On crystalline structure of TiO_2 films grown by plasma-enhanced atomic layer deposition

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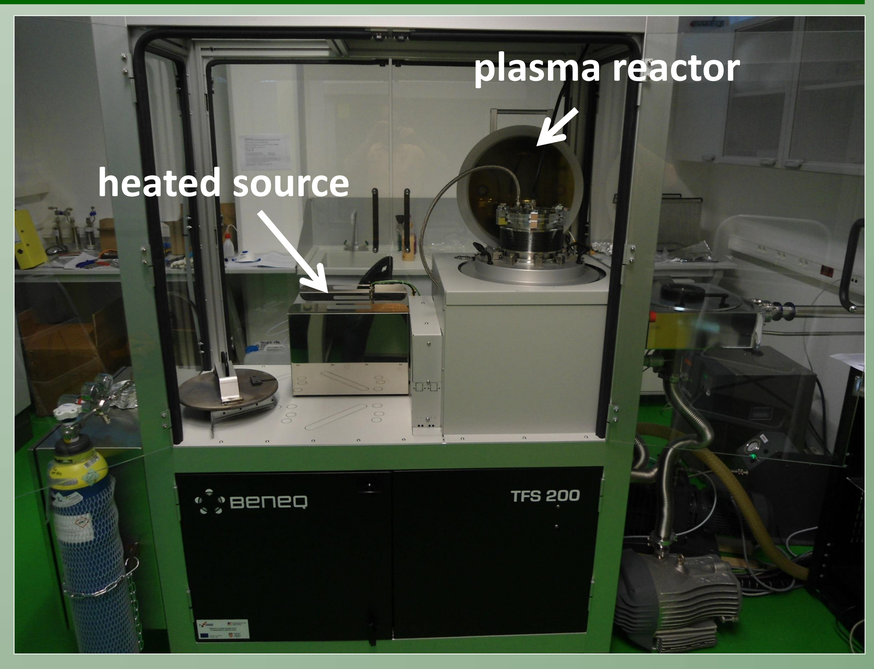
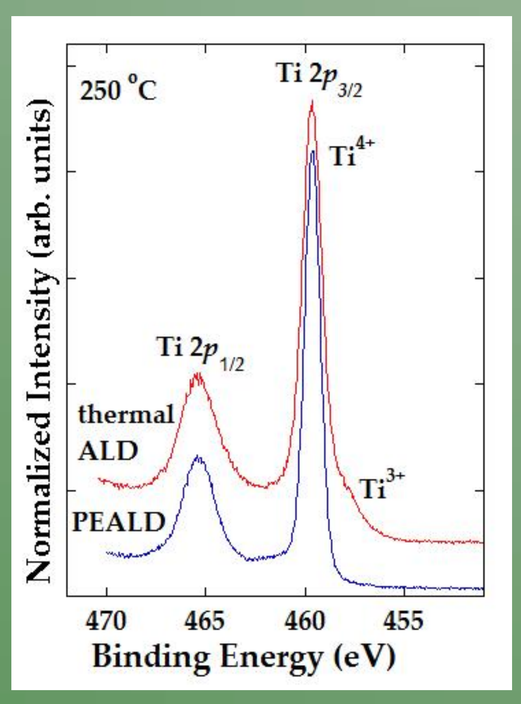
Introduction

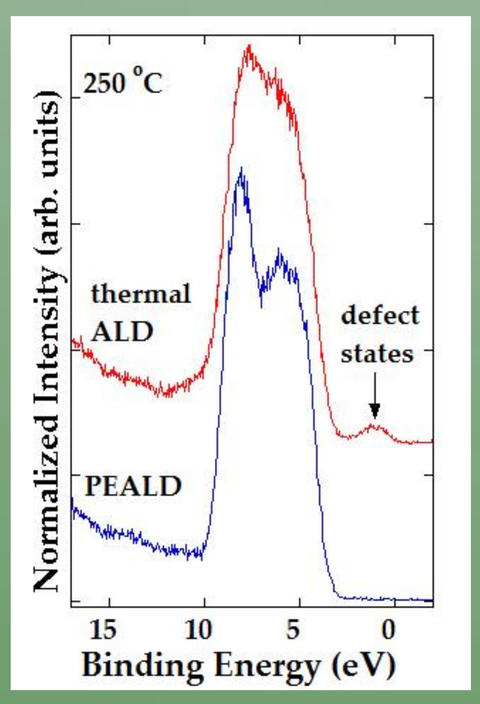
We have grown TiO_2 films using the heated source in **Beneq TFS 200 ALD** system for tetrakis(dimethylamino)titanium (TDMAT) as a Ti precursor. The films were synthesized on silicon substrates at temperatures from 100 °C – 250 °C using both thermal and plasma enhanced ALD (PEALD), with a remote RF plasma reactor operated at 13.56 MHz and 150 W.
For thermal ALD we have used H_2O as the oxygen source, while O_2 plasma has been employed in PEALD. TDMAT was heated to 50 °C for all depositions. The TiO_2 films are amorphous at deposition temperatures below 200 °C, while polycrystalline anatase phase is obtained above 200 °C.
All films were analysed with **XPS** (**SPECS** system), **SIMS** (**HIDEN** Workstation), while surface morphology was determined by **SEM** (**JEOL JSM–7800F**).



XPS analysis

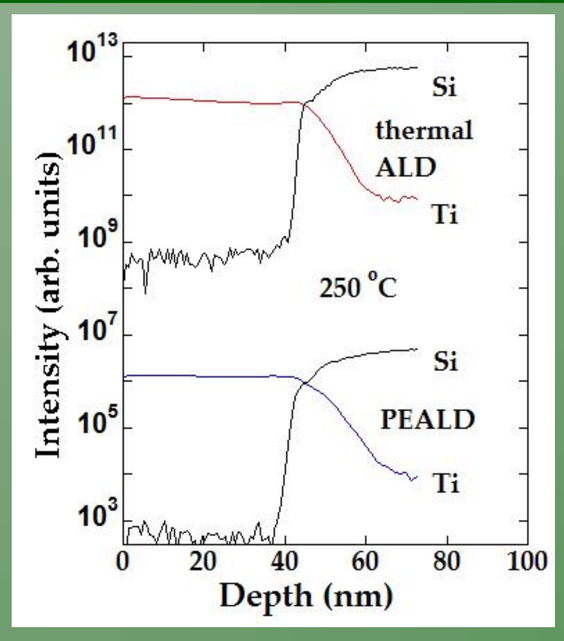
The core level and valence band photoemission spectra, measured on samples grown by thermal ALD and PEALD. Both Ti 2p spectra are dominated by a peak related to Ti^{4+} oxidation states (TiO_2), while the sample grown by thermal ALD shows a small contribution of Ti^{3+} states, which are responsible for some defect states within the energy gap.





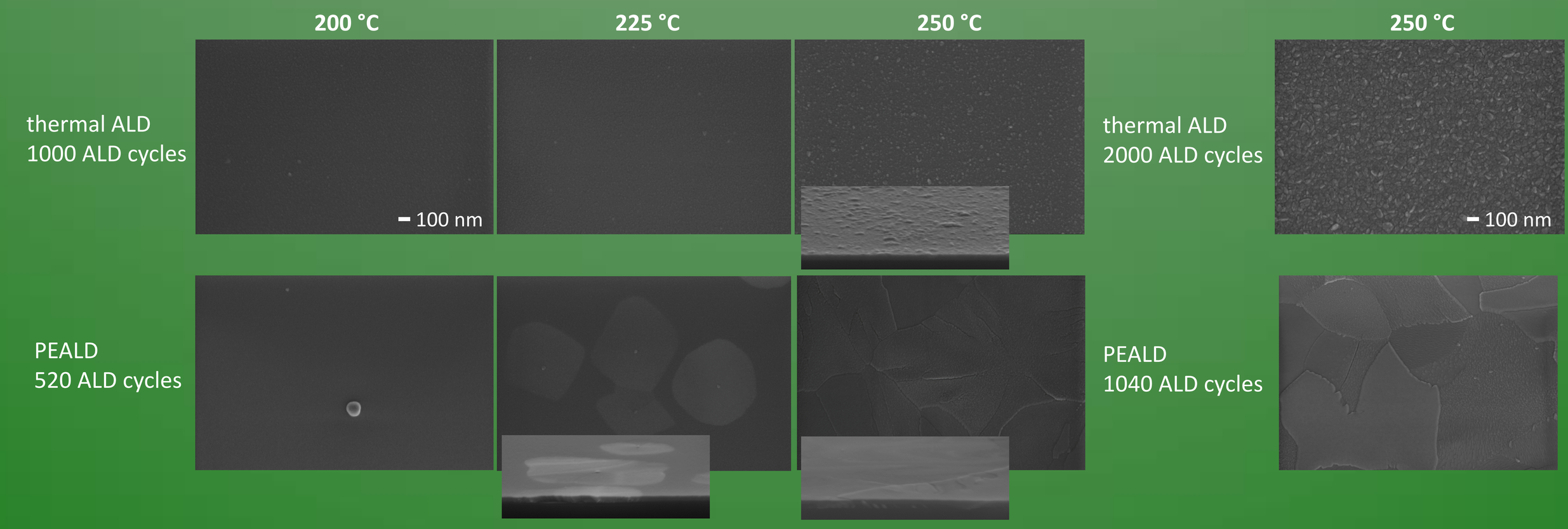
SIMS depth profiles

In-depth SIMS profiles of samples grown by thermal ALD and PEALD, recorded by measuring positive ions of Ti (using 3 keV O_2^+ primary ions), and negative ions of Si (with 5 keV Cs^+ primary ion beam).



SEM images

The surface morphology of TiO_2 films deposited at different substrate temperatures using thermal ALD and PEALD. Images were recorded at a magnification of 50000 times with the gentle electron beam of 0.7 keV. Small inserts are taken at a tilt angle of 10°.



Conclusion

1. Polycrystalline TiO_2 films were successfully grown at 250 °C by ALD and PEALD using TDMAT at 50 °C in a Beneq heated source.
2. Crystallization seeds were observed at 200 °C, while bellow that temperature purely amorphous films are formed.
3. ALD produces small crystalline grains (size in 100 nm range), while PEALD produces bigger seeds and large anatase plates of few micrometers.
4. The size of crystallites grows with film thickness.

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