Electrochemical nanowriting on CeO_2 thin films

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INTRODUCTION

CeO_2 is an oxide with variable chemical properties due to the external band structure, influenced by the f-orbitals of the rare earth metal Cerium.

We found multiple bias induced processes in oxide ceria thin films grown on different substrates by Pulsed Laser Deposition. Our measurements showed the formation of irreversible deformations on the oxide surface, as a consequence of the bias applied to the AFM tip. The exchange of electrons between tip and sample plays a pivotal role in the explanation of the electrochemical process.

The expansion of 7% of the total thickness is found to be compatible with ceria surface reduction, formation of oxygen vacancies and water physical adsorption.

Under reducing conditions, CeO_2 looses a fraction of oxygen ions, leaving oxygen vacancies, and becoming $CeO_{2-\delta}$. In the latter, the oxidation state of Cerium changes from +4 to +3.

$$O_o^x + 2Ce_{Ce}^x \longleftrightarrow \frac{1}{2}O_2(g) + V_o^{\bullet\bullet} + 2Ce'_{Ce}$$

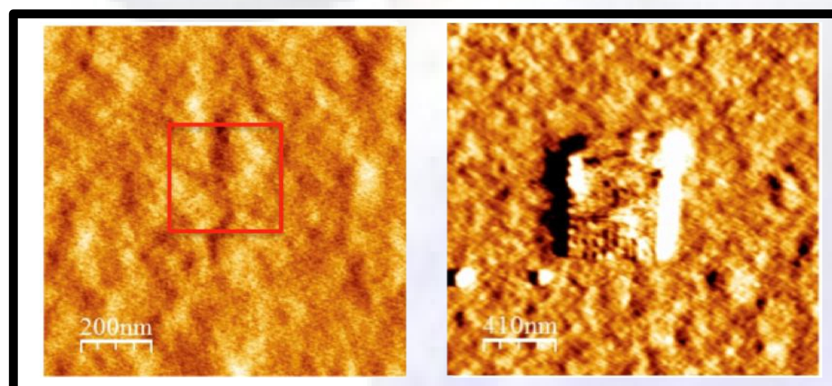


Fig 1: Oxide surface inside the Glove Box (left) and in air (right) after the application of a positive bias. Under reducing conditions the surface is unaltered.

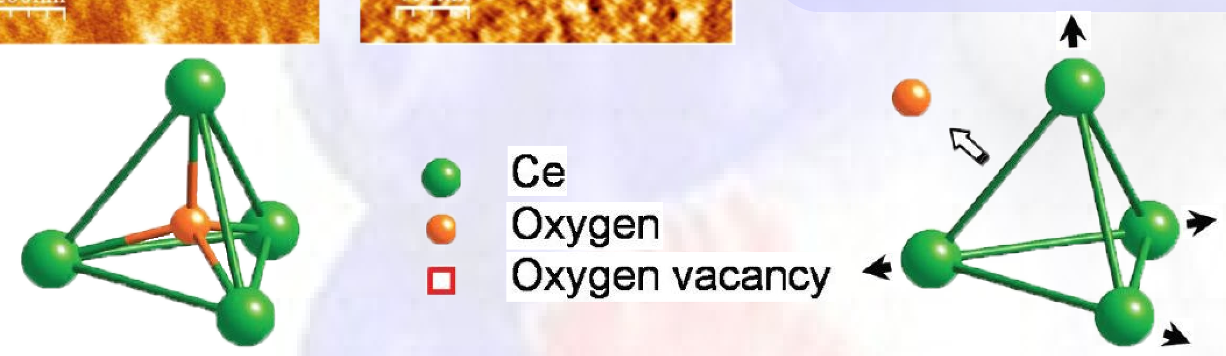


Fig 1: Expansion of the material due to the extraction of oxygen ion from the surface [1]

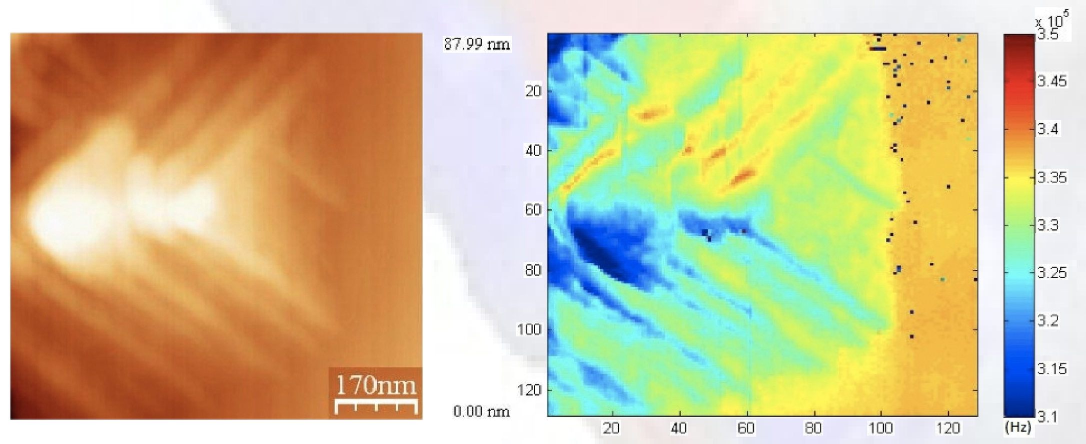
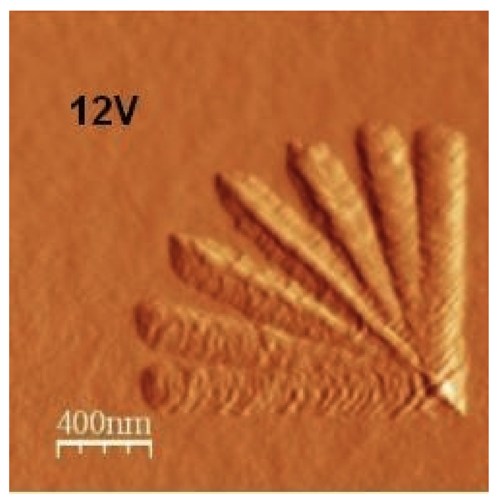
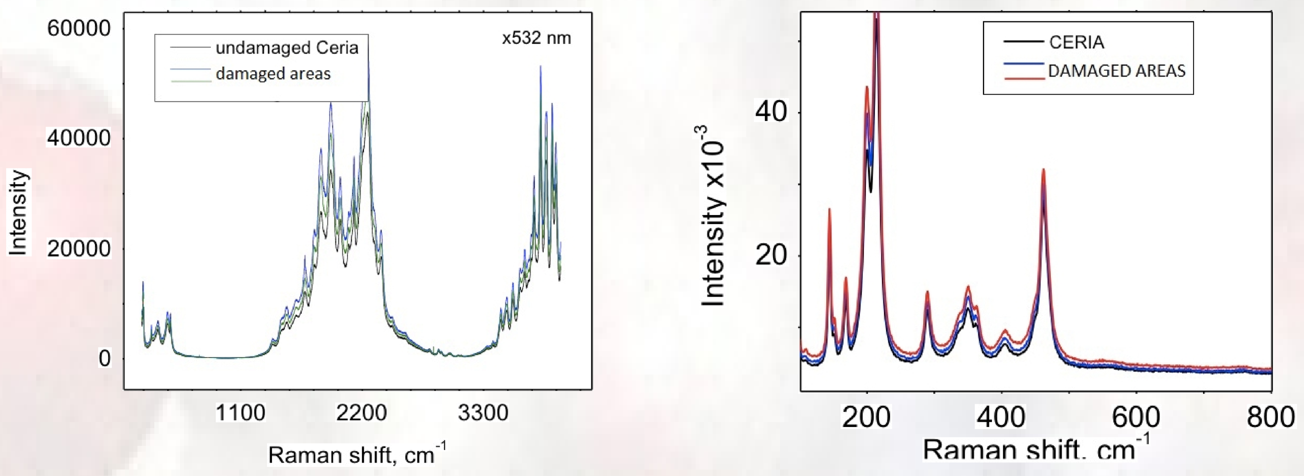


Fig 2: being the resonant frequency closely related with the tip-sample interaction through the spring constant and the reduced mass of the system in Hooke's approximation, the decrease of the resonant frequency is compatible with the decrease of the density surface sample after the induced bias process occurs. This can be explained by considering the extraction of oxygen ions from the lattice, leaving vacancies behind.



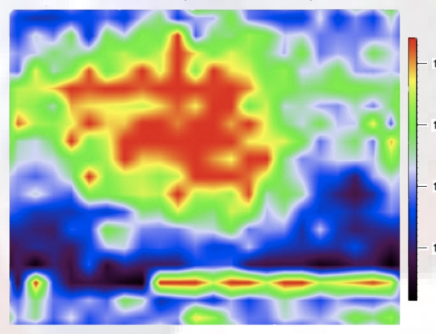
The electrochemical writing occurs for positive bias between + 5 V and + 41 V, and for negative bias, in the range between -26 V and -35 V. The lateral dimensions of the deformations exceed considerably the tip-surface contact area.

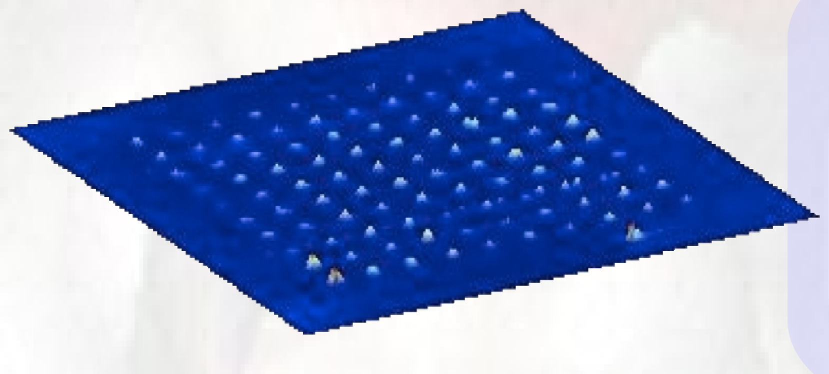
RAMAN SPECTROSCOPY



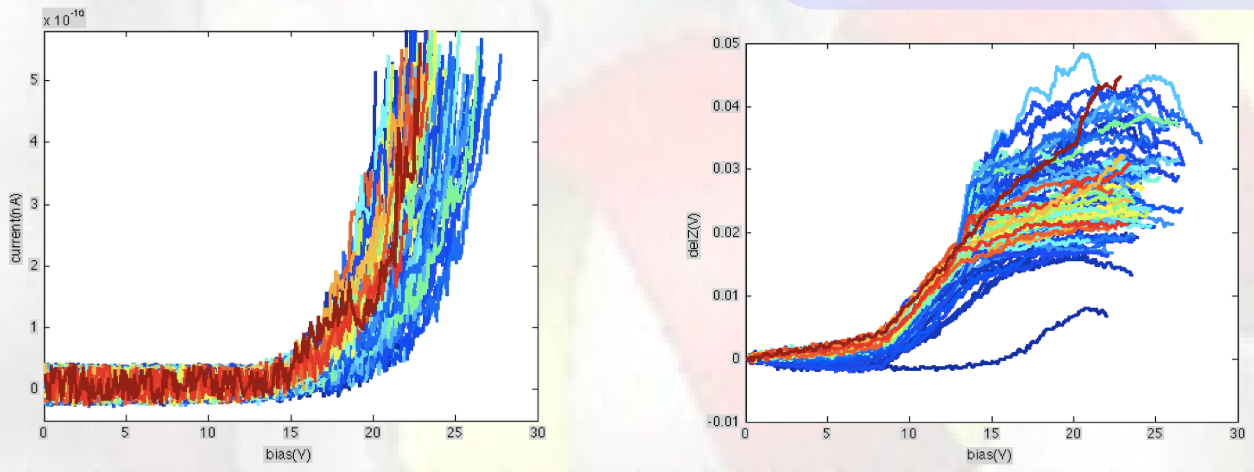
- Raman spectra didn't show significant number of defects on the surface.
- The density of defects is unchanged on etched areas and it is independent of Raman excitation.
- Observed higher intensity of Raman bands on etched areas.

individual band intensity analysis





The concurrent detection of current and z-component of piezo-scanner during the application of increasing d.c. pulses was carried out over a disperse grid of points on the surface, to prevent the reciprocal influence of close measurements.



- Current measurements showed that current and deformations are independent.

TEMPERATURE CONTROL

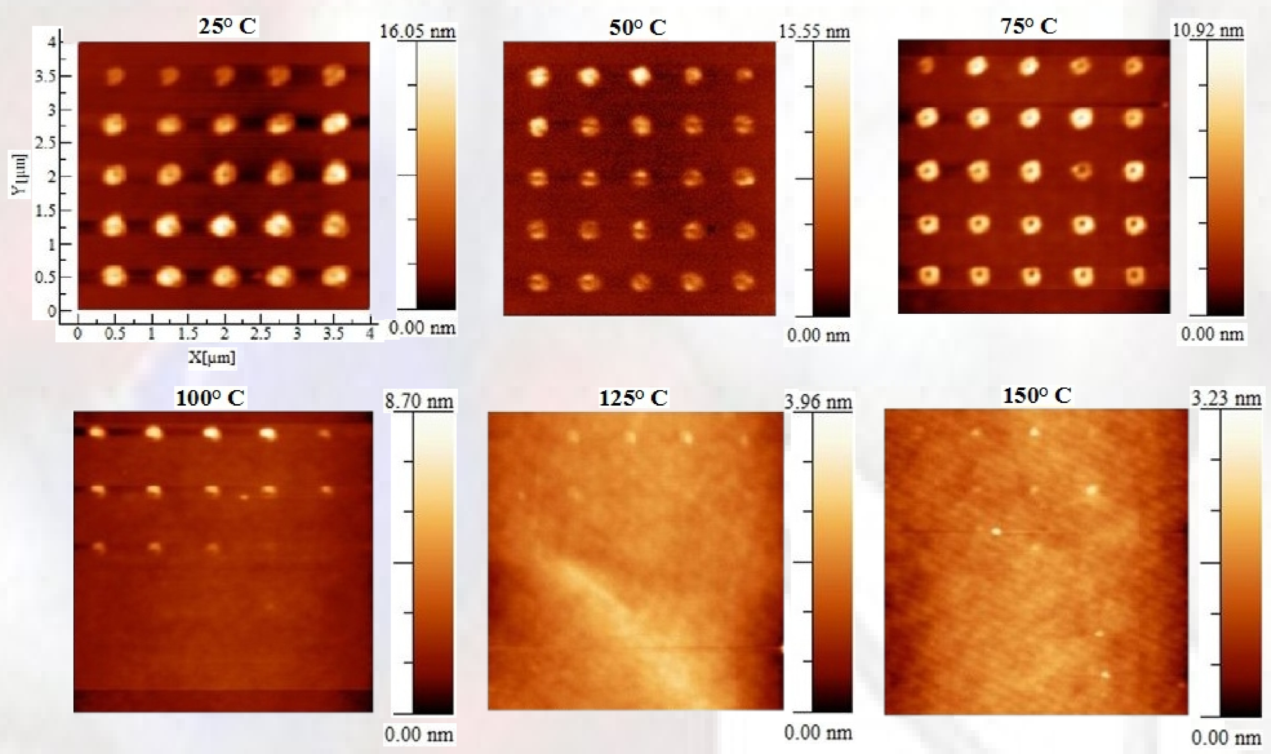


Fig 3: Over 100°C the number and size of particles decrease considerably. This result demonstrates the fundamental role of water in the electrochemical process. In dry atmosphere the poor tip-sample contact doesn't allow any change in Ceria-Oxygen bonds. In elevated humidity the presence of water droplet at the junction facilitate electrochemically-driven oxygen vacancies formation.

ELECTROCHEMICAL STRAIN MICROSCOPY

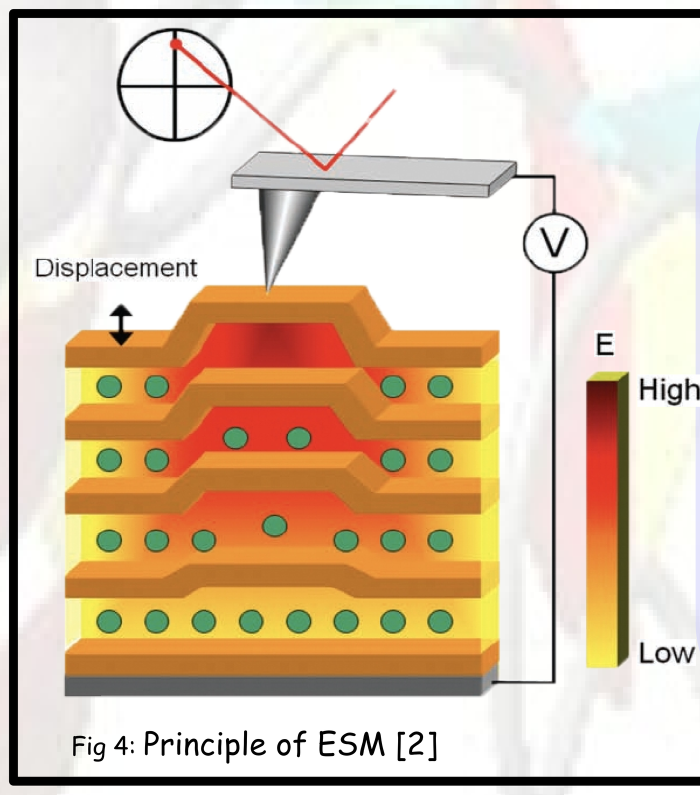


Fig 4: Principle of ESM [2]

- Bias applied to the AFM tip
- Electrochemical bias induced processes
- Local change in ions concentration with subsequent diffusion in the bulk
- Local volume change
- Local surface displacements
- Differential detection mode through the Band Excitation approach

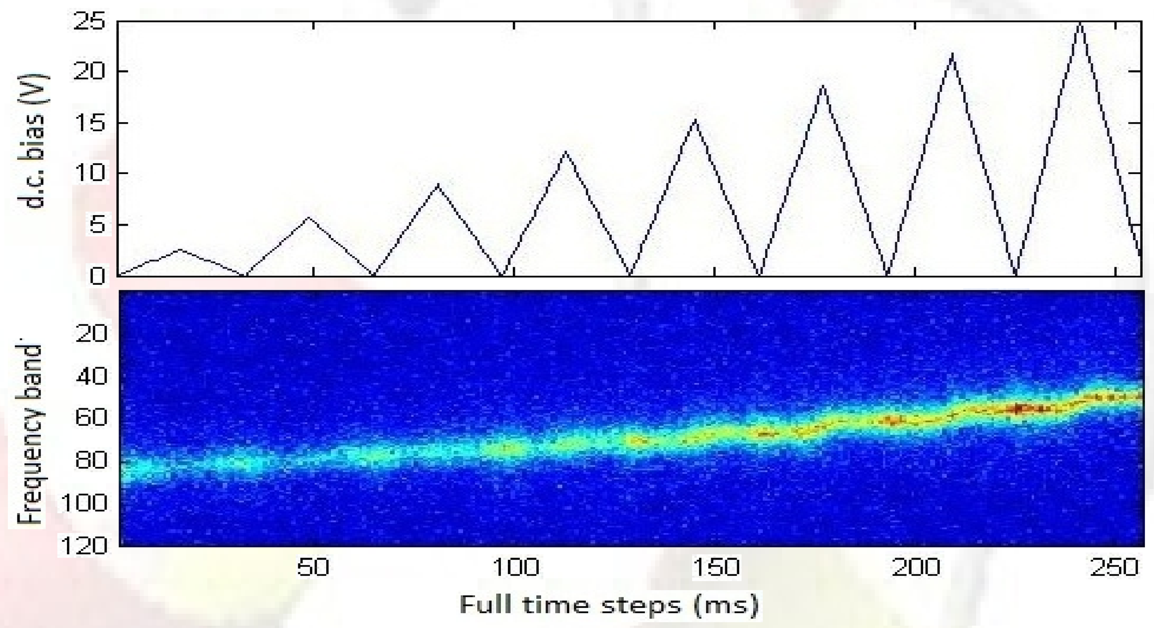
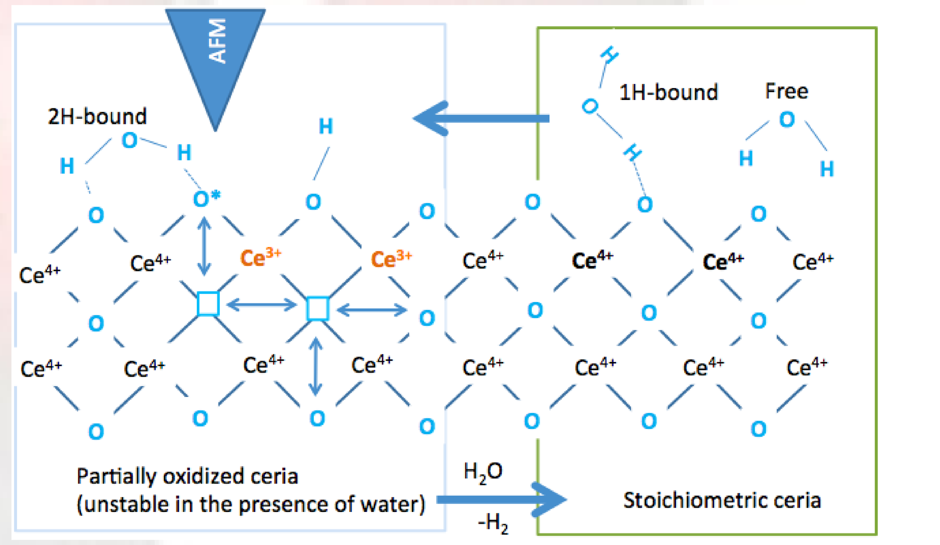


Fig 5: Unipolar first-order reversal curve (FORC) waveform. In this, the envelope of probe bias is an unipolar excitation waveform with increasing amplitude.

The discrete behavior of the amplitude spectrogram clearly shows the irreversible nature of the current process, and the shift of the resonant frequency to higher values reveals the increase in the tip-sample contact stiffness, due to the stronger interactions during the nanowriting process.

CONCLUSIONS



- Electrochemically driven oxygen vacancy formation. Energy requirement is about 2.87 eV:

$$E_v = E_{CeO_2\ (reduced)} + \frac{1}{2}E_{O_2} - E_{CeO_2\ (stoichiometric)}$$

- Electrochemically reduced ceria surface (oxygen defects) favors water physical adsorption in two forms (two H-bond structure and hydroxyl surface). Thermodynamically, both forms create favorable condition for water decomposition at low temperatures (<400°C) and low partial pressure of hydrogen:

$$H_2O + CeO_{2-\delta} \longleftrightarrow H_2 + CeO_2$$

REFERENCES

[1] Peng Gao et al., J. AM. CHEM. SOC. 2010, 132, 4197–4201
[2] Balke et al., Adv. Mater. 2010, 22, E193–E209

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