The Effects of Confined Core Volume on the Mechanical Behavior of Al/a-Si Core-Shell Nanostructures

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ABSTRACT

The mechanical behavior of novel Al/a-Si core-shell nanostructures (CSNs) is studied using instrumented nanoindentation to investigate the role that the confined core volume plays on the mechanical response of these structures. The CSNs are fabricated from truncated hemispherical Al nanodots with 100, 200, and 300 nm base diameters, which are then conformably coated with a-Si. CSNs with the smallest core diameter, and therefore the smallest confined core volume, have a unique load-displacement behavior characterized by nearly complete recovery of deformation beyond the elastic limit, which is enabled by dislocation activities within the confined Al core. In conjunction with this deformation recovery, discontinuous indentation signatures known as “load-drops” and “load-jumps” are observed during loading and unloading, respectively. As the size of the confined core volume increases, these indentation signatures are suppressed and the deformation-resistant properties are reduced. Supporting molecular dynamics simulations show that a smaller core volume results in a larger back-stress developed in the core during indentation, which further correlates with improved dislocation removal from the core after unloading. This complementary experimental and modeling investigation provides insight into the mechanisms that contribute to the unique mechanical properties of Al/a-Si CSNs.

Keywords: Core-shell nanostructure; nanoindentation; deformation-resistant; dislocations; molecular dynamics.

1. Introduction

Nanomaterials and nanostructures are well known to have mechanical properties that greatly differ from that of their bulk counterparts. This includes notable examples such as strengthening mechanisms in nano-grained metals [1-3], multilayer nanolaminate composites with enhanced hardness [4-6], material size effects [7-10], and dislocation starvation and mechanical annealing phenomena [11-13]. These unique mechanical properties provide potential avenues for engineering nanostructures and surfaces with desirable mechanical properties, benefiting such diverse fields as micro/nano-electro-mechanical systems (MEMS/NEMS), nanotribology, and biomedical applications.

Despite this promise of engineering nanostructures with unique mechanical properties, nearly all nanomaterials suffer from an underlying issue that reduces their effectiveness in real applications: permanent plastic deformation during contact loading. This is due to the nanoscale sizes of these structures and the resulting small contact areas during loading, which generates very high contact pressures, even at moderate contact loads. This lack of structural integrity is commonly an issue when nanostructures are used in nano-textured surfaces for low-friction applications [14-16], but is clearly an issue for all nanomaterials subjected to contact loading.

Several authors have reported what they termed “reverse plastic deformation” during nanoindentation experiments on nanoparticles. Gerberich *et al.* studied reversed plastic strain in single-crystal Si nanospheres [17,18], in which partial height recovery of the nanospheres was measured from scanning probe microscopy (SPM) after unloading, as compared to the cumulative residual displacement calculated from the load-displacement data. This mechanical

response was hypothesized to be the result of dislocations retracing their paths due to a high internal back-stress generated during nanosphere compression. Reverse plasticity has also been reported in CoB₂/SiO₂ core-shell nanostructures, although this strain recovery was attributed to magnetic effects in the CoB₂ core [19,20]. It should be noted that the nanostructure recovery observed in these studies is typically not complete and only appears for small deformations, with fracture occurring at larger deformations in some cases.

Complete deformation-resistant behavior has already been identified in a nano-textured surface composed of ~200 nm diameter polycrystalline Al nanodots protruding from an Al thin film, that were then conformably coated with 300 nm of a-Si, producing hemispherical core-shell nanostructures (CSNs) [14]. When subjected to nanoscratch testing, no plastic deformation of the surface was detected, even for contact loads as high as 8,000 μ N, while still maintaining a low coefficient of friction. Nanoindentation experiments on the individual CSNs revealed that the structures possess higher yield strengths than either Al or a-Si, and can also sustain up to 23% engineering strain without fracture [21]. Furthermore, the CSNs display unusual load-displacement behavior with no residual deformation, indicating little or no permanent deformation after unloading. This conclusion was further supported by SPM images showing no structure height change after indentation.

This unique mechanical behavior warrants further research into the underlying mechanisms responsible for the observed deformation resistance. However, the previous fabrication method provides little control over the size, shape, or location of the nanostructures, which convolutes the comparative analysis of multiple structures. To rectify this limitation, a new fabrication

method using electron beam lithography (EBL) has been developed to produce well-ordered arrays of nanostructures. In this study, the origin of the unique mechanical properties of Al/a-Si CSNs is explored through nanoindentation experiments and molecular dynamics (MD) modeling. The results show dislocation mechanisms in the Al core play a substantial role in the mechanical behavior of the CSNs, which is enabled by geometrical confinement of the soft Al core by the hard a-Si shell. In particular, the deformation behavior of these structures is critically dependent on the size of the confined core volume. As the core diameter increases, the mechanical response is significantly altered and the deformation resistance is reduced.

2. Experimental

2.1 Nanostructure Fabrication

EBL and a metal lift-off procedure were employed to fabricate the Al cores of the CSNs. A 4% dilution of 495k MW PMMA, a positive tone electron resist, was spin coated onto a (100) single crystal Si wafer at 3000 rpm. Patterned arrays of holes in the PMMA film were formed by selectively exposing the electron resist using a dedicated electron beam writer (JBX-9300FS, JEOL Ltd.), using 1 nA of current, a 50 kV accelerating voltage, and a beam dose of 775-1000 $\mu\text{C}/\text{cm}^2$. After exposure, the patterns were developed in a 1:3 mixture of methyl isobutyl ketone (MIBK) and isopropyl alcohol (IPA) for 45 s, and then rinsed in pure IPA for 15 seconds. This was followed by a low-pressure oxygen plasma etch to help smooth the edges of the holes opened in the PMMA film. Next, 100 nm of Al was deposited onto the patterned PMMA film using thermal evaporation (Auto 306D, Edwards Vacuum) at a rate of 0.4 nm/s. Finally, the remaining PMMA was selectively removed by immersion in a Remover PG (MicroChem Corp.) bath heated to 75° C for 48 hours, resulting in regular arrays of Al nanodots.

The patterned nanodot arrays were then coated with a-Si using plasma enhanced chemical vapor deposition (PECVD; Plasma-Therm SLR730). The substrate temperature, rf power, and silane flow rate were 250° C, 20 W, and 85 sccm, respectively, during a-Si deposition. Using this fabrication method, Al/a-Si CSNs with core base diameters of 100, 200, and 300 nm, with shell thicknesses of 100 and 300 nm, have been produced.

2.2 Mechanical Characterization

An instrumented nanoindenter (TriboIndenter, Hysitron) was used to characterize the mechanical behavior of the CSNs, primarily using displacement-controlled indentation, which is more sensitive to transient events during indentation [22]. The TriboIndenter features electrostatic force actuation and measures displacements using a capacitive sensing scheme, with a 3 nN force resolution and a 0.02 nm displacement resolution, respectively. A spherical diamond tip of 1 μm radius of curvature was used to indent individual CSNs with a feedback-controlled displacement rate of 3 nm/s while simultaneously measuring the applied force. The relatively large tip radius, as compared to the CSN size, was chosen to provide compression loading to the CSNs, rather than indenting the structures.

An integrated SPM on the TriboIndenter was used to accurately locate and indent individual CSNs, as well as measure nanostructure height before and after indentation. The nanoscale surface topography and morphology of the CSNs were also characterized with scanning electron microscopy (SEM; Nova NanoLab, FEI) and atomic force microscopy (AFM; Dimension Icon, Bruker).

3. Results and Discussion

3.1 CSN Morphology Characterization

The EBL fabrication method produced very uniform arrays of Al nanodots for the cores of the CSNs. Because the nanodots were fabricated with a lift-off technique, all the structures are ~100 nm tall, regardless of base diameter. SEM images of Al nanodots with 100, 200, and 300 nm base diameters are shown in Fig. 1. Based on X-ray diffraction measurements on a similarly prepared Al thin film, the individual nanodots are polycrystalline, with a mixture of (111) and (200) crystallites and a crystallite size of ~25 nm.

The nanodots were then coated with PECVD a-Si to produce arrays of regularly spaced CSNs that are rigidly attached to the underlying Si substrate, shown schematically in Fig. 2, along with a representative AFM image of a CSN with a 100 nm core diameter and 300 nm shell thickness. Note that only the top ~100 nm of the CSN is imaged by the AFM due to the shell skirting between structures.

3.2 Nanoindentation Results

3.2.1 Load-displacement Response

Fig. 3 shows representative load-displacement curves for 20, 40, 60, and 80 nm indents on CSNs with 100 nm diameter cores and 300 nm shell thickness. As can be seen, the indenter displacement returns to zero (or nearly to zero) for all loading conditions, which indicates that very little residual deformation remains after indentation and is consistent with our previous study [21]. As an example, SPM images of a CSN before and after an 80 nm indent are shown in

Fig. 4. After indentation, the measured height of the CSN decreases by 3.4 nm, but the structure morphology remains hemispherical (up to the resolution of the SPM), with no residual impression left from the indenter tip. This substantial deformation recovery beyond the elastic limit is especially remarkable considering the maximum indenter displacement is approximately 20% of the total structure height of ~400 nm.

Several types of indentation response are observed as a function of maximum indenter displacement. For 20 nm indents, the indentation response is either elastic or has a small hysteresis loop, indicating that this loading is at or near the elastic limit of the structures. The 40 nm indents are characterized by a smooth loading curve, but also exhibit a slope inflection during unloading that serves to bring the residual displacement back to zero. At 60 and 80 nm displacements, a large number of discontinuous indentation signatures appear during loading. These signatures, referred to as “load-drops,” represents microscopic events occurring beneath the indenter tip during loading, and are the displacement-control analogs of the pop-in events that are frequently observed in load-controlled nanoindentation experiments. During unloading, “load-jumps” occur in conjunction with a slope inflection. Notably, these anomalous increases in load while the indenter is retracting are an indication of rapid deformation recovery in the CSN.

3.2.2 Origin of the Indentation Signatures

While these indentation signatures are interesting, their origin and the role they play in the novel deformation-resistant properties of the CSNs are not readily apparent. In general, the microscopic origins of the indentation signatures are ambiguous and depend on the type of

material under investigation. These signatures can be the result of dislocation nucleation events and their propagation in metals [23], phase transformations in semiconductors [24], fracture in brittle materials [25], and thin film delamination [26]. For Al/a-Si CSNs, the load-drops/jumps could potentially be attributed to dislocation activities in the Al core, pressure-induced phase transformations in a-Si, and shell fracture/delamination events. Therefore, more detailed analysis is needed to identify the true origin of the indentation signatures.

Multiple repeated indents were performed on individual CSNs to gain insight into the origin of the load-drops/jumps. Load-displacement curves for 4 sequential 80 nm indents on a single CSN are shown in Fig. 5. As can be seen, consistent hardening behavior is observed after each indent. This hardening behavior is significant in that it precludes both shell delamination and shell fracture as the source of the indentation signatures, as these would both elicit a weakening effect in the CSNs. Furthermore, indents were performed on a 300 nm smooth a-Si thin film fabricated with the same process conditions as the a-Si shells used in this study to investigate the existence of pressure-induced phase transformations in the formulation of a-Si. Predicted a-Si phase transformations occur at contact pressures of 8.4 GPa, 16.25 GPa, and 19 GPa, and these phase transformations will appear as a discontinuity during the unloading portion of the load-displacement data [24,27]. As shown in Fig. 6, no evidence of a phase transformation is observed for contact pressures up to ~22 GPa. The elimination of shell delamination, shell fracture, and a-Si phase transformations as potential sources of the load-drops/jumps seen in the load-displacement curves strongly suggests that dislocation-based mechanisms in the Al core are instead responsible.

Further insight into the material deformation behavior can be found from analysis of the load vs. time and indenter displacement vs. time data. A plot of both contact load and indenter displacement vs. time for an 80 nm indent on an individual CSN is shown in Fig. 7. During loading, each drop in contact load corresponds to a forward indenter excursion as the contact stiffness suddenly and discontinuously decreases. More interesting, however, are the indenter signals observed during unloading, where each increase in the contact load correlates with an anomalous indenter retraction. Since this is a displacement-controlled indent, the only way the indenter can retract faster than the specified unloading rate is if something suddenly and unexpectedly pushes back against the indenter. This is a strong indication that the load-jumps during unloading are a result of rapid deformation recovery in the CSNs.

Given the substantial amount of deformation recovery during unloading, it is not reasonable to expect that much of this deformation can be attributed to typically-brittle a-Si. This is especially true for large indentation depths, as there is no evidence to suggest such large recoverable deformations of a-Si should be possible. Since very little residual deformation is observed and the CSNs remain hemispherical after nanoindentation, it is very likely that the harder and stronger a-Si shell is only deformed elastically during nanoindentation, with the primary deformation occurring due to compression of the softer Al core between the harder shell and Si substrate. At 20 nm indentation depth, where the CSNs behave elastically, the indenter is likely only interacting with the a-Si shell due to the relatively large thickness of the shell and the shallow indentation depth. As the indentation depth increases to 40 nm, the Al core is elastically compressed between the shell and the substrate, and during unloading, the elastic recovery correlates with the slope-inflection seen in the load-displacement curve. Further increases in

indentation depth result in plastic deformation within the Al core, as indicated by the load-drops during loading that correspond to the nucleation and propagation of dislocations in the 60 and 80 nm indentations.

With the knowledge that dislocation activities in the Al core play a vital role in the mechanical behavior of these structures, new insights into the mechanisms that enable deformation resistance can be attained. In accordance with our previous hypothesis [21] and that of others [17,18], the existence of reserve plastic deformation depends on the generation of a sufficient back-stress to cause dislocations to retrace their paths or otherwise annihilate during unloading. For CSNs, this back-stress is generated as the confined core volume is compressed between the hard a-Si shell and Si substrate. As the core diameter is increased, the confinement is reduced, which should have an effect on the mechanical behavior of these structures.

3.2.3 Effects of Increasing Confined Core Volume

To test this hypothesis, nanoindentation experiments were conducted on CSNs with 100, 200, and 300 nm core diameters and 300 nm shell thickness, representing different degrees of core confinement. Load-displacement curves for 60 and 80 nm indents on these structures are shown in Fig. 8. For the 60 nm indents, load-drops/jumps are observed for the 100 nm core CSN, as expected. As the core diameter increases, the indentation signatures are at first partially suppressed, as seen for the CSN with the 200 nm core diameter, resulting in a load-displacement response similar to that seen in Fig. 3 for a 40 nm indent on a CSN with a 100 nm diameter core and 300 nm shell thickness. The occurrence of these load-drops/jumps indicates that a sufficient back-stress to trigger dislocation annihilation during unloading can be generated in this structure.

With a further increase in core diameter, the displacement behavior completely changes, with full suppression of the load-drop/jump signatures. In addition, a residual displacement of 12.8 nm is seen in the load-displacement data. Similar results are obtained from the 80 nm indents.

It is worth noting that while core confinement is important for these structures, deformation resistance is not achieved for arbitrary shell thicknesses. Fig. 9 shows load-displacement curves for 80 nm indents on CSNs with 100 nm core diameters and 100 and 300 nm shell thicknesses, as well as SPM images of CSN height before and after indentation. While load-drops/jumps and reverse plastic deformation are present in both curves, more deformation recovery is observed with the 300 nm shell thickness compared to the 100 nm shell thickness. According to the SPM images, the height of the CSN with the 100 nm shell thickness decreases by 10.9 nm, compared to only 3.6 nm for the CSN with the 300 nm shell thickness. As mentioned previously, it is not reasonable to expect that this deformation is localized to within the a-Si shell. Rather, much of the deformations occurs as the soft Al core is compressed between the hard a-Si shell and Si substrate. Since both of these CSNs are indented to a depth of 80 nm, the thinner shell results in higher stress being transmitted to the Al core due to the close proximity of the core to the location of indentation contact, and this higher stress results in more plastic deformation than can be recovered. Clearly, core size, shell thickness, and indentation load/displacement can affect the desirable deformation-resistant properties of Al/a-Si CSNs, which will allow for further optimization of the CSN properties.

3.3 Molecular Dynamics Simulations

To further explore the dynamics of dislocations in the Al core during nanoindentation of CSNs, MD nanoindentation simulations were performed using LAMMPS [28]. All atomic interactions were modeled using the modified embedded atom method (MEAM), which has been shown to effectively model both Al [29] and Si [30], with a specialized Al-Si interatomic potential that also contains combinatorial parameters to model the interactions between Si and Al atoms at the core-shell interface [31]. The simulation domain consists of a single-crystal (001) FCC Al core on a 1 nm rigid substrate of frozen FCC Al atoms, covered by a shell of a-Si, as shown in Fig. 10. Since the substrate is completely rigid, an Al substrate was chosen to provide a commensurate core/substrate interface to prevent the formation of misfit dislocations at the core/substrate interface due to the lattice mismatch between Al and Si. The a-Si shell was constructed by first calculating the number of Si atoms that would be contained in the shell region if it were composed of Si atoms with a diamond cubic crystal structure, and then randomly populating the shell region with this number of Si atoms to form a fully-dense a-Si shell. The potential energy of the system was minimized using a conjugate gradient method with a relative energy tolerance of 10^{-6} , followed by equilibration to 300 K with a Nosé-Hoover thermostat [32] for 30 ps. The biggest limitation to using MEAM to model a-Si is the unrealistic densities obtained from the classical method of slowly quenching a Si melt [30]. To rectify this, prior to equilibration, the density of the a-Si shell was corrected by systematically removing Si atoms that were within 1.5 Å of another Si atom in order to achieve an experimentally validated shell density of 2.28 g/cm³ [33] after equilibration. During indentation, the indenter is modeled as a spherical repulsive potential of 100 nm radius and controlled to move into the CSN a specified depth with a constant velocity of 0.5 Å/ps while maintaining a system temperature of 300 K.

3.3.1 Dislocation Dynamics During Nanoindentation

Dislocation activities within the Al core were visualized using the dislocation extraction algorithm (DXA) [34] within the Open Visualization Tool (OVITO) [35]. Atomistic snapshots of dislocations generated during nanoindentation simulations in both the core of a CSN with a 20 nm diameter core and a 10 nm shell thickness, as well as a 20 nm diameter Al nanodot, are shown in Fig. 11. The dislocations are colored by Burgers' vector, with perfect FCC dislocations in blue, Shockley partials in green, Hirth dislocations in yellow, stair-rod dislocations in purple, and other dislocations colored red. In this illustration, these structures have comparable maximum dislocation densities of $7.02 \cdot 10^{16} \text{ 1/m}^2$ and $1.00 \cdot 10^{17} \text{ 1/m}^2$ for the CSN and Al nanodot, respectively; additional dislocations may be obscured by the visualization perspective. For the CSN, dislocations are first nucleated at the Al/a-Si interface and propagate into the Al core during loading, eventually reaching a maximum dislocation density at the maximum indenter displacement. Upon unloading, the number of dislocations within the core decreases as dislocations are absorbed by the Al/a-Si interface or annihilate through reactions with other dislocations. This process continues even after the indenter loses contact with the structure after unloading, eventually leading to the complete removal of all the dislocations in some circumstances. In comparison, the dislocation content within the Al nanodot is far more stable, with less dislocation annihilation occurring during unloading.

A more detailed look at the underlying dislocation dynamics yields some interesting observations about the behavior of dislocations in these structures. In the CSN, dislocations are first nucleated at the core-shell interface, and the resulting dislocation structure at the maximum indenter

displacement is primarily composed of glissile Shockley partials, as shown in Fig. 12. The high proportionality of mobile dislocations leads to significant egression of dislocations when the stress generated within the core is relieved during unloading, as indicated by the dislocation content within the core 22,000 time steps later. As these dislocations begin to be absorbed by the core-shell interface, the remaining sessile dislocation structures can become destabilized due to reactions with passing mobile dislocation, a phenomenon that has also been documented in MD simulations of amorphous/crystalline nanolaminates [36]. Note that further dislocation annihilation occurs after this time step, eventually leading to the dislocation-free state seen in Fig. 11.

Dislocations in the Al nanodot are instead nucleated at or slightly below the nanodot surface, which is in good agreement with the location of maximum shear stress predicted from contact mechanics theory for sphere-on-sphere contact with radii of 10 nm (nanodot) and 100 nm (indenter) and a contact interference of 2 nm. In contrast to the CSN, more prominent sessile dislocations structures involving Hirth dislocations, Frank dislocations, and Lomer-Cottrell locks are formed within the Al nanodot, as shown in Fig. 13. This disparity in mobile vs. sessile dislocations formed within the two structures is perhaps the result of the difference in dislocation nucleation site, i.e., interface-nucleation in the CSN and body-nucleation in the Al nanodot.

3.3.2 Effects of Core Size on Dislocation Density

To characterize the dislocation content within the Al core at various points during the indentation process, the dislocation densities at maximum indenter depth (full load), immediately after the indenter loses contact with the CSN during unloading (full unload), and at equilibrium after

indenter removal were calculated. Fig. 14 shows the calculated dislocation densities at several different maximum indenter displacements for CSNs consisting of 20 and 30 nm diameter cores, both with 10 nm shell thicknesses, as well as a 30 nm diameter Al nanodot. For the CSN with the 20 nm core diameter, 82% of the nucleated dislocations are removed from the core during unloading of a 9 nm indent, eventually reaching 100% removal at equilibrium. As the indentation depth is increased to 10 nm, fewer dislocations (64%) are removed at full unloading, while still reaching full removal at equilibrium. Finally, for the 11 nm indent, the dislocation removal at full unloading again decreases to 57%; in addition, dislocations are still present in the core volume even at equilibrium, with a residual dislocation density of 11% remaining. As the core diameter increases to 30 nm, dislocations are less readily removed from the core volume during unloading. For this structure, the reduction of dislocation content at equilibrium is 100%, 81%, and 71% for the 9, 10, and 11 nm indents, respectively. Far less dislocation annihilation during unloading is observed in the Al nanodot. Although the nanodot is subjected to lower maximum indenter displacements due to the lack of a shell, the resulting dislocation densities at full load are comparable to those of the CSNs. For these simulations, the amount of dislocation recovery at equilibrium ranges from 53%-61%, depending on indentation depth. Clearly, confinement of the Al core by the a-Si shell correlates with improved dislocation removal during unloading. In addition, smaller confined core volume further correlates with improved dislocation removal, which supports our hypothesis that core confinement is a critical component to the deformation-resistant properties of Al/a-Si CSNs.

3.3.3 Back-stress Calculations

The stress state in the core of the CSNs during nanoindentation was also studied. Since the stress within the Al core is inhomogeneous due to the CSN shape and tip curvature, this was characterized by defining a volume-weighted state of stress for the entire core and tracking this value as a function of time during nanoindentation. In LAMMPS, atomic stress is actually calculated using an energy equation [37], meaning that the computed quantity actually has units of stress·volume. As a result, the actual per-atom stress would be obtained by dividing the computed quantity by the per-atom volume to calculate a true stress. However, the volume of an individual atom is ill-defined in a deformed solid. To resolve this limitation, a global state of stress within the core was calculated by first computing the per-atom stress tensor (which has units of stress·volume) every 500 time steps, summing the value of each component over all atoms in the core, and then dividing these summed components by the total core volume to produce a volume-weighted global stress tensor. Finally, the components of the global stress tensor were used to calculate the von Mises stress in the core. Of particular interest is the residual stress that the core relaxes to after unloading, which can be interpreted as the back-stress generated within the core. Plots of von Mises stress vs. time for 10 nm indents on CSNs with both 20 nm and 30 nm core diameters are shown in Fig. 15. As can be seen, a substantially larger back-stress is generated in the CSN with the 20 nm core (208 MPa) compared to the CSN with the 30 nm core (62 MPa). The concurrence of increased back-stress and improved dislocation annihilation in the CSN with the 20 nm core strongly indicates that the removal of dislocation from the core is mediated by the higher residual stress developed in these structures.

3.3.4 Broader Implications

The MD simulations performed here provide a substantial improvement in the understanding of the mechanisms that contribute to the novel mechanical behavior of Al/a-Si CSNs. However, in this initial investigation, several aspects of the real-world CSNs were not considered in the models. Most notably, the models use a single-crystal Al core, whereas the as-fabricated Al cores are polycrystalline, with a grain size on the order of 25 nm. Based on the grain size, each 100 nm diameter Al core likely contains less than 25 grains, and the grain boundaries themselves can ostensibly act as sources for heterogeneous dislocation nucleation [38,39]. The annihilation mechanisms determined from this study likely very well describe the behavior of dislocations that are nucleated at the core-shell interface in grains on the surface of the Al core. However, for dislocations that are heterogeneously nucleated in the interior grains of the core far from the core-shell interface, the grain boundaries can act to obstruct dislocation motion and prevent the dislocations from annihilating at the core-shell interface. In this case, annihilation of dislocations may potentially be achieved by reverse dislocation motion enabled by the stress fields generated by dislocations piling up in front of grain boundaries, which has been observed in ultrafine-grained Al during *in-situ* TEM experiments [40]. Because of the small grain size (~500 nm, which is substantially larger than the grain size of the cores of the CSNs), the magnitude of reverse motion was large enough to result in dislocation annihilation at the original grain boundary source. It is plausible that such a mechanism could occur in the CSNs, with the dislocations that nucleate and propagate within interior grains moving back and annihilating at the nucleation source under the generated back-stress.

In consideration of MD length scales, there are significant computational challenges in modeling the polycrystalline structure of the CSN cores with 25 nm grains in order to capture similar

deformation mechanisms to the experiments. This is because the deformation mechanisms could change with grain size at nanoscale. The well-known Hall-Petch strengthening mechanism predicts an increase in material strength with decreasing grain size due to dislocation pile-ups at grain boundaries. However, this behavior breaks down when the grain size is below a critical value (typically in the range of 10-50 nm [41]) and transitions to a so-called “inverse Hall-Petch” regime where material softening with decreasing grain size is observed. Below this critical grain size, dislocation nucleation events are largely suppressed [42], and the mechanical behavior is dominated by grain boundary sliding [43]. MD simulations of nanocrystalline Al show that the critical grain size is less than 18 nm [44], which is less than the 25 nm Al core grain size in the fabricated CSNs. This means that simulations of CSNs with polycrystalline cores having grain sizes smaller than 18 nm will be modeling a situation that is not consistent with our experiments. However, an MD simulation of a CSN with a realistic core grain size (~25 nm) and enough grains to form at least one interior grain will require a core diameter of at least 75 nm plus addition shell thickness. A simulation of this size requires substantial computational resources that are beyond general accessibility.

In addition to the polycrystalline core structure, the as-fabricated Al cores are not expected to be pristine and should have a non-zero initial dislocation density, potentially including misfit dislocations at the core/substrate interface due to the lattice mismatch between Al and Si. Furthermore, there is an interest in how the amorphous/crystalline interphase region at the core/shell interface affects the underlying dislocation dynamics in the CSNs. More sophisticated and larger scale MD simulations investigating the effects of more realistic polycrystalline Al cores on Si substrates, non-zero initial dislocation densities, and the core/shell interphase

structure will be developed, as well as multiscale simulations using the coupled atomistics and discrete dislocation (CADD) method [45], which will allow access to more experimentally relevant length and time scales.

4. Conclusions

Nanoindentation experiments were performed to investigate the origin of the unique mechanical behavior observed in Al/a-Si CSNs. The results show that confinement of Al core, and particularly the size of confined core volume, are critically important for the deformation-resistant properties of these structures. Based on the indentation signatures exhibited by the CSNs with the smallest core diameter, the deformation behavior is mediated by dislocation activities within the confined core, with the deformation recovery resulting from dislocations retracing their paths or otherwise annihilating due to a back-stress generated during unloading. As the size of the confined core volume increases, the magnitude of this back-stress decreases, and deformation resistance is eventually completely suppressed as a result. Complimentary MD simulations show that smaller core diameters correlate with both a larger back-stress being developed and improved dislocation removal during unloading. These findings clarify the mechanisms that contribute to the desirable properties of Al/a-Si CSNs so that they can be designed to be effectively used in applications where the mechanical integrity of nanostructures is important.

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- [1] R.W. Armstrong, 60 years of hall-petch: Past to present nano-scale connections, *Mater. Trans.* 55 (2014) 2-12.
- [2] C.S. Pande, K.P. Cooper, Nanomechanics of Hall-Petch relationship in nanocrystalline materials, *Prog. Mater. Sci.* 54 (2009) 689-706.
- [3] K.E. Aifantis, A.A. Konstantinidis, Hall-Petch revisited at the nanoscale, *Mater. Sci. Eng. B.* 163 (2009) 139-144.
- [4] I.N. Mastorakos, A. Bellou, D.F. Bahr, H.M. Zbib, Size-dependent strength in nanolaminate metallic systems, *J. Mater. Res.* 26 (2011) 1179-1187.
- [5] A. Misra, R.G. Hoagland, Plastic flow stability of metallic nanolaminate composites, *J. Mater. Sci.* 42 (2007) 1765-1771.
- [6] N. Chawla, D.R.P. Singh, Y.-. Shen, G. Tang, K.K. Chawla, Indentation mechanics and fracture behavior of metal/ceramic nanolaminate composites, 43 (2008) 4383-4390.
- [7] A.T. Jennings, J.R. Greer, Heterogeneous dislocation nucleation from surfaces and interfaces as governing plasticity mechanism in nanoscale metals, *J. Mater. Res.* 26 (2011) 2803-2814.
- [8] D. Mordehai, M. Kazakevich, D.J. Srolovitz, E. Rabkin, Nanoindentation size effect in single-crystal nanoparticles and thin films: A comparative experimental and simulation study, *Acta Materialia.* 59 (2011) 2309-2321.
- [9] W. Wang, Y. Zhong, K. Lu, L. Lu, D.L. McDowell, T. Zhu, Size effects and strength fluctuation in nanoscale plasticity, *Acta Materialia.* 60 (2012) 3302-3309.
- [10] S.M. Han, T. Bozorg-Grayeli, J.R. Groves, W.D. Nix, Size effects on strength and plasticity of vanadium nanopillars, *Scr. Mater.* 63 (2010) 1153-1156.
- [11] W.D. Nix, J.R. Greer, G. Feng, E.T. Lilleodden, Deformation at the nanometer and micrometer length scales: Effects of strain gradients and dislocation starvation, *Thin Solid Films.* 515 (2007) 3152-3157.
- [12] K.J. Hemker, W.D. Nix, Nanoscale deformation: Seeing is believing, *Nature Materials.* 7 (2008) 97-98.
- [13] Z.W. Shan, R.K. Mishra, S.A. Syed Asif, O.L. Warren, A.M. Minor, Mechanical annealing and source-limited deformation in submicrometre- diameter Nicrystals, *Nature Materials.* 7 (2008) 115-119.
- [14] B.D. Morton, H. Wang, R.A. Fleming, M. Zou, Nanoscale Surface Engineering with Deformation-resistant Core-shell Nanostructures, *Tribology Letters.* 42 (2011) 51-8.

- [15] N.S. Tambe, B. Bhushan, Micro/nanotribological characterization of PDMS and PMMA used for BioMEMS/NEMS applications, 105 (2005) 238-247.
- [16] B. Bhushan, H. Liu, Micro/nanoscale tribological and mechanical characterization for MEMS/NEMS, 5343 (2004) 194-206.
- [17] W.W. Gerberich, W.M. Mook, C.R. Perrey, C.B. Carter, M.I. Baskes, R. Mukherjee, A. Gidwani, J. Heberlein, P.H. McMurtry, S.L. Girshick, Superhard silicon nanospheres, J. Mech. Phys. Solids. 51 (2003) 979-992.
- [18] W.W. Gerberich, W.M. Mook, M.J. Cordill, C.B. Carter, C.R. Perrey, J.V. Heberlein, S.L. Girshick, Reverse plasticity in single crystal silicon nanospheres, Int. J. Plast. 21 (2005) 2391-2405.
- [19] A. Rinaldi, M. Correa-Duarte, V. Salgueirino-Maceira, S. Licoccia, E. Traversa, A. Davila-Ibanez, P. Peralta, K. Sieradzki, Elastic properties of hard cobalt boride composite nanoparticles, Acta Materialia. 58 (2010) 6474-6486.
- [20] A. Rinaldi, S. Licoccia, E. Traversa, K. Sieradzki, P. Peralta, A. Davila-Ibanez, M. Correa-Duarte, V. Salgueirino, Radial inner morphology effects on the mechanical properties of amorphous composite cobalt boride nanoparticles, Journal of Physical Chemistry C. 114 (2010) 13451-13458.
- [21] W. Tidwell, D. Scott, H. Wang, R. Fleming, M. Zou, Nanoindentation study of deformation-resistant Al/a-Si core-shell nanostructures, Acta Materialia. 59 (2011) 6110-16.
- [22] O.L. Warren, S.A. Downs, T.J. Wyrobek, Challenges and interesting observations associated with feedback-controlled nanoindentation, 95 (2004) 287-296.
- [23] J. Li, K.J. Van Vliet, T. Zhu, S. Yip, S. Suresh, Atomistic mechanisms governing elastic limit and incipient plasticity in crystals, Nature. 418 (2002) 307-310.
- [24] V. Domnich, Y. Gogotsi, S. Dub, Effect of phase transformations on the shape of the unloading curve in the nanoindentation of silicon, Appl. Phys. Lett. 76 (2000) 2214-2214.
- [25] J.S. Field, M.V. Swain, R.D. Dukino, Determination of fracture toughness from the extra penetration produced by indentation-induced pop-in, J. Mater. Res. 18 (2003) 1412-1419.
- [26] C. Han, C. Huang, B. Wu, J. Lin, The nanoindentation applied to predict the interface delamination for the C/amorphous Si composite film, J. Appl. Phys. 106 (2009) 083517.
- [27] M. Durandurdu, D. Drabold, Ab initio simulation of first-order amorphous-to-amorphous phase transition of silicon, Physical Review B. 64 (2001) 014101.
- [28] S. Plimpton, Fast Parallel Algorithms for Short-Range Molecular Dynamics, J. Comput. Phys. 517 (1995) 1-19.

- [29] M.I. Baskes, Modified embedded-atom potentials for cubic materials and impurities, *Phys Rev B Condens Matter*. 46 (1992) 2727-2742.
- [30] S.J. Cook, P. Clancy, Comparison of semi-empirical potential functions for silicon and germanium, *Phys Rev B Condens Matter*. 47 (1993) 7686-7699.
- [31] B. Jelinek, S. Groh, M.F. Horstemeyer, J. Houze, S.G. Kim, G.J. Wagner, A. Moitra, M.I. Baskes, Modified embedded atom method potential for Al, Si, Mg, Cu, and Fe alloys, *Physical Review B: Condensed Matter & Materials Physics*. 85 (2012) 1-18.
- [32] W.G. Hoover, Canonical dynamics: Equilibrium phase-space distributions, *Phys Rev A*. 31 (1985) 1695-1697.
- [33] J. Custer, M.O. Thompson, D. Jacobson, J. Poate, S. Roorda, W. Sinke, F. Spaepen, Density of amorphous Si, *Appl. Phys. Lett.* 64 (1994) 437-439.
- [34] A. Stukowski, V.V. Bulatov, A. Arsenlis, Automated identification and indexing of dislocations in crystal interfaces, *Modell Simul Mater Sci Eng*. 20 (2012).
- [35] A. Stukowski, Visualization and analysis of atomistic simulation data with OVITO-the Open Visualization Tool, *Modell Simul Mater Sci Eng*. 18 (2010).
- [36] Y. Wang, J. Li, A.V. Hamza, T.W. Barbee Jr, Ductile crystalline-amorphous nanolaminates, *Proc. Natl. Acad. Sci. U. S. A.* 104 (2007) 11155-11160.
- [37] A.P. Thompson, S.J. Plimpton, W. Mattson, General formulation of pressure and stress tensor for arbitrary many-body interaction potentials under periodic boundary conditions, *J. Chem. Phys.* 131 (2009) 154107.
- [38] H. Van Swygenhoven, M. Spaczer, A. Caro, Microscopic description of plasticity in computer generated metallic nanophase samples: a comparison between Cu and Ni, *Acta Materialia*. 47 (1999) 3117-3126.
- [39] M. Tschopp, D. McDowell, Grain boundary dislocation sources in nanocrystalline copper, *Scr. Mater.* 58 (2008) 299-302.
- [40] F. Momprou, D. Caillard, M. Legros, H. Mughrabi, In situ TEM observations of reverse dislocation motion upon unloading in tensile-deformed UFG aluminium, *Acta Materialia*. 60 (2012) 3402-3414.
- [41] H. Conrad, J. Narayan, On the grain size softening in nanocrystalline materials, *Scr. Mater.* 42 (2000) 1025-1030.
- [42] V. Yamakov, D. Wolf, S. Phillpot, A. Mukherjee, H. Gleiter, Deformation-mechanism map for nanocrystalline metals by molecular-dynamics simulation, *Nature materials*. 3 (2004) 43-47.

- [43] H. Van Swygenhoven, P. Derlet, A. Hasnaoui, Atomic mechanism for dislocation emission from nanosized grain boundaries, *Physical Review B*. 66 (2002) 024101.
- [44] V. Yamakov, D. Wolf, S. Phillpot, A. Mukherjee, H. Gleiter, Deformation mechanism crossover and mechanical behaviour in nanocrystalline materials, *Philosophical magazine letters*. 83 (2003) 385-393.
- [45] B. Shiari, R.E. Miller, W.A. Curtin, Coupled atomistic/discrete dislocation simulations of nanoindentation at finite temperature, *Journal of engineering materials and technology*. 127 (2005) 358-368.