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Oxidation behavior of $Si_xH_yN_z$ films prepared via plasma-enhanced chemical vapor deposition

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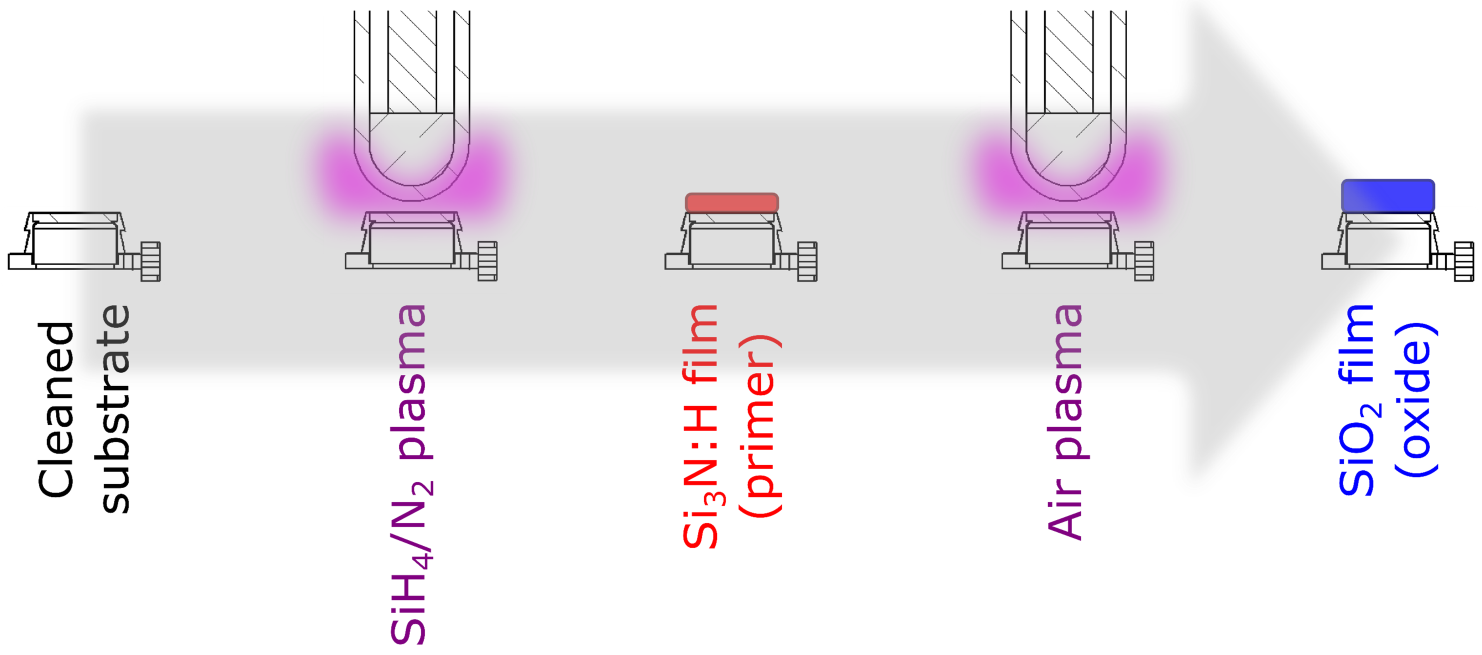
1. Introduction

The deposition of silicon-containing films is possible in a very simple manner via plasma-enhanced chemical vapor deposition (PECVD). A dielectric barrier discharge (DBD) plasma was used to prepare $Si_xH_yN_z$ films from 1.5% monosilane (SiH_4) diluted in nitrogen as a primer for silicon dioxide deposition. These films can be transformed easily into stoichiometric silicon dioxide (SiO_2) by a second DBD treatment in either oxygen or air. Further, the $Si_xH_yN_z$ films are sensitive to atmospheric air even without plasma excitation. This severely influences the conversion process within the second plasma, of course. Furthermore, the morphology of the resulting silicon oxide films severely depends on the pressure and the gas used to oxidize the PECVD primer films.

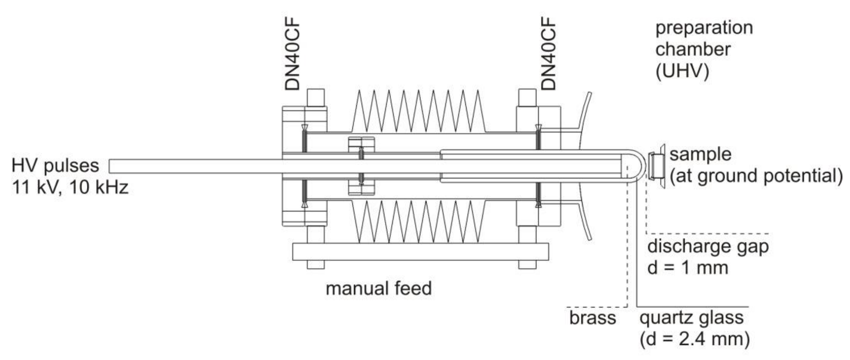


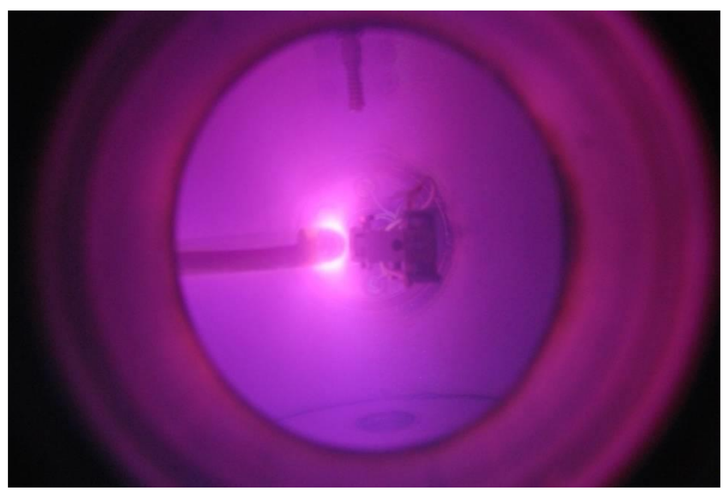
2. Experimental

Chemical analysis was performed via XPS utilizing a hemispherical analyzer (VSW HA100) and a commercial non-monochromatic X-ray source (Specs RQ20/38C) using Mg Kα at a photon energy of 1253.6 eV. Fit curves were gained using OriginPro 7G with the Peak Fitting Module.

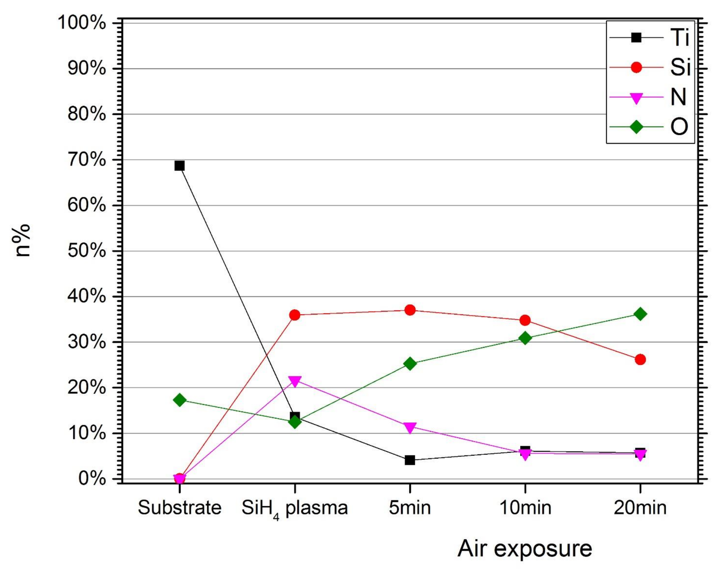
A Veeco Dimension 3100 SPM is employed for tapping mode atomic force microscopy (AFM) with silicon cantilevers (NSC15 with Al backside coating from Micromasch). All AFM images display sample areas of 5 x 5 µm².

Plasma treatments have been carried out employing a commercial high voltage generator (Ingenieurbüro Jürgen Klein, S/N 040-3) supplying alternating HV pulses with a peak voltage of 11kV, a pulse duration of 0.6µs and a pulse repetition rate of 1.6kHz. The silicon-containing primer films were produced from a 2s plasma using silane gas mixture (Linde Gas) consisting of 1.5% SiH_4 (99.999%) and 98.5% N_2 (99.9996%) at a pressure of 200mbar. Further process gases for plasma treatments were O_2 (Linde Gas, 99.995%) and atmospheric air.



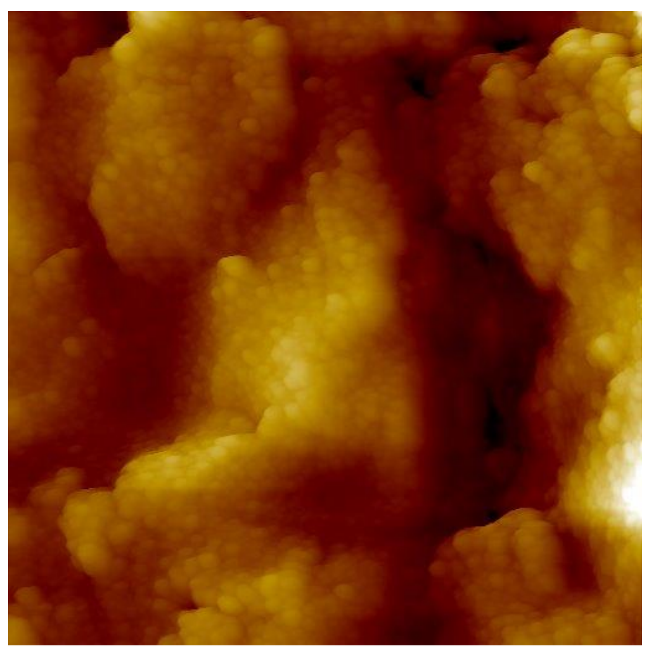


3. Film sensitivity: exposure to air

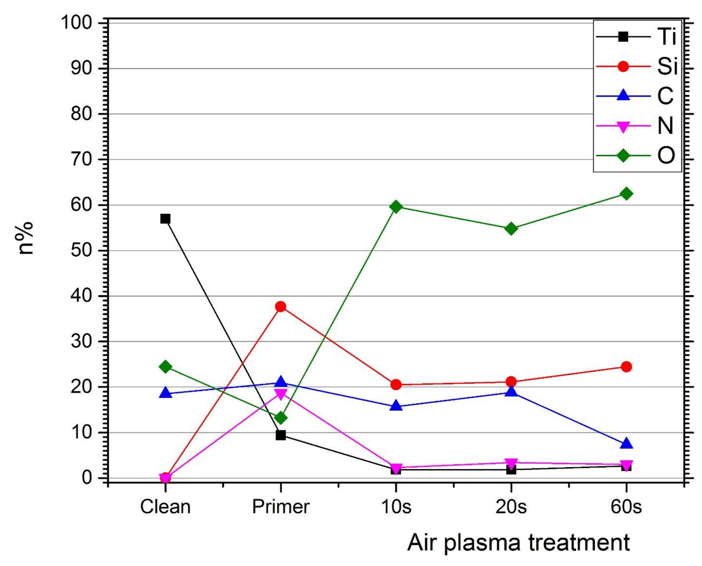


Film thickness	
Primer	4.8 nm
Vented	7.0 nm

Particles
~ 90 nm

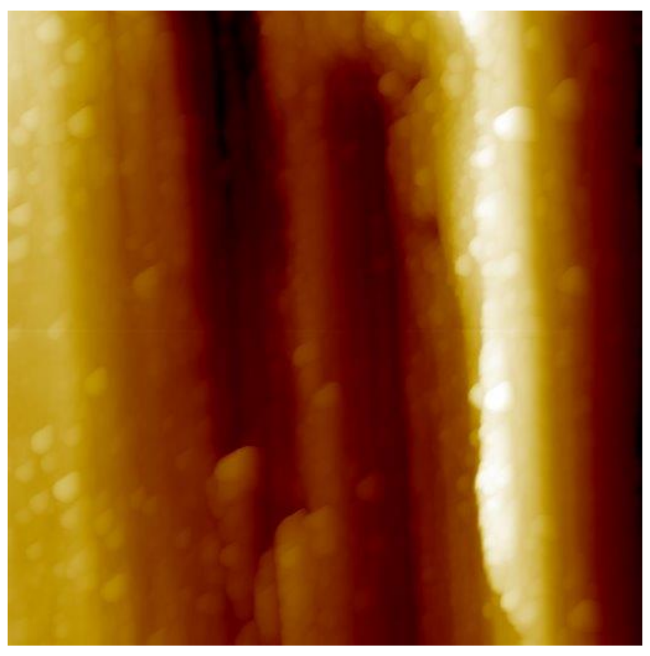


4. Film conversion: air plasma



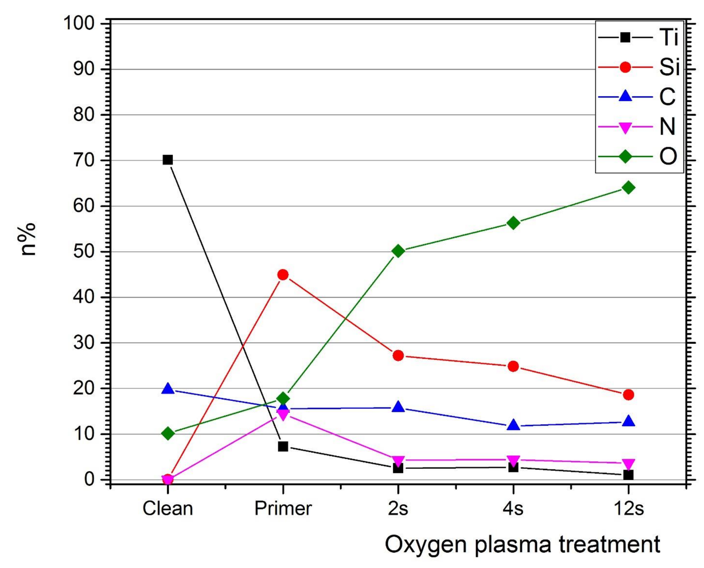
Film thickness	
Primer	4.4 nm
Oxide	6.7 nm

Particles
~ 200 nm



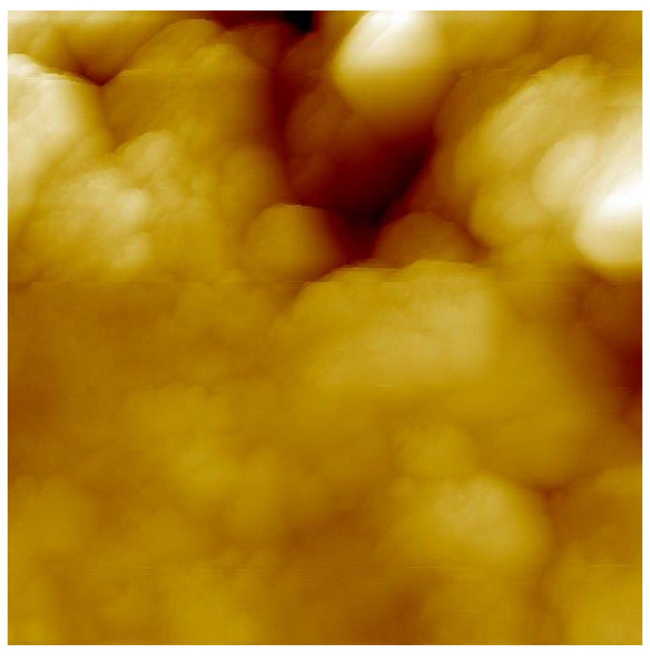
5. Film conversion: oxygen plasma

5.A at atmospheric pressure

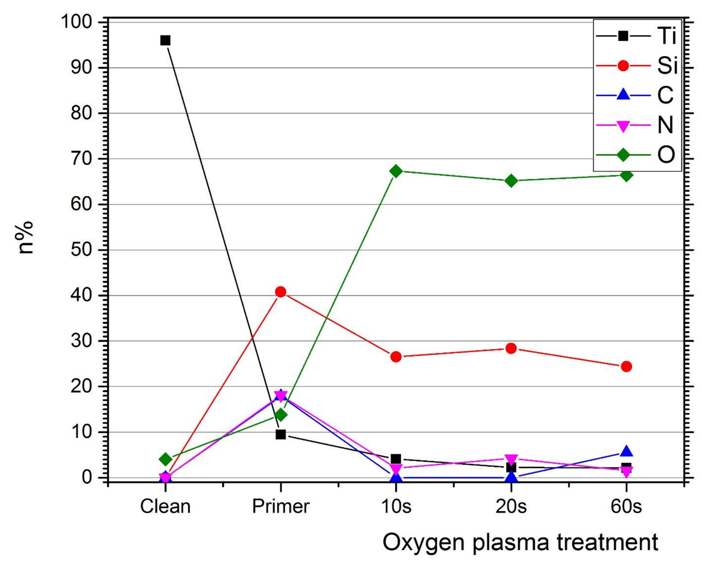


Film thickness	
Primer	4.8 nm
Oxide	9.8 nm

Particles
~ 600 nm



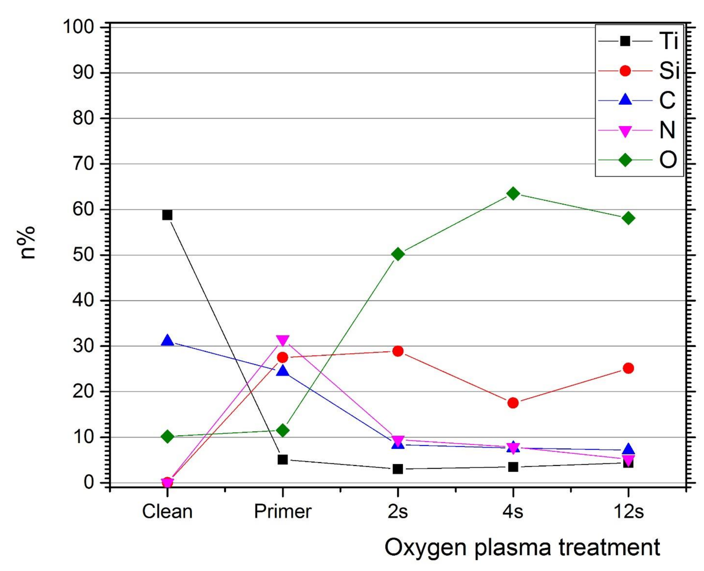
5.B at 200 mbar



Film thickness	
Primer	5.1 nm
Oxide	8.6 nm

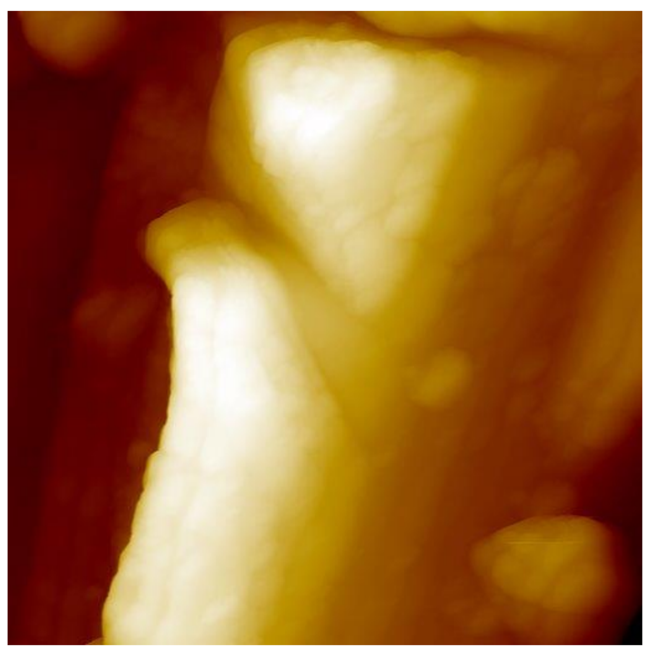
Particles
~ 800 nm

5.C at alterated HV pulse repetition rate



Film thickness	
Primer	5.8 nm
Oxide	6.6 nm

Particles
~ 400 nm



6. Summary

- Spontaneous oxidation at contact with air:
  O : Si = 1.38 after 20 min air exposure
  → AFM measurements (ex situ) for primer film impossible
- Plasma oxidation at least up to O : Si = 3.4
  → Possibly due to hydroxide formation inside the film?
- Higher power transfer leads to even higher intermediate O : Si ratios
  (e.g. O : Si = 3.6 after 4s in 5.C)

→ Film conversion mechanism proposedly via intermediate silicate state, i.e. $Si(OH)_4$

- Substantial growth in film thickness includes serious rearrangements throughout the bulk of the whole film
- During the rearrangements, a varying degree of particle formation is observed
- Size and number of particles strongly depend on parameters of conversion process, e.g.
  - Gas composition
  - Pressure
  - Plasma activation, especially:
  - Electrical power transferred via gas discharge
  - Resulting film thicknesses, i.e.
    significant degree of particle formation above 7 nm oxide film thickness

Yet it is unclear, whether smooth and closed oxide films with thicknesses larger than 10nm can be realized. The conversion mechanism, however, in all likelihood should allow to convert even much thicker films.

7. Acknowledgements

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