

Supporting information

Probing the Interfacial Chemistry of Ultra-Thin ALD-Grown TiO_2 Films: An In-Line XPS study

Aafke C. Bronneberg, Christian Höhn, and Roel van de Krol

Institute for Solar Fuels, Helmholtz-Zentrum Berlin für Materialien und Energie GmbH, Hahn-Meitner-Platz 1, 14109 Berlin, Germany

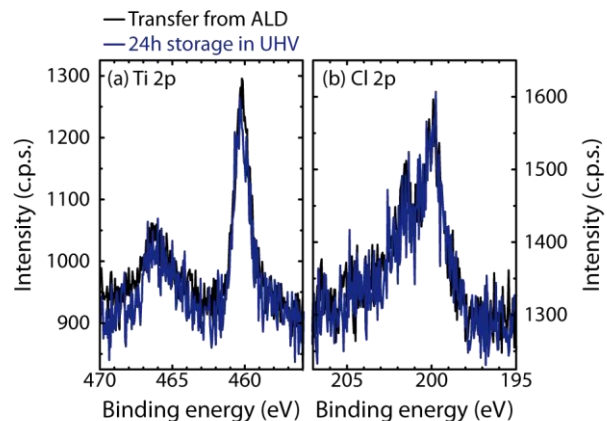


Figure S1: Fine spectra of the (a) Ti 2p and (b) Cl 2p region measured after the first TiCl_4 exposure immediately after transfer from the ALD chamber (black line) and after 24h storage under UHV conditions (i.e. at base pressure $<1 \times 10^{-9}$ mbar, blue line).

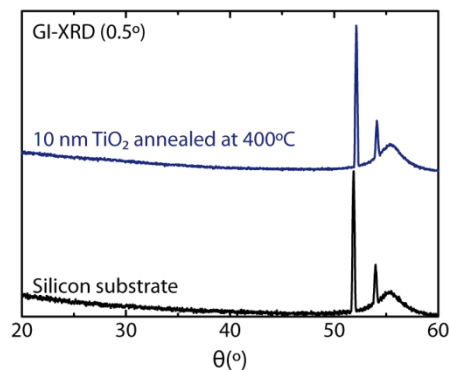


Figure S2: XRD pattern of the bare silicon substrate and of a silicon substrate coated with 10 nm TiO_2 which has been annealed in vacuum for 1 hour at 400°C . The XRD patterns were measured under grazing incidence (0.5°), and show no traces of crystalline TiO_2 .

Fine spectra of O 1s region

In Figure S3 fine spectra of O 1s core electrons are shown. Figure S3a shows the O 1s spectrum of the silicon substrate. The photoemission line in this spectrum is fitted with a single Voigt profile using a Shirley type background. The photoemission line is centered at 533 eV and corresponds to oxygen in SiO₂. One would expect the surface of SiO₂ to be covered by hydroxyl groups (Si-OH), but no signal was found at the corresponding binding energy of 533.7 eV¹.

The photoemission lines in the spectra of Figures S3b-j were fitted with two peaks. As outlined in the main text, the higher binding energy peak is assigned to oxygen in SiO₂ whereas the lower binding energy peak is assigned to oxygen in TiO₂. Similar as above, one would expect part of the oxygen to be present in the form of hydroxyl groups, now in the form of Ti-OH (~531.5 eV).¹ In addition, some of the oxygen may be present in the form of Si-O-Ti. However, the spectra shown in Figures S3b-i do not allow the individual O 1s contributions to be resolved. Only after 250 cycles, when the Si signal has completely disappeared, can we still see an O 1s contribution at higher energies than the O 1s in TiO₂. The binding energy of this peak matches with the binding energy of Ti-OH. This peak contributes up to 5% to the total peak area, resulting in an atomic concentration of 3 at.%. We assign this peak to titanium-bound hydroxyl groups, which could either be located on the surface as well as in the bulk.

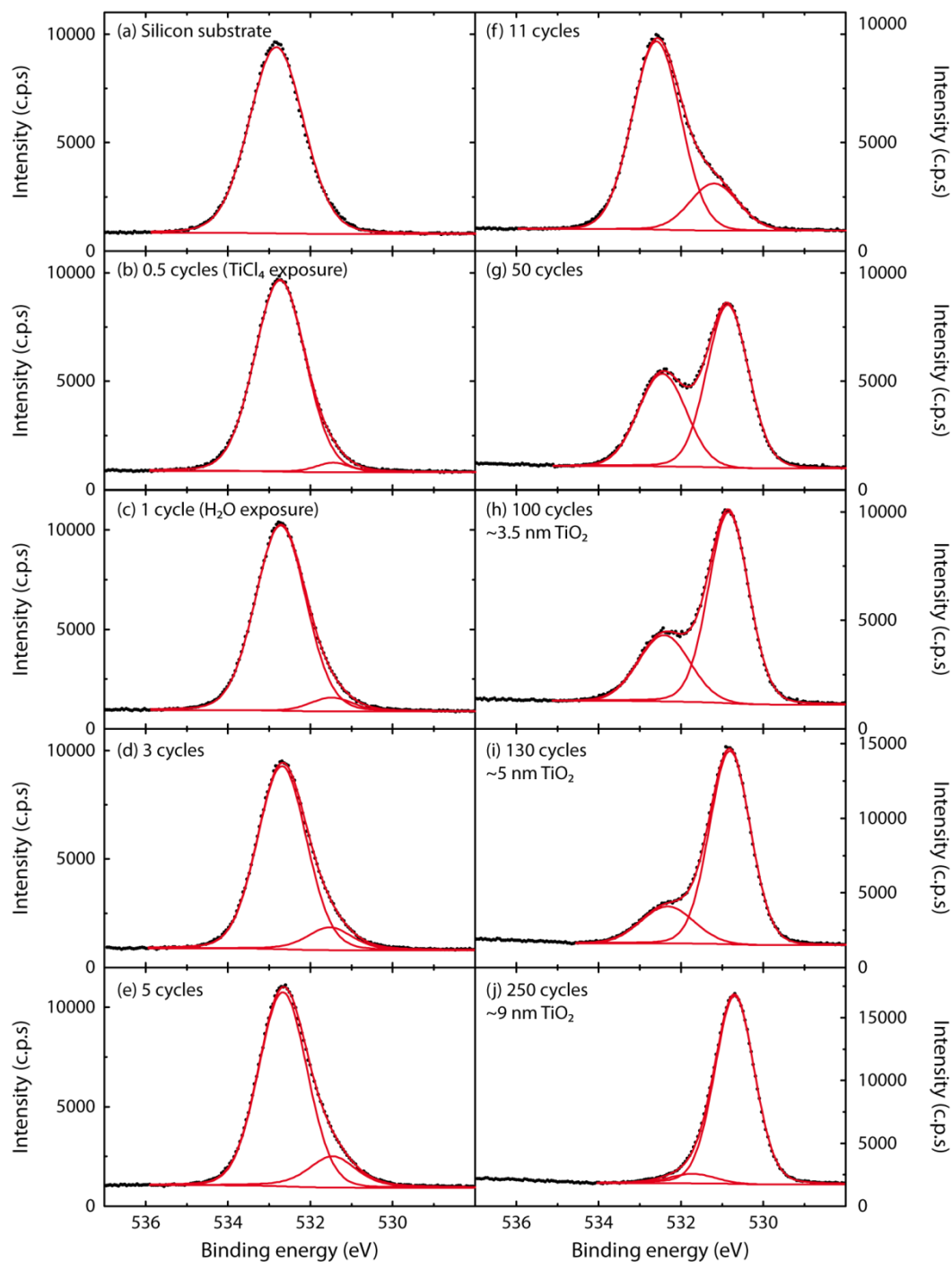


Figure S3: Fine spectra of O 1s region of (a) the silicon substrate, (b) after the TiCl_4 exposure (=0.5 cycles), (c) after H_2O exposure (=1 full ALD cycle), (d)-(j) after 3, 5, 11, 50, 100, and 250 full ALD cycles, respectively. The red lines represent the fit.

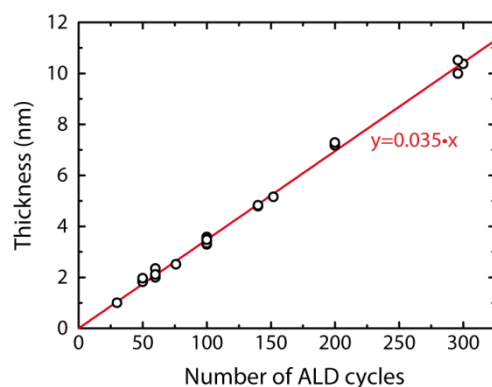


Figure S4: Film thickness as function of the number of ALD cycles. The red line is a linear fit. The slope represents the average GPC, i.e. 0.035 nm/cycle.

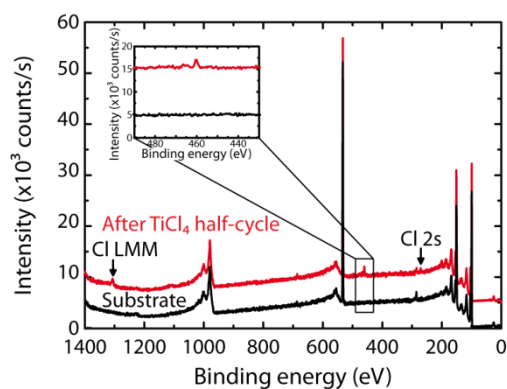


Figure S5: Survey spectra of the silicon substrate before deposition (black) and after the first TiCl₄ exposure (red). The inset shows a zoom of the Ti 2p region. No Ti 2p is observed before TiCl₄ exposure. After TiCl₄ exposure, the Cl 2s feature is visible at ~270 eV, as well as the Cl LMM Auger line at ~1305 eV.

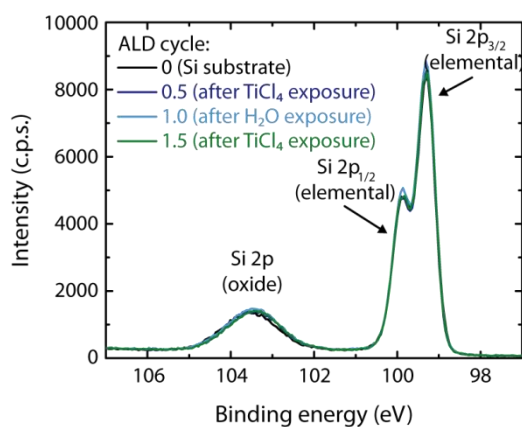


Figure S6: Fine spectra of the Si 2p region of the silicon substrate and after the first few ALD half-cycles. The peak at ~103.4 eV represents Si 2p in the form of a (native) oxide.

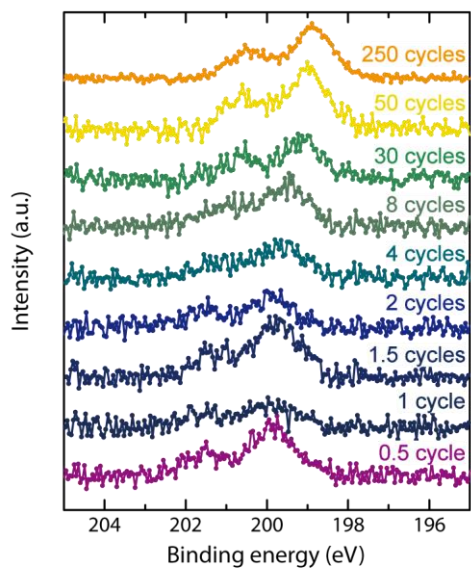


Figure S7: Fine spectra of the Cl 2p region measured after a varying number of ALD (half)cycles.

Table S1: Stoichiometry ([Ti]/[O]) of as-deposited and annealed TiO₂ films.

Number of ALD cycles	[Ti]/[O] as deposited	[Ti]/[O] annealed
100	0.55	0.53
200	0.50	0.49
300	0.48	0.49

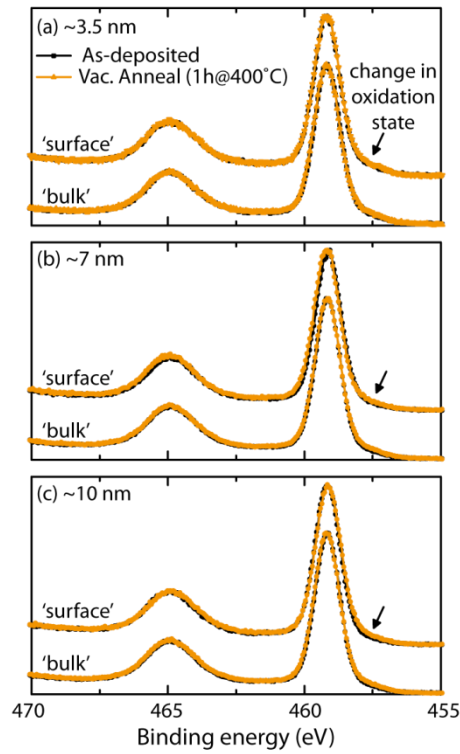


Figure S8: Fine spectra of Ti 2p region measured before (as-deposited, black data markers) and after annealing at 400°C in vacuum for 1 hour (orange data markers) of TiO₂ films with thicknesses of (a) ~3.5 nm (100 ALD cycles), (b) ~7 nm (200 ALD cycles), and (c) ~10 nm (300 ALD cycles). The spectra were measured at normal incidence (0°) and under a 60° angle, leading to more 'bulk' and 'surface' sensitivity. The arrow indicates the place where a possible change in oxidation state can be observed. No change in oxidation is observed after annealing.