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# Chemomechanical effects in thin film and bulk oxides

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# CHEMOMECHANICAL EFFECTS IN THIN FILM AND BULK OXIDES

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## Introduction

The long-term environmental sensitivity of the surface mechanical properties of materials has long been recognised and properties such as creep, fracture and fatigue are known to be susceptible to changes in environment [1]. A particular sub-group of these phenomena concerns the short-term effects of environment on the indentation hardness of ceramic materials, which, in the past, have been observed in small-scale near-surface-sensitive experiments such as microindentation tests.

## Objectives

The objective of this study is to use results from experiments using higher spatial resolution techniques than microindentation, such as nanoindentation, to try and resolve some of the previous controversies and ambiguities emerging from microindentation studies, thus enabling clearer mechanisms to be established for chemomechanical effects. The overall aim is to improve materials selection for tribological performance with due attention to in-service environmental effects.

## Experimental

Samples: A range of amorphous, as well as single and polycrystalline bulk oxide samples from commercial suppliers were compared to 400nm PVD coatings deposited onto architectural glass

### ➢Microindentation

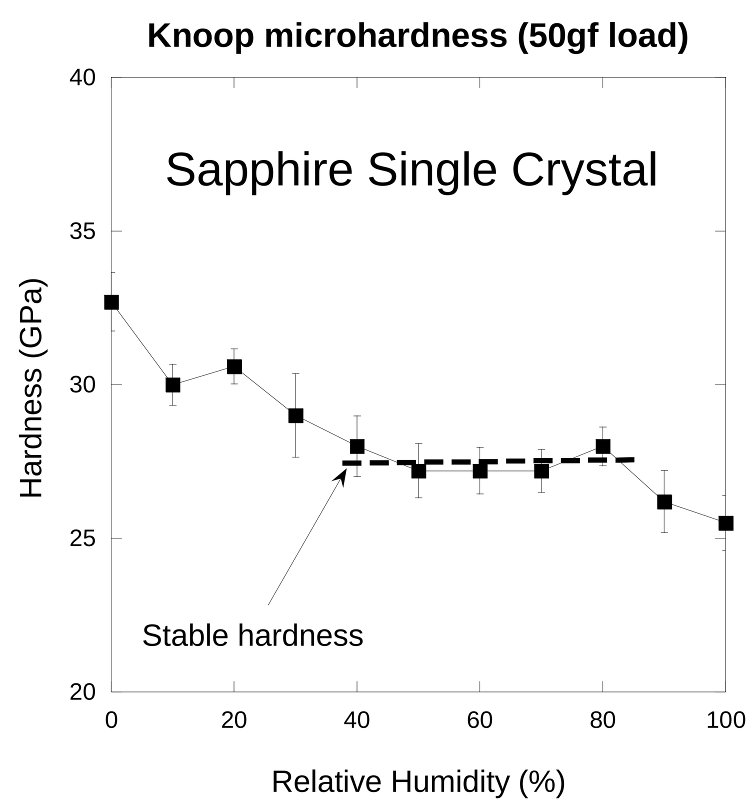
Indentations were performed using a Leitz Miniload fitted with a Vickers or Knoop indenter located in a humidity cabinet:

⌘ Samples were tested in three different conditions

- ⌘ As-received (stored in lab air).
- ⌘ Heated to 100ºC to drive off water and quenched in methanol (bulk oxides) or ethanol (coatings)
- ⌘ Heated to 100ºC and quenched into water.

⌘ Samples were removed from the liquid and dried at 50ºC in flowing air before testing

⌘ Hardness was determined from measurement of indentation diagonals by reflected light microscopy and SEM




Stable results between 40 and 80% RH

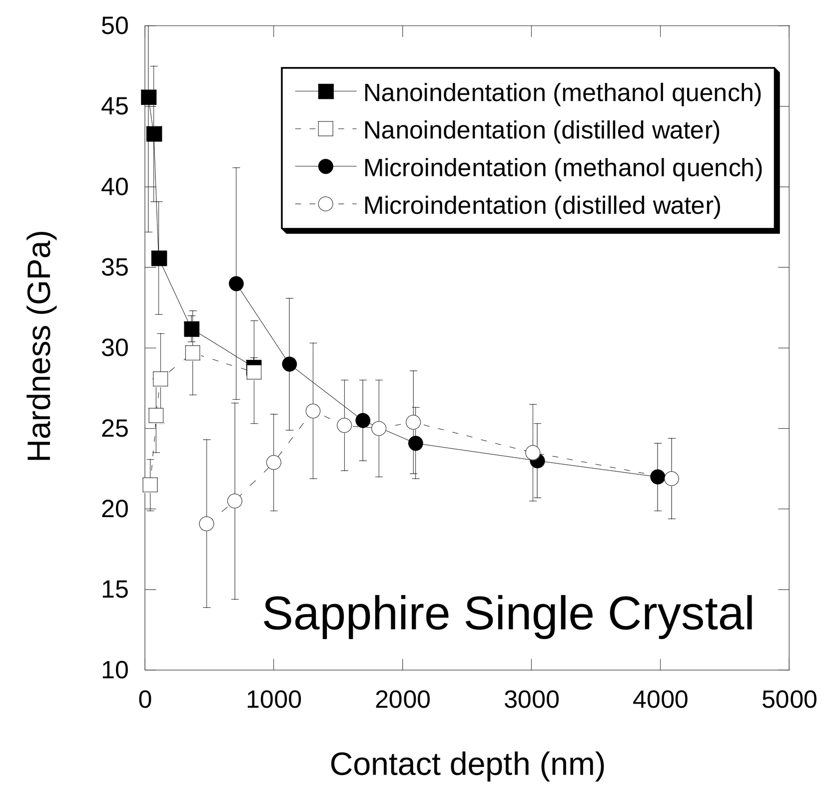
### ➢Nanoindentation

⌘ Nanoindentation tests carried out using a Hystiron Triboindenter fitted with a well-characterised Berkovich tip (end radius 109nm) located in a humidity controlled lab (50% RH).

⌘ Samples were prepared as for microhardness testing but were allowed to equilibrate in the lab for 2h after drying to reduce thermal drift

⌘ Indentation load-displacement curves were analysed by the Oliver and Pharr method to extract hardness.

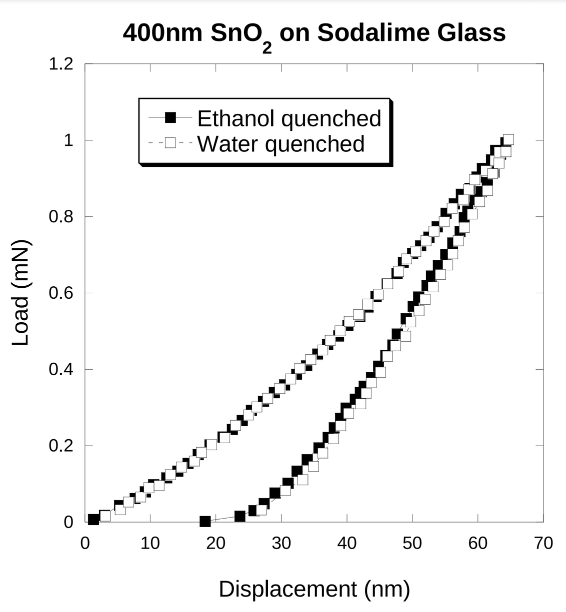
⌘ AFM images were obtained using the Berkovich indentation tip before and after indentation for pile-up assessment.

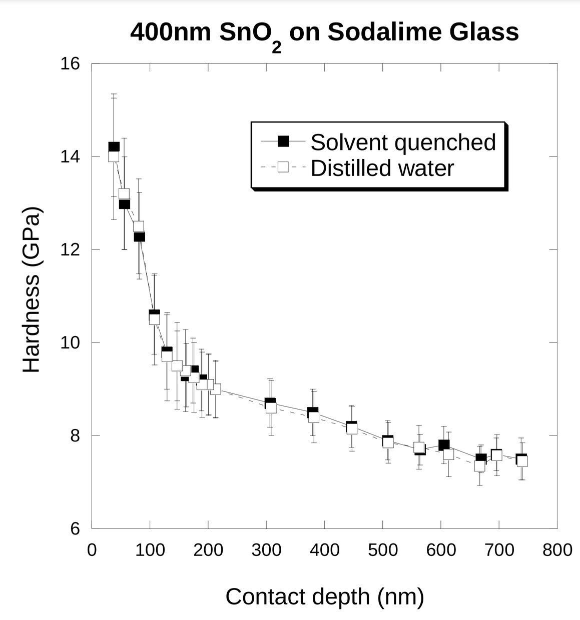


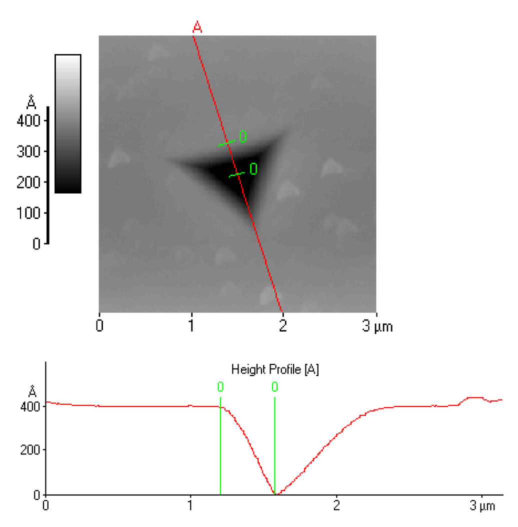

Chemomechanical effects clearly apparent in the nanoindentation data

## Factors Affecting Chemomechanical Effects

**PVD Tin Oxide on Soda-lime Silica Glass**

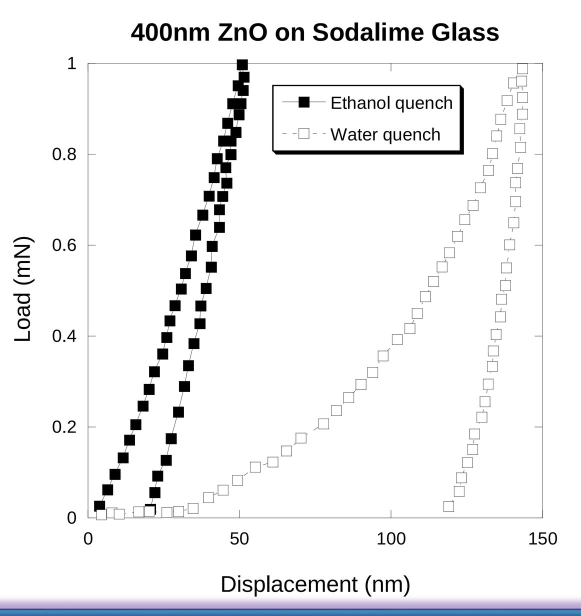


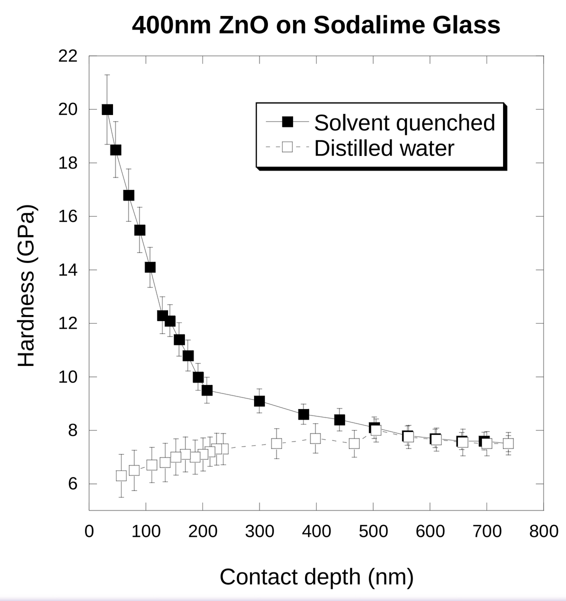



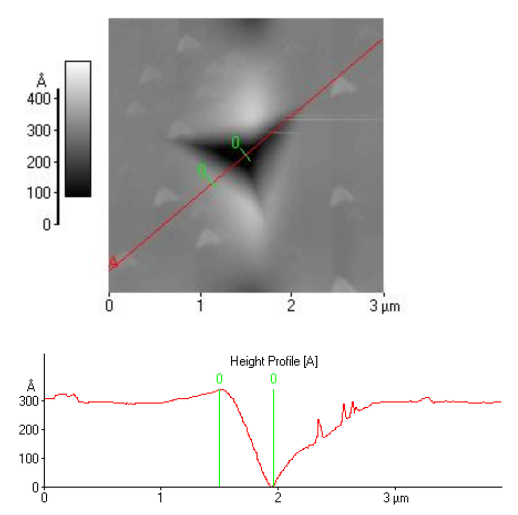



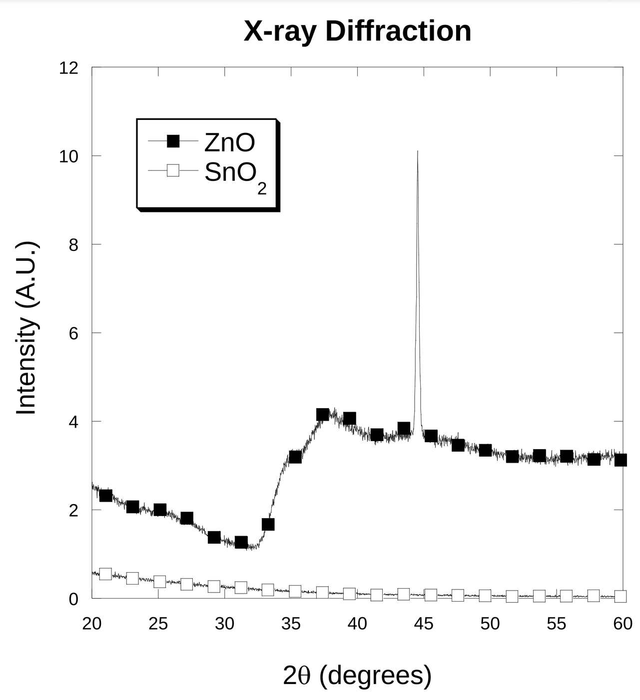
AFM of water-exposed indentations

**PVD ZnO on Soda-lime Silica Glass**

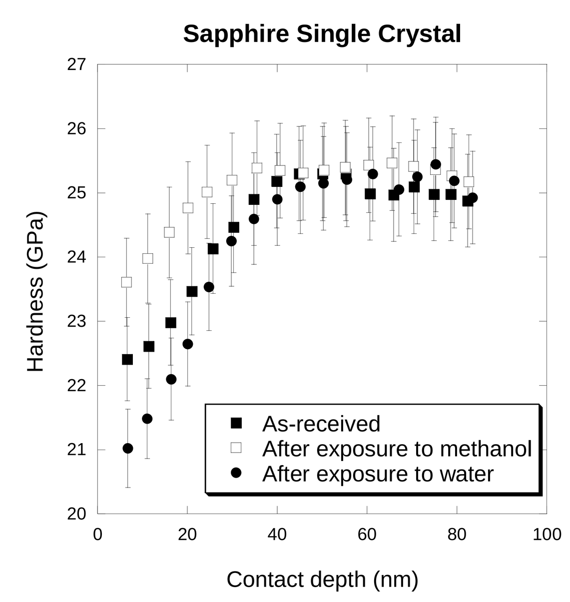


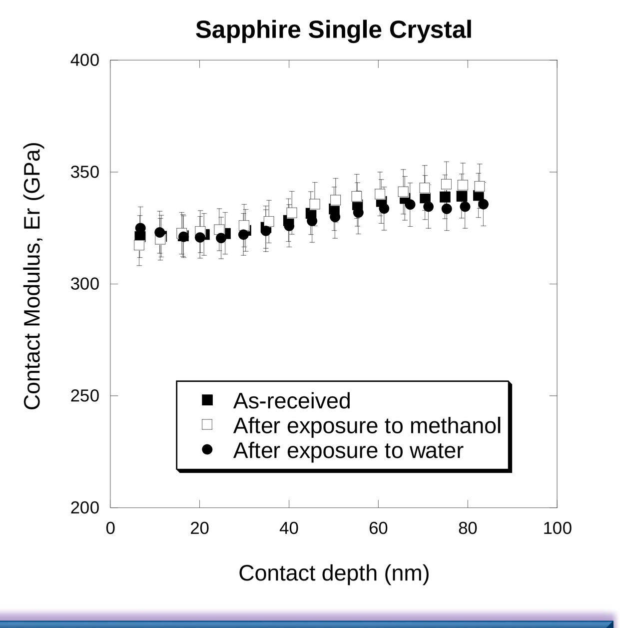






Strong chemomechanical effects only observed for crystalline bulk oxide materials and coatings. Chemomechanical effects only observed in plasticity, not in elastic response

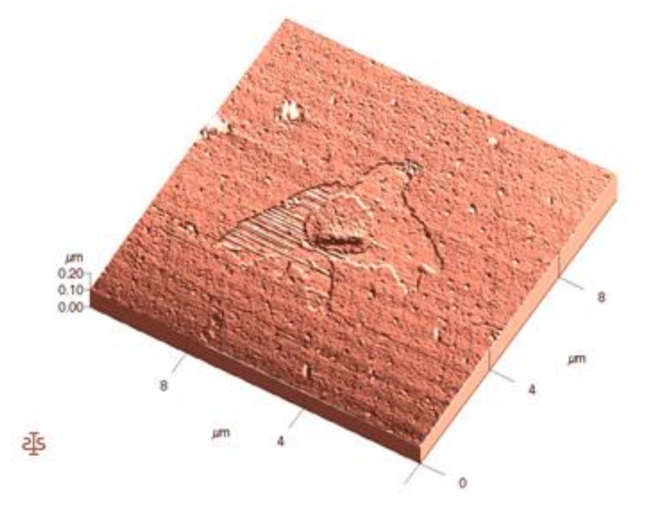


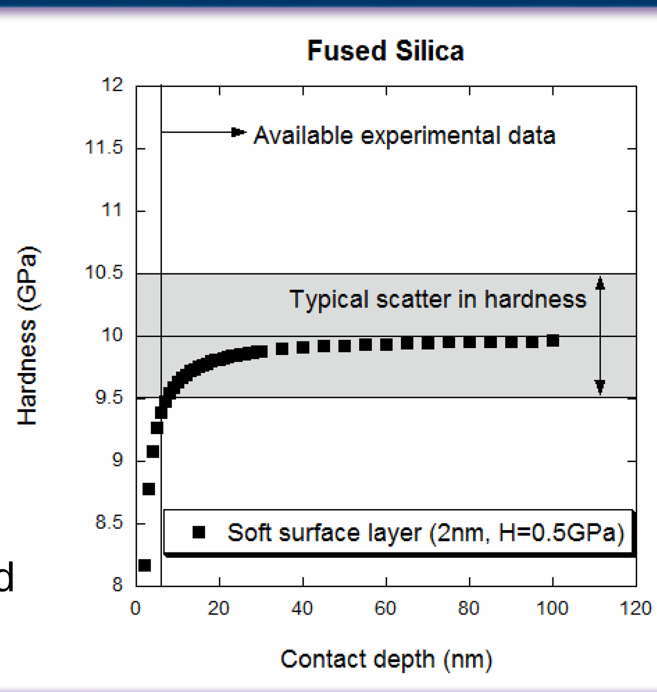

## Analysis and Discussion

Mechanisms for the effect [2]:

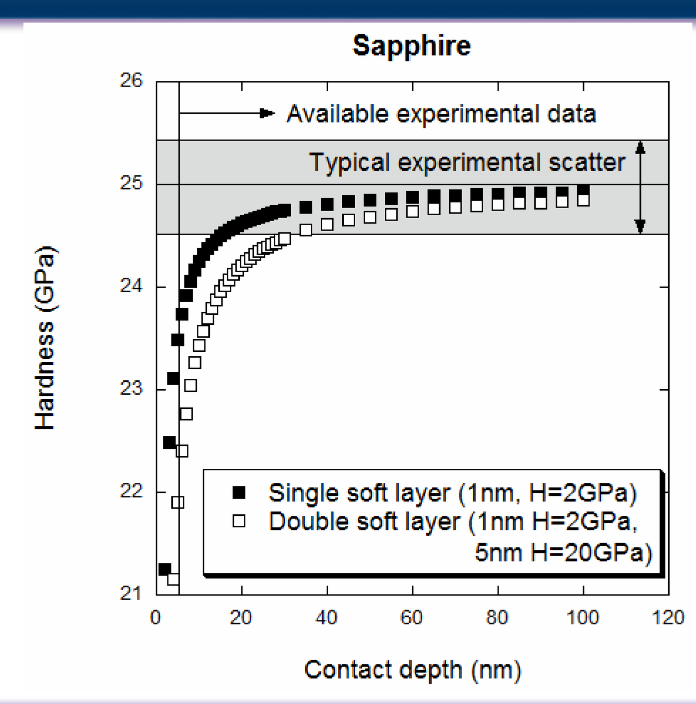
- Thick surface reaction layer (>5nm, not seen)
- Modification of indenter/surface friction (expected for all materials)
- Adsorbate effects
  - Thin surface reaction layer (2nm)
  - Dislocation mobility (crystalline materials)
  - Charged defects (small effect)



Water-affected layer scraped from fused silica during AFM analysis; 2nm thick




2nm Adsorbate modified layer too thin to explain sapphire results [3]. Thicker layer where dislocation mobility is increased by band bending due to surface adsorbates required.




## Concluding Remarks and Future Work

**Conclusions:**

⌘ Careful nanoindentation testing can give reliable data to unequivocally demonstrate chemomechanical effects for oxide ceramics

- ⌘ The hardness water-exposed alumina is lower than after solvent quenching in ethanol or methanol.
- ⌘The contact modulus is not affected by exposure.

⌘ The effect of the adsorbed layer is too small to be detected for most amorphous materials but in crystalline materials band bending-induced increases in dislocation mobility can generate considerable softening.

**Future work**:

⌘ Determine the effect of surface treatments which modify surface charge and adsorbate layers on chemomechanical effects.

⌘ Relate calculated surface band structure to chemomechanical response for different materials

**References**

1. Rehbinder P (1947) Nature, 159:866-867.
2. Westwood ARC, Ahearn JS, Mills JJ (1981) Colloids and Surfaces 2:1-35.
3. Bull SJ, Moharrami N, Hainsworth SV, Page TF (2015) J. Mater. Sci., in press.