Atom by Atom analysis of complex oxide materials

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Introduction

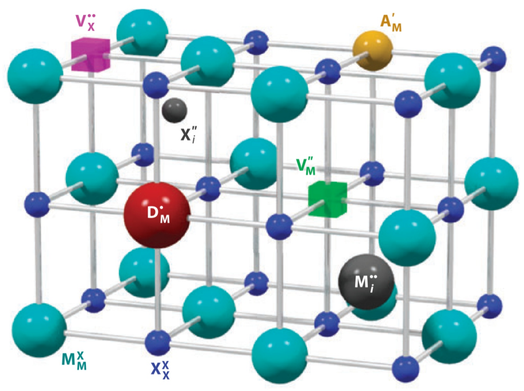
Complex oxide materials are of high technological relevance due to their wide range of electronic and magnetic properties. These properties can be tailored by introducing already small amounts of dopants and/or vacancies.

- Information about the structural/electronic configuration of defects is vital.
- Atom-by-atom characterisation by STEM still challenging, especially with vacancies and low defect concentrations
- New techniques in sample preparation, data aquisition and analysis are required

Point-defects in oxides

Most relevant complex oxides are metal oxides, which are **ionically bonded** solids with many types of defects that impact properties.

Point-defects (0D-defects) play a particularly important role in the control and optimization of these materials. See Figure 1 for a depiction of different point defects in ionic compounds.



M_i ... Cation interstitial
X_i ... Anion interstitial
V_M ... Cation vacancy
V_X ... Anion vacancy
D_M ... Donor substitutional
A_M ... Acceptor substi.

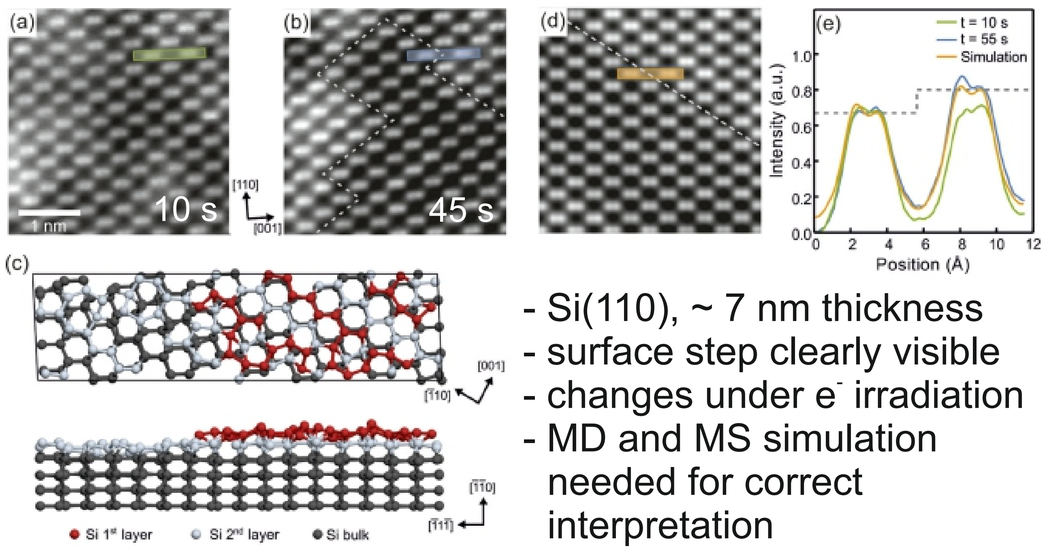
Figure 1: Types of point defects that can occur in a rock salt structure $M^{+2}X^{-2}$ compound. (adapted from [1])

STEM for the characterization of point defects

Aberration-corrected STEM combined with EDX and EDS gives structural, compositional and electronic information on atomic level.
Multislice (MS) **image simultions** based on realistic **atomistc models** (eg. from MD or DFT) needed for interpretation.

Requirements:

- Extremly thin samples needed (<20 unit cells)
- Precise thickness information (PACBED)
- information about **surface amorphization** and **surface-reconstruction** (Figure 2)
- „**Multi-modal**" information; EELS & EDX with (HA)ADF, (i)DPC + Diffraction)



- Si(110), ~ 7 nm thickness
- surface step clearly visible
- changes under e^- irradiation
- MD and MS simulation needed for correct interpretation

Figure 2: (a) ADF-STEM sequence of Si110 surface reconstruction under electron irradiation. (adapted from [2])

STO doped with Ta

We chose $SrTiO_3$ (STO) doped with different species (Nb, Ia, Ta) as a playing ground for method development and optimization.

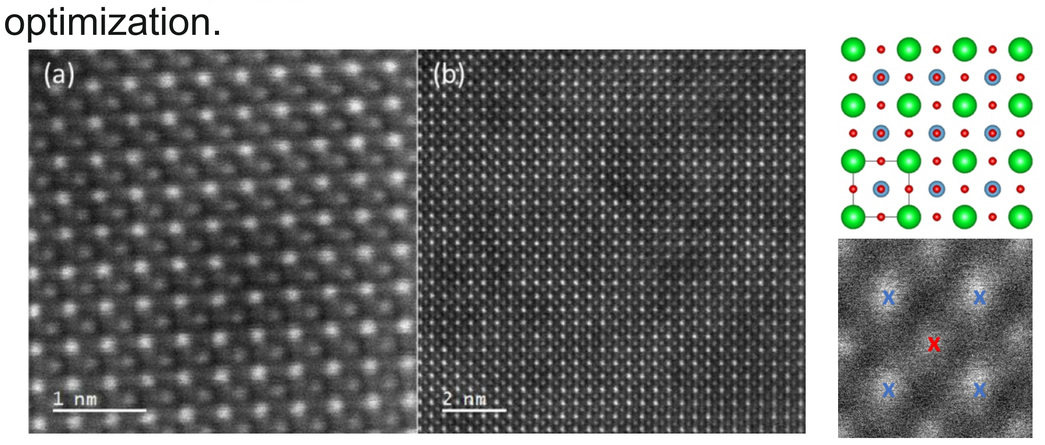
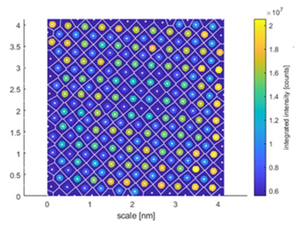


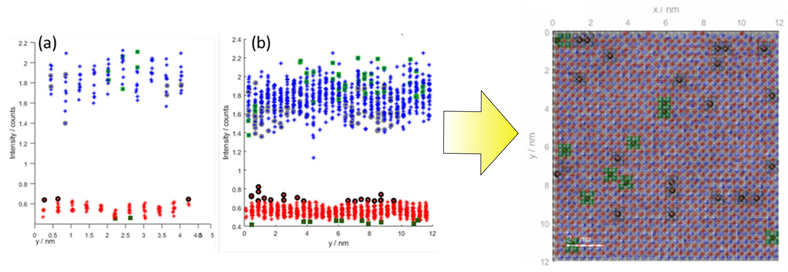
Figure 3: HAADF images of STO:Ta (100) with crystal model



- Intensity determination: Voronoi segmentation and column wise integration with in-house Matlab code (Seek'n'Integrate) [3].
- Threshold classification of columns to find outliers ($\mu \pm 2\sigma$)

$$I_{rel} = \frac{I_{TiO}}{I_{4\,Sr}}$$

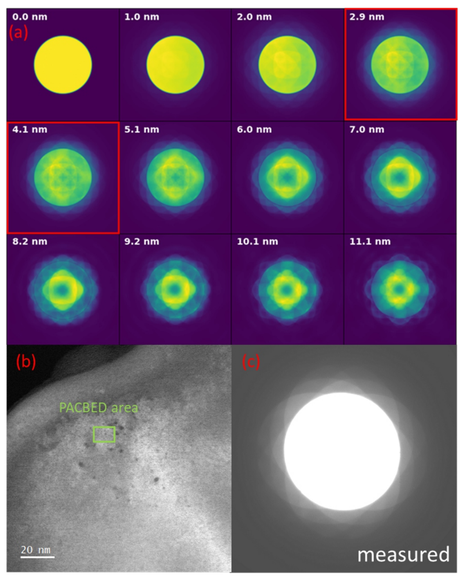
- PACBED thickness determination: 3-4 nm
- most likely 1 Ta atom/TiO column
- 30 % I increase of TiO, confirmed by MS



- Lower I for Sr postions: V_{Sr} ?
- Clustering for charge compensation [4]

PACBED thickness determination

- Quantitative comparison with MS simulations requires exact thickness information
- Position averaged convergent beam electron diffraction (PACBED) provides thickness of crystalline part if compared to MS simulations
- Tedious analysis process can be automatized by convolutional neural networks (see poster by Michael Oberaigner)



References/ Literature

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