Supplemental Information

Experimental:

ALD Reaction Conditions

Depositing a thin conformal hard coating on high-aspect ratio structures is non-trivial, with ALD being particularly suitable for these types of coatings as it offers atomic-level control of the depositing species one monolayer at a time (Figure 1c). Figure 1c shows a schematic of this process for an initially uncoated copper pillar whose surface is terminated with oxygen atoms . In the first step (1), a precursor gas is added into an ALD system where the precursor bonds with the oxygen to form a monolayer of the corresponding oxide. The following purge step (2) removes the remaining extra precursor as well as any additional reaction products from the chamber. This surface layer is then functionalized through reaction in a plasma (3) to produce a reactive oxygenated surface . The final step (4) is another purge step to remove the remaining reaction products. This process is repeated until the desired thickness is achieved. All reactions in our process were performed in an Oxford OpAL ALD system (Oxfordshire, UK); whereby 3nm of alumina was deposited with a precursor of trimethyl aluminum (SAFC Hitech, Allentown, PA) and the remaining thickness is titania formed from a titanium tetra-iso-propoxide precursor (SAFC Hitech).

The initial 3nm-thick Al_2O_3 layer was deposited first (1) with a reactant dose of precursor of trimethyl aluminum for 30ms at 120C. This was followed by (2) a 2 second purge followed by (3) a total of 6 seconds in a 300W plasma, 2 seconds for gas stabilization and 4 seconds for plasma power on. Finally, (4) the last purge step also lasted two seconds [1]. This process was repeated until the 3nm layer was complete. The following TiO_2 layer was added with a titanium tetra-iso-propoxide precursor at 200C. The remaining thicknesses of 2nm at pillar diameters, D, 75nm-150nm; 7nm at D~200nm, and 22nm at D ~ 500nm- 1000nm, respectively, were deposited via a process similar to the alumina deposition [2]. In both of these procedures, a remote oxygen plasma functionalized the surface with oxygen atoms such that the surface was identical to the initial conditions. It is expected that oxygen atoms and ozone are the most likely reactive species as there was a showerhead separating the plasma from the substrate.

Results

Methods of Calculating Axial Stress in the Copper Pillar:

In the case where the coating shares load with the copper pillar, we use a simple iso-strain model: $\frac{F}{A_{total}} = \left(A_f + (1 - A_f)\frac{E_{shell}}{E_{pillar}}\right)\sigma_{pillar}$ [3]. Here, F is the applied force, A_{total} is the cross-sectional area of the coated pillar. A_f is the cross-sectional area fraction of the copper pillar or $A_f = {}^{A_{pillar}}\!/_{A_{total}}$, E_{shell} and E_{pillar} are the elastic moduli for the coating and the copper pillar, respectively. This shared load model is most relevant for understanding the stress-state in the copper pillar at small strains, i.e. prior to catastrophic cracking of the coating. On the opposite end of the spectrum, we assume that the coating supports no load, and therefore the stress in the copper pillar is measured by $\sigma_{pillar} = {}^{F}\!/_{A_{pillar}}$ where F is still the applied force and A_{pillar} is the area of the copper pillar only. This model best estimates the stress-state in the copper pillar after the coating has cracked in multiple locations and is effectively "going along for the ride" as it is not capable of supporting any appreciable elastic stresses.

Discussion:

Strengthening from Dislocation Storage

Building upon analytical models for single arm sources [4-6], the general equation for overall shear stress in a small-scale sample is comprised of the lattice friction stress (first term on RHS in Eq. 1), the elastic interactions stress (2nd term on the RHS in Eq. 1), and the line tension stress (last term in Eq. 1):

$$\tau_i = \tau_0 + 0.5\mu b\sqrt{\rho_{tot}} + \frac{\mu b}{4\pi\lambda_i}\ln\left(\frac{\lambda_i}{b}\right), \tag{1}$$

where τ_i is the resolved shear stress for the activation of a single arm dislocation source, τ_0 is the lattice friction stress, μ is the isotropic shear modulus, b is the magnitude of the Burgers vector, and ρ_{tot} is the total dislocation density: material and microstructural parameters with identical applicability in the framework of classical bulk dislocation theory [7]. On the other hand, λ_i is a parameter relevant to single arm sources in pillars, as it represents the shortest distance between the source's pinning point and the free surface within the same elliptical slip plane.

In order to calculate the activation stress for a given nanopillar diameter, we first estimate the number of available single arm sources by following Parthasarathy's model, and by assuming that each dislocation segment represents a single-arm source, the average length of a dislocation segment is equal to the pillar diameter. The estimated number of single arm sources, *n*, can then be represented as:

$$n = \text{Integer}\left[\rho_{tot} \times \frac{\pi D h}{4}\right], \tag{2}$$

where D and h are the pillar diameter and height, and ρ_{tot} is the total dislocation density. The pinning points are then randomly distributed within a pillar, and the shortest length from each pinning point to the pillar surface, λ_i, is calculated.-The stress required to operate the weakest (i.e. longest) glissile dislocation source is taken as the stress required to produce the first strain burst. Statistics were calculated over 100 simulations. For each diameter, 100 simulations were performed, and the average and standard deviation of those results are shown in Figure 6, main text, along with the experimental results from Figure 2, main text. To calculate the resolved shear stress, τ_i, we adopt the model introduced by Parthasarathy *et al.*[6] modified appropriately to suit the <111> orientation of our pillars, i.e. a multiple-slip condition. In such orientations, any one of the 12 equivalent slip systems – as opposed to a single one - can be randomly assigned to a dislocation segment as proposed by Ng and Ngan [5].

It is reasonable to assume that the lattice friction stress is negligible in fcc metals and the shear modulus and the magnitude of the Burgers vector are taken as 44 GPa and 2.55 Å, respectively. Using these quantities, we calculate the stresses at the first strain burst for simulated samples with diameters D ~200, 250, 500, and 1000 nm and 3:1 (*h:D*) aspect ratio, and compare them with the experimental data. We intentionally did not include the samples with diameters smaller than D~200 nm because the plasticity mechanism at such small sizes is governed by dislocation nucleation at the free surfaces at the strain rates used in our experiments [8].

Hoop Stress

In these experiments, the source of the pressure normal to the coating and thus the hoop stress is primarily due to (1) the Poisson expansion of the copper pillar during the nearly elastic compressive loading and (2) the dislocation motion and resulting localized plastic flow of the copper pillar. As has been ubiquitously shown, the stress for dislocation motion and thus plastic flow in pillar compressions is size-dependent, suggesting that the strength for coated pillars may also size-dependent. The size-dependence in coated pillars appears to be reflected in the experimental results seen in Figure 2d and is also seen in other experimental and simulation work [9-11].

Threading Dislocations

Interestingly, in our investigations of initial pillar microstructure, TEM analysis of coated 500nm pillars reveals an extensive network of equally-spaced, ~40nm, threading dislocations originating from the pillar-coating interfaces, as shown in Figure 7. This observation may not be surprising since threading dislocations emanate from misfit dislocations which are typically found at thin film interfaces alleviating the strain across that interface [12]. The observed equilibrium threading dislocation spacing is a result of the balance between the energy required to produce threading dislocations and the resulting relieved elastic energy from the interfacial strain. As a result, the relative thickness of the coating with respect to the pillar diameter determines whether or not the threading dislocations will form. If the coating is too thin, few or no threading dislocations will be created because the elastic strain energy is insufficient to overcome the energy required to produce a misfit dislocation. Analogously, for sufficiently small pillars, the amount of stored elastic energy may be insufficient to drive the formation of dislocations, as consistent with our observations that misfit dislocations are not seen in pillars with $D < 500nm$. However, the lack of threading dislocations may result in an additional internal strain that may influence the pillar deformation resulting in an interesting, yet likely complex problem in smaller pillars. One consequence of threading dislocations in 500nm pillars may be that these threading dislocations weaken the coating, resulting in a smaller increase in hardening relative to that seen in 200nm pillars.

Bauschinger Analytical Model Detail

We take Cu as the representative materials and use it for all material properties. Beginning with the single-source in a dislocation-free plane, we incrementally apply a shear stress at a rate $\Delta\tau = \pm 0.01\tau_{source}$. When the force concentrated at the source reaches $F = \tau_{source} b$, a loop is emitted and two oppositely oriented point segments are introduced into the slip plane at a distance $\delta x = 0.2L$ on either side of the source, where

L is the length of the slip plane. The equilibrium positions of these dislocations are then determined through balance of the Peach-Kohler forces from long-range dislocation interactions and image forces caused by the hard coating. As an approximation, we truncate the image forces to the first image field. The Peach-Kohler force on the i^{th} dislocation in a system of *N* dislocations is given by:

$$F^i = \tau_{app} b - \frac{\mu b^2}{2\pi} \sum_{\substack{n=1 \\ n \neq i}}^{2N} \frac{sign(n,i)}{x_n - x_i}$$

Where we have treated the dislocations as screw-type, b is the Burgers vector and $sign\ (n, i)$ is read as the direction of the force on the i^{th} dislocation by the n^{th} dislocation. The summation is performed over both the real and image dislocations for *2N* total dislocations. Following the calculation of the equilibrium position of the dislocations, the force on the two dislocations closest to the coating is calculated to check if either exceeds their respective coating strength. This condition is:

$$\tau_{app} - \frac{\mu b}{2\pi} \sum_{n=2}^{N} \frac{1}{x_n - x_1} \geq \tau_{coating}$$

If this condition is met, this dislocation escapes through the coating and the equilibrium positions of the remaining dislocations are recalculated. If the condition is not met, the applied stress is incremented until the sum of the applied stress and the back-stresses are larger than the source strength:

$$\tau_{app} - \frac{\mu b}{2\pi} \sum_{n=0}^{N} \frac{1}{x_n} \geq \tau_{source}$$

This process is iterated through loading/unloading and at each stress, the total strain is calculated by the elastic strain given by Hooke's law and the plastic strain that is proportional to the distance swept out by the dislocations:

$$d\varepsilon_{plastic} = \frac{1}{2} b \frac{dA}{V}$$

For *y* indicating the direction normal to the plane and *z* directed out of Figure #, we can take a representative volume, $V = L_x L_y L_z = 3L^2 L_z$, L_z being arbitrary for the 1-dimensional problem. With $dA = L_z dx$, the expression for plastic strain simplifies to

$$d\varepsilon_{plastic} = \frac{1}{6}\frac{b}{L^2}dx$$

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