Determining the Mechanical Properties of Oxide-Coated Nano-Films using Reactive Molecular Dynamics

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Objectives

The goal of this study is to examine the effect of native-oxide layers on the mechanical properties of ultra-thin-films:

- Evaluate changes in modulus and yield stress.
- View structural and mechanistic changes in yielding.
- Apply thermodynamic yielding model to the simulation.

Introduction

Metal-oxide layers are likely to be present on metallic nano-structures due to either environmental exposure during use, or high temperature processing techniques, such as annealing. It is well known that nano-structured metals have vastly different mechanical properties from bulk metals; however, difficulties in modeling the transition between metallic and ionic bonding have prevented the computational investigation of the effects of oxide surface layers. Here we use newly developed potentials (COMB3) [1] to perform fully reactive molecular dynamics simulations which elucidate the effects that metal-oxide layers have on a copper nano-film's mechanical properties.

Yielding Features

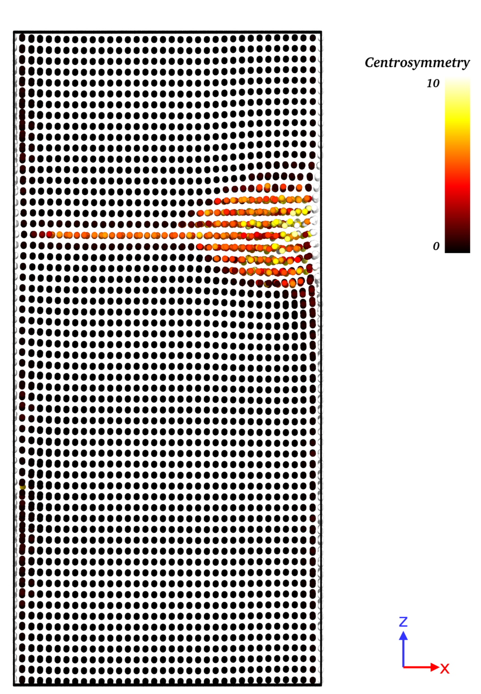

Figure 1: Initial defect colored by centrosymmetry.

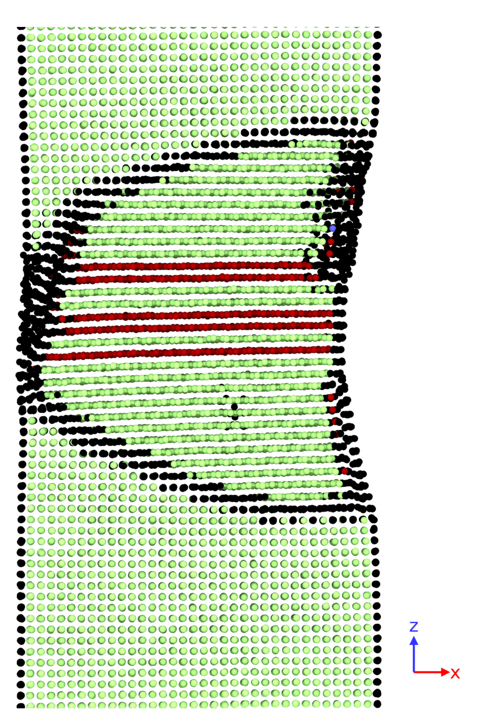

Figure 2: FCC reorientation loop with HCP stacking faults (red).

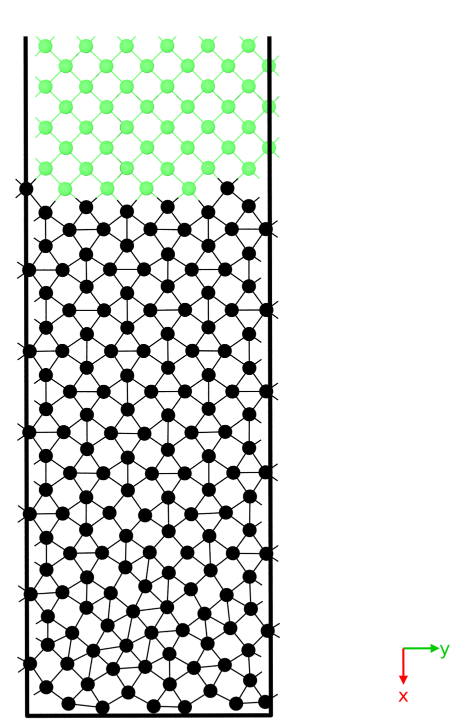

Figure 3: Top view of defect across thickness.

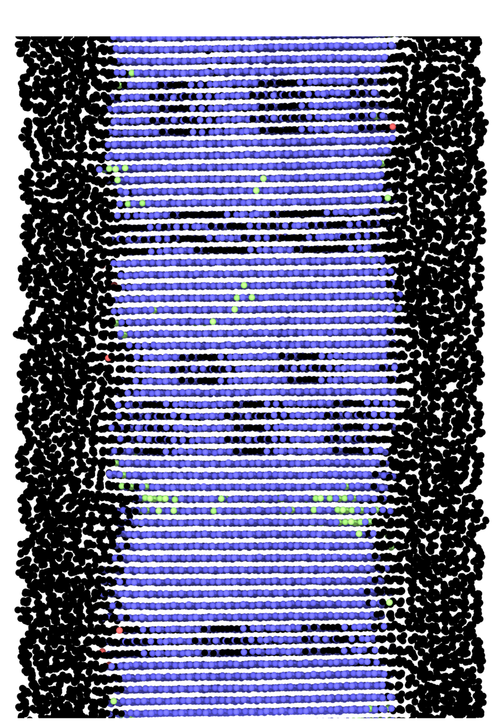

Figure 4: BCC (blue) transformation in the oxide simulation.

Oxide-Layer Structure

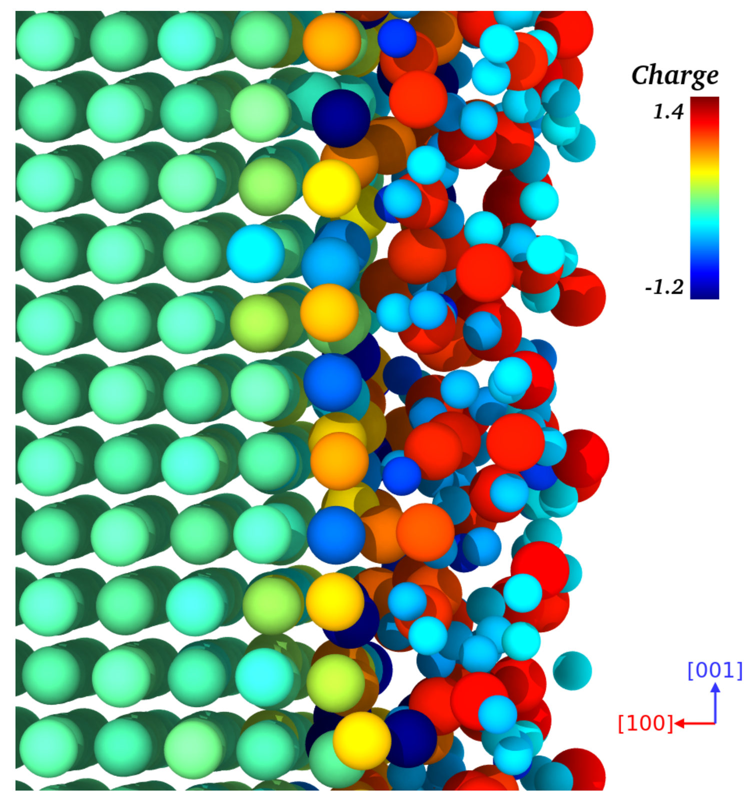

Figure 5: Close up of native oxide layer.

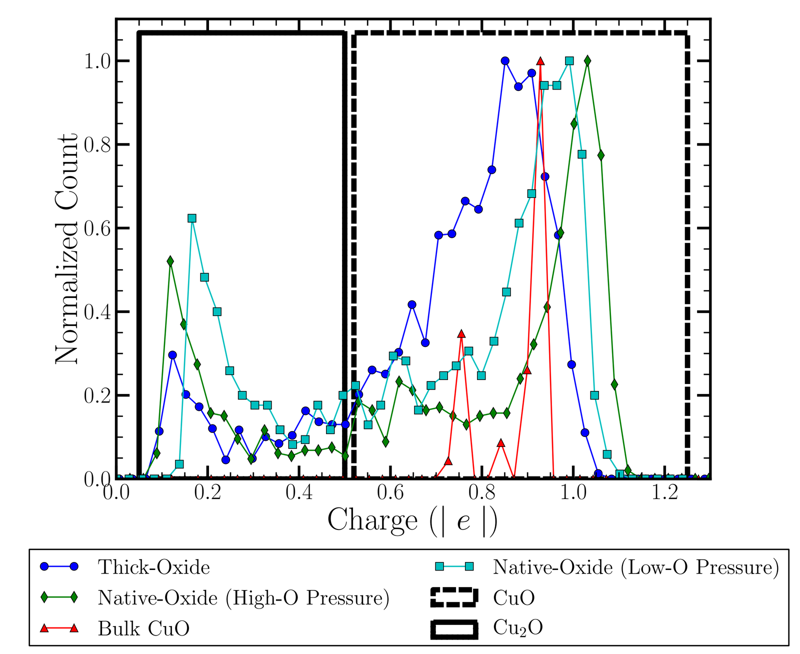

Figure 6: Charge distributions for oxide layers.

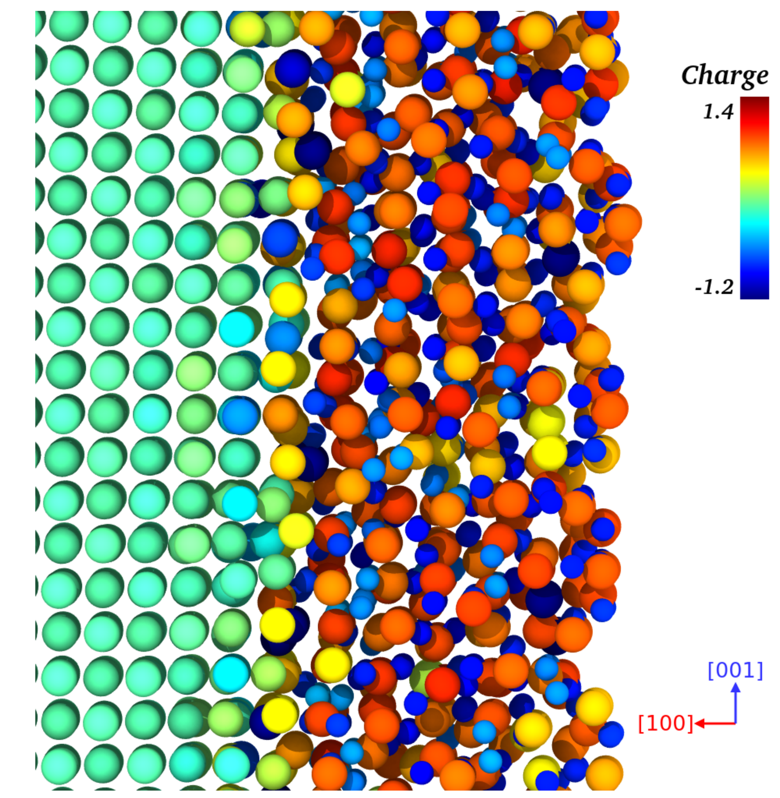

Figure 7: Close up of thick oxide layer.

Oxide Type	Stoichiometry (Cu:O)	Layer Thickness (Å)	Cu-O Bond Density ($\frac{bonds}{Å^3}$)	Density ($\frac{u}{Å^3}$)
Native-Oxide (2280 O)	0.85:1.0	7.3	0.141	3.30
Native-Oxide (960 O)	1.30:1.0	6.0	0.120	3.33
Thick-Oxide Layer	1.20:1.0	13.7	0.207	3.83
Bulk CuO	1.0:1.0	–	0.226	3.82

Methodology

Native layers were grown at 300K by exposing bare copper films to a high oxygen content atmosphere. The thick oxide layers sample was created by placing oxygen terminated CuO unit cells on the copper thin-film surface. Uniaxial tensile tests using copper nano-films with a thickness of 64 Å were simulated while varying the following parameters:

- Temperature (5K, 75K, 150K, 225K, 300K)
- Strain Rate (0.1%/ps, 0.05%/ps, 0.025%/ps)
- Oxide layer type (none, 5 Å, 15 Å)

The simulations were equilibrated, with a 1 fs timestep, for 150 ps in an NPT ensemble then strained under an NVT ensemble with a Nose-Hoover thermostat. Strain occured via 0.25% increments, with 2500, 5000, or 10000 steps of equilibration between each straining.

Model Description

A COMB3 [1] reactive potential was used to accommodate the transition between ionic and metallic bonding. It is based on a bond order/charge dependent term,

$$U^{bond} = \frac{1}{2}\sum_{i}\sum_{j\neq i}[V^{R}(r_{ik}, q_i, q_j) - (b^{angle} + b^{coord} + b^{torsion} + b^{conj})\sum_{n=1}^{3} V_n^{A}(r_{ij}, q_i, q_j)] \quad (1)$$

Where each atom's charge, q_i, is equilibrated by minimizing U^{es} at each timestep,

$$U^{es}[q; \mathbf{r}] = \sum_{i} V_i^{Self}(q) + \frac{1}{2}\sum_{i}\sum_{j} q_i J_{ij}^{qq} q_j + \sum_{i}\sum_{j\neq i} q_i J_{ij}^{qz} Z_j \quad (2)$$

Equilibration is achieved through charge dynamics that equalize electronegativity in the system.

Simulation Yielding Results

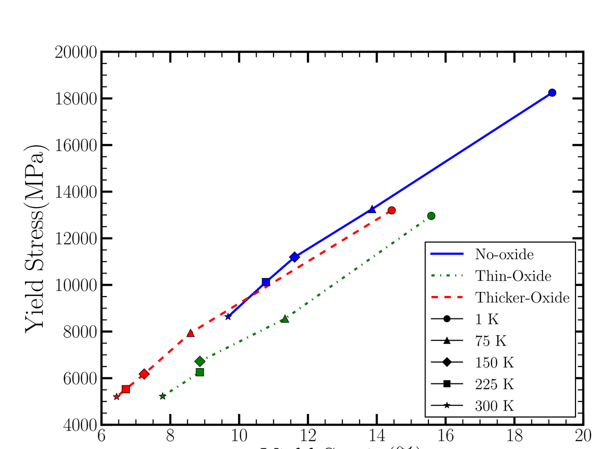

Figure 8: Yield stress and strain results.

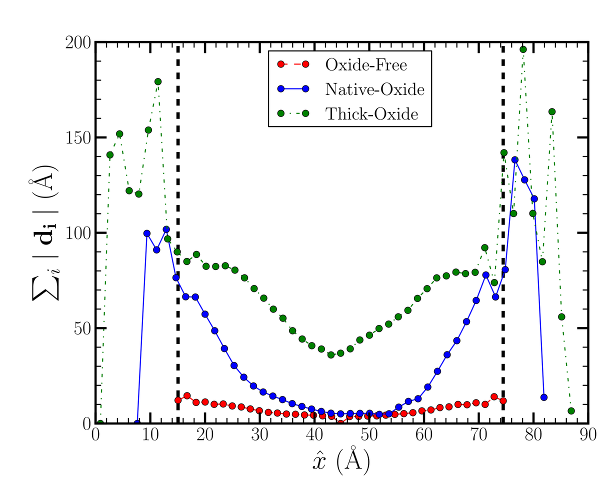

Figure 9: Binned atomic displacements at 1.3 % strain.

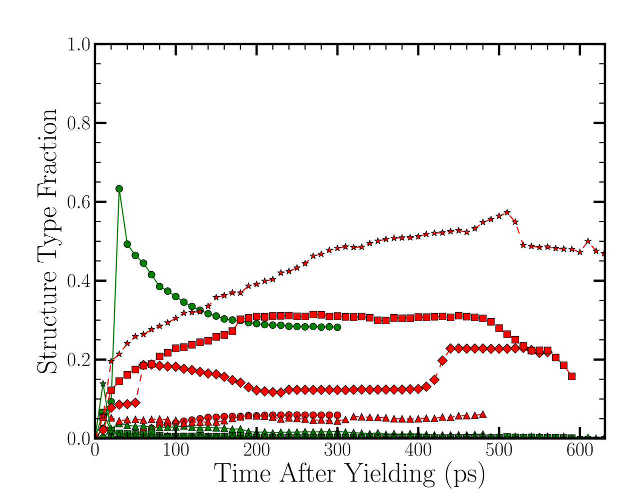

Figure 10: Oxide free thin-film structural progression after yield. (green=BCC, red=HCP)

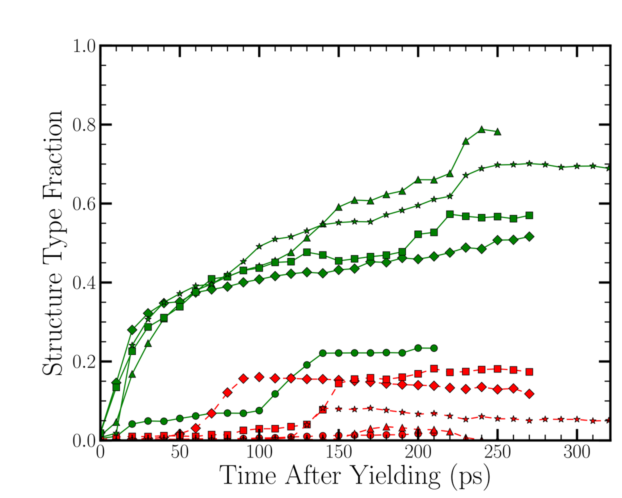

Figure 11: Thick oxide layer progression after yielding. (green=BCC, red=HCP)

Modulus Results

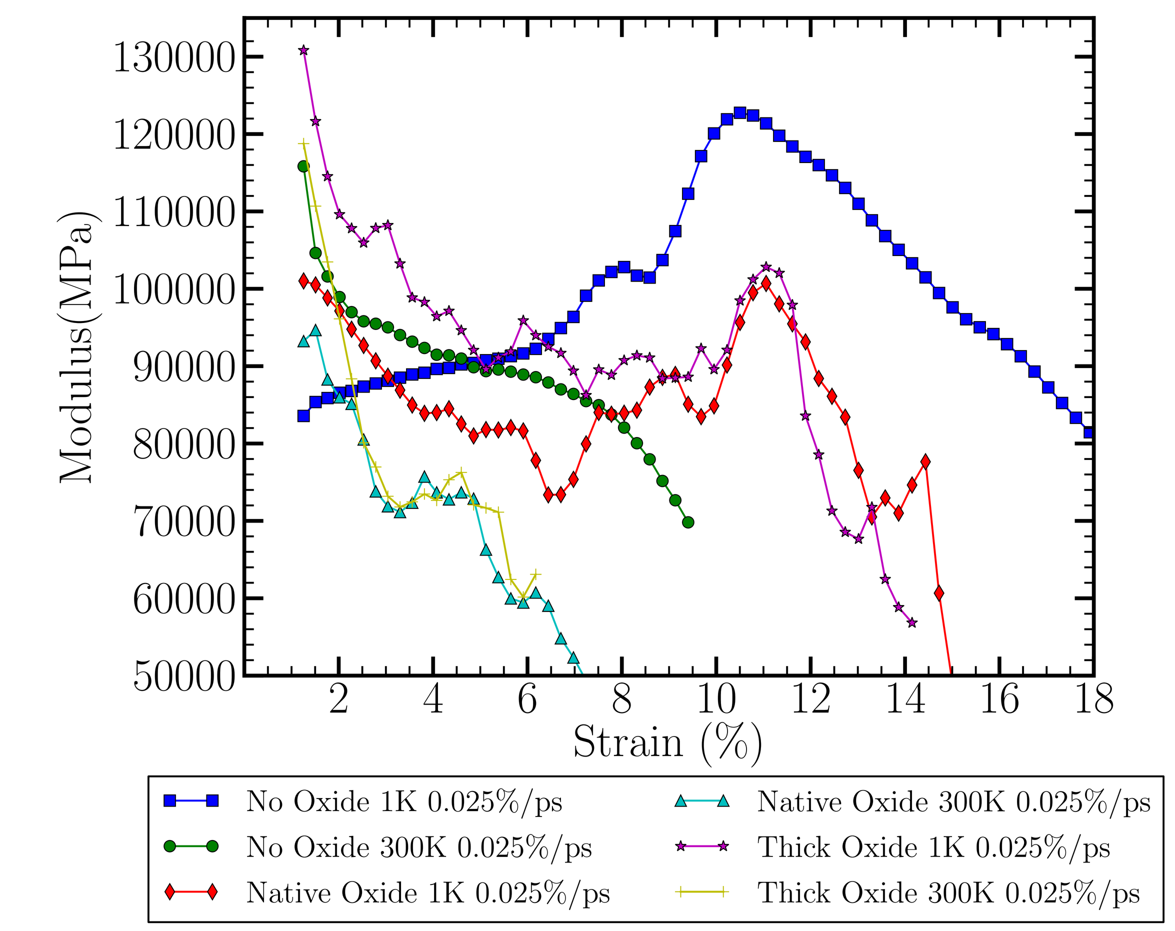

Figure 12: Rolling modulus results at 1K and 300K for thin-films, with a regression region of 1%.

Conclusions

These data represent a benchmark for further COMB mechanical testing:

- Oxide structure strongly effects the composite modulus, increasing the modulus at low strain and temperature values, while softening at higher temperatures.
- COMB potentials predict FCC [001]->[111] transitions as a yielding mechanism. Likely due to the higher generalized stacking fault energy with COMB potentials.
- Oxide layers squeeze the inner thin-film causing a FCC->BCC transition while under tension.
- Reorganization events within the oxide films nucleate defects, leading to brittle failure.

References

[1] Bryce Devine, Tzu-Ray Shan, Yu-Ting Cheng, Alan J. H. McGaughey, Minyoung Lee, Simon R. Phillpot, and Susan B. Sinnott. Atomistic simulations of copper oxidation and cu/cu_{2}o interfaces using charge-optimized many-body potentials. *Physical Review B*, 84(12):125308, 2011.

[2] Ting Zhu, Ju Li, Amit Samanta, Austin Leach, and Ken Gall. Temperature and Strain-Rate Dependence of Surface Dislocation Nucleation. *Physical Review Letters*, 100(2):025502, 2008.

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