

# PULSE

## For Dynamic XPS

### Application Note

#### Thermal Reduction of Titanium Oxides

The thermal reduction of Titanium oxides was observed in-situ by time-resolved XPS using snapshot acquisition of multiple spectral features. The oxygen reduction occurred within ~1 minute by applying a rapid temperature ramp and was found to be a step-wise process with an initial transition from 4+ to suboxide and the metallic state of Titanium at intermediate temperatures between 600 K and 725 K before further reduction of the 3+ oxidation state at temperatures > 725 K.

#### Setup

The SIGMA PULSE is a compact system and particularly suited for time-resolved XPS studies (figure 1).

The ASPECT hemispherical analyser with a mean radius of 160 mm and a true-counting multi-channel detector features high transmission, fast spectrometer electronics with short voltage settling times and fast detector read-out. With the NEO software multiple spectral features can be acquired continuously and sequentially in the Multi Peak Monitoring mode suitable for time-dependent measurements in the millisecond range.

The MECS monochromated X-ray source is located at 54.7° to the analyser and is routinely run at 600 W for the generation of Al K $\alpha$  radiation.

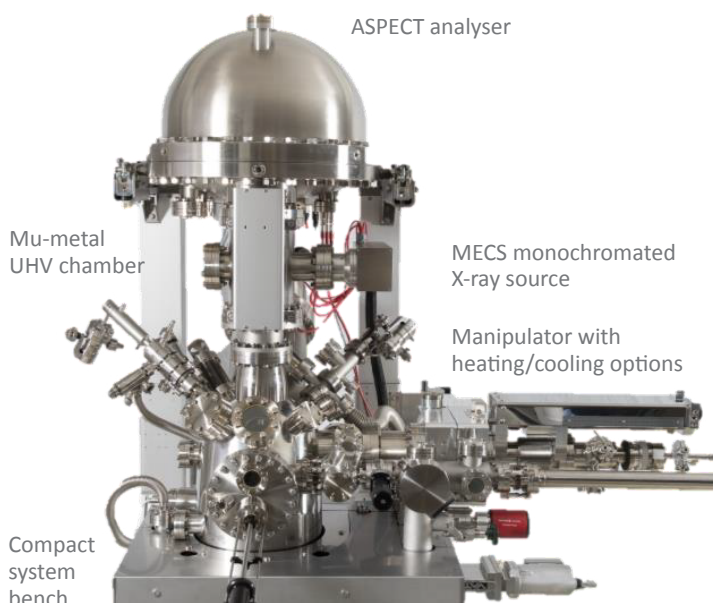


Figure 1: An example of customised PULSE system for time-dependent XPS.

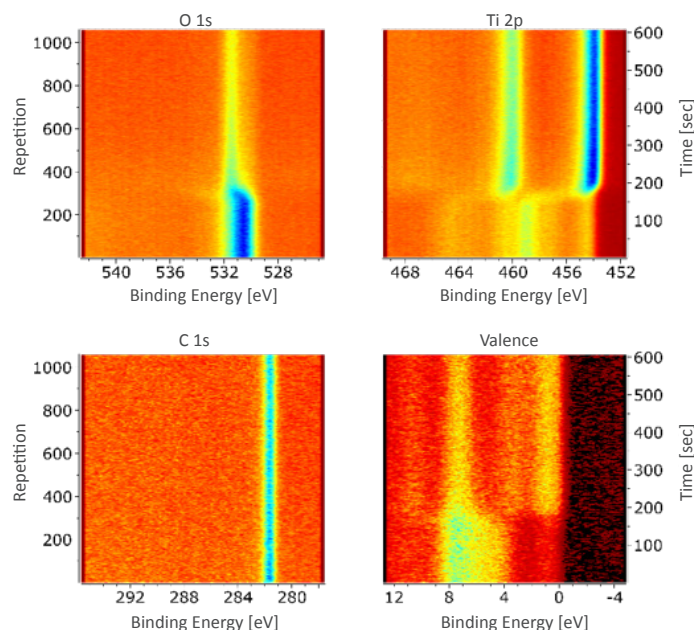


Figure 2: Colour-coded intensity representation of O 1s, Ti 2p, the valence band and C 1s (clockwise from top left) as a function of time during sample heating.

The UHV analysis chamber is made from mu-metal for magnetic shielding. For the temperature dependent studies described here the sample manipulator was equipped with a heater stage. Furthermore, a gas inlet was attached to the analysis chamber for the controlled dosing of the sample with process gas. The sample material was 0.5 mm thick polycrystalline Titanium with a purity of > 99.6% and a thermocouple in direct thermal contact to the analysed surface.

#### Reduction Measurements

The Titanium surface was analysed by XPS using the new Multi Peak Monitoring acquisition mode in order to continuously observe the spectral evolution of O 1s, Ti 2p, C 1s and the valence band (figure 2). After 2 minutes into the data acquisition the temperature was ramped from 550 K to 900 K within ~ 2 min. Each acquisition cycle consisting of the four spectra took ~ 570 ms with 500 ms detection time and was repeated over a period of 10 minutes of total acquisition time.

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Initially, the Titanium surface shows mixed oxidation states (figure 3a) with contributions from the Ti 4+, 3+, 2+ and the metallic state [2] at binding energies of 458.9 eV, 457.5 eV, 455.3 eV and 454.1 eV. The main peaks can be clearly seen in the colour-coded representation of the Ti 2p interval (figure 2). A strong O 1s peak at binding energy 530.3 eV is observed at the beginning (figure 2) which can be attributed mainly to the Titanium oxides TiO<sub>2</sub> and Ti<sub>2</sub>O<sub>3</sub>.

After the thermal reduction of the 4+ and 3+ oxidic states of Titanium only the metallic 2p doublet is evident (figure 3b). It can be seen from the colour-coded spectra in figure 2 that the O 1s peak is shifted to a higher BE of 531.8 eV, associated with =.

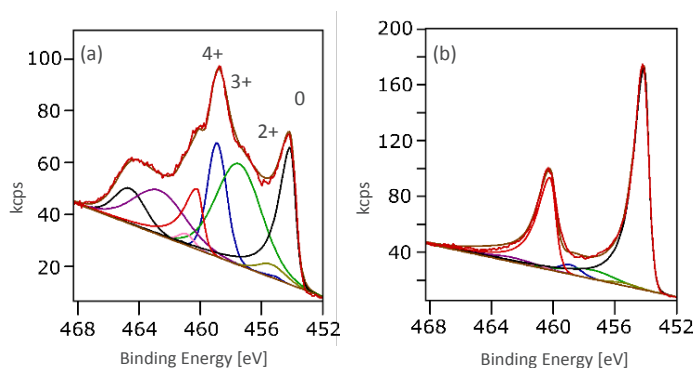


Figure 3: XPS spectra of Titanium 2p before (a) and after (b) thermal reduction of surface oxides.

The rapid change from pre-dominantly 3+ and 4+ to metallic Titanium when ramping the temperature takes place within < 1 minute each time and can be seen after 2 minutes of starting the data acquisition (figure 4a).

The changes in distribution of the Titanium states is also shown as a function of temperature in figure 4b.

The 4+ contribution starts to decrease from ca. 600 K, where all other contributing states increase. From about 725 K the 3+ state starts to decrease with temperature while mainly the contribution from the metallic peak increases.

It can be seen that a slower increase of the metallic Ti signal during the 4+ reduction is followed by a faster increase during the 3+ reduction. The redistribution of the Titanium states appears to proceed in a step-wise manner with the reduction of the 3+ state taking place only after the 4+ state has vanished.

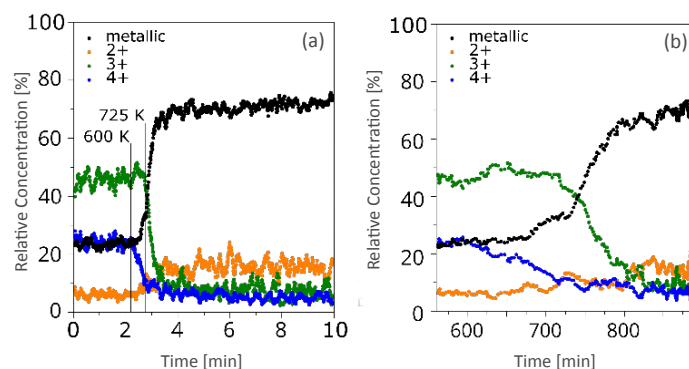


Figure 4: Changes of the distribution of the metallic and oxidic Titanium content in the probed region as a function of time (a) and temperature (b) determined from the snapshot spectra acquired in the Multi Peak Monitoring mode.

As expected, the intensity of the oxygen peak is greatly reduced at the same time (figure 2). Oxidised Titanium shows a higher concentration of the 4+ state at the surface whereas the suboxides are mainly present near the oxide-metal interface and on heating metallic Titanium can diffuse into the oxide overlayer [2]. Due to the observation in ref. [1] desorption of Titanium oxides from the surface does not take place under similar conditions and it can therefore be concluded from the decrease of the 4+ state and the initial increase of the 3+ state that a TiO<sub>2</sub> overlayer is first reduced followed by further reduction of 3+. This step-wise redistribution is likely to be accompanied by oxygen desorption and a rearrangement of the surface structure [3].

### Conclusion

The SIGMA PULSE system was used to observe and measure the temperature dependent reduction of the oxidic states of Titanium. From the determined relative concentrations it was concluded that the reduction takes place via a step-wise redistribution from the oxidic state 4+ and then 3+ to the metallic state of Titanium. Finally, it was shown that time-dependent XPS is a useful analysis technique for monitoring thin film and surface reactions and furthermore can be utilised for process control.

- [1] G. Lu et al., Surface Science **458** (2000), 80
- [2] A.F. Carley et al., J. Chem. Soc. Faraday Trans. I **83** (1987), 351
- [3] T. Leichtweiss et al., J. Mater. Chem. A, 2014, **2**, 6631

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