Material Dimensionality Effects on the Nanoindentation Behavior of Al/a-Si Core-Shell Nanostructures

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ABSTRACT

The nanoindentation behavior of hemispherical Al/a-Si core-shell nanostructures (CSNs), horizontally-aligned Al/a-Si core-shell nanorods (CSRs) with various lengths, and an Al/a-Si layered thin film has been studied to understand the effects of geometrical confinement of the Al core on the CSN deformation behavior. When loaded beyond the elastic limit, the CSNs have an unconventional load-displacement behavior with no residual displacement after unloading, resulting in no net shape change after indentation. This behavior is enabled by dislocation activities within the confined Al core, as indicated by discontinuous indentation signatures (load-drops and load-jumps) observed in the load-displacement data. When the geometrical confinement of the core is slightly reduced, as in the case of CSRs with the shortest rod length, the discontinuous indentation signatures and deformation resistance are heavily reduced. Further decreases in core confinement result in conventional nanoindentation behavior, regardless of geometry. Supporting molecular dynamics simulations show that dislocations nucleated in the core of a CSN are more effectively removed during unloading compared to CSRs, which supports the hypothesis that the unique deformation resistance of Al/a-Si CSNs are enabled by 3-dimensional confinement of the Al core.

Keywords: Core-shell nanostructure; nanoindentation; core confinement; dislocations; molecular dynamics.

1. Introduction

It is well known that the mechanical properties of nanostructures and thin films can differ greatly from those of their bulk counterparts. As the critical dimension of these structures decreases below the sub-micron length scale, the mechanical behavior becomes much more dependent on the dynamics of the included dislocations, leading to a host of effects that are typically not observed in bulk materials. This includes not only the familiar Hall-Petch strengthening mechanism in nano-grained metals [1-3], but also more unusual material behaviors such as size effects [4-6], dislocation starvation [7,8], and mechanical annealing phenomena [9]. Utilizing these unique mechanical properties allows for the design and fabrication of engineered nanostructures and surfaces that can potentially benefit a number of micro- and nanomechanical applications.

Currently, nanostructures are seldom used in applications that rely on significant contact interactions. Due to the nanoscale sizes of these materials and the resulting small contact areas, very high contact pressures can be generated, resulting in permanent plastic deformation of the nanostructures at even the moderate loads experienced in micro- and nano-systems. However, as a potential solution to this issue, deformation-resistant behavior has been identified in several different nanomaterials. Reverse plastic strains in response to compression loading have been observed in pristine, single-crystal Si nanospheres [10,11], which were attributed to dislocations retracing their paths and annihilating during unloading. $\text{CoB}_2/\text{SiO}_2$ core-shell nanostructures have been shown to also exhibit similar reverse plasticity [12,13]. In both materials, the deformation recovery is typically incomplete and is limited to small deformations. Notably, complete deformation resistance has been demonstrated in certain core/shell materials. Ag/SiO_2

core-shell nanowires have been shown to have enhanced fracture resistance and nearly complete shape restoration after bending deformation, even up to bending deflections approaching 90° [14]. This behavior was only observed in the core-shell nanowires, and not in identically prepared Ag nanowires and hollow SiO_2 nanotubes, which indicates that this behavior is explicitly tied to the core-shell structure.

Al/a-Si core-shell nanostructures (CSNs), composed of a nanotextured Al thin film coated with a conformal shell of a-Si, have also been shown to have deformation resistant properties [15]. When loaded beyond the elastic limit, the CSNs have an unconventional load-displacement behavior with no residual displacement after unloading, resulting in no net shape change after indentation. This was theorized to be the result of confinement of the soft Al core within the hard a-Si shell. Furthermore, surfaces textured with these CSNs are found to have superior tribological and deformation-resistant properties compared to Al nanodots and single-crystal Si [16]. When subjected to nanoscratch testing with a $100\ \mu\text{m}$ diamond tip, the CSN-textured surfaces had both a lower coefficient of friction and no observable surface deformation, even for contact loads as high as $8000\ \mu\text{N}$.

The idea that material “dimensionality” can affect the mechanical behavior of materials with sub-micron dimensions was studied by Mordehai *et al.*, who performed indentation experiments on several different Au nanomaterials, including symmetric single-crystal nanoparticles, laterally-elongated nanostructures, and thin films [17]. They found that the mechanical behavior of the nanoparticles was dominated by dislocation annihilation events at the free surfaces of the nanoparticles, while indentation of the thin films resulted in dislocation pile-up beneath the

indenter. Furthermore, the laterally-elongated structures exhibited an intermediate behavior, due to competition between dislocation annihilation at free surfaces and the formation of sessile dislocation structures.

With this knowledge that material dimensionality can affect the mechanical behavior of small-scale structures, it is therefore of interest to determine how changes in the dimensionality of the Al core will influence the deformation resistant properties of Al/a-Si CSNs. In this study, the role of geometric dimensionality on the mechanical behavior of several different geometries of nanostructures is assessed. Specifically, this includes hemispherical Al/a-Si CSNs, horizontally-aligned Al/a-Si core-shell nanorods (CSRs) of various lengths, and an Al/a-Si layered thin film, which represent 3-, 2-, and 1-dimensional confinement of the Al core, respectively. The results show that the hemispherical CSNs are deformation resistant, with nearly complete deformation recovery after indentation, even when loaded beyond the elastic limit. This deformation resistance is found to be enabled by the 3-dimensional confinement of the Al core in this structure. As this confinement is reduced, more conventional indentation behavior is observed with permanent residual deformation of the nanostructures.

2. Experimental

2.1 Nanostructure Fabrication

Patterned arrays of Al nanodots and horizontally-aligned Al nanorods were fabricated using electron beam lithography (EBL) and a metal lift-off procedure. First, 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. An electron beam writer (JBX-9300FS, JEOL Ltd.) was used to selectively expose

the electron resist using 1 nA of current, a 50 kV accelerating voltage, and a beam dose of 1000 $\mu\text{C}/\text{cm}^2$. After exposure, the sample was 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, resulting in patterned arrays of holes in the PMMA film. Next, 100 nm of Al was deposited onto the patterned PMMA film using thermal evaporation (Auto 306D, Edwards Vacuum) with a deposition 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. The end result is patterned arrays of Al nanostructures (nanodots and horizontally-aligned nanorods) that are rigidly attached to the Si substrate. Using this fabrication method, hemispherical Al nanodots with 100 nm diameters and horizontally-aligned Al nanorods with diameters of 100 nm and lengths of 100 nm, 500 nm, and 10 μm were fabricated. A schematic of the rod geometry is shown in Fig. 1; note that the specified rod length excludes the hemispherical end-caps of each rod. A 100 nm Al thin film was also fabricated with thermal evaporation using the same deposition parameters as in the EBL procedure.

The patterned nanostructure arrays and Al thin film were then coated with 300 nm of a-Si using plasma enhanced chemical vapor deposition (PECVD; SLR730, Plasma-Therm). The substrate temperature, rf power, and silane flow rate were 250° C, 20 W, and 85 sccm, respectively, during a-Si deposition. This results in 3 different geometries of Al/a-Si nanostructures, with different levels of core confinement: hemispherical CSNs, in which the Al core is axisymmetrically confined by the a-Si shell and by the Si substrate; CSRs, which have reduced core confinement along the longitudinal axis of the rod; and an Al/a-Si layered thin film, where the Al layer is only

confined between the Si substrate and the a-Si film, with no lateral confinement. These 3 geometries are shown schematically in Fig. 2.

2.2 Mechanical Characterization

An instrumented nanoindenter (TriboIndenter, Hysitron) was used to characterize the mechanical behavior of the nanostructures, primarily using displacement-controlled indentation, which is more sensitive to transient events during indentation than load-controlled indentation [18]. The nanoindenter utilizes electrostatic force actuation and a capacitive displacement-sensing scheme, with a 3 nN force resolution and a 0.02 nm displacement resolution, respectively. The structures were indented with a feedback-controlled displacement rate of 3 nm/s while simultaneously measuring the applied force, using a conical diamond tip of 1 μm tip radius of curvature. A large tip radius, compared to a more conventional Berkovich indenter, was chosen to provide compression loading to the CSNs and CSRs, rather than indenting the structures.

The nanoscale surface topography and morphology of the nanostructures were characterized with a combination of scanning electron microscopy (SEM; Nova NanoLab, FEI), atomic force microscopy (AFM; Dimension Icon, Bruker), and an integrated scanning probe microscope (SPM) on the nanoindenter using the same 1 μm tip.

3. Results and Discussion

3.1 Nanostructure Morphology Characterization

Using the EBL fabrication method, very uniform arrays of Al nanodots and nanorods were fabricated for the cores of the CSNs and CSRs, respectively. SEM micrographs of 100 nm

diameter Al nanodots and 100 nm, 500 nm, and 10 μm Al nanorods are shown in Fig. 3. The Al nanostructures are polycrystalline, with a mixture of (111) and (200) crystallites, based on X-ray diffraction measurements of a similarly prepared Al thin film. Deposition of a-Si on these nanostructures results in a conformal shell on the nanostructures, as seen in SEM images in Fig. 4. Due to the conformal nature of the coating, the lateral dimensions of the visible portion of the individual nanostructures measured from the SEM images uniformly increases by 300 nm for both the CSNs and the CSRs, with only the top ~ 100 nm of the structure protruding from the surface. The diameter of the CSNs increases to 400 nm, while the width of the CSRs increases to 400 nm, regardless of core length, and the length of the CSRs increases by 300 nm compared to the lengths of Al nanorods. Some small-scale roughness is evident in the shell morphology, as seen in the AFM images in Fig. 5, but since it is substantially smaller than the tip radius used during nanoindentation, it is not expected to interfere with the mechanical characterization.

3.2 Nanoindentation Measurements

3.2.1 Deformation Resistant CSNs

Nanoindentation experiments were performed to characterize the mechanical response of hemispherical CSNs to compression loading. Several different types of mechanical response are observed as function of indentation depth, as can be seen from load-displacement curves for 20, 40, 60, and 80 nm displacement-controlled indentations in Fig. 6. The 20 nm indentation has an indentation response that is either elastic or a small hysteresis loop, which indicates that this displacement is at or just beyond the elastic limit of the CSN. The 40 nm indentation has a smooth loading curve, as well as a smooth unloading curve with a slope inflection that brings the indenter displacement back to zero. At the highest indentation displacements of 60 and 80 nm, a

large number of discontinuous indentation signatures, called load-drops and load-jumps, are evident during loading and unloading, respectively, as well as a slope inflection during unloading similar to that seen in the 40 nm indent. As can be seen, the indenter displacement returns to zero (or nearly to zero) regardless of the applied maximum indenter displacement, which indicates that very little residual deformation remains after indentation. In light of the fact that for the 80 nm indents, the maximum indentation depth is 20% of the total structure height of 400 nm, this deformation resistance is especially notable and is consistent with previously reported measurements on Al/a-Si nanostructures fabricated from a nanotextured Al thin film [15,16].

The observed indentation signatures correspond to micro- or nanoscale events happening beneath the indenter tip and are analogous to the pop-in/pop-out events commonly seen in load-controlled nanoindentation experiments. The origin of these signatures depends heavily on the type of material being investigated and can be the result of a variety of distinct mechanisms, including dislocation nucleation and propagation events in metals [19,20], phase transformations in semiconductors [21], cracking in brittle materials [22], and thin film delamination [23]. However, the latter three mechanisms can be discounted as a potential source of the indentation signatures observed in Al/a-Si CSNs. Multiple repeated indents on individual CSNs show consistent hardening behavior after each subsequent indent, as shown in Fig. 7 for 80 nm displacement-controlled indents, which precludes both cracking of the a-Si film or delamination at the Al/a-Si interface as the source of the indentation signatures. If such cracking or delamination occurred, subsequent indents would result in further crack growth or delamination, which would elicit a weakened response in the CSNs. This conclusion is further supported by high resolution SEM images of focused ion beam (FIB) milled cross-sections of an unindented

CSN and a CSN that has been subjected to 4 sequential 1000 μN load-controlled indentations, shown in Fig. 8. In comparison to the unindented CSN, the apex of the indented nanostructure is slightly flattened; however, it should be noted this CSN was indented to almost twice the maximum contact load than the CSN characterized in Fig. 7. Even at this much larger contact load, no evidence of shell delamination or crack formation is observed. In addition, nanoindentation experiments on a smooth a-Si thin film showed no evidence of a pressure-induced phase transformation up to an estimated contact pressure of ~ 22 GPa.

Since shell fracture, shell delamination, and a-Si phase transformations have all been eliminated as potential sources of the indentation signatures seen in the load-displacement curves, this strongly suggests that dislocation activities within the Al core are responsible. The hardening behavior that is observed upon repeated indentation further suggests that dislocations play a significant role in the mechanical behavior of CSNs, as it is consistent with strain hardening. It is hypothesized that the 3-dimensional confinement of the Al core in the hemispherical CSNs creates conditions that are favorable to allow dislocations that are generated in the Al core during loading to retrace their paths or otherwise annihilate during unloading. Structures with reduced core confinement, namely horizontally aligned CSRs and layered thin films, should display different mechanical behavior as the core confinement is decreased.

3.2.2 Effects of Decreased Core Confinement

Nanoindentation experiments were conducted on CSRs with a core length of 100 nm to test this hypothesis. The elongated core of this structure breaks the axisymmetric core confinement of the CSNs, which we define as 2-dimensional core confinement due to the additional core volume

along the longitudinal axis of the rod. A load-displacement curve for an 80 nm displacement-controlled indentation on a CSR is shown in Fig. 9, along with an AFM image of the structure morphology after indentation. The load signatures seen in the load-displacement data of the CSNs are still evident in the CSR, but the number and magnitude are significantly changed. For example, in the 80 nm indent in Fig. 6, approximately 9 load-drops and 8 load jumps are observed, with average magnitudes of 13.7 μN and 10.7 μN , respectively. In comparison, approximately 4 load-drops and 5 load-jumps are seen in Fig. 9(b), with the indentation signature populations dominated by a single, large magnitude signature, along with several much smaller secondary load signatures. During loading, a large load-drop with a magnitude of 63.2 μN occurs near the maximum indenter displacement, as well as 3 other load-drops with an average magnitude of 1.5 μN . Similarly, during unloading, a 30.2 μN load-jump occurs in addition to 4 other load-jumps with an average magnitude of 9.4 μN . In addition, the indenter displacement no longer returns to zero during unloading and residual deformation of the structure is clearly seen from the AFM image, meaning that the CSRs are not deformation resistant.

Multiple repeated indents on a single CSR results in an increase in maximum indentation load after each indentation, as seen in the load-displacement curves for 4 sequential indents on a CSR in Fig. 10. Although this behavior was attributed to strain hardening in the CSNs, the residual deformation on the CSRs after indentation (Fig. 9(b)) results in an increase in contact area for each subsequent indentation, which can also explain the increase in maximum indentation load for multiple indentations. Even so, the presence of load-drops and load-jumps suggests that dislocations activities within the confined Al core of the CSR still play a key role on the mechanical behavior, but the reduced confinement perhaps inhibits the ability of dislocations to

annihilate during unloading. To further explore this, nanoindentation experiments were also performed on CSRs with core lengths of 500 nm and 10 μm , as well as an Al/a-Si thin film. Representative load-displacement curves for 80 nm displacement-controlled indents on all 5 geometries, including the hemispherical CSNs and the 100 nm CSRs, are shown in Fig. 11. As previously noted, the CSN has an unconventional mechanical response characterized by numerous discontinuous indentation signatures and deformation-resistant behavior as indicated by zero residual displacement after unloading. When the confinement of the Al core is slightly reduced, as in the 100 nm CSR, the number and magnitude of the observed indentation signatures are heavily reduced, along with the deformation resistance. As the core confinement is reduced further, however, there is a sharp transition in the mechanical behavior. The 500 nm and 10 μm CSRs, as well as the layered thin film, all have a more conventional load-displacement response, with no indentation signatures observed during loading and unloading and a substantial residual displacement evident in the load-displacement curve. This residual displacement accompanies the residual impressions left on the structures after indentation, as shown in SPM images in Fig. 12.

Analysis of the contact stiffness provides further insights into the mechanical behavior of these structures. A plot of contact stiffness vs. maximum indentation depth for all 5 geometries is shown in Fig. 13. For the CSNs, the contact stiffness increases with indentation depth up to 60 nm, at which point it becomes practically constant. Combined with the CSN load-displacement curves in Fig. 6, this trend provides information about the evolution of the indentation response of the CSNs with increasing indentation depth. For the 20 nm indents, where the CSNs behave elastically, the indenter is only interacting with the a-Si shell due to the thickness of the shell and

the shallow depth of the indent. When the indentation depth increases to 40 nm, the contact stiffness increases as the Al core begins to be elastically compressed between the a-Si shell and the Si substrate. During unloading, this elastic recovery coincides with the slope inflection that is observed in the load-displacement data. At 60 and 80 nm indentation depths, the contact stiffness reaches a maximum value that is largely independent of indentation depth. At these depths, the Al core begins to be plastically deformed, resulting in the nucleation and propagation of dislocations which are evident by the load-drops and load-jumps during loading and unloading, respectively. Similar contact stiffness behavior is also observed in the 100 nm CSRs, which also show some evidence of dislocation activities during indentation, as noted in Fig. 9 and Fig. 10.

The contact stiffnesses of the 500 nm CSRs, 10 μ m CSRs, and layered thin film, however, all increase linearly with indentation depth, with values that generally overlap. In effect, the longer CSRs have a mechanical response that is largely indistinguishable from that of the layered thin film geometry. Moreover, the transition from the deformation-resistant behavior in the CSNs to the conventional indentation behavior of the layered thin films occurs abruptly, i.e., when the 3-dimensional core confinement of the CSN is reduced slightly, as in the 100 nm CSR, the deformation resistance and the accompanying indentation signatures are heavily reduced. More drastic reductions in core confinement result in a conventional indentation response, regardless of the dimensionality of the core confinement. As a result, it is very clear that 3-dimensional core confinement plays a critical role in the novel deformation-resistant behavior of Al/a-Si CSNs.

3.3 Molecular Dynamics (MD) Simulations

Supporting MD simulations using LAMMPS [24] were undertaken to further explore the role that core confinement plays on the dynamics of the dislocations nucleated during indentation of these structures. The modified embedded atom method (MEAM) [25] was used to model all atomic interactions with a specialized Al-Si interatomic potential [26]. The simulation domain consists of a single-crystal (001) FCC Al core covered by a shell of a-Si, shown schematically in Fig. 14. Prior to nanoindentation, 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 using a Nosé-Hoover thermostat for 30,000 time steps with a time step of 1 fs. The a-Si shell was constructed by randomly populating the shell region with Si atoms and then systemically removing atoms that are too close together in order to achieve an equilibrium shell density of 2.28 g/cm^3 , which is the measured density of a-Si [27].

3.3.1 Nanoindentation Simulations and Dislocation Density Calculations

Nanoindentation simulations were performed on several different geometries of Al/a-Si nanostructures: a CSN with a 15 nm core radius and CSRs with a rod radius of 15 nm and core lengths of 15, 25, and 35 nm, all with a 5 nm shell thickness. For these simulations, the indenter is modeled as a purely repulsive spherical potential with a radius of 100 nm and controlled to move 6 nm into the nanostructure at a constant rate of $0.5 \text{ \AA/ps}$ while maintaining a system temperature of 300 K. After reaching the specified indenter displacement, the indenter is completely retracted at the same displacement rate. Dislocation activities within the Al core are characterized using the dislocation extraction algorithm (DXA) [28] within the Open Visualization Tool (OVITO) [29].

A snapshot of the atomic distortion resulting from dislocations nucleated in the core of a CSN at maximum indenter displacement is shown in Fig. 15(a). The core has been sliced down the middle to visualize an interior plain of atoms, which are colored by lattice structure. The green atoms are in a face-centered cubic (FCC) arrangement and the red atoms are hexagonal close-packed (HCP) atoms representing a stacking fault formed by the nucleation of Shockley partial dislocations. A more detailed view of the dislocation content is provided in Fig. 15(b), showing only the HCP atoms that primarily comprise the stacking faults, with the leading and trailing Shockley partials represented as green lines. As indicated, one pair of Shockley partials has cross-slipped into an adjacent slip plane. This cross-slipped dislocation structure is far less mobile than in-plane Shockley partial dislocations, which will potentially affect the dynamics of these dislocations after the removal of the applied indentation load. To visualize this, the time evolution of the dislocation content within the core is shown in Fig. 15(c), with all atoms removed to show only the dislocations within the interior of the core. The individual dislocation lines are colored by Burgers vector, with perfect FCC dislocations, Shockley partials, Hirth dislocations, and other dislocations colored blue, green, black, and red, respectively. As the nanostructure is indented, dislocations, consisting primarily of glissile Shockley partials, are nucleated at the core/shell interface and further propagate. This continues until a maximum dislocation density is reached at the maximum indenter displacement. During unloading, a notable egression of dislocations occurs as the mobile dislocations are reabsorbed by the core/shell interface. This continues even after the indenter loses contact with the CSN, eventually reaching an equilibrium dislocation density. A non-zero equilibrium dislocation density is typically due to the formation of sessile dislocation structures, either due to cross-slip

(as demonstrated here) or other dislocation reactions. In this case, ~93% of the dislocations nucleated during loading have been reabsorbed by the core/shell interface or otherwise annihilated. It should be noted that this phenomenon is specific to the core-shell structure, as similar simulations performed on Al nanodots result in stable dislocation densities that do not substantially decrease during unloading.

To characterize how the dimensionality of core confinement affects the behavior of dislocations in CSNs and CSRs, the dislocations densities at key points during the nanoindentation simulations were calculated. Fig. 16 shows the calculated dislocations densities at maximum indenter displacement, immediately after the indenter loses contact with the nanostructure during unloading, and at equilibrium (at least 85,000 time steps after the indenter has lost contact with the nanostructure). For the CSN, which is the structure with the most highly confined core, approximately 65% of the dislocations nucleated during indentation are removed when the structure is fully unloaded and further increases to 93% at equilibrium. When this confinement is reduced, as in the CSRs, the dislocation density relaxes to a nearly constant value when fully unloaded, regardless of core length, with minimal additional recovery occurring at equilibrium. For these structures, the proportion of dislocations removed at equilibrium from the core of the CSRs decreases from 89% to 85% and then to 83% as the core length increases from 15 nm to 25 nm and 35 nm, respectively. The reduced lateral confinement exhibited in the CSRs allows more opportunity for dislocations to cross-slip or otherwise form sessile dislocations, such as Hirth or Stair-rod dislocations, resulting in less dislocation recovery compared to the CSN.

4. Conclusions

Nanoindentation experiments were performed on several different geometries of Al/a-Si nanostructures, including hemispherical CSNs, horizontally-aligned CSRs, and a layered thin film, to investigate the effects of geometrical confinement of the Al core on the CSN deformation behavior. The CSNs have deformation-resistant properties, as indicated by complete recovery of deformation beyond the elastic limit. When the core confinement is slightly reduced, the deformation resistance that is observed in the CSNs is substantially reduced. A further reduction in core confinement results in more conventional indentation behavior regardless of geometry. Supporting molecular dynamics simulations show that dislocations nucleated in the core of CSNs are more readily removed during unloading compared to CSRs, which indicates that the 3-dimensional core confinement of the CSNs plays an important role in the deformation resistant properties of CSNs. This study elucidates the effects that core confinement plays on the novel nanoindentation behavior of hemispherical Al/a-Si CSNs, which will allow for the rational design and effective implementation of these structures in nanomechanical applications.

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Figure 1

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Figure 16

The “dimensionality” of core confinement greatly influences the mechanical behavior of Al/a-Si core-shell nanostructures

Hemispherical Core-Shell Nanostructure

Core-Shell Nanorod

Layered Thin Film