IN SITU TRANSMISSION ELECTRON MICROSCOPY (TEM) STUDY OF THE REDUCTION OF TiO_2 TO Ti_nO_{2n-1} MAGNÉLI PHASE

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INTRODUCTION AND OBJECTIVES

The Magnéli phases are titanium suboxides derived from rutile TiO_2 to which oxygen vacancies were introduced, yielding compounds with the general stoichiometry Ti_nO_{2n-1} ($4 \leq n \leq 10$). These materials exhibit interesting properties, such as enhanced conductivity vs. TiO_2.

Regarding the rutile → Magnéli transition, little is known on the transition mechanism, and especially experimental data is lacking to determine how this transition operates.

Herein, we use *in situ* gas phase transmission electron microscopy (TEM), allowing us to observe the reduction process in real time and space, which is essential for proposing a true phenomenological model.

Goals of the study:

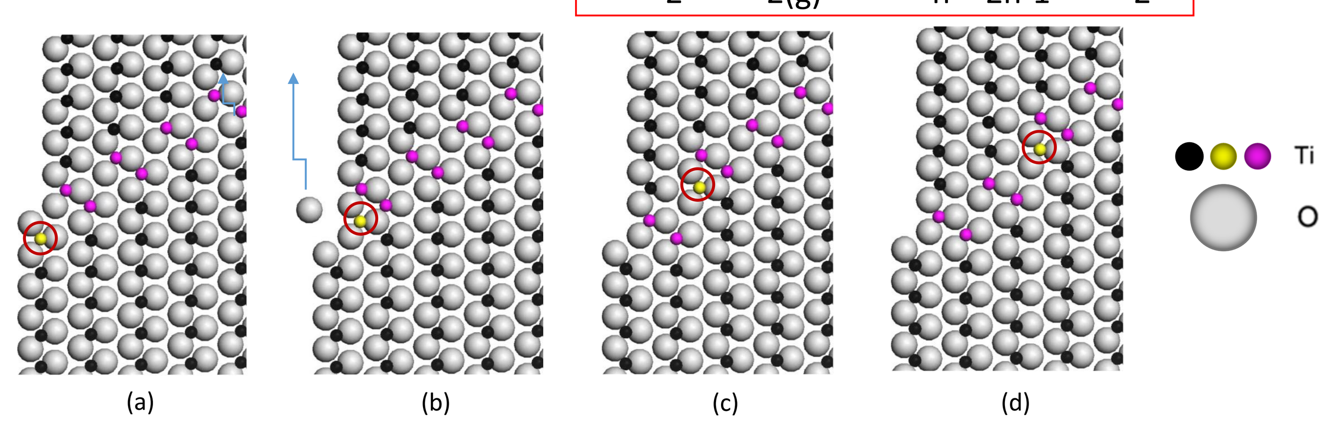
- Observe the formation and propagation of the structural transformation in real time and space
- Put into evidence the crystallographic shear plane (121)

3 pathways for the synthesis:

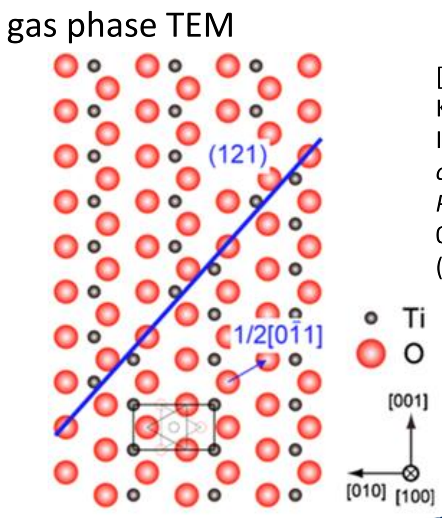
$TiO_2 + C_{(s)} \rightarrow Ti_nO_{2n-1} + CO$

$(2n-1)TiO_2 + Ti_{(s)} \rightarrow 2\, Ti_nO_{2n-1}$

$TiO_2 + H_{2(g)} \rightarrow Ti_nO_{2n-1} + H_2O$ → *in situ* gas phase TEM



[1] L. Liborio, N. Harrison, *Phys. Rev. B*. **77**, 104104 (2008).



[2] S. Harada, K. Tanaka, H. Inui, *Journal of Applied Physics*. **108**, 083703 (2010).

EXPERIMENTAL DEVICE

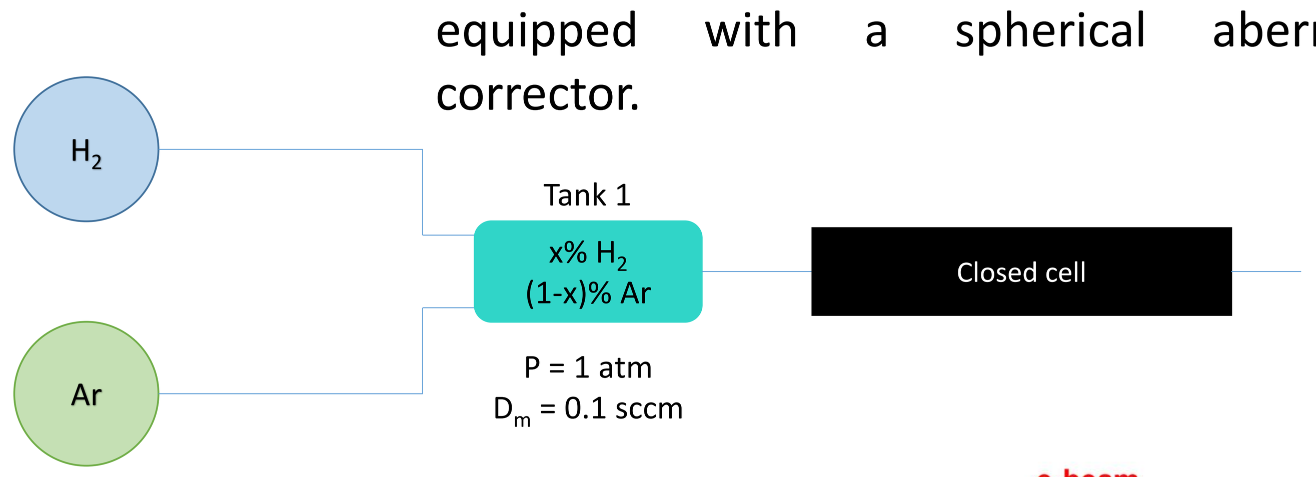
[3] "TEM Environmental Gas Cell: Atmosphere," *Protochips*. https://www.protochips.com/products/atmosphere/

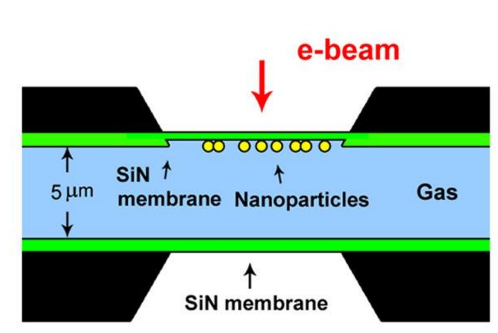
In situ gas TEM (closed-cell)

- TiO_2 nanoparticles dispersed in EtOH
- Drop-casted onto MEMS device with observation window (SiN) and cell assembly
- Heating via Joule effect + flow of H_2 ⇒ *in situ* conditions

$$TiO_2 + H_2 \xrightarrow{\Delta} Ti_nO_{2n-1} + H_2O$$

This experiment was conducted on a JEOL JEM 2100F transmission electron microscope equipped with a spherical aberration corrector.





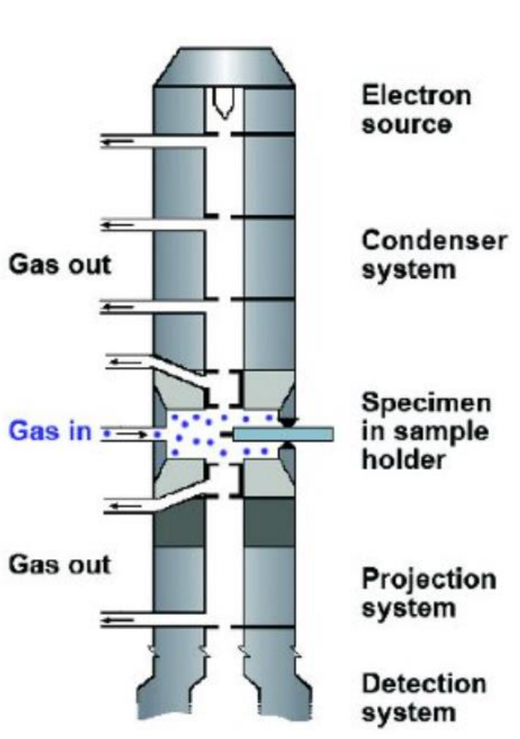
Environmental TEM (differential pumping)

Preparation ≅ closed-cell

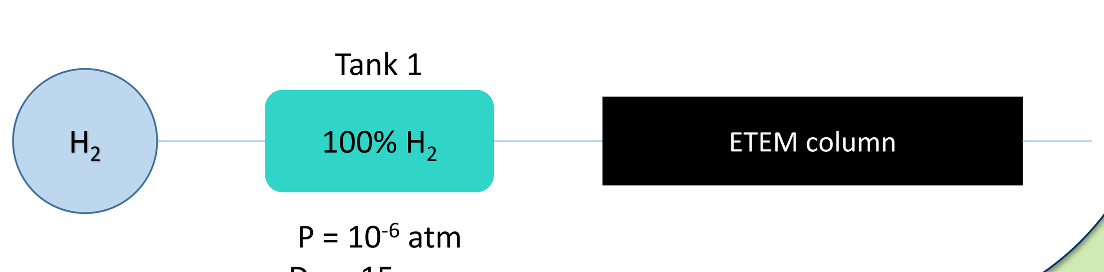
Differences :

- MEMS device only for heating
- Gas inserted via TEM column

This experiment was conducted on a FEI Titan 60-300 environmental TEM (ETEM) equipped with a spherical aberration corrector.



[4] J. R. Jinschek, S. Helveg, *Micron*. **43**, 1156–1168 (2012).

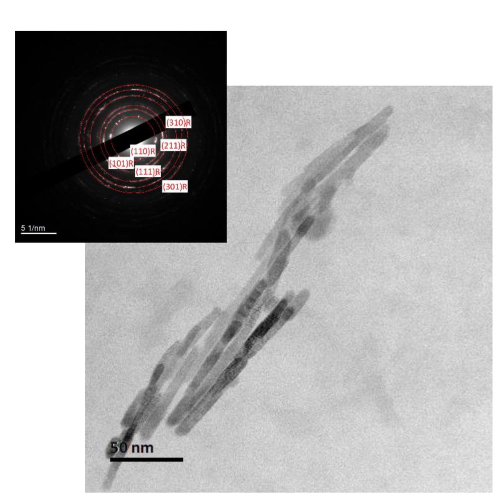


RESULTS & DISCUSSION

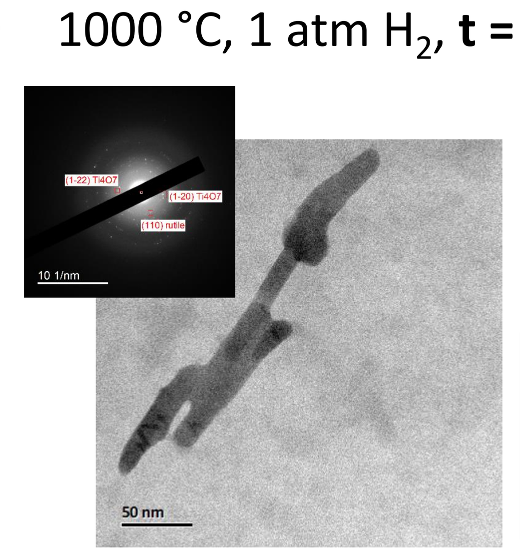
Acquisitions were made in conventional imaging mode to follow the morphology, as well as high-resolution imaging (HRTEM) and electron diffraction (SAED) to follow the crystalline structure, as a function of time, temperature, and the environment applied to the sample.

In situ gas TEM (closed-cell)

25 °C, Vacuum, **t = 0**



1000 °C, 1 atm H_2, **t = 7 h**



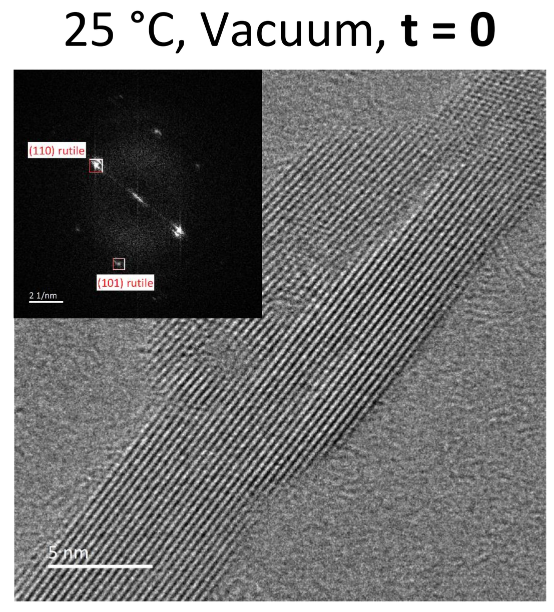
Difficult to follow the phase transition due to long duration of transition

- Effect of the electron beam difficult to quantify
- Sintering induced by elevated T°

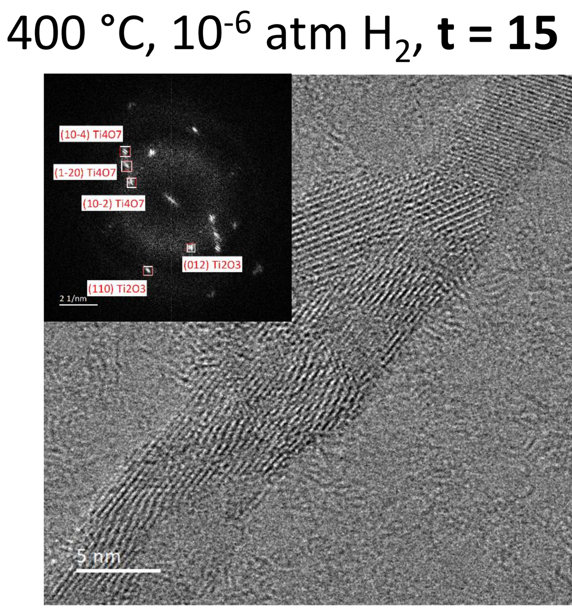
Solution : Use of ETEM → different reactivity (linked to P, D_m)
+ better signal/noise ratio due to reduced membrane thickness → HRTEM & e- dose↘

Environmental TEM (differential pumping)

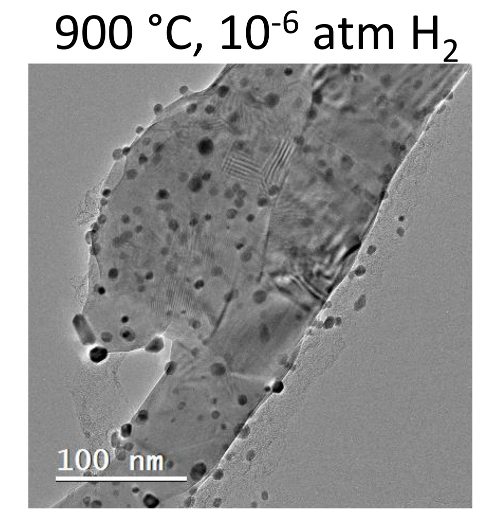
25 °C, Vacuum, **t = 0**



400 °C, 10^{-6} atm H_2, **t = 15 min**



900 °C, 10^{-6} atm H_2



- Reactivity ↗↗
- Introduction of planar defects to crystal structure

CONCLUSION AND PERSPECTIVES

- Difference in reactivity for each experimental configuration → parameters : pressure, gas flow, substrate…
- Observation: discontinuity of atomic planes ⇒ presence of planar defects in the structure introduced during the reaction
- Other experiments in environmental TEM with slower temperature ramp are required, to slow down the reaction and allow better observation of dynamic phenomena occurring during the structural transformation