Field induced oxygen vacancy migration in anatase thin films studied by *in situ* biasing TEM

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Introduction

- Interest in memristors revived since a first memristor device based on TiO_2 was reported by HP Laboratories in 2008 [1].
- Memristive behaviour of TiO2 is determined by the presence of oxygen vacancies (VO).
- VO induce localized electronic states within the band gap, correlated to the formation of Ti^{3+} ions [1].
- We present an in situ biasing TEM study of the atomic structure of oxygen deficient anatase thin films, epitaxially grown on LaAlO3 (LAO) substrates by Pulsed Laser Deposition (PLD).

Anatase: Structure and properties

Titanium dioxide TiO2 is the most prominent representative within the class of transition metal oxides. Anatase is one of the 3 polymorphs of TiO2 with a large number of applications due to its optical properties, memristive behaviour, catalytic activity and electrochemical stability.

- Wide band gap n-type semiconductor (ΔE = 3.2 eV)
- VO act as donors introducing excess electrons
- Localized electronic states within the band gap correlated to the formation of T3+ ions.

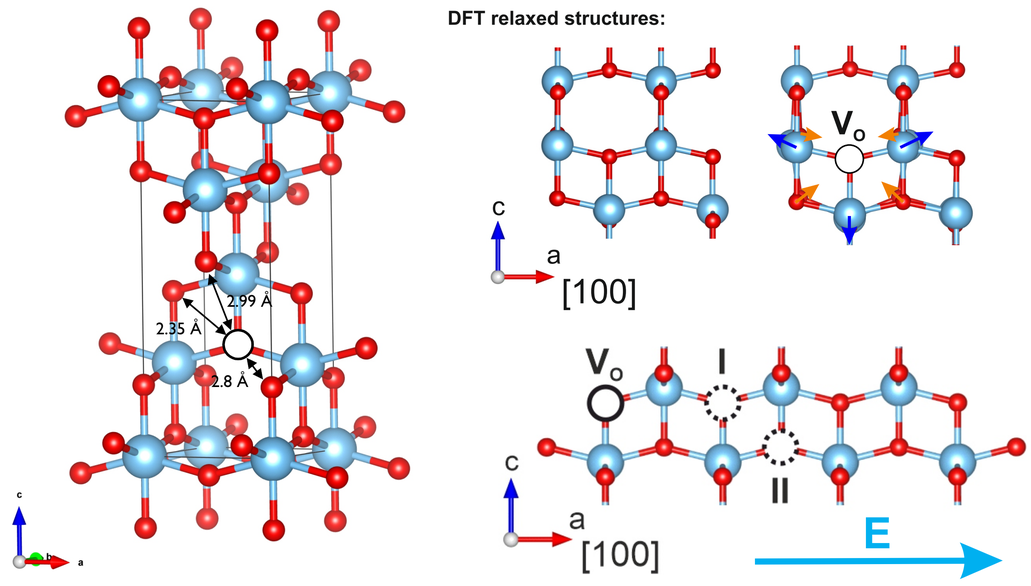


Figure 1: Structure of TiO2 anatase and VO arrangement. Applied E field vector parallel to [100] orientation.

- Attractive forces between VO but Coulomb repulsion prevents clustering, leads to arrangments I and II
- Preferred VO movement along [100] crystallographic orientation [3]

Oxygen vacancy superstructures in anatase

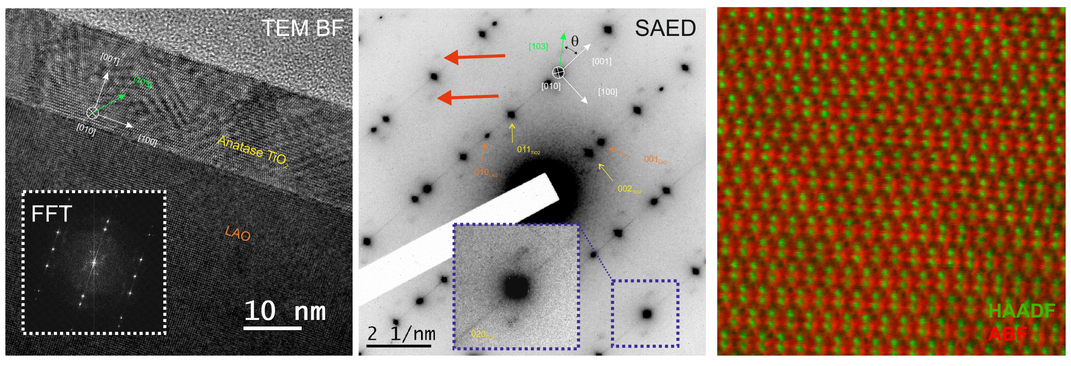


Figure 2: Structure of TiO2 anatase and VO arrangement

- slight displacements of Ti ions in vicinity to VO
- dechannelling effects lead to HAADF intensity variations
- VO planar arrangements without strong atomic restructuring (balance VO induced displacements) [4]

Sample preparation and geometry

- Cross-sectional sample preparation by focused ion beam (FIB) cutting
- Cover sample with insulating layer (eg. spin coating)
- Avoid initial Pt deposit to prevent short circuits
- Field direction has to be aligned parallel to interface in [100] orientation of the film
- Field is applied over the outer contacts the inner contacts are left open

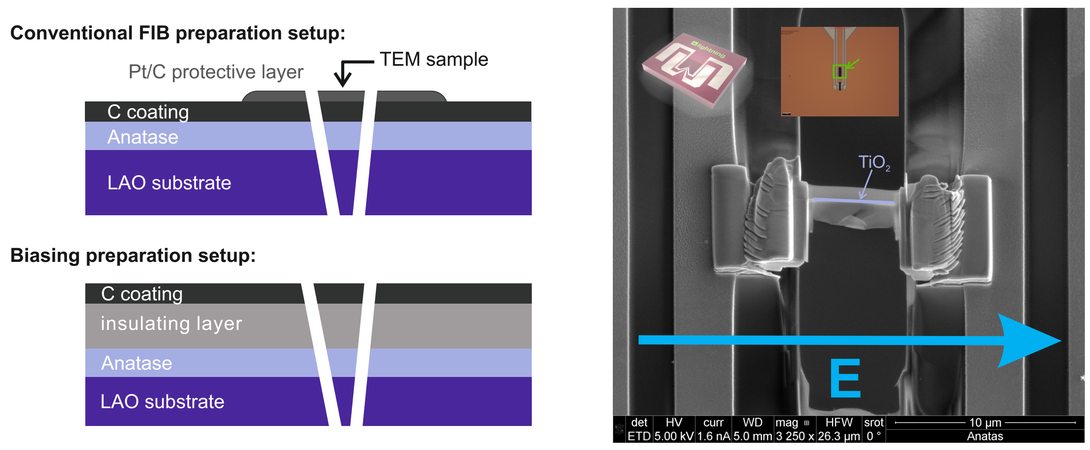
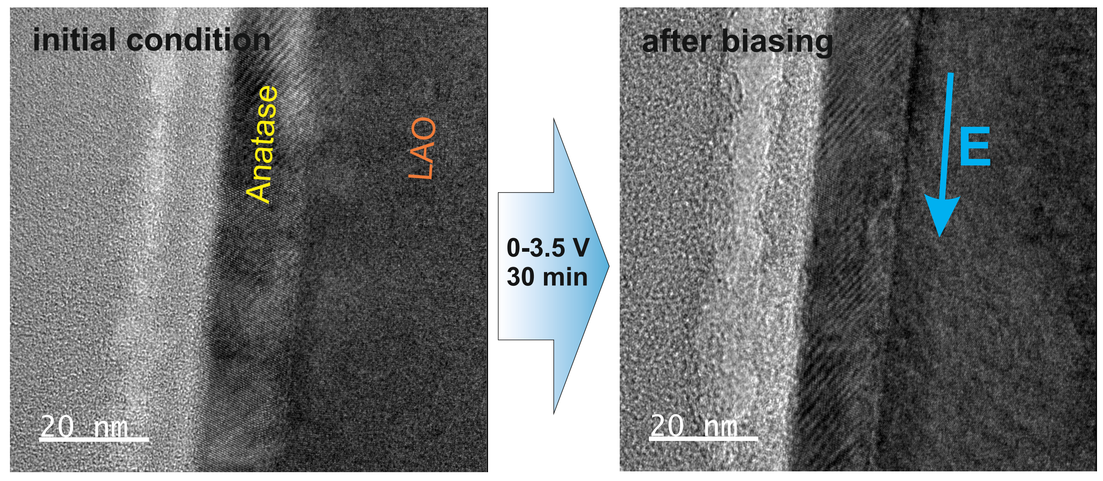


Figure 3: TEM biasing sample preparation procedure

TEM *in situ* biasing experiment - first results



- VO superstructures clearly visible on both images
- Higher occurence of superstructures after biasing

Challenges and Outlook

- Beam damage effects need to be considered
- Reversibility of the observed effect?
- Improvement of sample preparation in terms of reproducibility and Pt spray

References/ Literature

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