Investigation of residual chlorine in TiO_2 films grown by Atomic Layer Deposition

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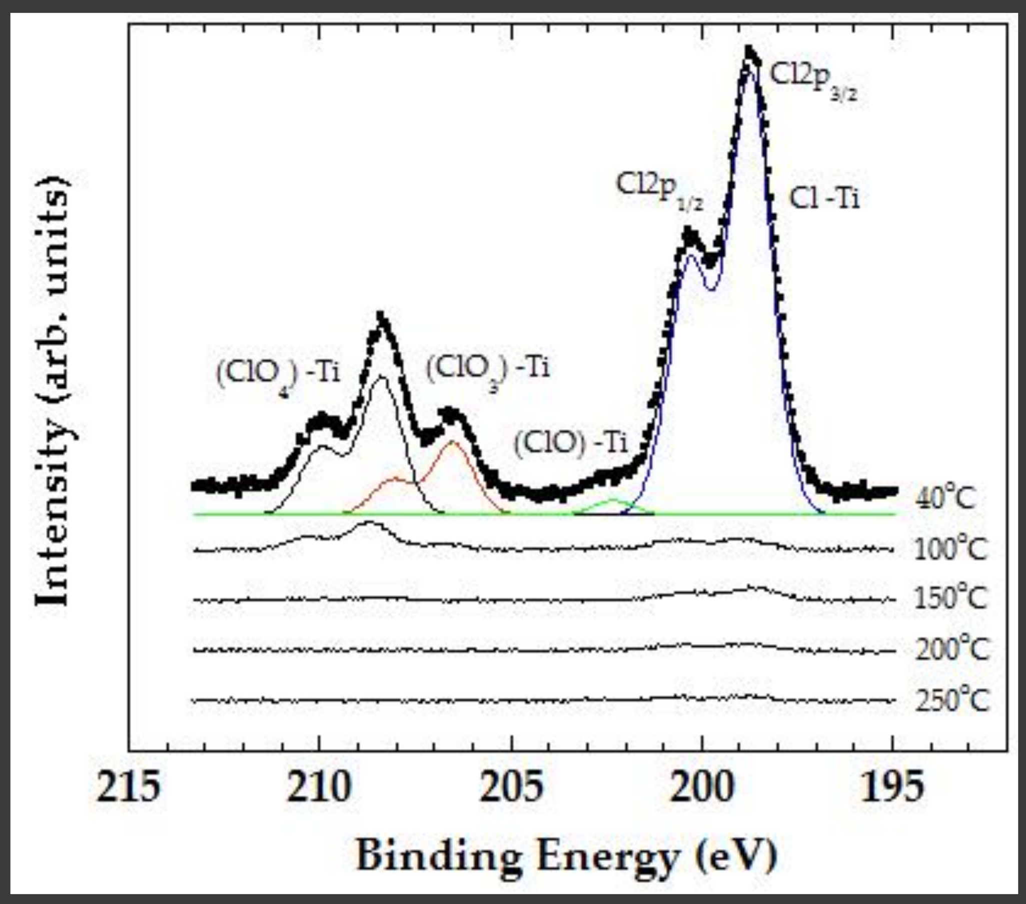
Introduction

Among metal-oxide semiconductors, titanium dioxide (TiO_2) is one of the most promising materials for many applications, ranging from microelectronics to photo catalysis or medical device materials. In recent years, atomic layer deposition (ALD) technique has been extensively used for the growth of thin TiO_2 films because of its excellent thickness control and the high conformity of the obtained films. When titanium tetrachloride ($TiCl_4$) is used as the ALD precursor for the synthesis of thin TiO_2 films, some chlorine impurities remain present in the resulting inorganic material. The assessment of Cl impurities is particularly important for the photocatalytical applications where the incorporated chlorine lowers the energy gap of TiO_2, thus affecting performances of the TiO_2-based catalytic systems. In the present work we present a comprehensive study of residual chlorine impurities within the TiO_2 films grown on silicon substrates using ALD and plasma-enhanced ALD (PEALD) techniques at a wide temperature range.

Sample preparation

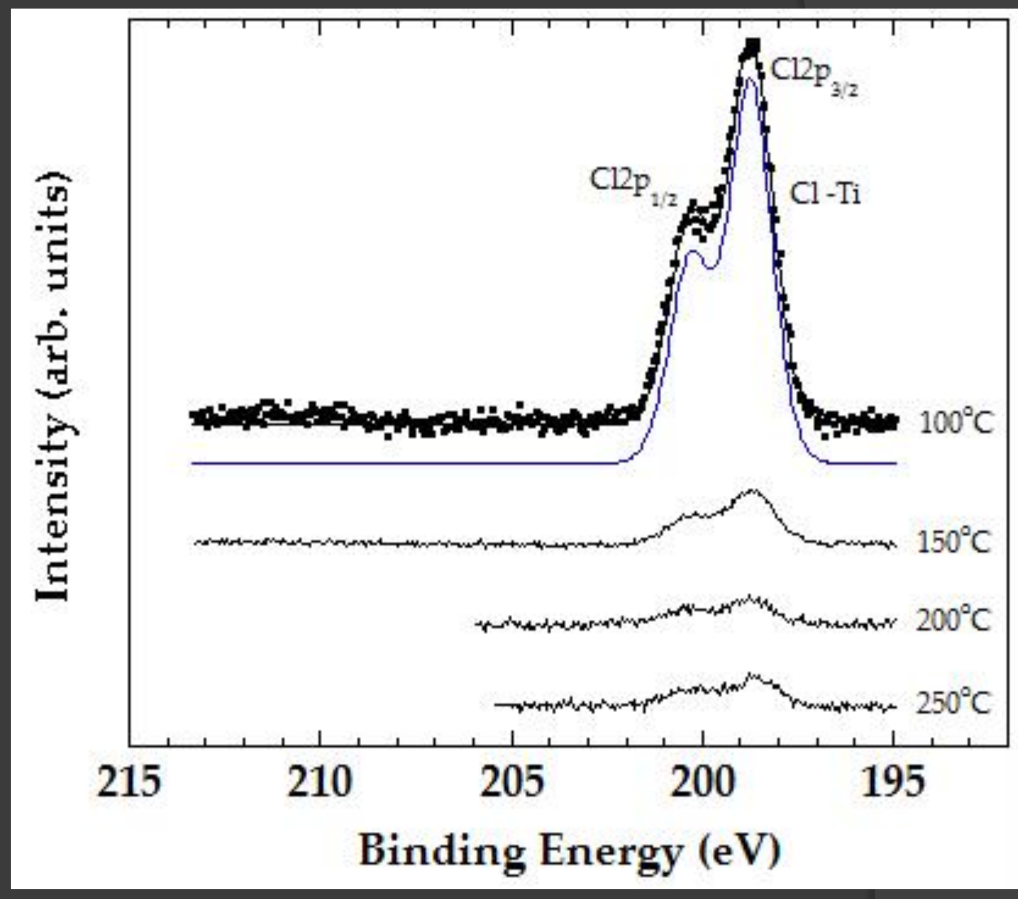
Thermal ALD: Precursors $TiCl_4$ and H_2O (1000 cycles, 250 ms exposure to $TiCl_4$, 3 s N_2 purge, 180 ms exposure to H_2O, 2 s N_2 purge)

PEALD: Precursors $TiCl_4$ and O_2 plasma, 150 W (522 cycles, double pulse of $TiCl_4$, 300 and 350 ms, 4 s N_2 purge, 3 s O_2 plasma, 6 s N_2 purge)

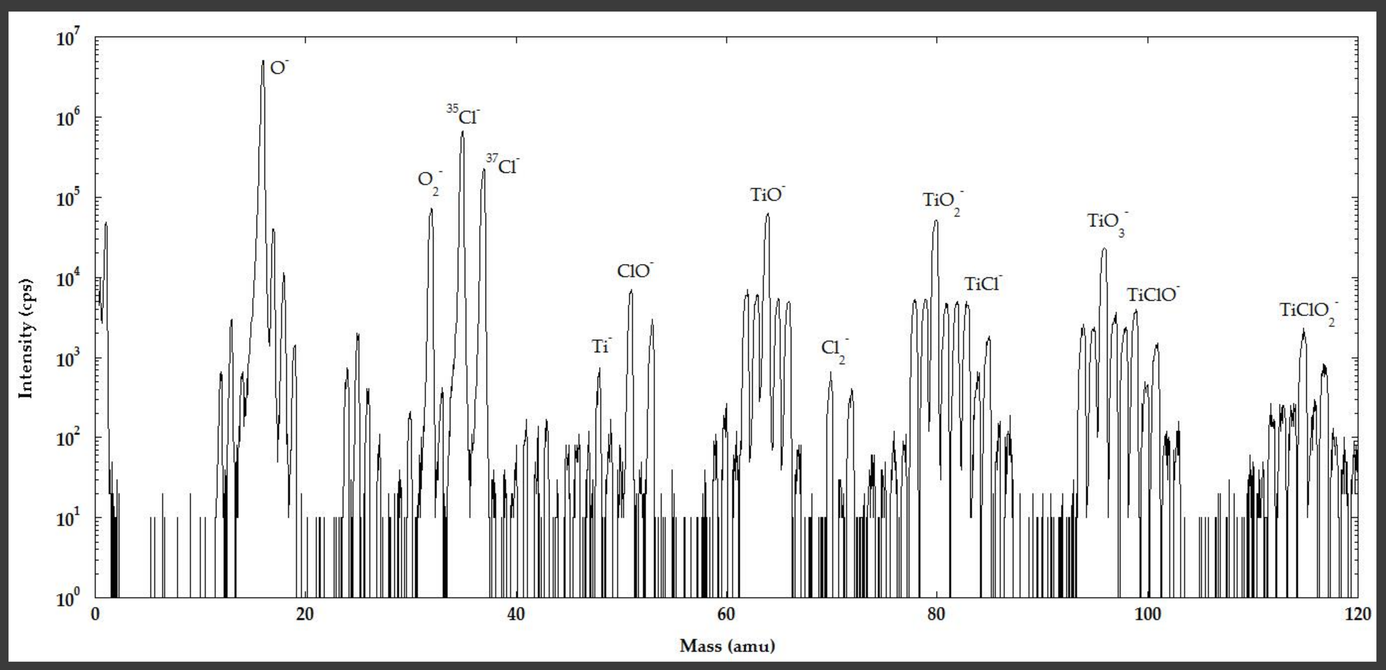


XPS analysis

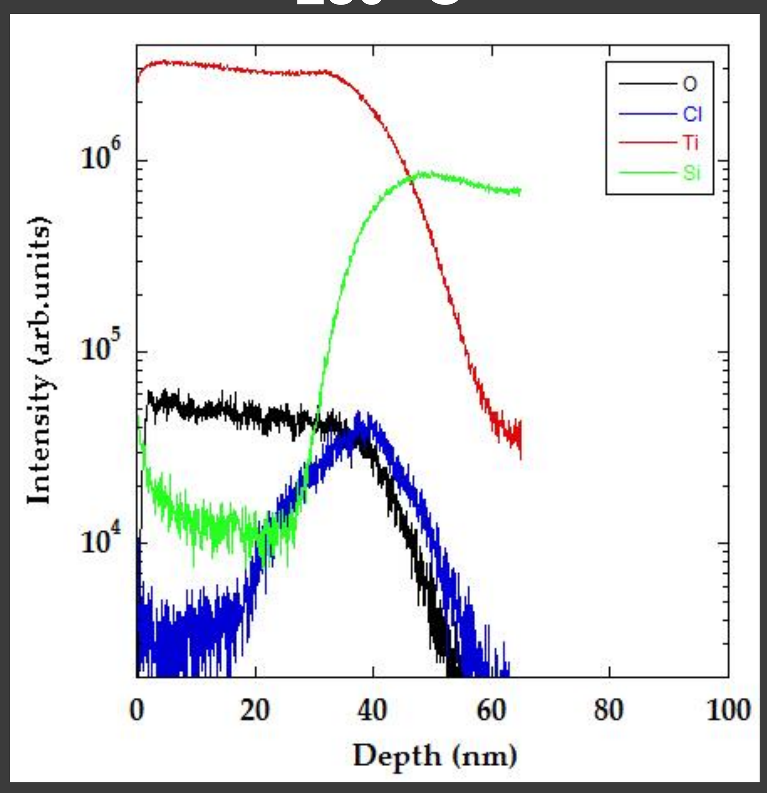
Photoemission spectra taken around Cl 2p core levels measured on TiO_2 samples grown by thermal ALD and PEALD. Residual chlorine is present at all temperatures. Characteristic Cl-O bonds of chlorine in +1, +5 and +7 oxidation states, are present only in PEALD grown samples with concentration decreasing rapidly with temperature. On the other hand, only $TiCl_4$ contribution is present in samples grown by thermal ALD. In both samples chlorine becomes quite low for temperatures above 200 ^{0}C.



SIMS mass spectrum of PEALD grown sample at 40 °C, recorded with 5 keV Cs^+ primary ions and collecting the negative secondary ions.

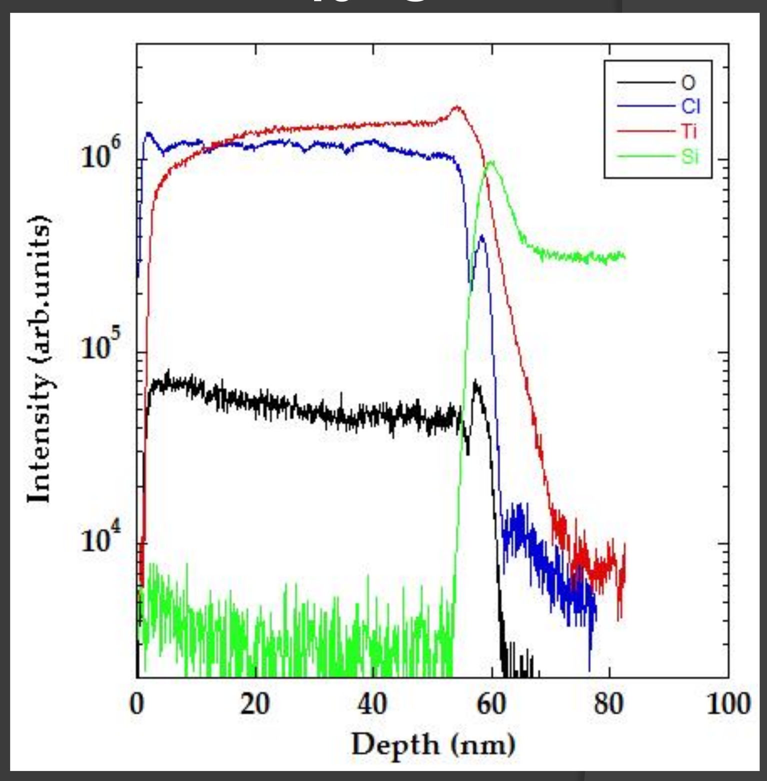


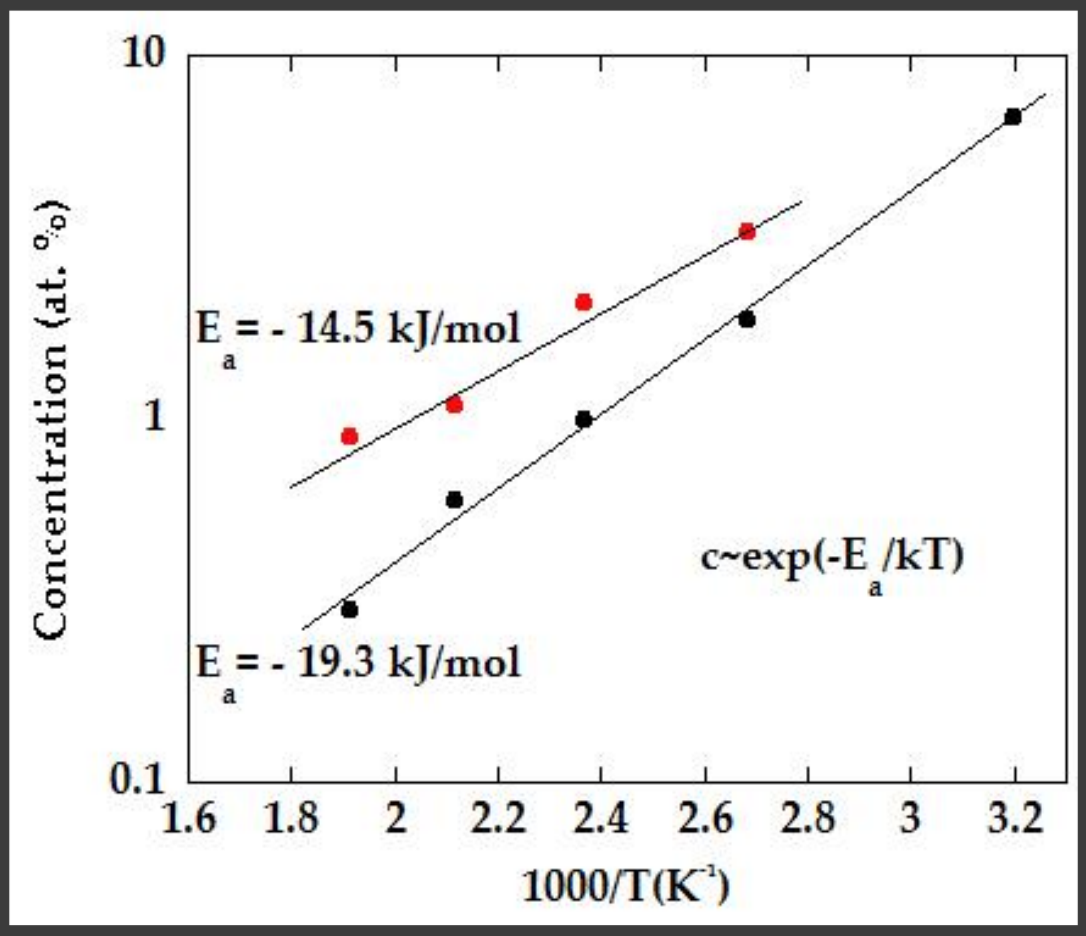
250 °C



SIMS depth profiles at TiO_2 films grown on 40 °C and 250 °C using plasma-enhanced ALD. Spectra were recorded by measuring positive ions of Ti and Si (using 3 keV O_2^+ primary ions), and negative ions of O and Cl (with 5 keV Cs^+ primary ion beam).

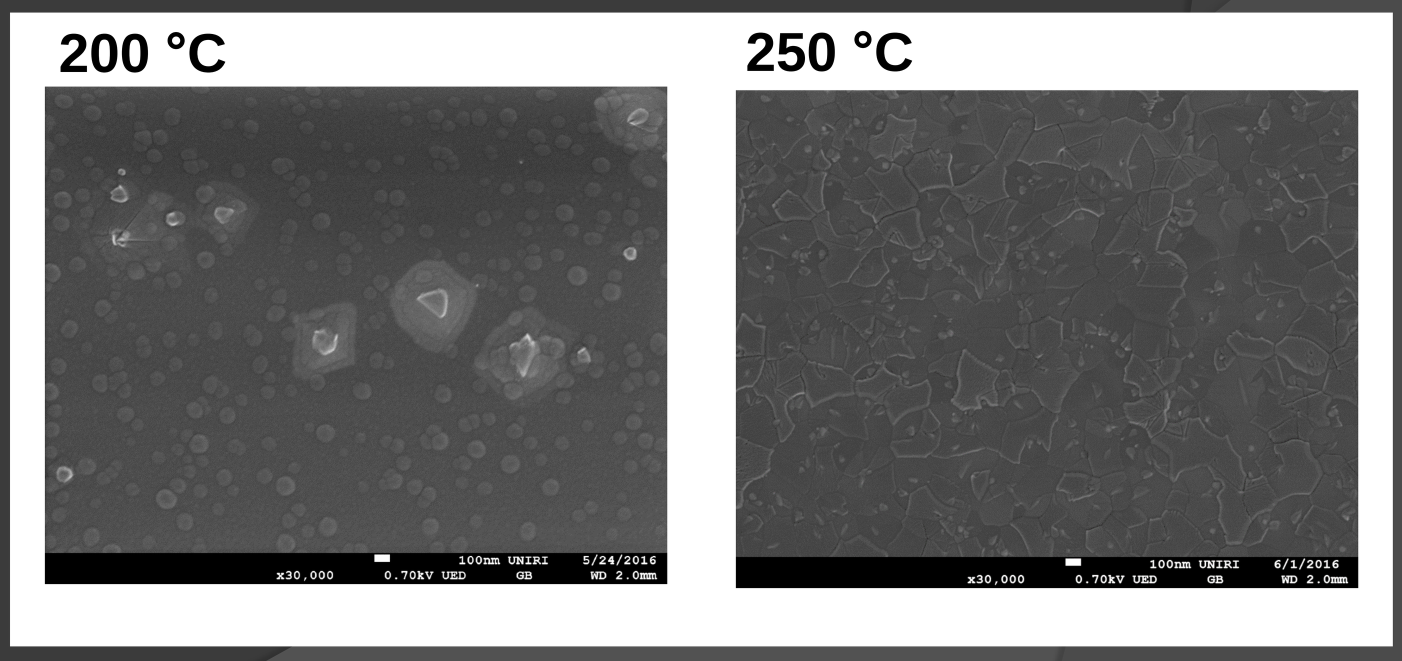
40 °C





Arrhenius plot of Cl concentration vs reciprocal temperature (1000/T) for samples grown by thermal ALD and PEALD. The linear fitted lines were used to calculate the activation energy.

SEM images of the surfaces of TiO_2 films grown at 200 °C and 250 °C using PEALD, recorded with the gentle electron beam of 0.7 keV.



Conclusion

Films deposited with PEALD show lower residual concentration of Cl, but also some additional Cl bonding (ClO^-, ClO_3^-, ClO_4^-).

In both thermal ALD and PEALD the temperature dependence of Cl concentration follows Arrhenius behaviour with activation energy E_a= - 14.5 kJ/mol for thermal ALD, and E_a= - 19.3 kJ/mol for PEALD.

This behaviour may explain unconventional temperature dependence of TiO_2 film and grain growth at low T, as found in the literature (W.J. Lee and M.H. Hon, *J. Phys. Chem. C 2010, 114*, 6917).