EELS & EDX spectrum imaging : pushing the limits

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Note : Seven slides showing unpublished data removed
Acknowledgements

• Center for Electron Microscopy & Analysis at The Ohio State University
  – Frank Scheltens, Robert Williams, Dan Huber, Hamish Fraser, Srini Rajagopalan

• FEI Company
  – Anna Carlsson, Dmitri Klenov

• Imperial College London
  – John Kilner, Stuart Cook, Monica Burriel

• CSIC-ICN, Barcelona
  – A.Cavallaro, J.Roqueta, A. Apostolidis, A.Bernardi, A.Tarancón, J.Santiso

• Universidad Complutense, Madrid
  – Jacobo Santamaria, Carlos Leon, Alberto Rivera
Motivation

IONIC CONDUCTORS

Feel the strain

The high temperatures required for oxygen ion conductivity have hampered the development of practical applications of ionic conductors. Now superlattices made of yttria-stabilized zirconia and strontium titanate show promise for room-temperature devices.

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In 1897, Nernst discovered that he could improve the high-temperature electrical conductivity of oxides by making certain mixtures. He used these mixtures to patent the first practical application of oxygen ion conductors, an incandescent lamp filament which became known as the ‘Nernst Glober’. Later the composition of the filament material was simplified to the Nernst mass (85% ZrO2, 15% Y2O3), now known as yttria-stabilized zirconia (YSZ), in which the oxygen ion conductivity is achieved by the oxygen ions migrating by a vacancy mechanism through the cubic fluorite lattice. Since that early start, the continued optimization of oxygen ion conductors has become essential to the development of devices such as the

Figure 1 Ionic conductivity of YSZ. a, Logarithm of the long-range ionic conductivity (in S cm⁻¹) of the bilayers STO/YSZ/STO versus inverse temperature. The thickness range of the YSZ layer is 1–82 nm. Also included are the data for a single crystalline YSZ and a thin film (ti), 700 nm thick, with the same nominal composition. b, Conductance at 400 K of superlattices consisting of repeated layers of 1-nm YSZ/10-nm STO, as a function of the number of interfaces (the number of [YSZ/STO] repeats is half the number of interfaces). Reprinted with permission from ref. 1. © 2008 AAS.
Surprising....but enormous potential if a real effect!
PLD grown: SrTiO$_3$ – YSZ – SrTiO$_3$ multilayer

- Extensive mixing initially (consistent with in-situ RHEED).
- Change to layer-by-layer after 3 repeats (RHEED)

PLD: SrTiO$_3$ – YSZ – SrTiO$_3$ multilayer

- Incoherent islands
- Coherent or semi-coherent chains

PLD : EELS analysis – the limits

EDX hyperspectral mapping

[110] SrTiO3
Care: There are non-local effects in spectroscopic imaging

- Split signal into elastically scattered electrons and thermally diffused electrons
- EDX map for oxygen K-edge in SrTiO$_3$ [001]:

Contribution of thermally scattered electrons to atomic resolution elemental maps.
Oxygen and Titanium Signals Collected from Ti/O – O – Ti/O Columns

300 kV
\( \alpha = 24 \text{ mrad} \)
\( \beta = 39 \text{ mrad} \)
\( t/\lambda = .19\lambda \)
Quantification: entire multilayer

\[ \frac{C_A}{C_B} = k_{AB} \frac{I_A}{I_B} \]

Fit background – remove Bremsstrahlung
Fit peaks – overlap issues
Integrate to obtain net counts
Quantify – Cliff Lorimer k-factor
Why calculated k-factors are dangerous!

\[ k_{AB} = \frac{1}{Z} = \frac{(Q\omega a)_A}{(Q\omega a)_B} \frac{A_B}{A_A} \frac{\epsilon_A}{\epsilon_B} \]

**A**: atomic weight
**Q**: ionization cross-section
**\( \rho \)**: density
**\( \mu \)**: linear absorption coeff.
**a**: relative transition probability
**t**: thickness
**\( \omega \)**: fluorescence yield
**\( \epsilon \)**: detector efficiency

Calculated values much have higher errors than the experimental data.
Determine Experimental k-factors

• Bulk SrTiO$_3$ wafer/substrate

• Bulk Y$_2$O$_3$-ZrO$_2$ crystal: composition established by SEM-EDX with elemental standards and Laser Ablation Inductively Coupled Plasma Mass Spectrometry (LA-ICP-MS)

\[
\frac{C_A}{C_B} = k_{AB} \frac{I_A}{I_B}
\]
Coherent layers in RF sputtered STO-YSZ-STO

Samples grown & provided by J Santamaria et al
RF sputtered STO-YSZ-STO

- Four 1nm layers of YSZ
- EDX shows that substrate – STO buffer interface is Sr-rich
- YSZ layers appear to be continuous

Samples grown & provided by J Santamaria et al
EDX mapping of RF sputtered STO-YSZ-STO PLD
Quant 1: RF sputtered STO-YSZ-STO

Entire Layer: 13.6 mol% Y$_2$O$_3$
Quantification 2: RF sputtered STO-YSZ-STO

- Divide sample into 10 sub-regions
- Sub-regions are (256 x 4) pixels i.e. each box is 0.4nm in height
- Quantify each box for Sr, Ti, Y & Zr
• Samples grown by **BOTH** PLD and RF sputtering show Y/Zr rich layers that are coherent with STO
• Sr & Ti present throughout the layer
• Ti concentration is more reduced than Sr in the Zr-layer
• Averaged composition of layers is higher than nominal target values
• Lower STO-YSZ interface is smoother/flatter than upper YSZ-STO interface
Computational study of structures of $\text{Y}_2\text{O}_3$-stabilised $\text{ZrO}_2$/SrTiO$_3$ multilayers

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YSZ/STO supercell

Initial configuration for the genetic algorithm

- Supercell with SrO-terminated STO interfaces

STO

$\text{ZrO}_2$ with 2 Zr$^{4+}$ replaced with Y$^{3+}$ and one O$^{2-}$ removed

STO

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0. O
1. Zr
2. Ti
3. Sr

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Result from the genetic algorithm and CASTEP

Fluorite YSZ structure unstable

- Spontaneously transforms into a different structure
- Low energy structure from genetic algorithm confirmed with energy calculations within CASTEP
- This structure only with excess SrO? What about stoichiometric STO/excess TiO$_2$?
Intermixing of YSZ and STO:
- $\text{Y}^{3+}$ in $\text{Sr}^{2+}$ lattice site
- $\text{Sr}^{2+}$ in $\text{Zr}^{4+}$ lattice site
- $\text{Zr}^{4+}$ in $\text{Ti}^{4+}$ lattice site
- $\text{Ti}^{4+}$ in $\text{Zr}^{4+}$ lattice site

“The lowest energy YSZ structure in a YSZ/STO multilayer, determined using a combination of classical and first principles-based methods, is different from the expected fluorite lattice and appears to favour interdiffusion.”

Conclusions & Comments

• EDX spectrum imaging is easier to quantify than EELS mapping.

• Quantification on the sub-nanometre scale achievable provided due care is given to determination of experimental k-factors (or z-factors) and channelling effects.

• Atomic scale chemical maps provide qualitative insights but....

• Quantification on the atomic scale requires simulation of the images/maps due to non-local contributions in both EELS & EDX

• How do we relate the role of compositional fluctuations on ionic conductivity properties.
Thanks to

• Ohio Research Scholar Award (ODOD Third Frontier program)
• A*STAR programme (Wei Li Cheah)
• UK Engineering and Physical Sciences Research Council (EPSRC)