The adsorption and DBD-plasma-polymerization of thiophene on titania

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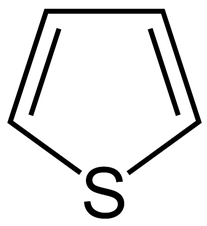
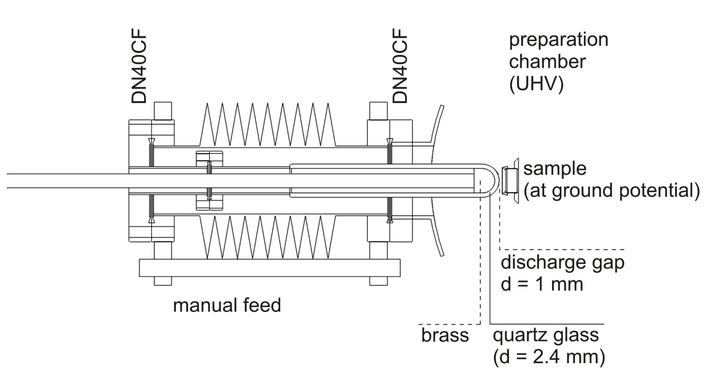
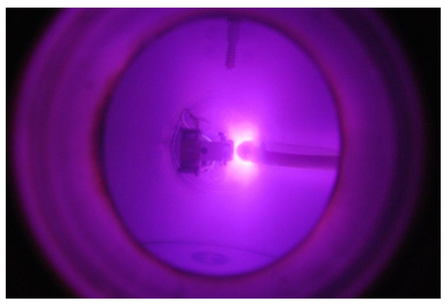
1. Introduction

The adsorption of thiophene from the gas phase onto clean (see below, 3.) and Plasma-oxidized titanium foils (see below, 4.) as well as onto perchloric acid (see below, 5.) or bromine pretreated titanium foils (see below, 6.) did not yield any chemical interaction or even stable adsorption. Thus, the oxidative polymerization as classical approach for the synthesis and deposition of polythiophene cannot be employed for titania substrates. Using a dielectric barrier discharge (DBD) plasma during the gas dosage from a 8 hPa thiophene atmosphere (see below, 7.) results in the deposition of Plasma-polymerized thiophene films at quite large deposition rates. The deposition mode, however, changes from a Frank-van-der-Merwe- type growth within the first seconds towards the deposition of two different classes of particles presumably originating from gas phase agglomeration.



2. Plasma treatments

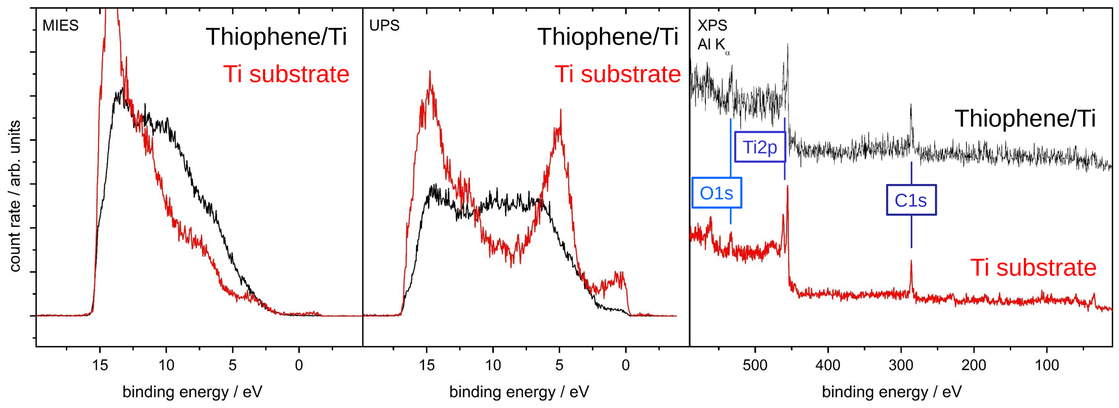




Dielectric Barrier Discharge (DBD)

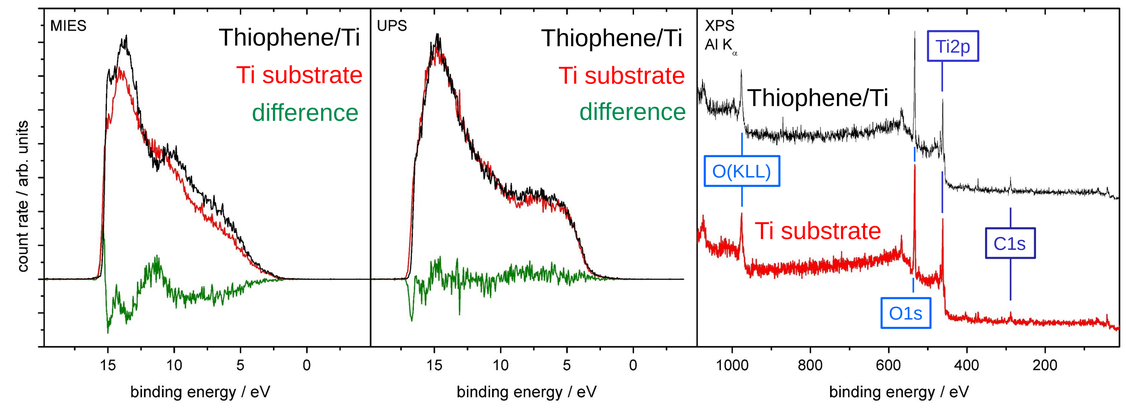
- HV-pulses 11kV
- Pulse width 0.6µs
- Repetition rate 1.6 kHz

3. Adsorption of thiophene on clean titanium



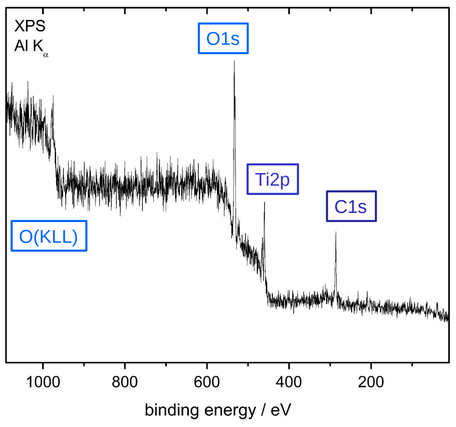
- Slight oxidation of the Ti substrate
- No stable adsorption of thiophene

4. Adsorption of thiophene on Plasma-oxidized titanium



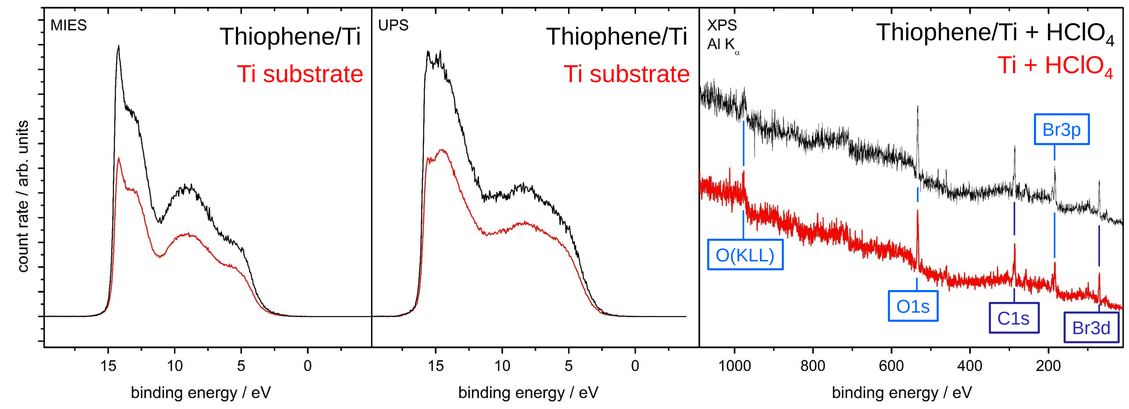
- No effect on the titanium substrate at all after the thiophene dosage

5. Adsorption of thiophene on perchlorated titanium



- Significant amounts of adventitious carbon
- No perchlorate anions found

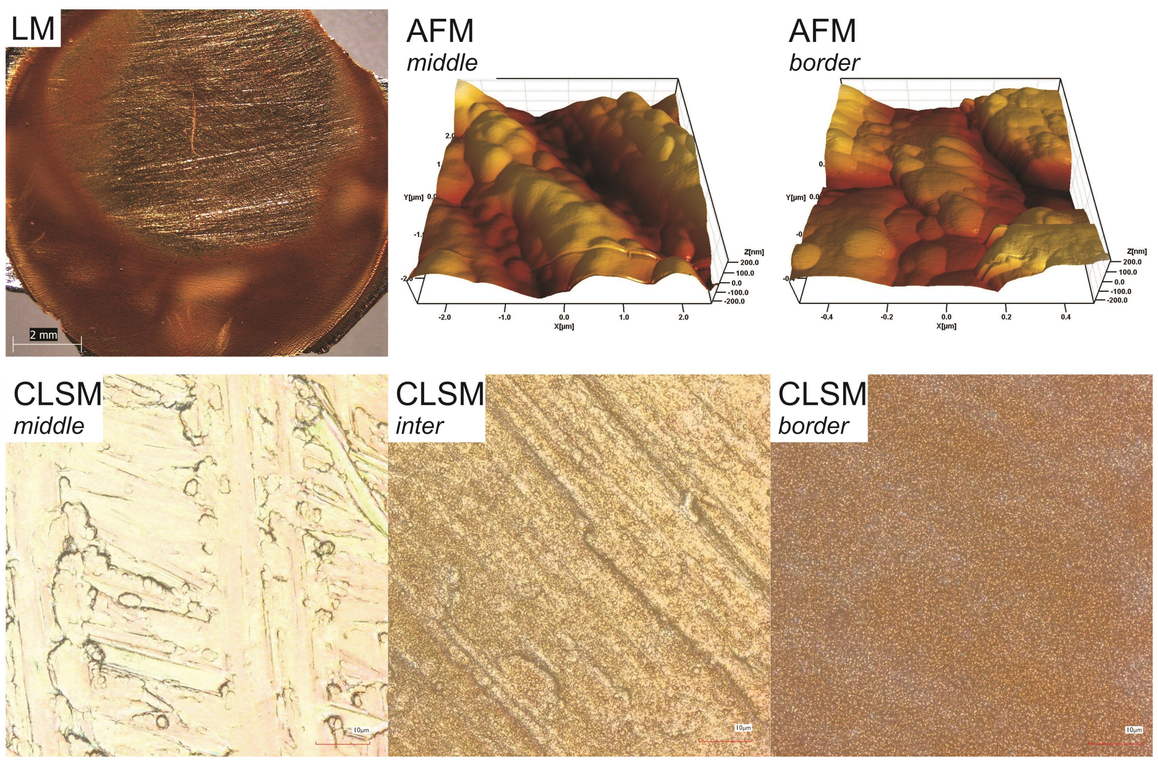
6. Adsorption of thiophene on bromated titanium



- Huge amounts of bromate anions
- Still no stable adsorption of thiophene

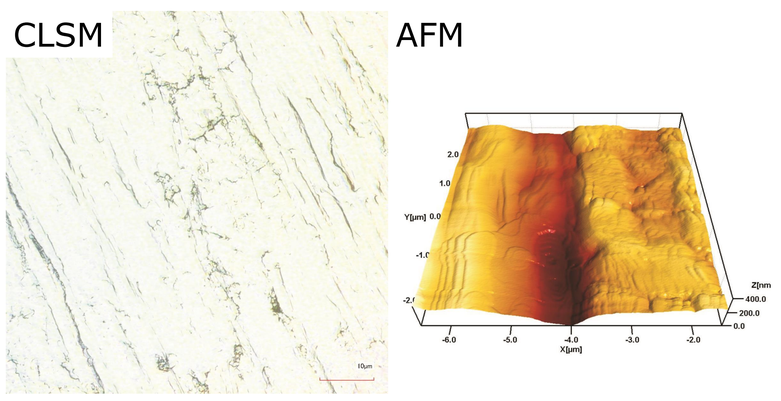
7. Plasma-polymerization of thiophene on titanium

7.a deposition time 60s



- Deposition of a thick film of polythiophene
- Roughly structured film morphology
- High dependance of the thickness on the discharge gap

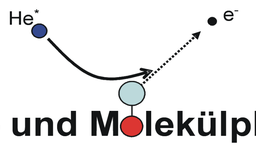
7.b deposition time 0.5s



- Slighty oxidized titanium at the interface
- Highly cross-linked thiophene polymer
- Atomically plain films during the first seconds of deposition

8. Summary

The exposition of clean, plasma-oxidized, perchlorated and bromated titanium films to thiophene atmospheres did neither lead to a stable adsorption of thiophene, nor to a polymerization at the electronegative centers at the surface.
The excitation of a plasma discharge within thiophene atmospheres, however, leads to the plasma-polymerization of highly cross-linked polythiophene onto titanium. The titanium substrate gets slightly oxidized at the interface to the film during to the deposition process. The film growth rates and morphology drastically change from the slow deposition of a homogeneous, flat film towards the fast deposition of a roughly structured, particle-based film.



Atom- und Molekülphysik an Oberflächen

9. Acknowledgements

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