anealing up to 1100°C apart from Titanium also Oxygen and Sulfur in slight concentrations have been detected
- however Ti2p analysis shows no significant broadening according to chemical shift

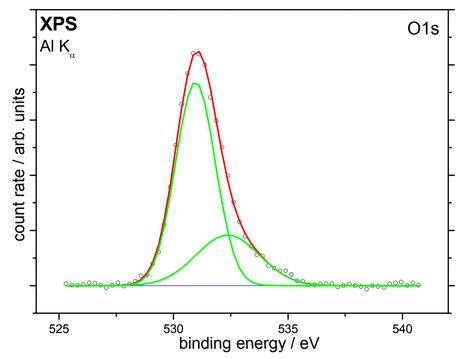
O_2/N_2-Plasma

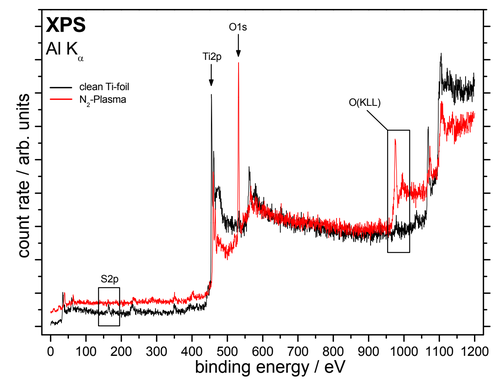


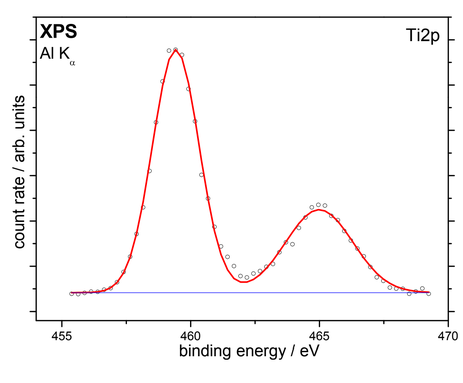


Stoichiometry:
Ti: 24% S: <1%
O: 76% C: <1%

- plasma treatment in O_2 led to a distinct increase in Oxygen concentration evident in XPS survey spectrum
- compared to clean Titanium, the Ti2p offeres a characteristic energy shift, which can refere to Ti^{4+} (459.5 eV) whereas no metallic Ti or suboxides are observable

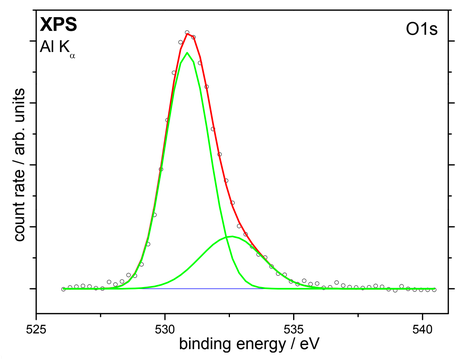




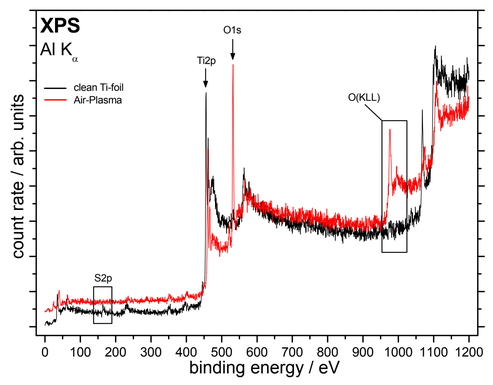


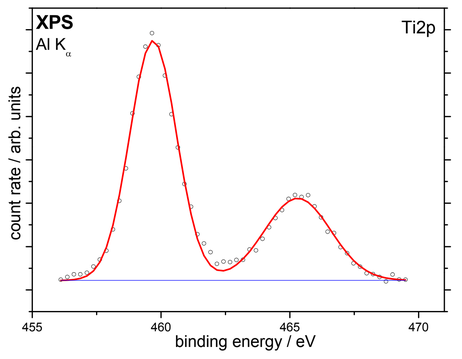
Stoichiometry:
Ti: 24% S: <1% N: <1%
O: 76% C: <1%

- N_2-plasma as well resulted in the oxidation of the Ti surface maybe due to Oxygen impurities in the process gas
- Ti2p analysis shows the same contribution for Ti^{4+} (459.4 eV)
- no nitrogen incorporation can be detected
- similarly to O_2 plasma no Sulfur impurities have been found



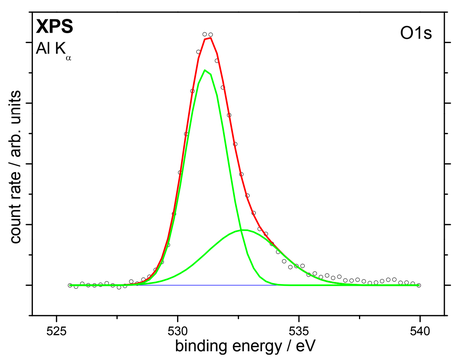
Air-Plasma





Stoichiometry:
Ti: 24% S: <1% N:<1%
O: 76% C: <1%

- compared to the plasma treatment in O_2 and N_2, Air-plasma shows the same stoichiometry and contributions of Ti2p (459.7 eV) and O1s (531.2 eV) which can be related to Ti^{4+}
- besides no other contaminations like Sulfur and Nitrogen can be found



References

[1] A. Wold, *Chem. Mater. 5 (1993) 280-283*
[2] M. Wittmer, H. Melchior *Thin Solid Films 93 (1982) 397*
[3] F.M. El-Hossary, N.Z. Negm, S.M. Khalil, M. Raaif *Appl. Surf. Sci. 239 (2005) 142-153*
[4] G.P. Burns, I.S. Baldwin, M.P. Hastings, J.G. Wilkes *J. Appl. Phys. 66 (1989) 2320*

Summary

- the plasma treatment of Titanium in Oxygen, Nitrogen and Air led to a reproducible formation of a TiO_2 surface layer independet of the applied process gas, whereas no Nitrogen incorporation took place
- in addition existing surface contaminations are removed

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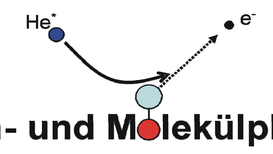

Atom- und Molekülphysik an Oberflächen