Effect of native oxide layers on copper thin-film tensile properties: A reactive molecular dynamics study

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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. Newly developed charge-optimized many body [Liang et al., Mater. Sci. Eng., R 74, 255 (2013)] potentials are used to perform fully reactive molecular dynamics simulations which elucidate the effects that metal-oxide layers have on the mechanical properties of a copper thin-film. Simulated tensile tests are performed on thin-films while using different strain-rates, temperatures, and oxide thicknesses to evaluate changes in yield stress, modulus, and failure mechanisms. Findings indicate that copper-thin film mechanical properties are strongly affected by native oxide layers. The formed oxide layers have an amorphous structure with lower Cu-O bond-densities than bulk CuO, and a mixture of Cu$_2$O and CuO charge character. It is found that oxidation will cause modifications to the strain response of the elastic modulii, producing a stiffened modulii at low temperatures (<75 K) and low strain values (<5%), and a softened modulii at higher temperatures. While under strain, structural reorganization within the oxide layers facilitates brittle yielding through nucleation of defects across the oxide/metal interface. The oxide-free copper thin-film yielding mechanism is found to be a tensile-axis reorientation and grain creation. The oxide layers change the observed yielding mechanism, allowing for the inner copper thin-film to sustain an FCC-to-BCC transition during yielding. The mechanical properties are fit to a thermodynamic model based on classical nucleation theory. The fit implies that the oxidation of the films reduces the activation volume for yielding.

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I. INTRODUCTION

Nano-structured materials such as nano-wires and nano-films have been a popular subject of research due to their unique mechanical, electrical, chemical, and optical properties when compared with their bulk properties. They have found applications as flexible, transparent, conducting thin-films, catalysts, and frameworks for NEMS devices. In terms of mechanical properties, nano-wires and thin-films are known to have greatly increased yield stresses. This has been thoroughly demonstrated in simulations for compressive and tensile yielding of copper nano-pillars and uniaxial and biaxial tensile simulations of copper ultra-thin-films. Experimental verification of these simulations have been performed using tensile tests with copper nanowires and bulge tests of copper ultra thin films. Furthermore, copper nanowire tensile simulations show both increased and decreased modulii depending on the orientation and interatomic potentials being tested. These physical property changes are largely a result of the high surface to volume ratios present in nano-structured materials. It is known that at high surface-area to volume ratios, FCC metal surface atoms will develop tensile surface stresses (1.0–2.5 J/m$^2$) as a response to coordination reduction. These atoms will then apply compressive strains to the core atoms of the nano-structure. For thin-films and nanowires, this compressive core-stress is proportional to the ratio of the surface stress to the diameter or thickness. At film or nanowire thicknesses less than 50 nanometers, the core stresses can range from 100s of MPa to several GPa, strongly affecting the mechanical properties.

Both experimental and simulation studies have indicated that surface features such as roughness, corners, thin-film misfit strains, or thin-film passivated coatings will cause significant changes to mechanical properties of a nano-scaled material. Additionally, nano-structures are often “dislocation-starved,” implying that deformation mechanisms must result from surface nucleation at a much higher stress value than bulk-dislocation generation mechanisms.

Due to the importance of surface stress and surface nucleation of dislocations on the mechanical properties of nano-structures, it is expected that the presence of native oxide layers will have a profound effect on mechanical properties. Here we study the effects that these initial oxidation layers have on the mechanical properties of ultra-thin copper films. While there are currently no experiments at the scales we are capable of simulating, several studies have been performed at a slightly larger scale where this work may help to elucidate results. Experimentally, it has been found in Cu
nanowires, with an approximate radius of 300 nm, that oxidation initially softens and then stiffens the material along with a corresponding decrease and increase in yield stress during tensile testing. However, no explanation for this mechanism has been provided. In terms of structure, Ozkan et al. found from XRD data that Cu$_2$O was formed in the completely oxidized copper nanowires. They also found that the Cu$_2$O nanowires had a relatively low modulus of 25 GPa. The authors attributed the intermediate strengthening behavior to structural reorganization within the nanowire core, rather than production of the stiffer CuO phase. In additional XRD studies of copper nanostructures, the CuO phase oxide has been found to grow from copper thin films, possibly from a mechanism where Cu$_2$O transforms to CuO.

While studying CuO nanowire growth on copper substrates, Xu et al. found Cu$_2$O as the initial oxidation product on copper films, which then transformed to mostly CuO. These experimental studies were reinforced by Lim et al. who used X-ray photoelectron spectroscopy to find that native oxide films will eventually develop into an inner Cu$_2$O layer, and an outer CuO layer. We aim to determine if these mechanisms are replicated in our simulated oxidation experiments, as well as provide insight into the differences in mechanical properties that develop with oxidation.

The complex bonding environment present at a metal-oxide layer interface, which must smoothly transition from metallic to ionic character, is modeled through the use of Charge-Optimized Many Body (COMB) reactive MD force fields. While mixed bonding environments are accurately handled implicitly by ab initio techniques such as Density Functional Theory (DFT), the size-scales necessary for determining nano-structured mechanical properties makes these techniques prohibitively expensive. Streitz and Mintmire developed a popular inter-atomic potential for metal-oxide interfaces; however, their potentials were inaccurate in their prediction of interface structure. The ability to efficiently and accurately simulate the bonding environment transition between metallic and ionic bonding has only been recently developed with the advent of reactive, bond-order-based potentials such as COMB and ReaxFF. These allows for the unique investigations into these metal/metal-oxide structures with classical potentials.

Pure copper nano-wires and thin-films have been extensively studied through simulations with embedded-atom method (EAM) potentials, providing ample benchmarking for comparison with COMB potentials, and the effect of oxide layers. While there has been previous work in the use of MD simulations in studying multi-layered metal thin films, none of these studies have focused on modeling metal-oxide interfaces in thin-films. The early stages of the copper oxidation process have been investigated by Jeon et al. using ReaxFF potentials. The authors found that surface reconstruction was key to continuing oxidation, and the oxide structure strongly depended on surface orientation and defects. Jeon et al. noted a mixture of stoichiometric oxides, with CuO fractions increasing at higher temperatures. Additional reactive MD studies, using ReaxFF potentials, have examined the effect of oxidation on the mechanical properties of aluminum nanowires.

It was found that an initial oxide layer on aluminum allows for super ductile behavior, where oxide bonds can continually reform on the surface of the wire as it deforms. The aluminum oxide layers formed differed in stoichiometry when compared with bulk Al$_2$O$_3$, leading to a decrease in modulus. The formed oxide layers then softened the nanowires in a manner consistent with the rule of mixing. Here we examine if analogous behavior can be found in copper thin-films, using COMB potentials. To evaluate this behavior, simulated tensile tests are performed on oxide-free and two variants of oxide coated ultra-thin films, at a variety of strain rates and temperatures.

II. METHODS

Simulations were performed with the Large-scale Atomic/Molecular Massively Parallel Simulator or LAMMPS simulation software. To correctly capture the complex bonding environment that exists at the interface between an ionically bonded oxide and metallic copper, a bond-order dependent, 3rd generation COMB potential was used. This particular parameterization evolved from a Cu-Cu$_2$O parameterization developed by Devine et al. Their initial Cu-Cu$_2$O parameterization was referred to as a 2nd-generation COMB potential, and was split into two forms, COMB2A and COMB2B. COMB2B differs from COMB2A in that it has an additional polarization function and core-charges interactions to prevent the overstabilization of O$_2$ molecules. The Cu-O COMB potentials were further refined into 3rd-generation, COMB3 potentials by Liang et al. Modifications were made in the self-energy and short-range bond order potentials which allowed for increased accuracy in the energetics of molecular systems, and uniform parameters across all bonding types. The basic form of the total energy expression for a COMB3 potential is

$$E_{\text{COMB}} = E_{\text{self}} + E_{\text{Coul}} + E_{\text{polar}} + E_{\text{vdW}} + E_{\text{bond}} + E_{\text{others}}.$$  \hspace{1cm} (1)

The self energy, $E_{\text{self}}$, is comprised of an atomic ionization energy term and an embedded atom term, to account for the change in atomic hardness when in a lattice. The ionization term is a 4th order Taylor Series expansion with respect to atomic charge. The embedded-atom term, known as the field-effect correction, is a multi-body pair potential with $1/r^6$ and $1/r^5$ expressions to characterize changes in the bonding environment. Atoms are modeled as having radially decaying charge densities similarly to the ES + model using ReaxFF potentials. The authors found that surface reconstruction was key to continuing oxidation, and the oxide structure strongly depended on surface orientation and defects. Jeon et al. noted a mixture of stoichiometric oxides, with CuO fractions increasing at higher temperatures. Additional reactive MD studies, using ReaxFF potentials, have examined the effect of oxidation on the mechanical properties of aluminum nanowires.

The Coulombic energy, $E_{\text{Coul}}$ is formed as a sum of the electrostatic energy between atomic charge densities,
\[ E^\text{q}[\rho(r)] = \frac{1}{2} \int \left( \rho(r_1) \rho(r_2) \right) \frac{d^3r_1 d^3r_2}{|r_1 - r_2|}. \] (4)

Molecular polarization terms, \( E^\text{polar} \), can be included, which include the effects of dipole–dipole, dipole–charge, and dipole–self interactions. In this simulation, the polarization terms were neglected, allowing only for charge redistribution within oxygen molecules. No noticeable differences in oxide structure were noticed with the inclusion of polarization terms. The \( E_{\text{vdW}} \) term captures the van der Waals interactions with a Lennard–Jones expression.

The \( E_{\text{bond}} \) term is the bond-order dependent term which depends on atomic spatial location, \( r \), and charge, \( q \), allowing the capture of charge-transfer events

\[ E_{\text{bond}} = \frac{1}{2} \sum_i \sum_{j \neq i} \left[ V_R(r_{ij}, q_i, q_j) - (b_{\text{angle}} + b_{\text{coord}} + b_{\text{bond}}) \right] \]

\[ + b_{\text{torsion}} + b_{\text{coord}} + b_{\text{conjug}} \sum_{n=1}^3 V_n^A(r_{ij}, q_i, q_j), \] (5)

where \( V_R(r_{ij}, q_i, q_j) \) and \( V_n^A(r_{ij}, q_i, q_j) \) are exponentially decaying pair-wise repulsive and attractive terms, \( b_{\text{angle}} \), \( b_{\text{coord}} \), \( b_{\text{bond}} \), \( b_{\text{torsion}} \), and \( b_{\text{conjug}} \) adjust the total energy according to bond angle, coordination environment, torsion, and conjugation. \( E_{\text{others}} \) is left as a term able to adjust and correct for errors in bonding energy.

Charges, \( q \), on each atom are adjusted dynamically using an extended Lagrangian method developed by Rick et al.

\[ L = \sum_{i=1}^{N} \left( \frac{1}{2} m_i \dot{q}_i^2 + \sum_{i=1}^{N} \frac{1}{2} M_i q_i^2 - E_{\text{COMB}} - \lambda_t \sum_{i=1}^{N} q_i \right), \] (6)

where the first term is the kinetic energy of the atomic nuclei with mass \( m \), the second term is the kinetic energy of the charges with a fictitious mass, \( M \), and \( \lambda_t \) is a multiplier which enforces charge neutrality. The equation of motion for the dynamic charges is as follows:

\[ M_i \ddot{q}_i = -\frac{\partial E_{\text{COMB}}}{\partial q_i} - \lambda_t = -\chi_i - \lambda_t, \] (7)

where \( \chi_i \) is the electronegativity of atom \( i \). Using the fact that the total charge is conserved leads to the following expression for motion in charge space:

\[ M_0 \ddot{q}_i = \ddot{\chi}_i, \] (8)

where it becomes clear that electronegativity is being equilibrated to a mean value. The previous equation is solved using a velocity Verlet integration \( \text{ between atomic-motion timesteps. More thorough summaries and descriptions of COMB3 potentials can be found in Liang et al.}^{38,41} \)

The thin-film simulations were oriented in the [100], [010], and [001] directions for each face, which will be referred to as the \( \hat{x} \), \( \hat{y} \), and \( \hat{z} \) directions, respectively. The initial cells were 18 unit-cells (63 Å) thick in the \( \hat{z} \) direction, 30 unit-cells high (108.3 Å) in the \( \hat{z} \) direction, and 6 unit-cells deep (22 Å) in the \( \hat{y} \) direction, with periodic boundary conditions in the \( \hat{y} \) and \( \hat{z} \) directions.

Two different oxidized films were simulated to examine the effect of the oxide layers. The first was created by exposing both sides of a copper thin-film to oxygen atoms at 300 K with a Nose-Hoover NPT ensemble with a chain length of 10. The simulation was allowed to oxidize for 500 ps. The oxygen atoms were initially placed in a cubic lattice 3.0 Å apart, and 7 Å from the copper surface. Initially, two different oxidation simulations were performed with different amounts of oxygen atoms, one with 2280 and the other with 960. The structure were compared to evaluate differences under different oxygen pressures. Ultimately the high-pressure, 2280 oxygen atom system was used for the native copper oxide mechanical simulations.

Since the first simulation’s stoichiometry was more similar to CuO than Cu2O, the second film was made by inserting a perfect CuO lattice at the Cu thin-film surface and allowing it to equilibrate. The idea was to create an interface which emulates the effect of significant surface reorganization events, leading to a thicker oxide structure. The unit cell of the CuO was tetragonal with a space group of P42/mmc; each unit cell had initial lengths of 3.03 Å in the [100] and [010] directions, with an elongated [001] axis at 5.25 Å. The oxide was oriented such that the CuO [001] axis was aligned with the simulation \( \hat{y} \) axis, and the CuO [100] axis was aligned with the \( \hat{z} \) axis. The film was oxygen terminated at the interface to allow for Cu-O bonds to readily form. The Cu-O layers were 30 cells in the CuO-[100] direction, 2 cells in the CuO-[010] direction, and 4 cells in the CuO-[001] directions. Due to the lattice mismatch between the oxide and the bare Cu surface, a 1.2 Å gap was placed between each 2 cells in the CuO-[100] direction to achieve the same total simulation cell size. The interface was initially equilibrated through the use of a conjugate gradient minimization.43 Throughout the rest of this work, the oxygen exposed simulation will be referred to as the native-oxide and the CuO-slab simulation will be referred to as the thick-oxide sample.

Mechanical properties were evaluated by performing strain-controlled tensile tests. First, the simulation cells are equilibrated for 50 ps with a 10-chain Nose-Hoover barostat, to relax the pressure in the [010] and [001] directions using a timestep of 1 fs. The uniaxial tensile tests were executed by expanding the cell in the \( \hat{z} \) direction by 0.25% increments, then equilibrating to relax the [010] direction. Simulations were equilibrated between each straining event for 2.5, 5.0, and 10.0 ps, corresponding to strain rates of 0.1%/ps, 0.05%/ps, and 0.025%/ps. Pure CuO tensile-test simulations were also performed in a small (5 × 5 × 4) unit cell to evaluate the mechanical properties for comparison. Periodic conditions were removed from either the [100] or the [010] direction to find the effect of a free surface on the modulus values. The stress was recorded at each timestep utilizing the kinetic energy tensor and the virial tensor as follows:

\[ P_{ij} = \frac{1}{V} \sum_{i} m_i v_{ik} v_{jk} + \frac{1}{V} \sum_{k} r_{ki} f_{ki}, \] (9)

where \( P_{ij} \) is the pressure tensor for the \( ij \)-th component, \( m_i \), \( v_{ik} \), and \( f_{ki} \) are, respectively, the mass, \( i \)-th velocity...
component, and \( i \)-th force component on the \( k \)-th atom. \( V \) is the total system volume, requiring an adjustment for vacuum in simulations whose borders expand beyond the thin-film. The failure mechanisms can be directly observed by tracking defects (such as stacking faults) or phase changes during amorphous deformation. The defects are quantified and visualized using both Centrosymmetry parameters\(^{44} \) and common neighbor analysis.\(^{45} \) Ovito\(^{46} \) was used for visualization and analysis of atomic positions.

### III. RESULTS AND DISCUSSION

#### A. Oxide structure

Qualitative differences in the oxide layer structures can be seen in Fig. 1; it is clear that surface restructuring of the FCC copper is present at the interface of both thick (Fig. 1(c)) and native (Fig. 1(a)) layer samples. We see that in the native oxide sample, not all oxygen atoms were participating in the oxide layer. A region of \( \text{O}_2 \) molecules can be seen hovering near the slab in Fig. 1(b), which was removed in Fig. 1(a). We note that the oxide layer relaxation times provided during equilibration (500 ps) may be too short for significant rearrangement or relaxation of the oxide layers. While large structural changes in the native oxide layers were observed in the first 25 ps of equilibration, the oxide structure stagnated at this point, indicating that higher temperature or longer time scales were necessary to progress beyond this threshold. We chose to continue the study from this point due to the computational burden associated with COMB potentials. The native oxide layers in this study are representative of the initial oxidation structures formed, rather than structures in final equilibrium. This issue was alleviated slightly in the thick oxide samples, where conjugate gradient minimization was able to accelerate equilibrium. However, it should be noted that these structures may not have fully relaxed in the time allotted. These results are still quite useful for comparison with future works and the establishment of a benchmark for oxide-coated metal thin-film tensile simulations.

The thin-film oxidation process was analyzed in the native-oxide layer samples by plotting the number of copper atoms with \( |q| > 0.1 \) as a function of simulation time. Fig. 2 shows the progression of oxidized Cu atoms, where a plateau for low oxygen pressure simulations begins near 10 ps and that for the high pressure simulation begins near 20 ps. It appears that an initial oxide layer occurs within the first 10–20 ps, and limits further oxidation in both samples. Similar saturated copper oxide behavior at 300 K has also been reported by Jeon et al.\(^{33} \) Table I shows the resultant thickness for the oxide layers. The slab geometry was thickest, and both of the native oxide samples formed self limiting layers. The high oxygen-pressure native oxide was thicker than the low-pressure simulation.

The stoichiometry of the oxide layers indicated compositional differences between the native and thick oxide simulations. Copper and oxygen atoms with \( |q| > 0.1 \) were considered as part of the oxide layer for analysis. The results in Table I were gathered under this criterion, indicating that the native-oxide stoichiometry was dependent on the exposed oxygen pressure. The high O-pressure native oxide formed Cu\(_{0.85}\)O, while the low O-pressure simulation had a copper rich stoichiometry of Cu\(_{1.30}\)O. The thick-oxide layer also bonded with an excess of copper atoms to form Cu\(_{1.20}\)O. In the thick oxide simulation, the stoichiometry of the initial slabs was 1:1, indicating that Cu atoms are pulled from the

![Fig. 1. Close-up view of (a) native, (b) native with \( \text{O}_2 \), and (c) thick copper oxide interface structures, shown with smaller O atoms and larger Cu atoms.](image1)

![Fig. 2. First 150 ps of Cu atom oxidation for low O-pressure (960 atoms) and high O-pressure (2260 atoms).](image2)
surface during the oxide equilibration. In terms of atomic density, the thick-oxide layer is quite similar to the bulk CuO density. However, the native-oxide layer has a slightly lower density, indicating that initial oxide layers are less compact than bulk CuO.

Charge distributions were analyzed to ensure the presence of ionic bonds within the oxide layers. Although the stoichiometry implies that Cu(II)O is formed, the charge distributions indicate that the COMB potentials stabilize CuO with charges near $\pm1\text{e}$. It is assumed that within this parameterization a magnitude of $\pm1\text{e}$ represents fully oxidized oxygen/copper ions, similarly to calculations performed in previous studies. Fig. 3 shows the distributions for the native and thick oxides. As expected from the stoichiometric results, the copper ion charges in the thick oxide layer are slightly less positive than the native oxide layer. The excess copper allows for less charge-per-atom, making the positive ions have a slightly lower charge peak. We can separate the positive, copper, charges into Cu$_2$O and CuO regions through charge magnitude. We find that a mixture of oxide types occurs with each sample. In all three samples investigated, the charge distributions show more CuO character than Cu$_2$O. This coincides with the initial CuO configuration chosen for the thick oxide sample. The native oxide samples’ behavior can be explained by examining the Cu-O phase diagram. We see that high partial pressures of oxygen lead to CuO formation, while a mixture region (between molar fractions of O at 0.33 to 0.5) would be present in the simulation as free oxygen atoms are oxidized. From this analysis it seems that a mixed Cu$_2$O-CuO oxide layer is likely to occur at the interface under these conditions. The low-O pressure sample had a relative excess of Cu$_2$O-type atoms compared with the high-O pressure simulation as would be expected from the phase diagram.

The surface restructuring and oxide-layer crystallinity were evaluated with a 2-D structure factor. Only copper atoms within the oxide layer were considered, and the following structure factor was calculated for the $\hat{y}$ and $\hat{z}$ directions,

$$S(r) = \sum_j N \exp \left( \frac{k}{L_y} r_{jy}^2 + \frac{l}{L_z} r_{jz}^2 \right),$$  

where $r_{jy}^2$ is the $a=x, y, z$ component of the $j$-th atomic position, $k$ and $l$ are the plane index numbers, and $L_a$ is the cell size in the $a=x, y, z$ direction. Structure factor calculations for only the copper atoms in the native-oxide, thick-oxide, and bulk-CuO structures can be seen in Fig. 4. In the native and thick oxides, some structure is present from (010) planes in the interfacial atoms, as can be seen in Figs. 4(b) and 4(c). However, the layers are relatively amorphous compared with the peaks found in the pure Cu sample (Fig. 4(a)). The lack of structure in both the native and thick oxide layers can be seen at higher order coefficients. These results are supported by previous ReaxFF reactive molecular dynamics simulations, where an amorphous oxide is formed on room temperature copper surfaces.

Bonding environments in each of the oxide layers were investigated through radial distribution functions as well as bond-density comparisons. The radial distribution functions (rdf) are shown in Fig. 5. The rdf peaks at 1.2 Å show that the O$_2$ bonds are still present in both the native and thick

<table>
<thead>
<tr>
<th>Oxide type</th>
<th>Stoichiometry (Cu:O)</th>
<th>Layer thickness (Å)</th>
<th>Cu-O bond density (bonds/Å$^2$)</th>
<th>Density (Å$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Native-oxide (2280 O)</td>
<td>0.85:1.0</td>
<td>7.3</td>
<td>0.141</td>
<td>3.30</td>
</tr>
<tr>
<td>Native-oxide (960 O)</td>
<td>1.30:1.0</td>
<td>6.0</td>
<td>0.120</td>
<td>3.33</td>
</tr>
<tr>
<td>Thick-oxide layer</td>
<td>1.20:1.0</td>
<td>13.7</td>
<td>0.207</td>
<td>3.83</td>
</tr>
<tr>
<td>Bulk CuO</td>
<td>1.0:1.0</td>
<td>...</td>
<td>0.226</td>
<td>3.82</td>
</tr>
</tbody>
</table>

FIG. 3. Normalized copper atom charge distributions in different copper oxide layers. Rectangular regions indicated CuO or Cu$_2$O character.

FIG. 4. 2-D structure factors for (a) oxide-free, (b) thick, and (c) native oxide layers (high-O).
oxide film samples. The 1.8 Å peak represents the Cu-O bonding, and it can be seen that the thick-oxide has a relative increase in Cu-O to O-O bond ratio. Since the Cu-O bonds are relatively less present in the native-oxide samples it implies that some degree of O-O bonding is still present in the native oxide samples. When looking at the density of Cu-O bonds (defined by any inter-atomic separation less than 2 Å between O and Cu), the thick oxide has slightly less bonds per unit volume than bulk CuO and both native-oxide samples have a significant decrease in bond density, once again implying a layer with impartially dissociated O₂ molecules. Different mixtures of Cu-O compositions appear to create differences in bonding-density. Mechanical testing was performed on the thick-oxide layers as well as the high O content native oxide layers (from here on referred to as only native oxide layers), to give a perspective on the tensile properties at different oxidation stages.

B. Mechanical properties

A summary of thin-film mechanical properties is included in Table II. Despite the apparent stress-strain linearity before yielding in Fig. 6, variations in modulus values were observed such that the choice of strain values over which the regression was performed would affect results. For this reason, we chose to represent the modulus as a function of strain for several of the simulations as shown in Fig. 7. This rolling modulus was calculated over strain range intervals of 1.25%. It is expected that the modulus will decrease with strain and temperature since interatomic forces typically decrease with increasing atomic separation. Reduction in modulus with increasing temperature has been observed experimentally in Ref. 49 and computationally8,50 for copper thin films; however, the films used in each of these studies were considerably thicker than the films simulated here. For the non-oxide copper samples, the low temperature tensile tests show behavior which indicates an increasing modulus with strain. The simulation results also indicate that the low-temperature, oxide-free thin-films are softer at low tensile-strain values. The effect was not an artifact specific to COMB potentials, as we were able to replicate the same behavior with several popular copper EAM potentials51,52 for stacking fault studies. These tensile tests were performed on identical oxide-free copper thin films. We have included these results in Fig. 7 for comparison with COMB potentials. In Mishin et al.52 potential, the variations in modulus are larger at lower temperatures, with an increasing modulus until about 8% strain. We note that these variations may occur in many simulations with similar inter-atomic potentials and geometries. Here, the 1 K oxide-free modulus increases until a small decrease near 9% strain and a large decrease at 11% strain. This increasing modulus behavior produces no artifacts structurally, and only occurs in the 1 K and 75 K oxide-free simulations. The increasing modulus values may be due to a slight over-coordination at low temperatures. When the modulus is measured between 0 strain and the yield strain, the oxide-free modulus agrees closely with previous copper nanowire values: 100 GPa at 0 K and 80 GPa at 300 K.7 The oxide-coated thin-films also experience some modulus increases in limited strain regions, which vary with temperature. There are significant displacements

<table>
<thead>
<tr>
<th>Type</th>
<th>Temperature (0.1, 0.05, 0.025%/ps)</th>
<th>Yield stress $\epsilon = 0.05$ (GPa)</th>
<th>Elastic modulus $\epsilon = \epsilon_{y}$ (GPa)</th>
</tr>
</thead>
<tbody>
<tr>
<td>No oxide 1</td>
<td>16.8</td>
<td>18.4</td>
<td>18.2</td>
</tr>
<tr>
<td>No oxide 75</td>
<td>13.9</td>
<td>13.7</td>
<td>13.2</td>
</tr>
<tr>
<td>No oxide 300</td>
<td>8.60</td>
<td>8.52</td>
<td>8.50</td>
</tr>
<tr>
<td>Native oxide 1</td>
<td>13.2</td>
<td>13.5</td>
<td>13.0</td>
</tr>
<tr>
<td>Native oxide 75</td>
<td>9.08</td>
<td>8.99</td>
<td>8.52</td>
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<tr>
<td>Native oxide 300</td>
<td>5.41</td>
<td>5.52</td>
<td>5.21</td>
</tr>
<tr>
<td>Thick oxide 1</td>
<td>13.2</td>
<td>13.2</td>
<td>13.1</td>
</tr>
<tr>
<td>Thick oxide 75</td>
<td>8.89</td>
<td>8.57</td>
<td>8.72</td>
</tr>
<tr>
<td>Thick oxide 300</td>
<td>5.83</td>
<td>5.77</td>
<td>5.51</td>
</tr>
</tbody>
</table>

FIG. 5. Radial distribution function for copper oxide layers.

TABLE II. Thin-film mechanical properties.
of atoms within the oxide layers during yielding, and these variations are likely to adjust the composite modulus.

The oxide-metal composite modulus values are higher for the thick-oxide layers than the native-oxide layers, at all temperatures studied. It is likely that this is due to the higher Cu-O bond density values found in Table I. When analyzed with the rule of mixtures for composite materials, an effective modulus can be determined for the oxide layer. The expression for the effective modulus from the rule of mixtures for uniform thickness thin-films simplifies to

$$E_{\text{oxide}} = \frac{E_{\text{total}} t_{\text{total}} - E_{\text{Cu}} t_{\text{Cu}}}{t_{\text{oxide}}}$$

(11)

where $t_{\text{total}}$, $t_{\text{Cu}}$, and $t_{\text{oxide}}$ are the thickness of the entire thin-film, metallic copper layer, and oxide layers, respectively. Rather than choosing a representative modulus for the no-oxide copper, we calculated the effective modulus for all values of strain using Eq. (11). Fig. 8 shows the results of these calculations. The pure oxide simulations had a modulus of 282 GPa when strained in the [010] direction; however, the modulus was quite sensitive to structure. The effective modulus for the thin-film oxides near 0 strain is lower than the calculated modulus for the pure oxide. Furthermore, the modulus of the oxide when removed from the thick oxide simulation was only 90.0 GPa, indicating that structural differences can easily soften the oxide layer.

At low temperatures (75 K or less), the oxide coated samples have a higher modulus than the bare thin-films up until strains near 5%. At larger strain values, the copper-only films become stiffer relative to the oxide coated films. In the high temperature region, over small strain ranges (<2%), it appears that the thicker, higher bond-density oxide layers actually serve to stiffen copper nano-films. However, due to the rapid decline in effective modulus, softening behavior is observed for larger strain values. The native-oxide sample softens the copper thin-film across all strain values at 300 K. The fact that the low Cu-O bond density, native oxide layers seem to initially decrease the modulus near room temperature may help to explain the experimental findings in Ozkan et al.,23 where the initial stages of oxidation softened copper nanowires in tensile testing. We note that this study used much thicker nanowires than the film thicknesses present here (300 nm), and we are simulating limited time scales. Thus, many other mechanisms, such as annealing, may have a large softening effect as well.

Yielding behavior is summarized in Fig. 9. For a given temperature, the oxide samples yield at lower stresses than the oxide-free sample. The native and thick oxide samples are very similar in yield stress values; however, the native oxide layer yields at strain values approximately 20% larger than the thick oxide samples. Both oxide-coated films are considerably less ductile than the oxide-free film. The higher
bond density in the thick-oxide layers appears to enhance the embrittled response of the composite thin-film compared with the native thin-film. Furthermore, neither oxide sample saw breakage of the oxide layer after yielding. In general, yield stresses increased at higher strain rates; however, variations were on the order of 100 MPa, and several simulations did not follow this trend. Previous studies on copper thin-films have found that below a critical strain rate of 0.0417%/ps, the yield stress is essentially independent of strain rate. Since these studies are performed nearly above and below this value, some strain-rate invariant behavior is expected.

Since it is difficult to characterize yielding behavior within the amorphous films, we used the atomic displacement from the equilibrium position to examine restructuring within the oxide layers. Homogeneous cell displacement was subtracted such that only relative atomic displacement was recorded. The resulting displacements were summed in bins along the $x$ axis to visualize the transition in relative displacement through the oxide interface; we chose 1.3% strain, well before yielding in all samples, to demonstrate that significant atomic displacement occurs in the oxide films before the yield strain. The results of this analysis are shown in Fig. 10. It is obvious from Fig. 10(a) that more relative atomic displacement has occurred within the oxide layers, which has lead to increased displacement within the metallic layer, when compared with the oxide-free simulation. A view of the thin film along the $y$ axis is shown in Fig. 10(b), where it can be seen that much of the displacement is localized to defects within the oxide layer. These displacement events served to nucleate defects within the inner metallic layers at much lower strain values than in the oxide free simulations. Since the nucleations events appear to be related to oxide structure, we re-iterate that the oxide layers formed in both the native and the thick samples may not have fully relaxed into the structures found in physical systems. Thus, these nucleation events may be caused by structures more closely related to those formed in the initial stages of oxidation. The oxide-free copper thin films simulated in this work have different yielding behavior than previously reported in the literature for tensile simulations of ultra-thin copper films with EAM potentials. Rather than the nucleation of partial dislocations on (111) planes, which has been predicted with EAM potentials, the COMB potentials used here predict phase-transformations or reorientations in addition to partial dislocation nucleation as a yielding mechanism. It is important to note that we are using smaller size scales (63 Å in this work vs. 108 Å (Ref. 9) and 202 Å (Ref. 8)), which could potentially affect the differences between these tensile tests. To help with comparison between this work and previous studies, the same geometries were also tested using Mishin et al. EAM potentials. For the geometries selected in this work, uniaxial tensile stresses with COMB potentials initially cause either a transformation into a re-oriented FCC crystal, such that the [111] direction aligns with the $z$, tensile axis, or a transformation into a BCC structure with the BCC [110] direction aligned with the $z$ axis. It is likely that this effect is due to the larger unrelaxed generalized stacking-fault energy (GSFE) (224 mJ/m$^2$) with COMB potentials, when compared with EAM potentials (158 mJ/m$^2$). These results are a much better fit to the DFT results for the copper GSFE, with a value of 210 mJ/m$^2$, which suggests that the COMB potential is more accurate in predicting stacking fault defects. The higher GSFE implies that slip between FCC (111) planes is made significantly more difficult in the COMB system than previous EAM studies, which leads to increased difficulty in slip such that an ABCABC repeat structure is formed. Rather, an ABAB structure is formed such that closely packed BCC layers are formed with the [110] axis aligned with the tensile ($z$) direction. This result is supported with the relatively low phase transition energy from FCC to BCC, which is 0.008 eV with COMB potentials and 0.046 eV for the EAM potentials.

Similar results have been seen in the literature previously. Thin-film uniaxial tensile test simulations of Copper with EAM potentials have shown similar yielding-based crystalline re-orientation to those reported in this work. Reorientation along the tensile axis has been seen in previous MD simulations of Au FCC nanowires. Experimentally, FCC to BCC transitions have been found within copper precipitate particles, while under tensile stresses in Iron based alloys. Martensitic, hexagonal close packed (HCP), transformations have been previously reported in simulations of bi-axially strained copper thin films with two different EAM potentials at large strain rates. We performed our simulations at much lower strain rates, but it is possible that the 0.25% scaling used as strain increments is capable of inducing shock-like conditions for this simulation. However, we note that strain rates in this regime have been successfully used in previous tensile simulations. Since our results have not been well reported in the literature, here we present the yielding mechanisms as a means of comparison between the oxide coated and bare thin films, and a benchmark for future COMB potential-based mechanical tests.

The phase transformation is well characterized in the oxide-free thin-films; first they undergo a surface reorganization within the two closest (010) planes to the surface. The re-organizational slip is shown in Fig. 11(a), where slip occurs in the [001], or strain, direction. These slipped sites allow for the nucleation of (001) planar defects which propagate across the crystal in the [100] direction, and spread in the strain ([001]) direction, as shown in Fig. 11(b). The yield
stress occurs as this defect-loop crosses the thickness of the thin-film. The initial state of the planar defect is shown as a cross section in Fig. 11(c), rows of atoms in the [100] direction are alternately compressed or elongated such that the FCC “diamonds” are either distorted or rotated around the [001] axis. Under further compressive strain in the [100] direction, the rotated FCC diamonds collapse to form a close packed plane as shown in Fig. 11(d). After this collapse, the behavior diverges depending on temperature, and the presence of an oxide layer.

At low temperatures (<75 K) in the oxide-free simulations, it appears that there is not enough thermal energy to promote slip between (001) planes such that an ABCABC repeating pattern is formed in the [001] direction. Rather, only every other plane is allowed to slip forming an ABAB structure, which is effectively a BCC cell with its [110] direction co-aligned with the simulation cell’s [001] direction. For the oxide-free thin-films, this stacking requires a considerable expansion in the [010] direction, seen in Fig. 11(d). The sort of stacking seen in the BCC transformation is

FIG. 10. Displacement in oxide layers: (a) summed atomic displacements (\(\sum d_{ij}\)) binned in the [100] direction at 1.3% strain with a dotted line to separate the oxide and metallic regions; (b) displacement magnitude color-chart to indicate displacement localization.

FIG. 11. Yield mechanisms: (a) thin-film surface slip showing that the transformations initially result from surface abnormalities; (b) (001) planar defect loop colored by centrosymmetry parameter; (c) a top view of the leading planar defect in (b), where the untransformed, FCC region can be seen in green; (d) fully compacted close-packed plane formed from (c); (e) example of the multi-layered structure (ABAB) formed when a BCC transformation occurs, with black atoms as the top layer, grey as the middle layer, and white as the bottom layer; (f) example of the multi-layered structure (ABCABC) formed when a (111)-reorientation event occurs, with black atoms as the top layer, grey as the middle layer, and white as the bottom layer.
shown in Fig. 11(e). An idea of the post-yielding relative phase behavior within each thin-film can be gathered from Fig. 12, which shows structure type calculated with adaptive common neighbor analysis. Here we see that after yielding, the low-temperature oxide-free simulations rapidly develop BCC structured regions within the defect loops.

As the temperature increases, inter-planar slip seems to become more energetically favorable, where an ABCABC structure can be achieved. This structure can be seen in Fig. 11(f). This leads to the formation of a re-oriented FCC lattice, rather than a BCC lattice, such that the FCC [111] direction is aligned with the simulation’s z direction. A defect loop formed with this mechanism is shown in Fig. 13(a). This orientation favors the typical HCP stacking faults with (112)-dissociated partial dislocations. Fig. 12 shows that the BCC transition is suppressed in the post-yielded high temperature oxide-free samples, and FCC (111) plane stacking faults are generated soon after yielding. These leave HCP structures behind as the leading partial dislocations move through the film. Fig. 12 shows this with an increasing HCP fraction of atoms after yielding in the higher temperature oxide-free samples. When more than one FCC re-orientation loop is nucleated (as is the case with temperatures above 75 K), grains are formed as the defect loops meet within the film. This leads to the formation of grain boundaries during yielding in the thin-film samples as demonstrated in Fig. 13(b). In each of the samples with temperatures above 1 K, partial dislocation nucleation occurred in tandem with any structural re-arrangement or gain formation. This is again seen as HCP structures in Fig. 12 for higher temperature oxide-free samples. The re-orientation based yielding behavior may not be an artifact which is limited to COMB potentials, as we performed identical tensile experiments with oxide-free copper thin films at 1 K and 300 K using the Mishin et al. potential. While these potentials generated substantially more stacking faults, in closer agreement to previous Cu thin film simulations, we still observed some reoriented domains during yielding, as shown in Fig. 13(d). This leads us to believe that these extremely thin-films (<70 Å) may be prone to reorganization in tensile simulations.

The displacements shown in Fig. 10 indicate that restructuring events occur within the oxide layers prior to the yield stress being reached in the composite thin-film. From centrosymmetry calculations and common neighbor analysis of the inner copper film (Fig. 12), we see that the initial planar FCC-to-BCC type defects are nucleated as the restructuring occurs. The increase in these nucleation events essentially embrittles the oxide films, causing yield at much lower strain values. The native oxide sample nucleates defect structures which are similar to the oxide-free sample; however, from Fig. 12 it appears that the presence of the film prevents the same (001) planar slip necessary to achieve the FCC [001] → [111] re-orientation. We observe that the oxide-films apply a compressive stress in the [100] direction while under tensile load. This increased compressive stress may prevent the slip necessary for [001] → [111] re-orientation. In terms of strain in the [100] direction, at 150 K, the native oxide metallic layer is compressed by 16%, while the oxide-free thin-film has only compressed by 9%. For the native oxide layers, the BCC structured atoms out-number the HCP oriented atoms up until 300 K. At 300 K, the increased ductility of the oxide layer allows for partial dislocation emission with (112) type Burgers vectors on (111) planes. This can be seen schematically with the increase in slipped-HCP structure after yielding in Fig. 12(b).

The thick-oxide sample shows a much clearer trend with regards to the oxide’s effect on yield mechanism. The simulations saw similar embrittling behavior to the native-oxide thin films, where many FCC-to-BCC type defects were emitted on (100) planes from oxide rearrangement. These defects propagated across the crystal in surface terminating loops, transferring a significant portion of the film to BCC structure. Even in the higher temperature thick-oxide samples, the nucleated FCC-to-BCC defects completely spread across the crystal, with a relatively small portion of HCP sacking-faults, as seen in the other 300 K samples. Fig. 13(c) shows that a nearly complete transition is made to BCC structure within the inner metallic film, in the 75 K structure. Similar to the native oxide results, the thick oxide provides a compressive stress in the [100] direction. At 150 K, the inner metallic layer experiences a [100] compressive strain of 14% relative to the 9% in the oxide-free layer. The increased modulus and applied compressive stress in the [100] direction seems to facilitate the FCC to BCC transition.

From these results it appears as though the partially amorphous copper oxide layers nucleate defects in the...
thin-films via rapid strain release during restructuring events. The defects are nucleated more rapidly in the thicker, higher Cu-O bond density sample, leading to enhanced embrittlement compared with the thinner, native oxide layer. From examining the failure mechanisms, it appears that for COMB potentials, the FCC-to-BCC transformation competes with partial dislocation emission and FCC reorientation to a [111] tensile axis. The ability of the sample to compress in the [001] direction seems to dictate the formation of BCC layers or stacking-fault-based, HCP layered defects. Therefore, [100] compressive stresses caused by [001] tensile stresses in the oxide layers prevent the necessary slip to form the reoriented (111) FCC planes. This argument is supported by the increased observed modulus and bond-density in the thick-oxide samples, where tensile forces should produce a larger [100] compressive stress than the native layers, resulting in an excess of BCC-structured defects.

C. Thermodynamic model

Zhu et al.\textsuperscript{21} have developed a classical nucleation theory based yielding model for nanowires, which is general enough to remain applicable to dislocation free-thin film geometries as well. The following implicit expression was derived for the dislocation nucleation stress while under a constant strain rate

\[
\frac{Q(\sigma, T)}{k_B T} = \ln \frac{k_B T N \nu_0}{E \varepsilon \Omega(\sigma, T)}.
\]

Here, \(k_B T\) is the thermal energy, \(N\) is the number of surface nucleation sites, \(\nu_0\) is the frequency of attempted nucleation events, \(E\) is the elastic modulus, \(\varepsilon\) is the strain rate, and \(\sigma\) is the nucleation stress. \(Q(\sigma, T)\) is the activation free-energy for dislocation nucleation, and \(\Omega\) is the activation volume, defined as \(\Omega(\sigma, T) \equiv -\partial Q(\sigma, T)/\partial \sigma\)|. Thermal activation is
achieved by performing work on the activation volume, and it is proportional to the number of atoms involved in the process. To better understand our yielding behavior, we fit a linearized version of this model to simulation data so that the activation energies and volumes can be determined. The first-order approximation was taken for the stress response such that \( Q(\sigma) = Q^* - \sigma \Omega \), where \( Q^* \) is the activation energy in the absence of stress. The nucleation stress can then be represented by

\[
\sigma = \frac{Q^*}{\Omega} - \frac{k_B T}{\Omega} \ln \frac{k_B T N v_0}{E \varepsilon \Omega},
\]

(13)

With the knowledge that the athermal nucleation stress, \( \frac{Q^*}{\Omega} \), will be approximately the yield stress at 1 K, we can solve Eq. (13) to find the activation energy and volume as a function of temperature. The copper Debye’s frequency of \( 10^{13} \) s\(^{-1} \) was used for a \( v_0 \) value, and since failure occurs along planes in the [001] direction, there were \( N = 60 \) nucleation sites. The tensile modulus, \( E \), was modeled as a function of temperature as well, using a linear interpolation between measured points. The moduli values where the regression range spanned all strain values up to the yield stress were used for the fitting. Results were fit using yielding data at temperatures of 1 K, 75 K, 150 K, 225 K, and 300 K and strain rates of 0.1%/ps, 0.05%/ps, and 0.025%/ps.

The temperature dependent activation volume and activation energy are shown in Fig. 14. Activation energies for multi-mechanism, high-temperature copper yield stress upon the initial stages of oxidation. These results were replicated by using EAM potentials to test the same structures, leading us to conclude that the non-linearity was not unique to COMB potentials. At low temperatures, the oxide layers were found to stiffen the thin-films at lower strain values and soften the films at higher strains, while at high temperatures the oxide layers only softened the copper films. The oxide layers lowered the yield stress by 30%–40%, and embrittled the material such that yield occurred at much lower strains. The cause of the embrittlement was restructuring events within the oxide layers which nucleated defects into the inner copper film before yielding. These results may help explain experimental findings for larger copper nanowires which showed a decreased modulus and yield stress upon the initial stages of oxidation.

In the oxide-free simulations, at higher temperatures, grain formation and an FCC [001] \( \rightarrow \) [111] transition with partial dislocation generation were the preferred yielding mechanisms, while near 0 K an FCC-to-BCC transition dominates yielding behavior. The BCC lattices were oriented with the BCC [110] axis aligned with the FCC-[001] axis. It is possible that this trend is a non-physical artifact of the

IV. CONCLUSIONS

We have used reactive COMB potentials to evaluate the tensile properties of oxide-coated-copper thin films for the first time. Due to computational limitations with the COMB potentials, we studied the effects of the initial oxide structures rather than fully relaxed structures. Structural differences were found between the natively formed oxide, with simulated exposure to oxygen atoms, and the pre-formed, then relaxed, oxide interface. The natively formed oxide layers had lower Cu-O bond densities, lower atomic densities, and a lower Cu:O ratio than the pre-formed layers. Charge distribution plots indicated that a mixture of CuO and Cu2O phases were present at the interface, and structural analysis showed a primarily amorphous crystal structure. It seems that to achieve an atomistically sharp, crystalline interface, either a much longer equilibrium time is needed (>500 ps) or adjustments need to be made to the COMB Cu-O parameters.

The lower Cu-O bond density present in the native oxide layer decreased its modulus relative to the thick oxide simulation, and both oxide layers had effective modulii lower than bulk CuO. Significant variations in modulii values were found over the strain ranges measured. Several of these results were replicated by using EAM potentials to test the same structures, leading us to conclude that the non-linearity was not unique to COMB potentials. At low temperatures, the oxide layers were found to stiffen the thin-films at lower strain values and soften the films at higher strains, while at high temperatures the oxide layers only softened the copper films. The oxide layers lowered the yield stress by 30%–40%, and embrittled the material such that yield occurred at much lower strains. The cause of the embrittlement was restructuring events within the oxide layers which nucleated defects into the inner copper film before yielding. These results may help explain experimental findings for larger copper nanowires which showed a decreased modulus and yield stress upon the initial stages of oxidation.

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COMB parameterization, as it has not been observed in experimental studies. Although the results differ from previous simulation studies, they are supported by the fact that COMB potentials have significantly larger GSFEs than previously studied EAM potentials, giving more similar results to DFT studies in copper. They are further supported by the observation of similar restructuring behavior in tensile simulations of FCC Au nanowires, and the presence of similar restructuring events when using Mishin et al. EAM potentials on our same structures. The FCC-to-BCC yielding mechanism was reinforced by the presence of the oxide layers, as they facilitated the [100] contraction necessary to prevent the formation of a new orientation of FCC grains. This allowed for large portions of the inner-copper film to be transformed to a BCC structure in the thick oxide simulations. In support of previous simulations, the oxide’s effect on yielding behavior can be characterized by a decrease in activation volume necessary for surface defect nucleation. To our knowledge, there currently are no experimental studies to validate these results; hopefully, this manuscript will help to support future experimental works. These results provide a benchmark for further study investigating the effects of oxide layers on metal nanostructures.

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