Redox-based switching mechanisms in memristive devices studied by synchrotron-based spectromicroscopy

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Outline

1. **Motivation:** Memristive devices for nonvolatile memory

2. ***Operando* spectromicroscopy:** Comprehensive understanding of memristive processes: oxygen vacancy motion

3. **Post mortem spectromicroscopy:** Design rules to prevent retention failure

4. **Beam-sample interaction**

5. **Conclusion**

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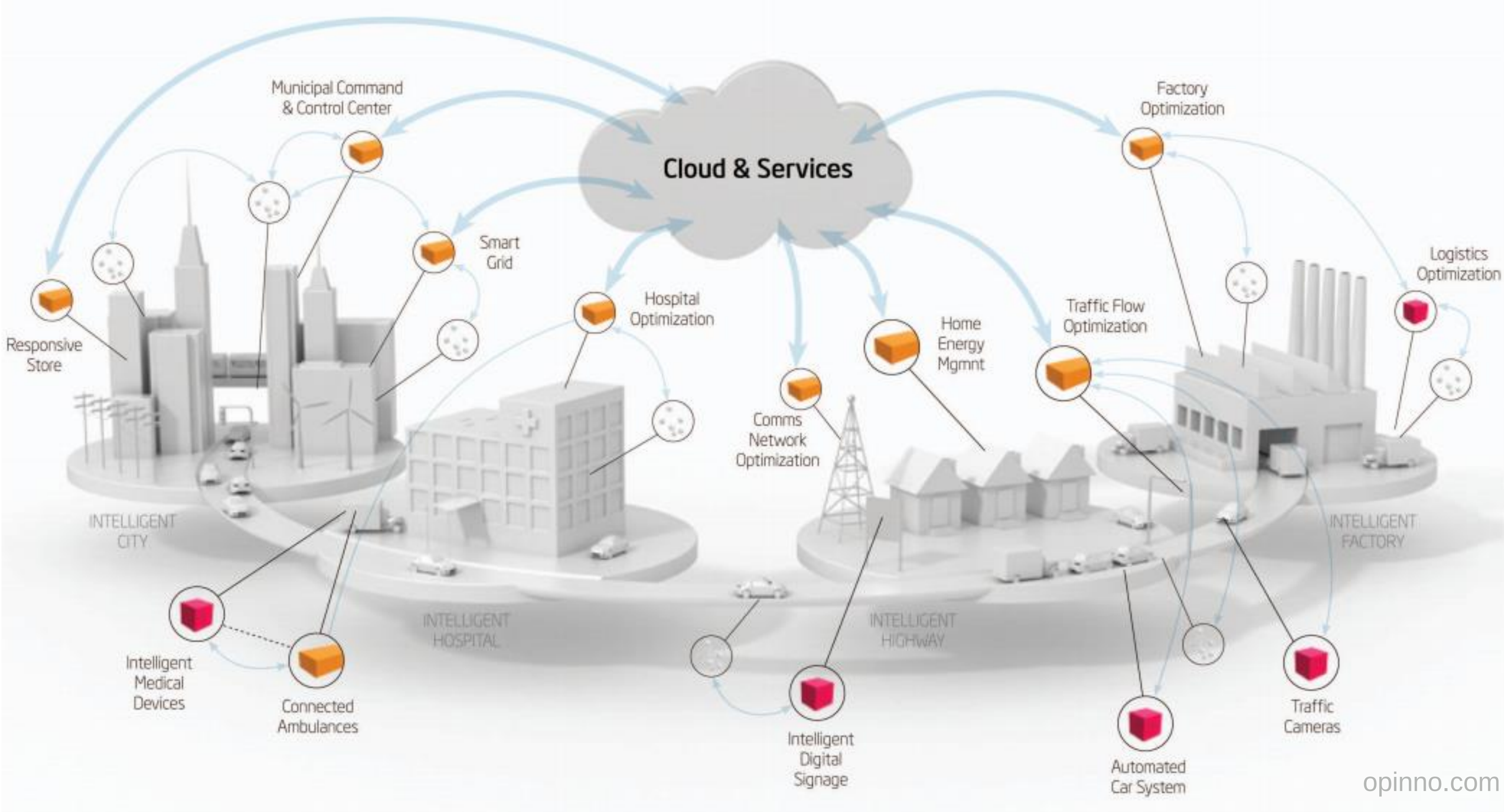
A connected world: The Internet of Things



Technological revolution requires new concepts in data storage and mobile computing

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Electronic data storage systems

Flash

https://en.wikipedia.org/

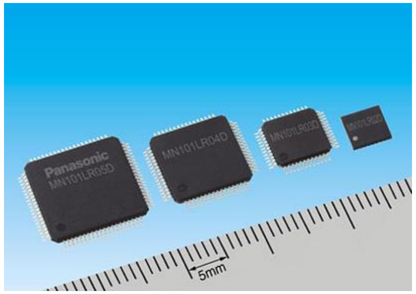
- non-volatile
- slow
- switching time: µs
- high voltage required

DRAM

https://en.wikipedia.org/

- volatile
- fast
- switching time: ns
- refresh power and time

ReRAM



http://news.panasonic.com/

- non-volatile
- fast
- switching time: ns
- **Complex mechanisms**

Kent, *Nat. Nanotech.* **10** (2015)

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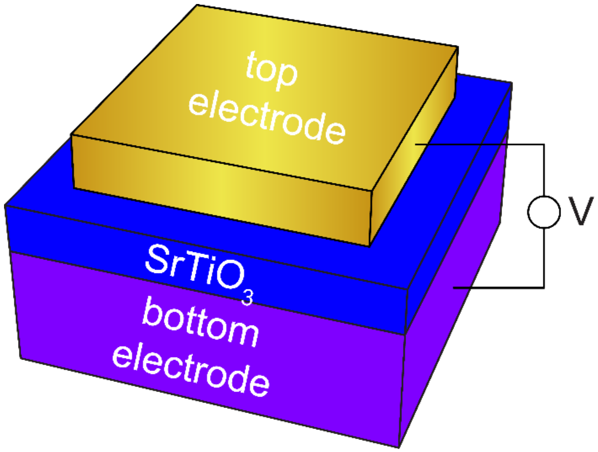
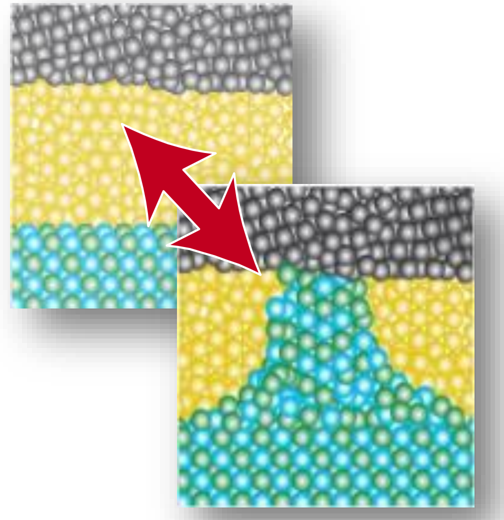
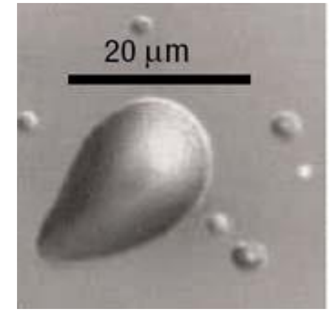
Resistive Switching for non-volatile memory

Szot *et al.*, Nat. Mater. **5** (2006)
Waser *et al.*, *Nat. Mater* **6** (2007)
Waser *et al.*, *Adv. Mater.* **21** (2009)
Wong *et al.*, *Proceedings of the IEEE **100** (2012)*
Cooper *et al.*, *Adv. Mater.* (accepted, 2017)

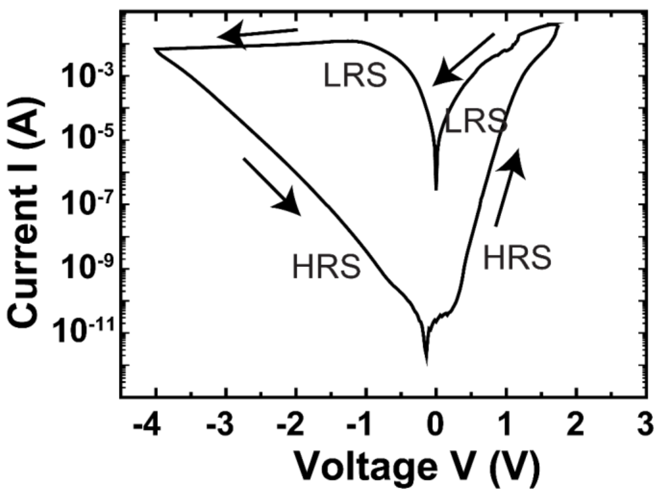






Oxygen evolution underneath the anode:

$$2\,Ti^{4+} + O_O \leftrightarrow 2\,Ti^{3+} + V_O^{\cdot\cdot} + \tfrac{1}{2}O_2 \uparrow$$



Baeumer *et al.*, *Nat. Commun.* **6** (2015)

- Oxygen vacancy generation and redistribution under applied field → local redox reaction
- Spatial confinement: filamentary switching

? Quantitative details

? Impact on electronic transport

→ **Spectromicroscopic quantification mandatory**

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Model material of choice: $SrTiO_3$

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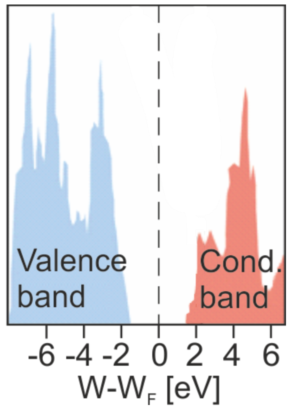
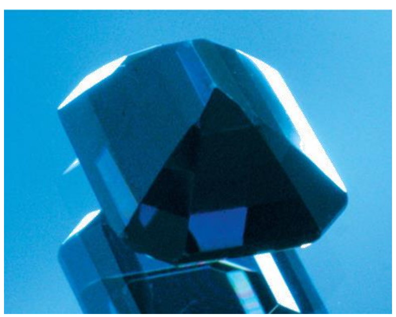
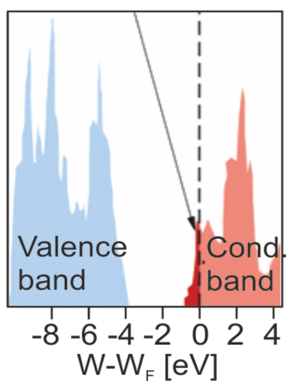
- Stoichiometric $SrTiO_3$: transparent, insulating



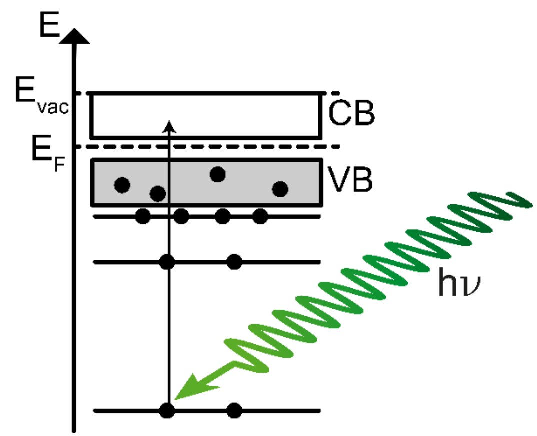
- Oxygen deficient $SrTiO_{3-\delta}$: opaque, conducting



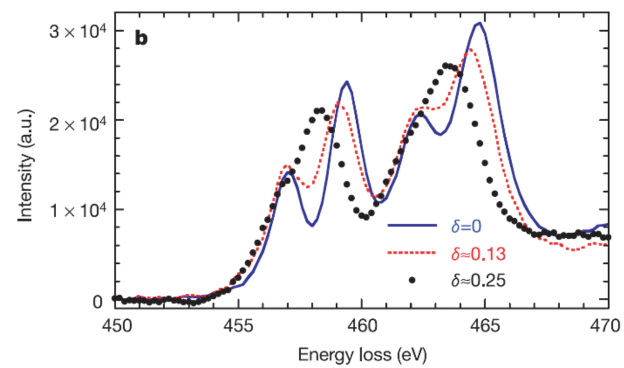


Waser, *Adv. Mater.* **21** (2009)

- X-ray absorption spectroscopy, EELS



- oxygen vacancies cause significant spectral changes



Muller, *Nature* **430** (2004)

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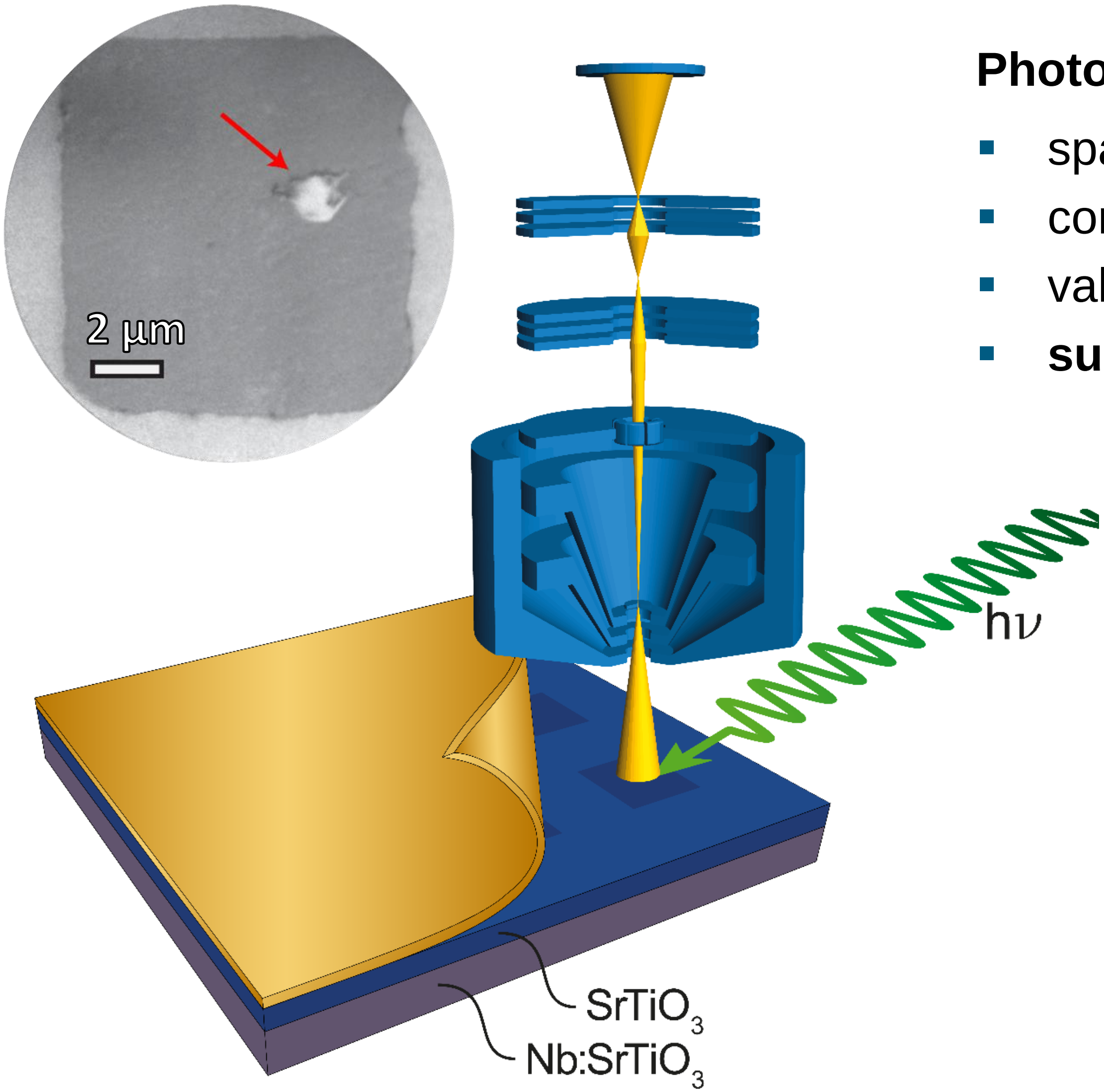
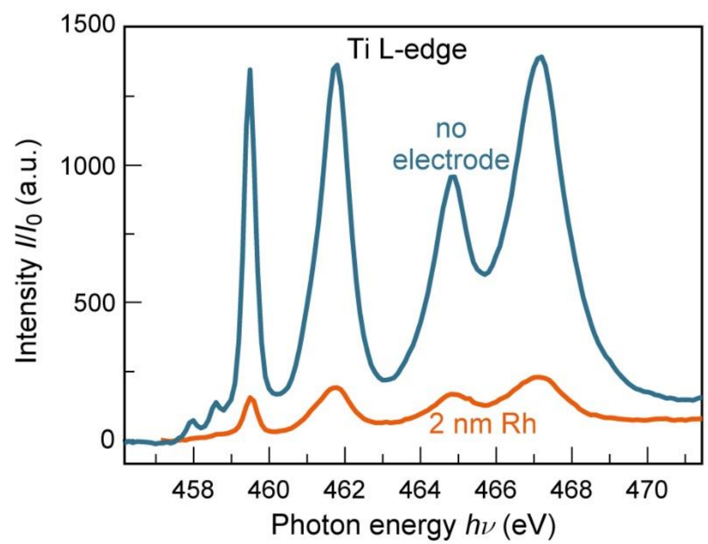
Method of choice: Spectromicroscopy



Photoelectron emission microscopy

- spatially resolved XPS and XAS
- composition sensitive
- valence state sensitive
- **surface sensitive**



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Evidence of localized valence changes

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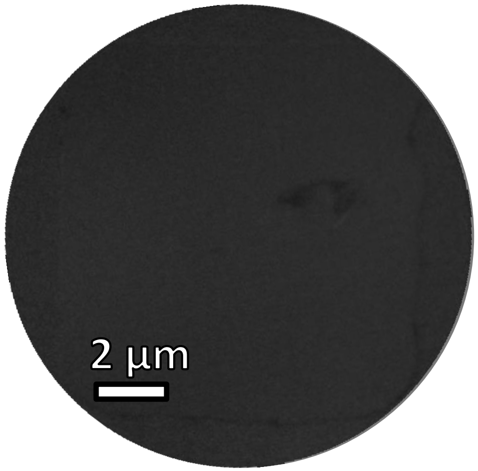
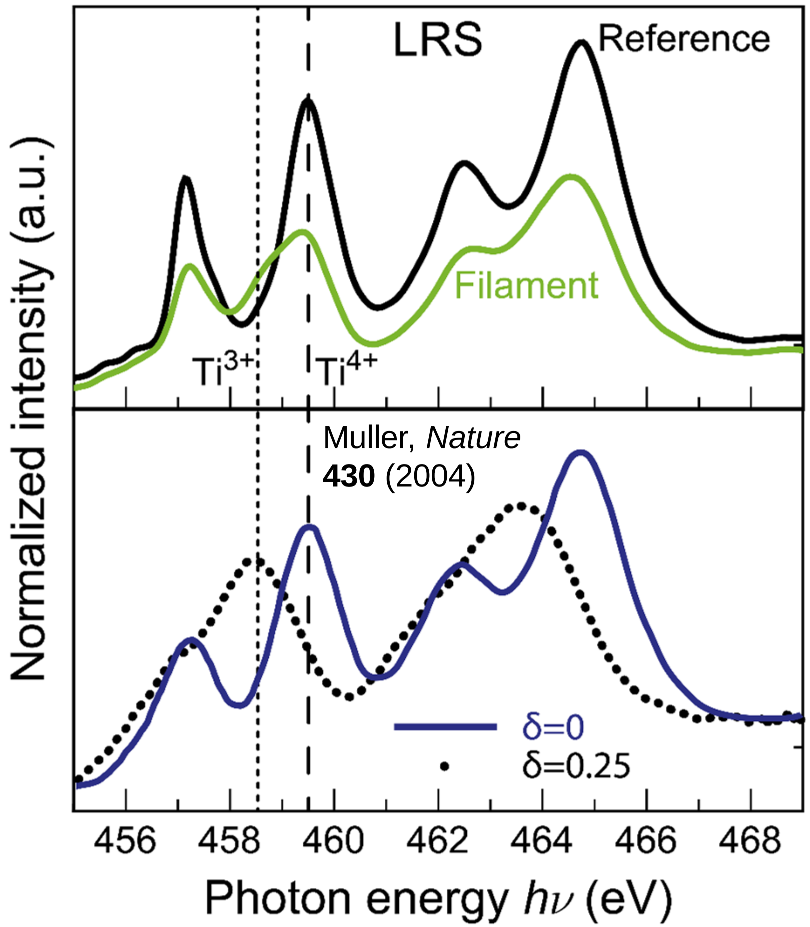
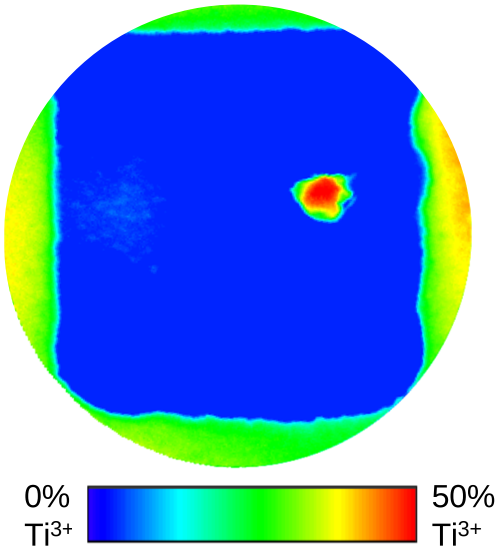
PEEM image stack



Ti L-edge spectra



False color map



- Identification of switching filament
- LRS: Ti^{3+} filament in Ti^{4+} matrix

? Switching details

Baeumer, *Nat. Commun.* **6** (2015)
Baeumer, *Nanoscale* ***8*** (2016)

In-operando PEEM: Graphene electrode

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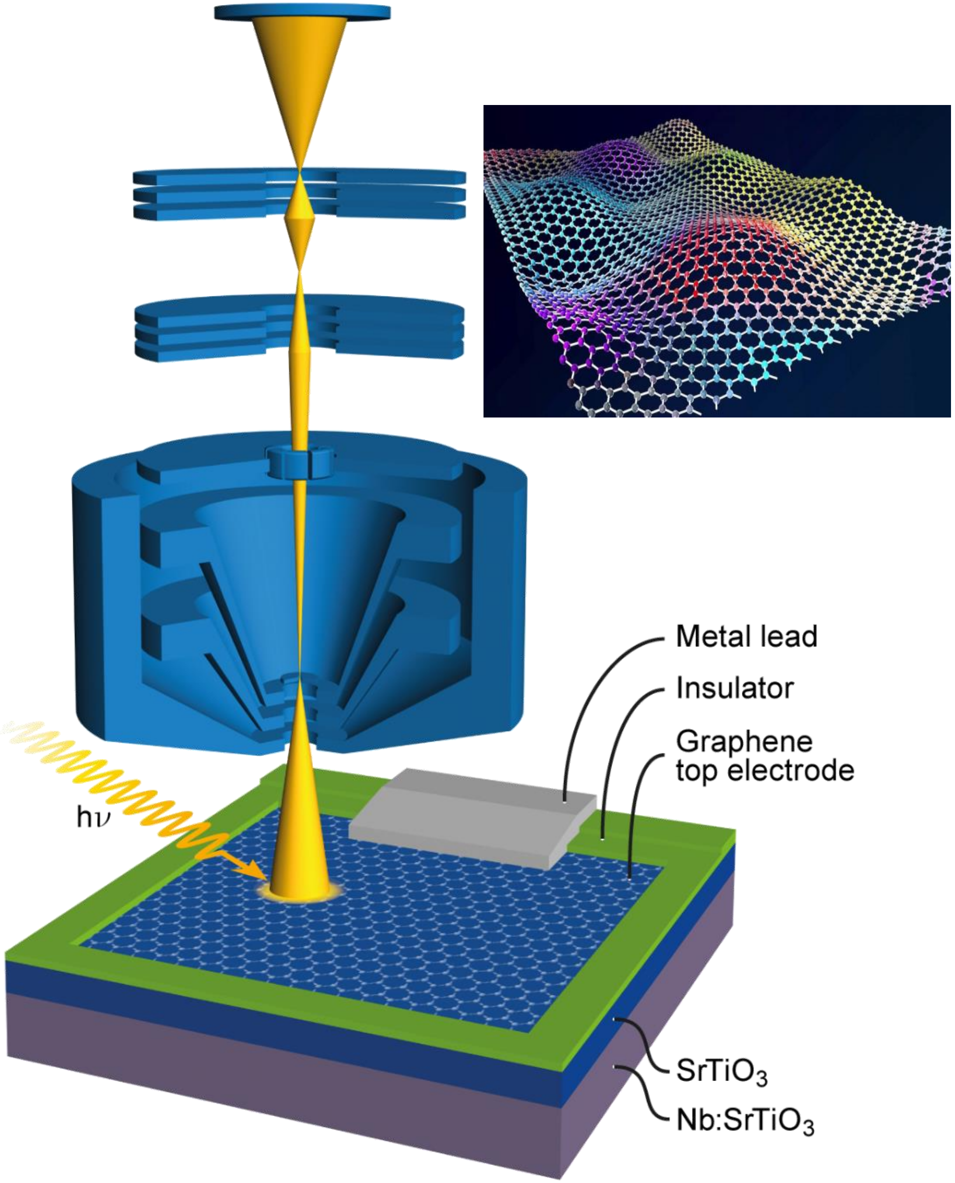
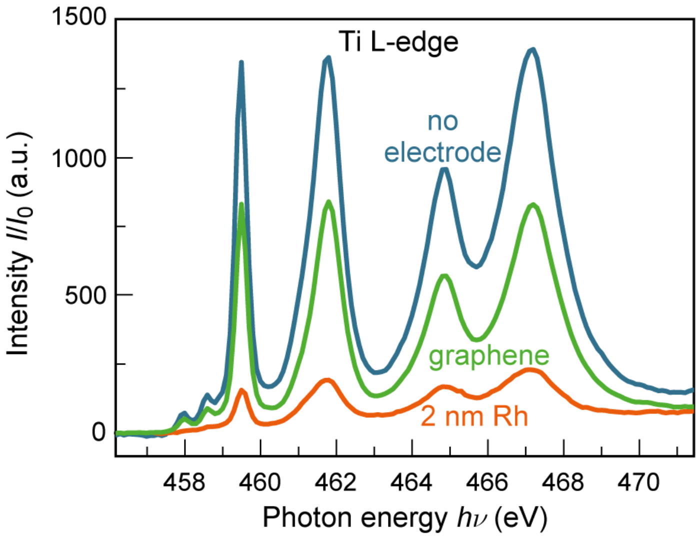


Photoelectron emission microscopy

- surface sensitivity:
  need for ultra-thin electrode
- graphene is the ideal candidate
- excellent signal-to-noise ratio



Baeumer *et al.*, *Nat. Commun.* **7** (2016)

graphene growth:
S. Rogers, M. Shim, University of Illinois

Spectroscopic fingerprint of valence changes

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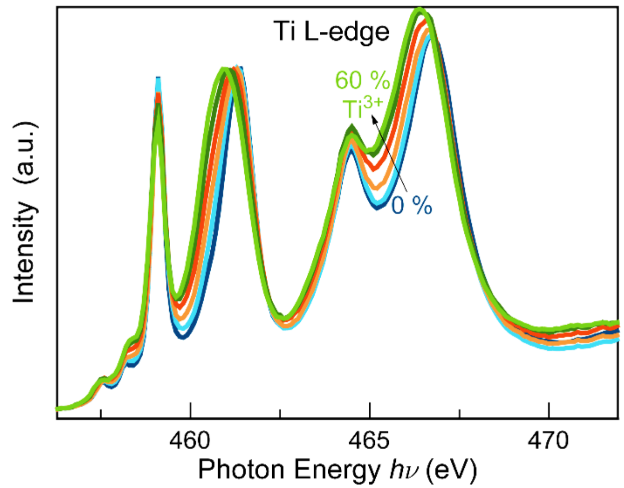
$$2Ti^{4+}+O_O \leftrightarrow 2\,Ti^{3+}+V_O^{\bullet\bullet}+ \tfrac{1}{2}O_2\uparrow$$

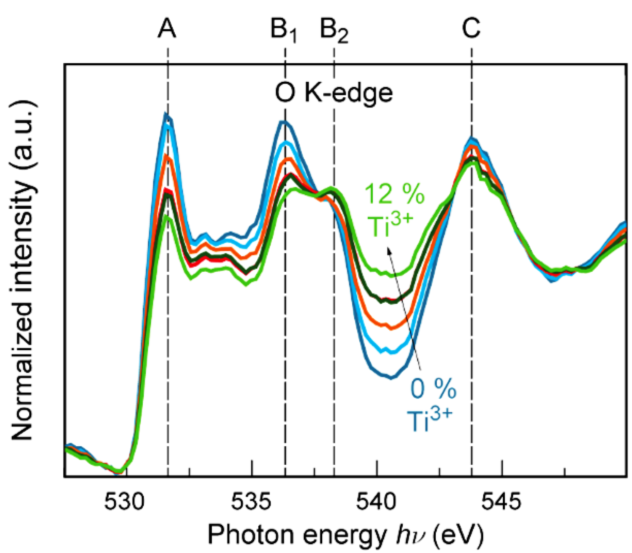


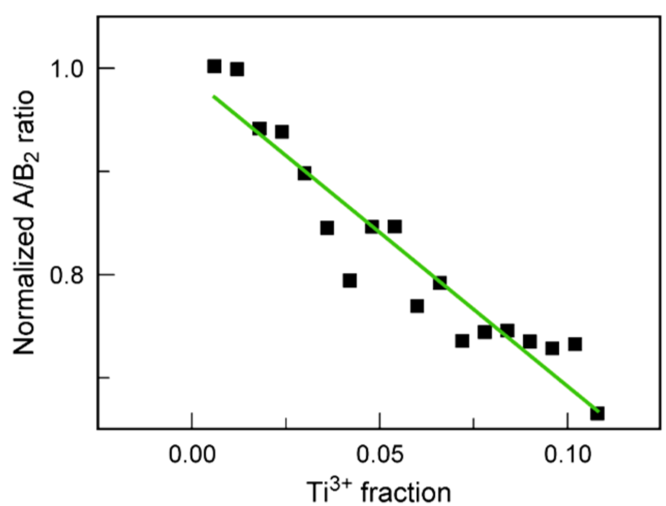
Ti L edge

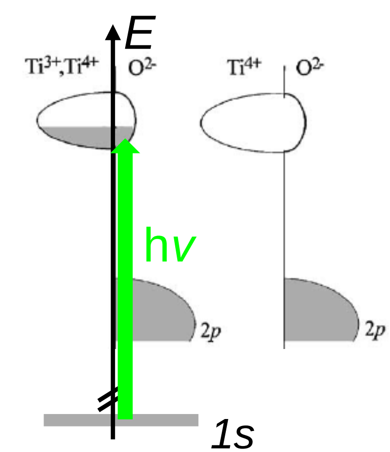
- Large changes: significant spectral changes
- Subtle changes: spectral features hard to detect

O K edge

- Subtle changes: O K-edge very sensitive
- Direct measure for electrons in conduction band







Baeumer, *Nat. Commun.* **7** (2016), Abbate, *PRB* **46**, 4511 (1992)

Sefat, *Solid State Chem.* **178** (2005)

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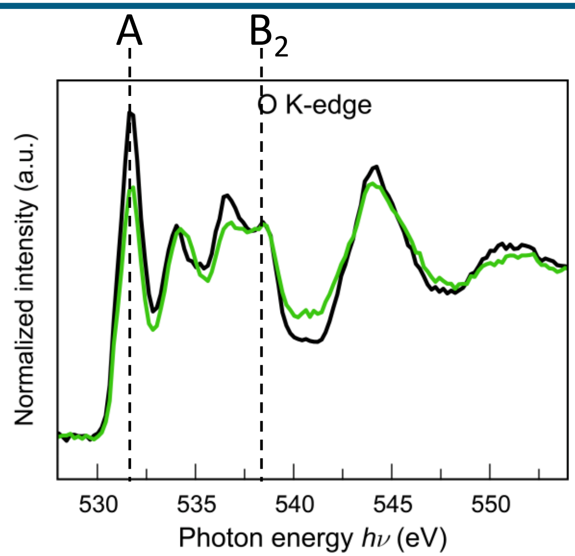
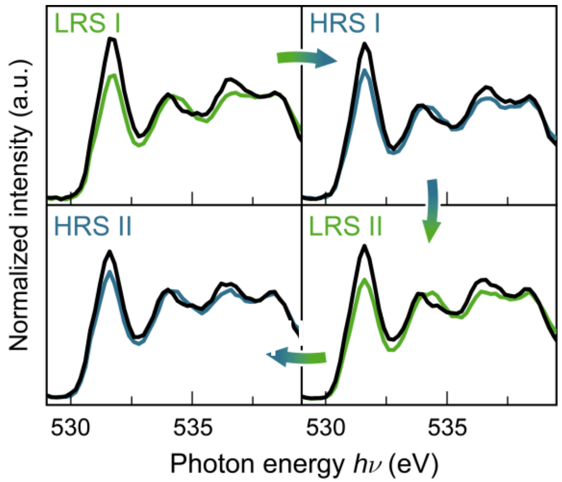
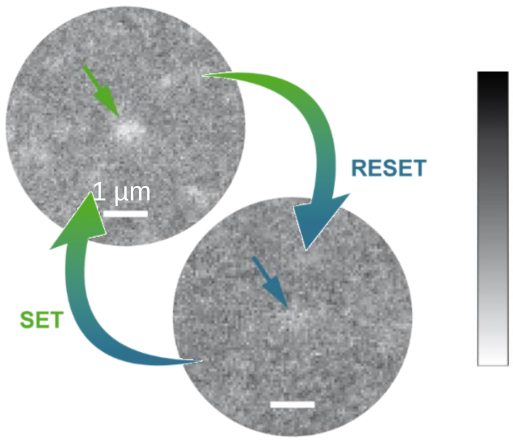
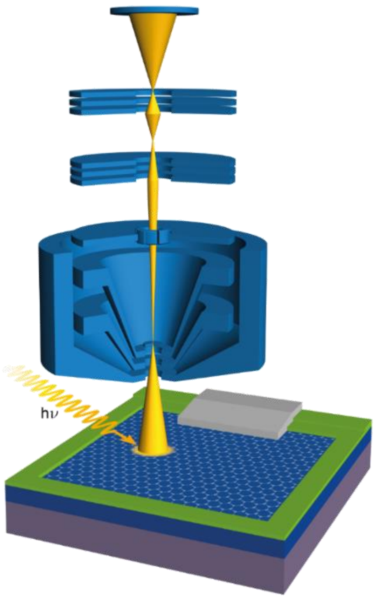
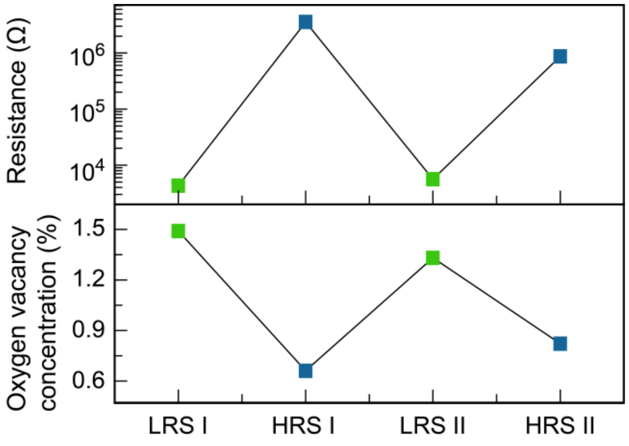
Quantifying oxygen vacancy variations











- Switching-induced modulation in oxygen vacancy concentration
- Variation by factor 2-3
- Agreement with resistance change
- Variation by 10^2-10^3

Baeumer, *Nat. Commun.* **7** (2016)

Quantification of carrier density modulations

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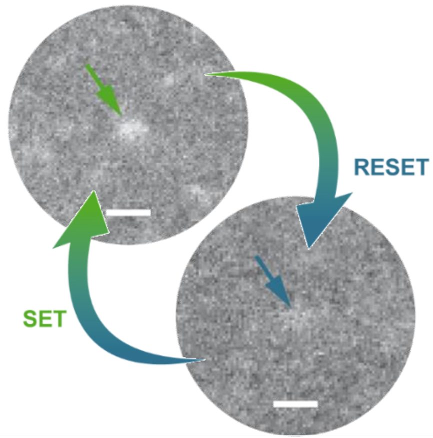
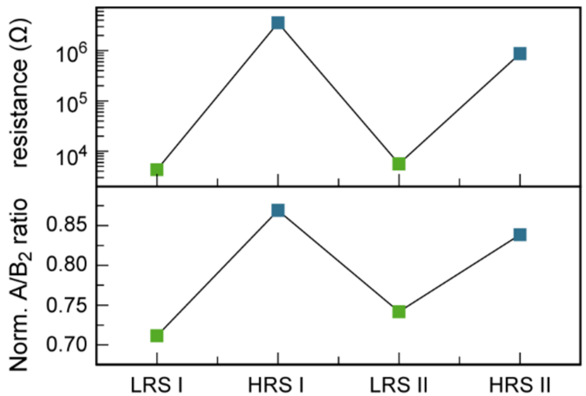
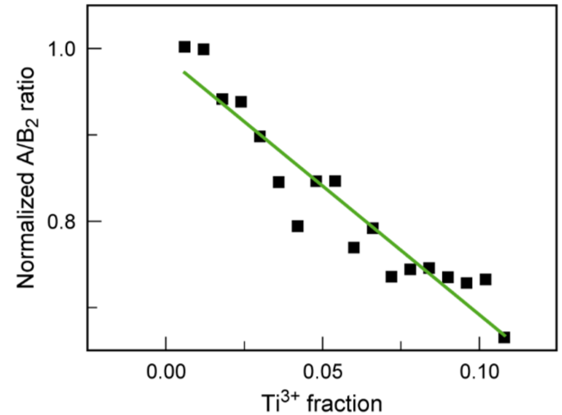
Spectroscopic change





Comparison with calibration



	LRS	HRS
N_{VO}	3.35×10^{20} cm^{-3}	7.5×10^{20} cm^{-3}
n	**1.5×10^{21} cm^{-3}**	**6.7×10^{20} cm^{-3}**

$$2Ti^{4+} + O_O \leftrightarrow 2Ti^{3+} + V_O^{\bullet\bullet} + \tfrac{1}{2}O_2\uparrow$$

- ✓ Redox-induced carrier density modulations
- ✓ Variation by factor 2-3
- ✓ Agreement with resistance change
- ✓ Variation by 10^2-10^3

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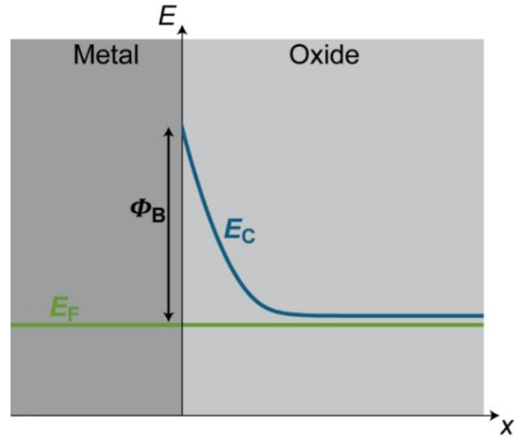
Quantitative treatment of VCM switching

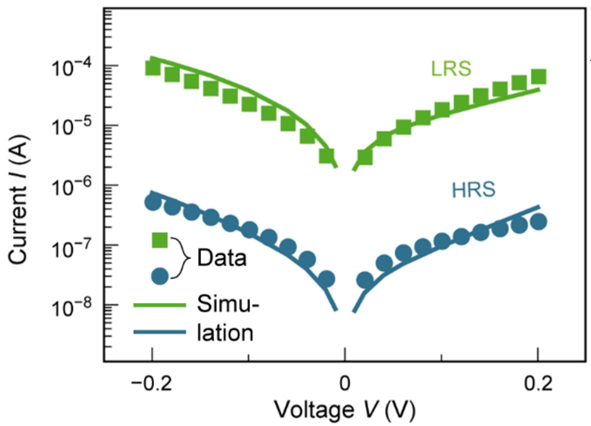
- experimental quantities:
resistance + vacancy concentration

	LRS	HRS
N_{VO}	3.35×10^{20} cm^{-3}	7.5×10^{20} cm^{-3}
n	**1.5×10^{21} cm^{-3}**	**6.7×10^{20} cm^{-3}**

- understanding the device resistance: A Schottky barrier

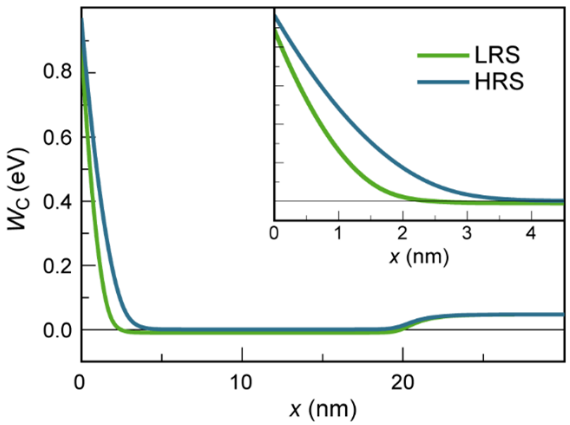


- transport model based on experimental quantities



transport model from
A. Marchewka, SISPAD 2015

- oxygen vacanciy variation causes Schottky barrier modification



Baeumer, *Nat. Commun.* **7** (2016). **Simulation: A. Marchwka & S. Menzel, RWTH Aachen & FZJ**

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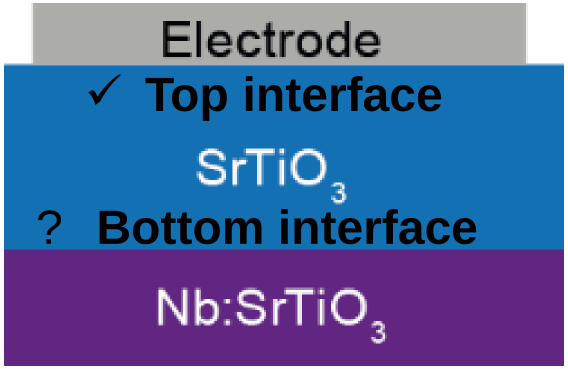
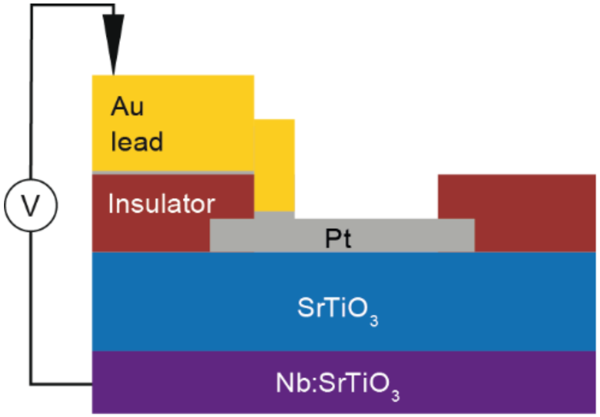
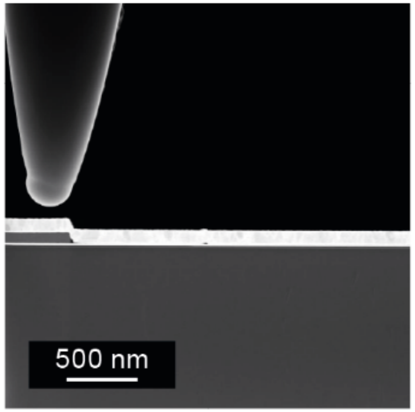
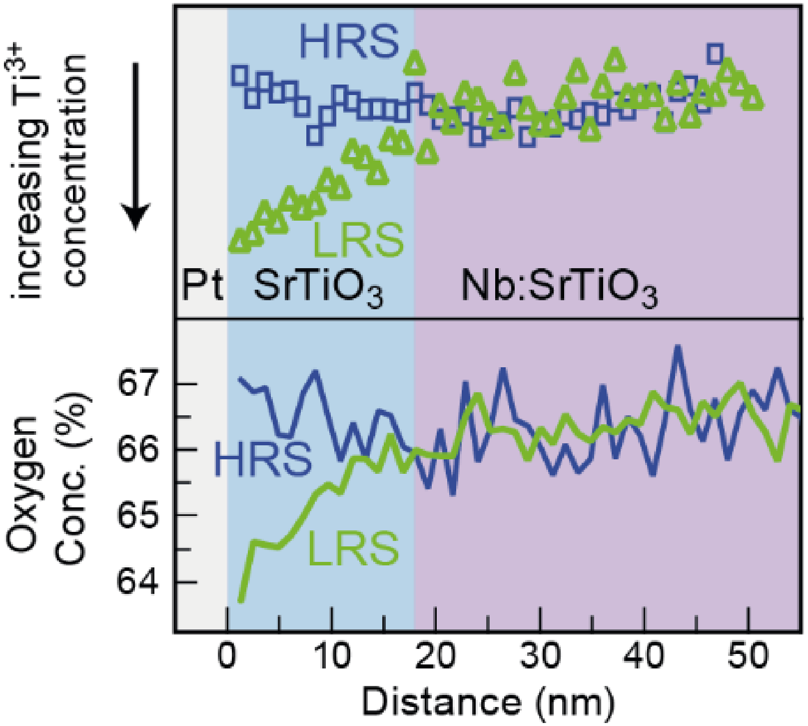
TEM-based oxygen vacancy mapping









Cooper, Baeumer *et al.*, *Adv. Mater.* (accepted, 2017)

- ✓ *In operando* TEM clarifies switching details
- ✓ Concentration variation only at top interface
- ✓ Agreement with PEEM data
- ✓ LRS: decrease of the total oxygen concentration in the film
- ✓ LRS: Ti^{3+} gradient
- ✓ HRS: Nearly stoichiometric $SrTiO_3$

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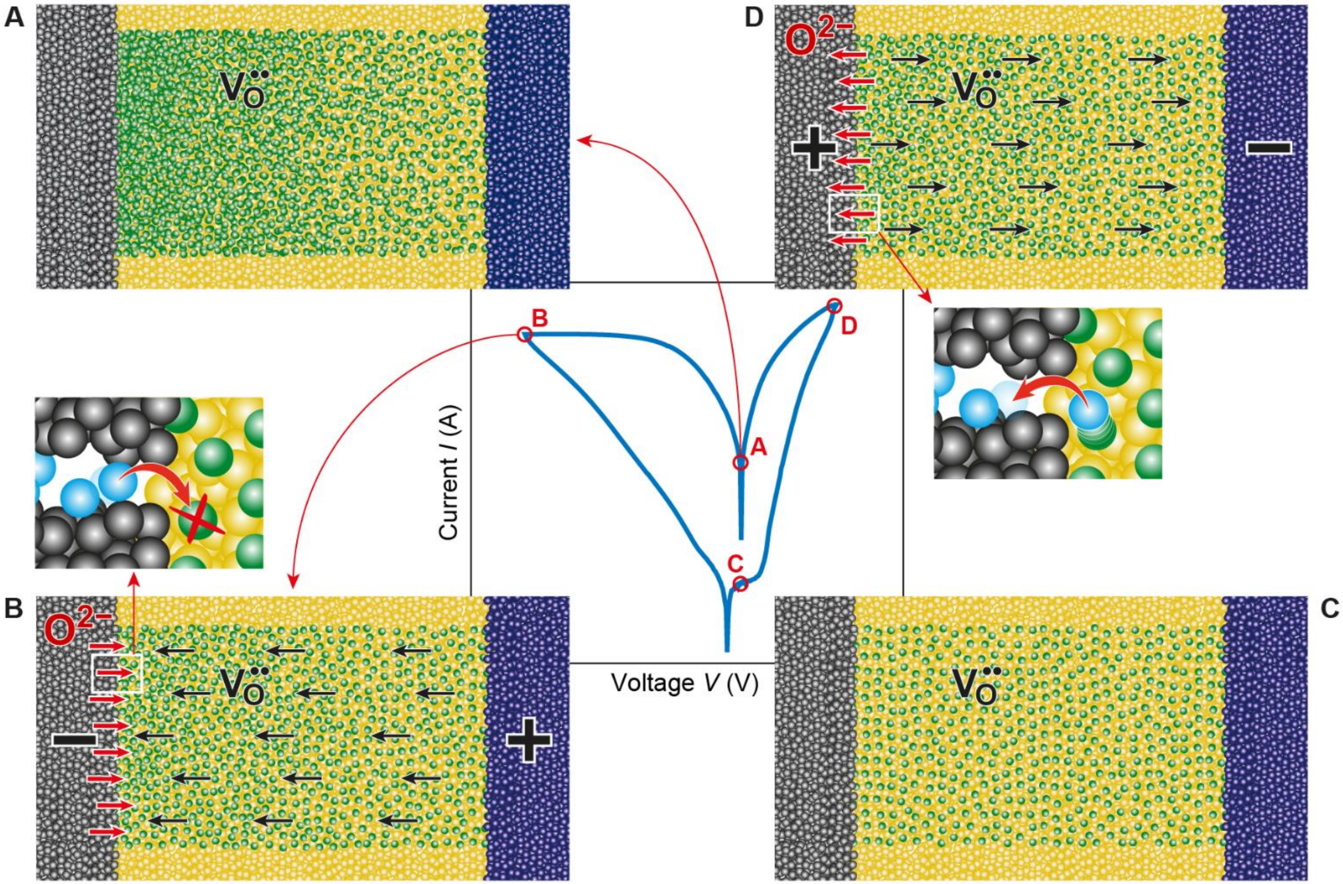
Microscopic origin of resistive switching in $SrTiO_3$

Oxygen evolution and reincorporation reaction: $2Ti^{4+} + O_O \leftrightarrow 2\,Ti^{3+} + V_O^{\bullet\bullet} + \frac{1}{2}O_2\uparrow$

Set: left to right

Reset: right to left



Cooper, Baeumer *et al.*, *Adv. Mater.* (accepted, 2017)

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Nonvolatile memory: Data retention

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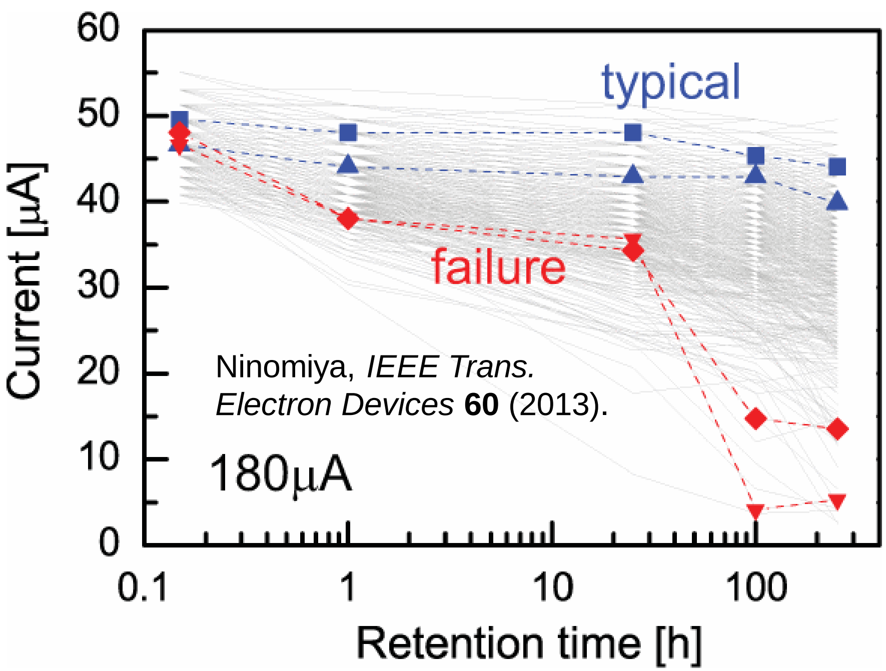
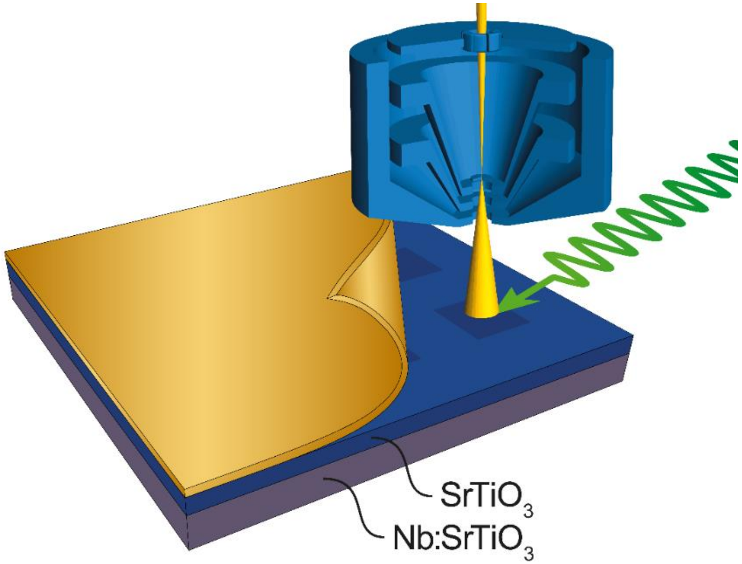
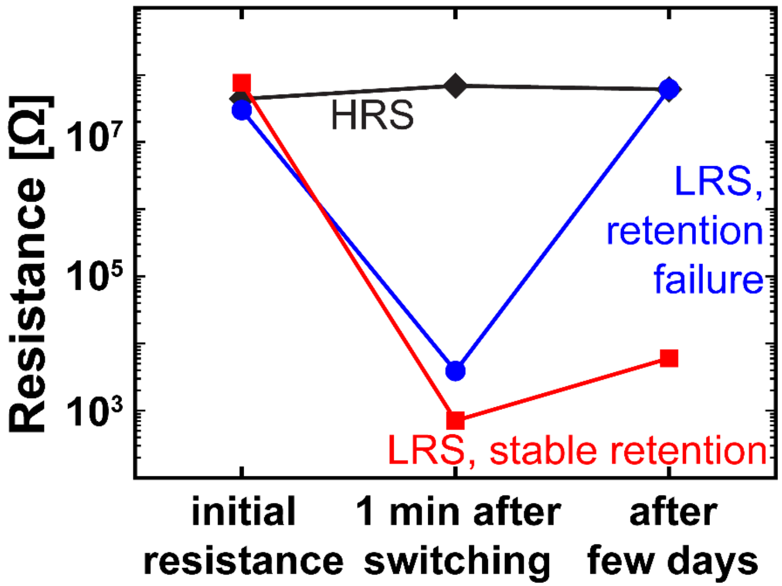
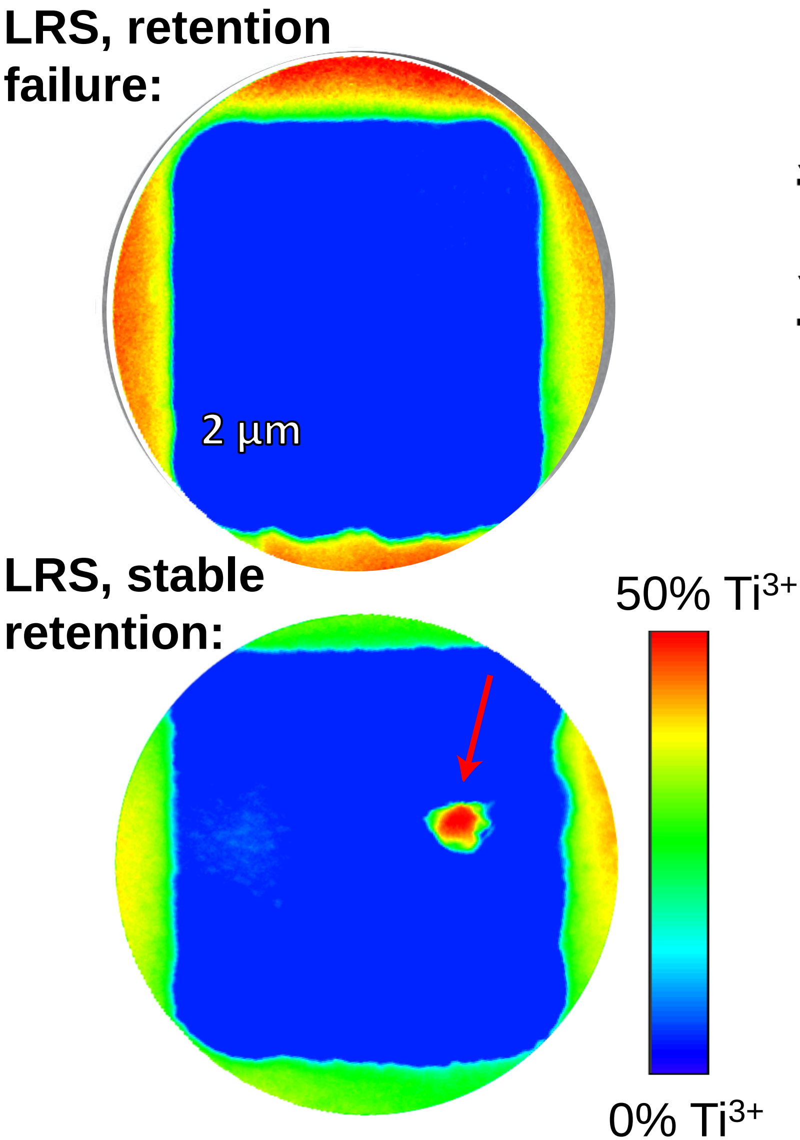


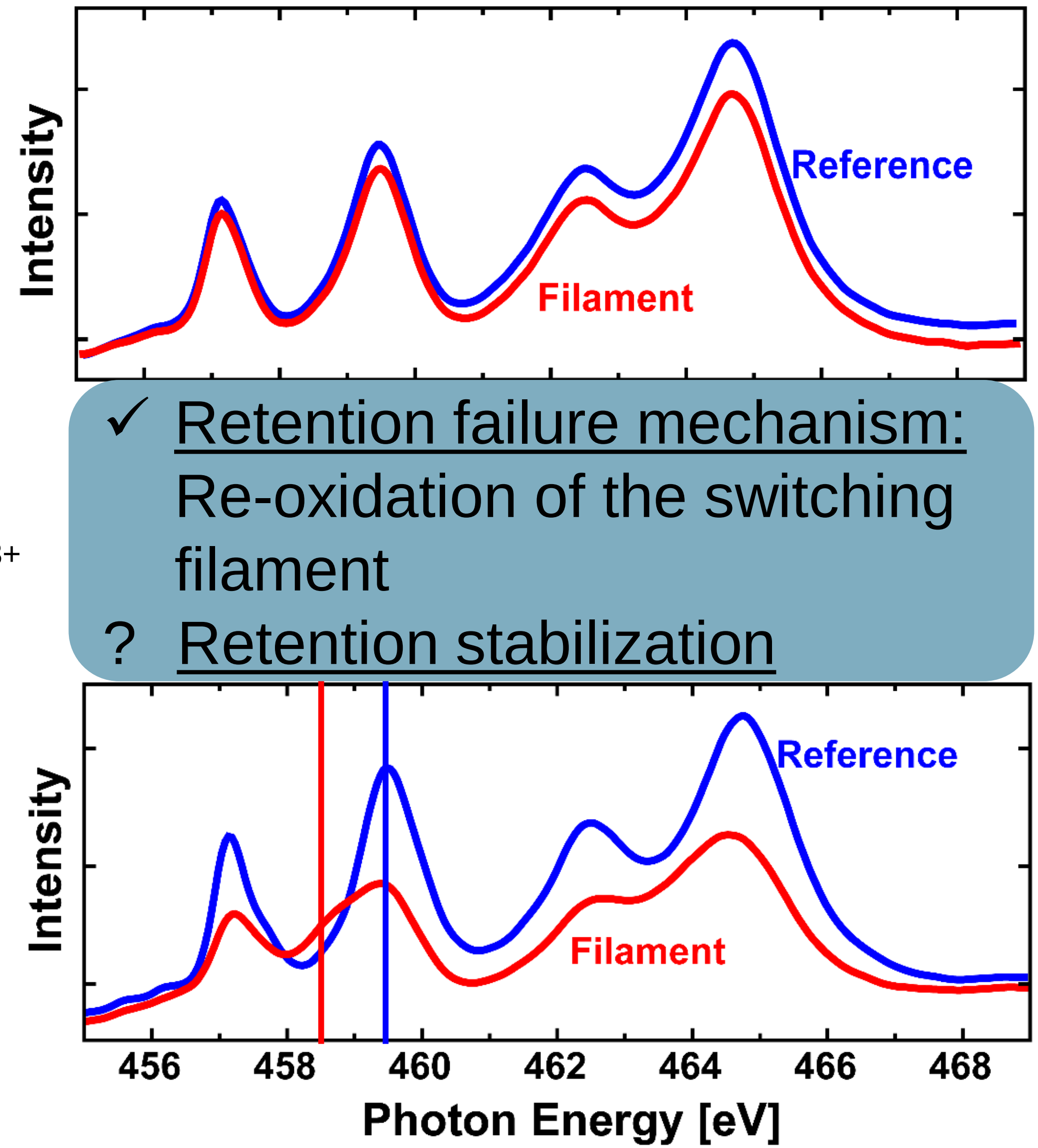


- ✓ Long retention for some devices
- ? Operation mechanism
- ? Failure mechanism
- ? Design rules



LRS Retention Failure: Re-oxidation





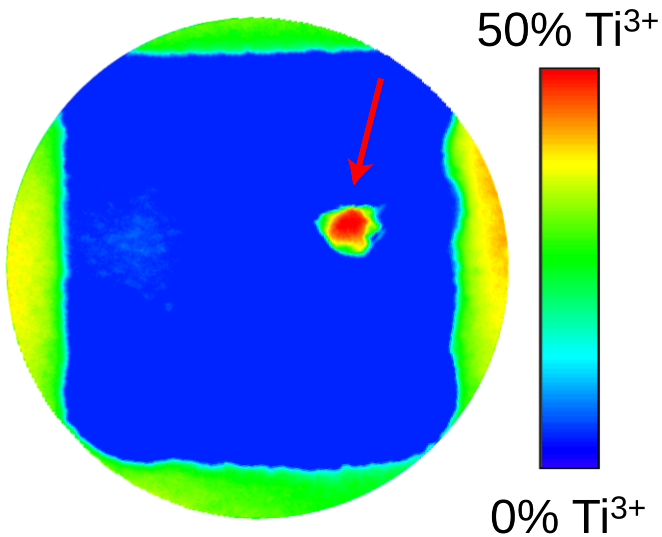
✓ <u>Retention failure mechanism:</u> Re-oxidation of the switching filament

? <u>Retention stabilization</u>

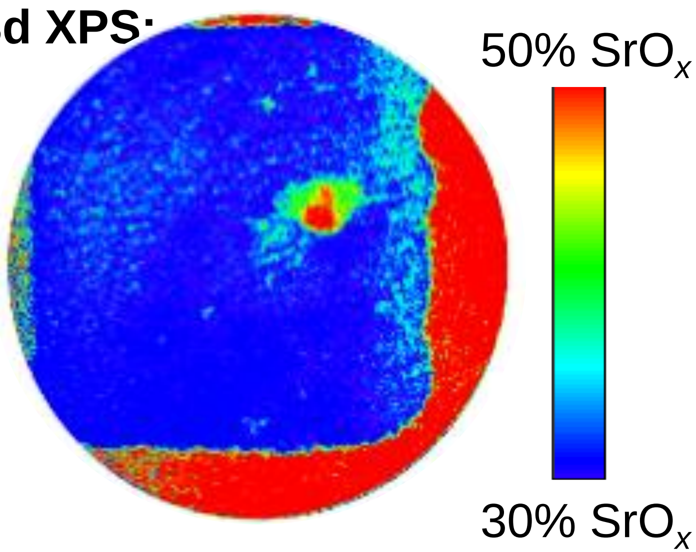
Baeumer *et al.*, *Nat. Commun.* **6** (2015)

Filament chemistry

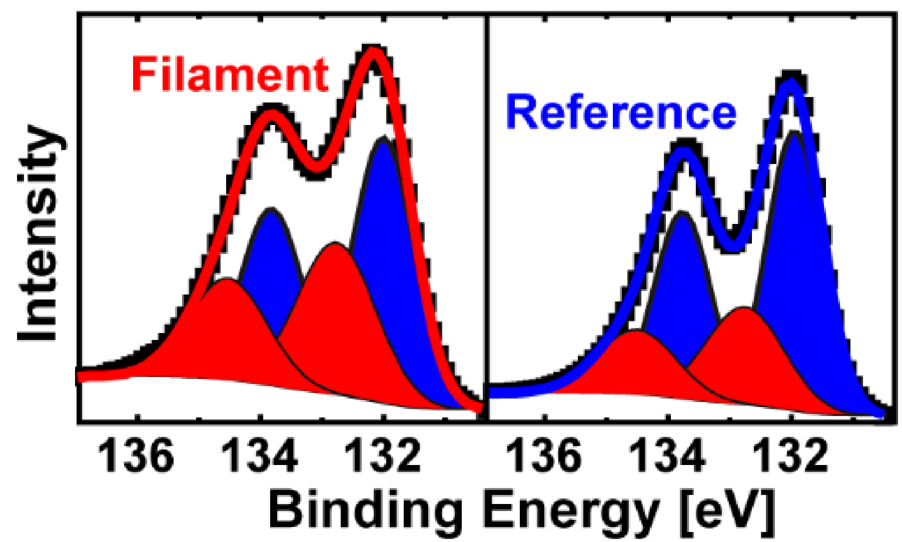
Ti valence state:



Sr 3d XPS:



- ✓ <u>Stable retention</u>: Microscopic phase separation into Sr-deficient $SrTiO_3$ and SrO surface layer
- ? Side effect or origin of retention stabilization



Baeumer *et al.*, *Nat. Commun.* **6** (2015)

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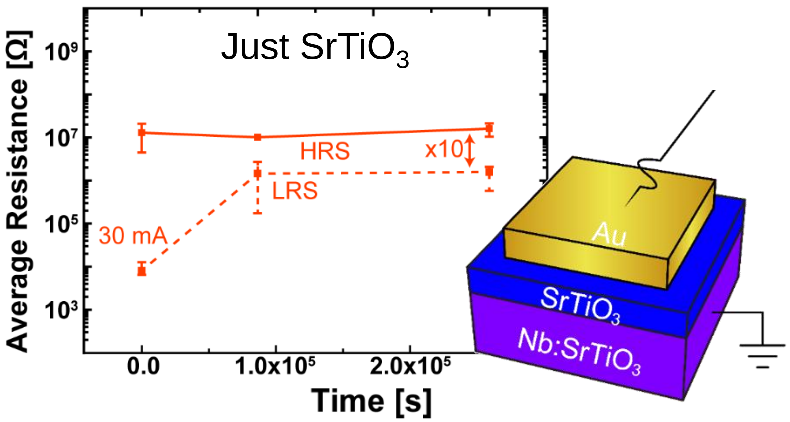
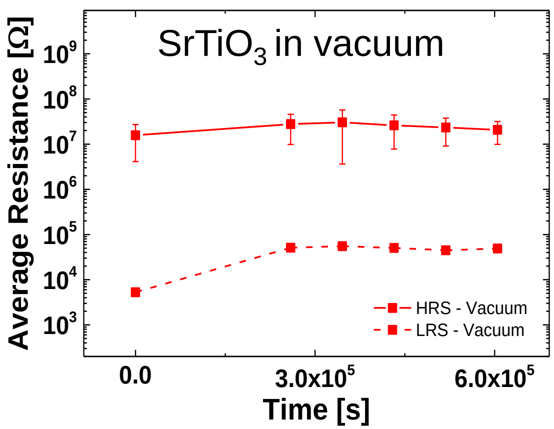
Design Rule for Stable Retention

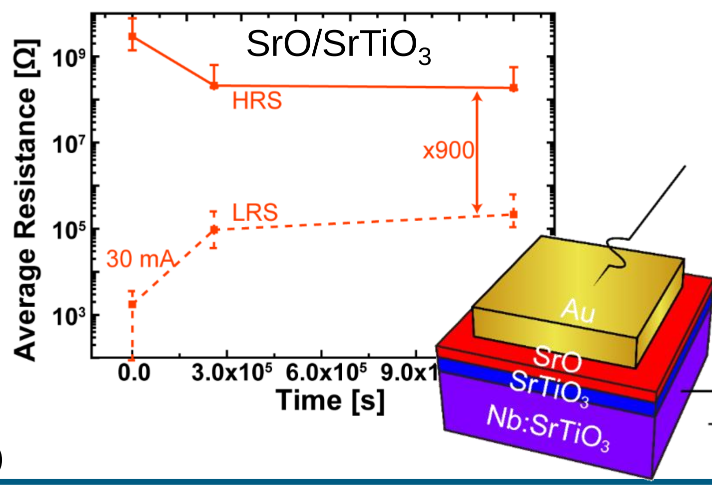
Stoichiometric $SrTiO_3$: Retention failure

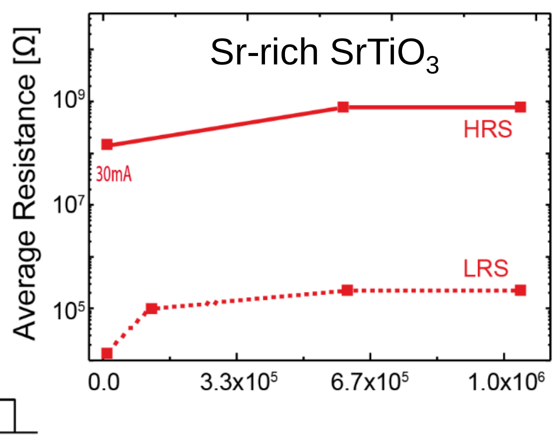


- ✓ $SrO/SrTiO_3$ interface inhibits re-oxidation
- ? <u>SrO = Oxygen reservoir</u>
- ? <u>Role of oxygen diffusion coefficient</u>

Operation in **vacuum** or **SrO interlayer** or **Sr-rich $SrTiO_3$: Retention stabilization**



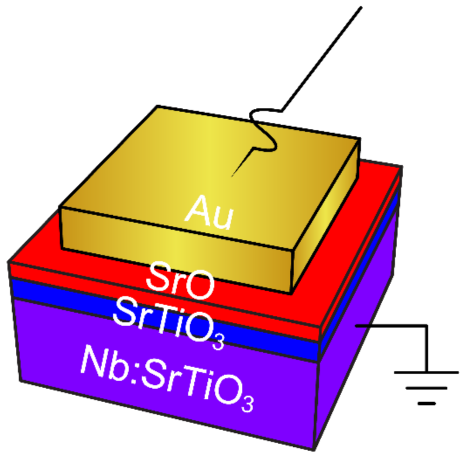




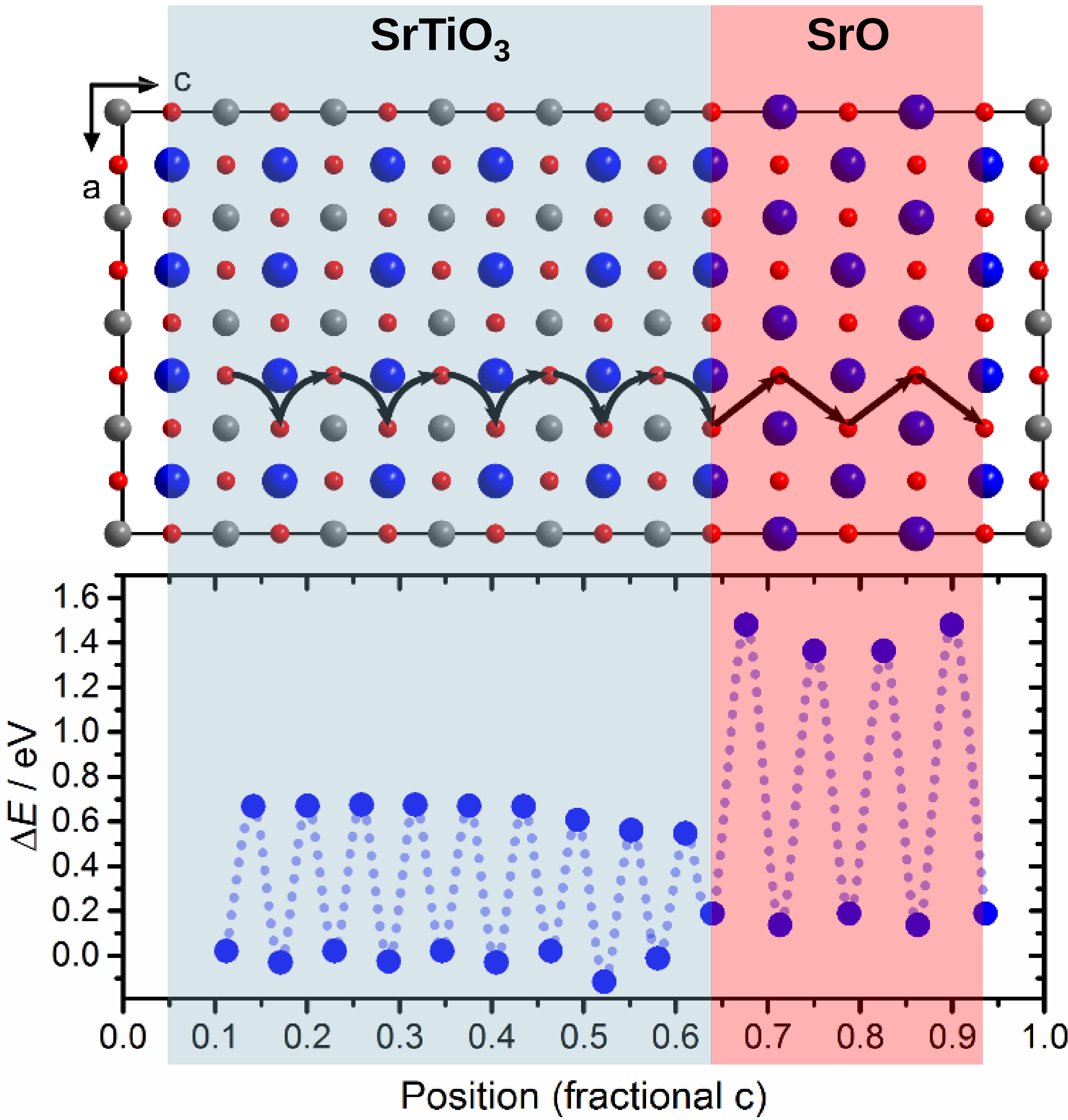
Baeumer *et al.*, *Nat. Commun.* **6** (2015)

Raab *et al.*, *AIP Advances* **5** (2015)

Design Rule for Stable Retention



- ✓ $SrO/SrTiO_3$ interface inhibits re-oxidation
- ✓ Impeded oxygen diffusion in SrO



Baeumer *et al.*, *Nat. Commun.* **6** (2015)

Design Rule for Stable Retention

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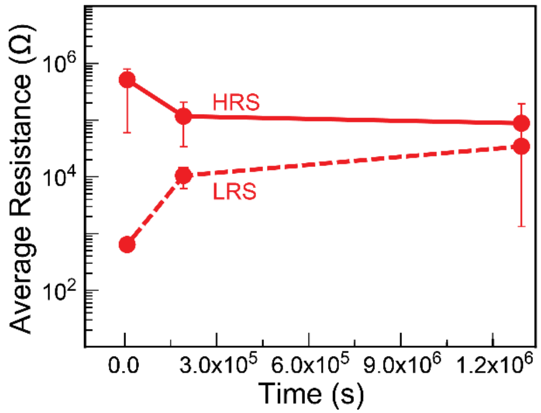
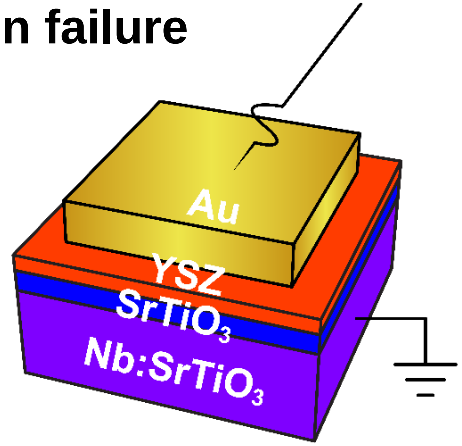
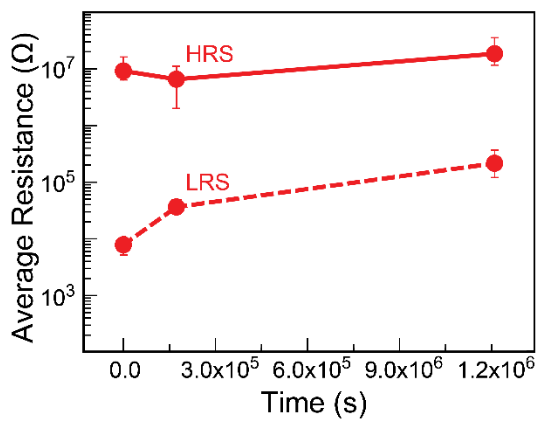
Enhanced oxygen migration: YSZ
(D(500 K)=10^{-13} cm^2s^{-1}): **Retention failure**

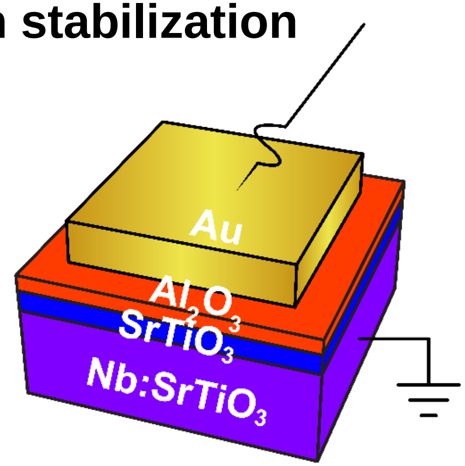


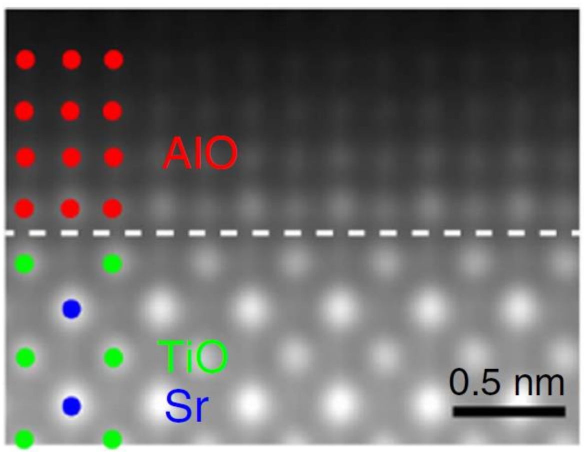


- ✓ Oxygen diffusion coefficient determines retention
- ✓ Al_2O_3 layer: good retention without structural changes

Inbited oxygen migration: Al_2O_3
D(500 K)=10^{-65} cm^2s^{-1}: **Retention stabilization**







Baeumer *et al.*, *Nat. Commun.* **6** (2015)

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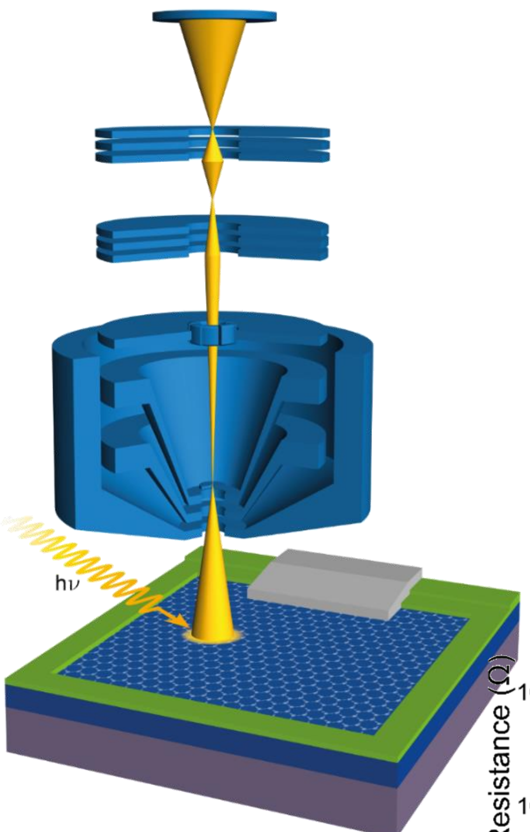
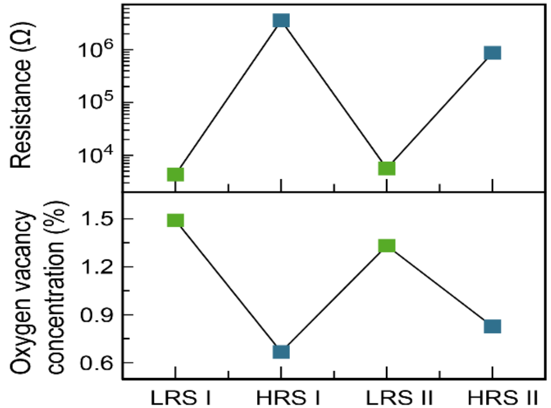
Conclusions

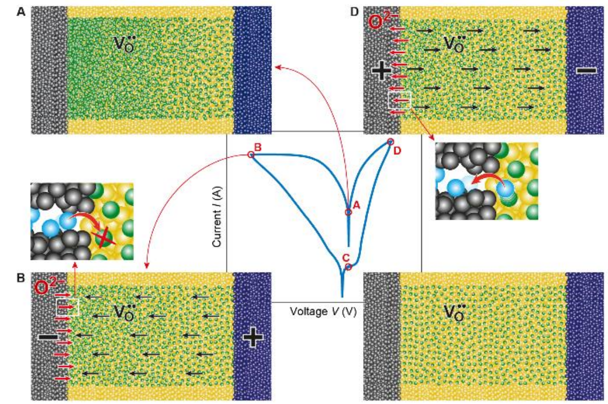
Spectromicroscopy: Post mortem & in-operando insights



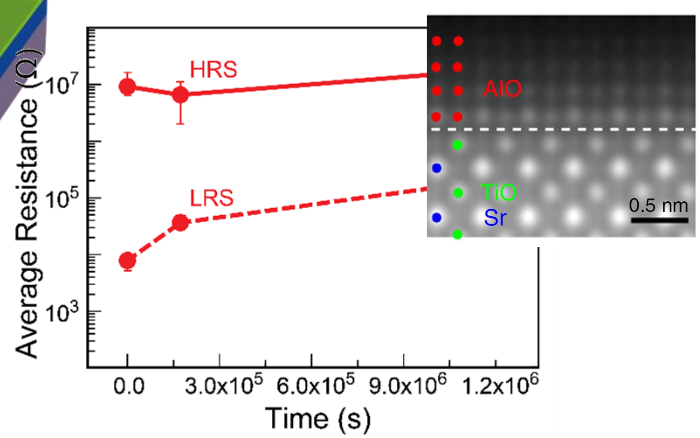
Quantitative evidence of local redox reaction



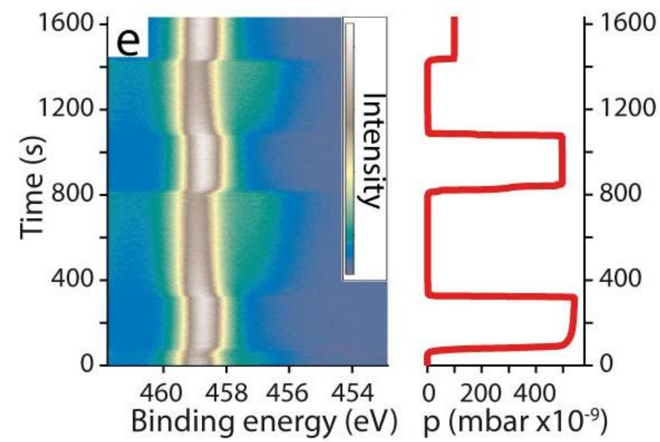
Mechanistic understanding of the switching process



Design rule: Prevent re-oxidation of filament



X-ray interaction: possible creation of defects (and second phases)



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