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Published in:
AIP Advances

Published: 01/07/2015

Document Version:
Final Published version, also known as Publisher’s PDF, Publisher’s Final version or Version of Record

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Publication record in CityU Scholars:
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Published version (DOI):
10.1063/1.4927509

Publication details:
Yang, L., Bian, J. J., Zhang, H., Niu, X. R., & Wang, G. F. (2015). Size-dependent deformation mechanisms in hollow silicon nanoparticles. AIP Advances, 5(7), [77162]. https://doi.org/10.1063/1.4927509

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Citation: AIP Advances 5, 077162 (2015); doi: 10.1063/1.4927509
View online: https://doi.org/10.1063/1.4927509
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Size-dependent deformation mechanisms in hollow silicon nanoparticles

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(Received 14 June 2015; accepted 16 July 2015; published online 23 July 2015)

Even inherently brittle hollow silicon nanoparticles (NPs) can withstand larger strain to failure than solid NPs. However, the influence of wall thickness on the mechanical behavior of hollow Si NPs is not fully understood. Using molecular dynamics simulations, we investigate the compressive behavior of hollow Si NPs. Three distinct failure mechanisms of hollow NPs are uncovered, and their strength and deformability are analyzed quantitatively. For extra-thick-walled NPs, dislocations will nucleate below the contact area and cut through the particles till failure. For mid-thick-walled NPs, however, dislocations will emit from the inner surface and slip towards the outer surface. For thin-walled NPs, elastic buckling is the cause of failure. Compared to solid NPs, hollow NPs with wall thickness being around half of its outer radius can achieve significant improvement in both strength and deformability.

Nanoparticles have exhibited a wide range of applications in micro-/nano-electro-mechanical systems, pharmaceuticals, catalysts, and environment protections. 1,2 In fulfilling the diverse application functions of NPs, it is of critical importance to characterize the mechanical properties of NPs and understand the underlying deformation mechanisms, which typically display size dependence and are evidently different from their macroscopic counterparts. 3,4

Both atomistic simulations and experiments by atomic force microscopes (AFM) have been carried out to study the mechanical behaviors of Si NPs. For example, Gerberich et al. 5 measured the hardness of Si NPs ranging from 20 nm to 100 nm and found that the hardness was up to 50 GPa, four times greater than that of bulk silicon. They attributed the plastic deformation in Si NPs to heterogeneous dislocation nucleated at the contact edges and followed by dislocation propagation along a glide cylinder. Using the Tersoff potential, Valentini et al. 6 simulated the compression of Si NPs with radii up to 10 nm at 0 K, and found that the phase transformation is dominant in the particle core. Further simulation works 7 revealed that dislocations can nucleate in NPs larger than 10 nm in radius at elevated temperatures. Zhang et al. 8 found that phase transformation is followed by dislocation nucleation within the newly formed phase region, depending on the size of the particle.

Since the Tersoff potential was initially developed to represent the phase transformation of silicon, dislocations were scarcely observed in silicon NPs using this potential. The Stillinger-Weber (SW) potential, 9 however, has been shown to be superior in representing the shearing behavior and generalized stacking fault energies for silicon at low temperature. Compared to the Tersoff potentials, the SW potential provides the closest match to ab initio dislocation nucleation results in defect-free silicon. 10 Recently, using SW potential, Chrobak et al. 4 pointed out that the plasticity

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of bulk silicon is dominated by phase transformation due to the relative constraint, while NPs are less constrained and their plasticity is mainly driven by dislocations. For the compression of Si NPs using SW potential, Hale et al.\textsuperscript{11} revealed that dislocations are nucleated near the contact points and grow on both \{110\} and \{111\} crystallographic planes.

Although NPs demonstrate greatly improved strength, it is found to be at the expense of deformability. Hollow NPs have evoked great interests owing to the ability to keep both strength and admiring ductility. For example, through in situ compression, Shan et al.\textsuperscript{12} found that hollow CdS NPs can not only withstand extreme stresses but also exhibit considerable deformation to failure. Recently, through chemical vapor deposition and etching, it is possible to fabricate Si hollow NPs,\textsuperscript{13} which are capable of accommodating large volume changes without pulverization under cyclic loading. The collective mechanical behavior of hollow silica NPs was also explored by nanoindentation.\textsuperscript{14} It was found that each compressed hollow NP experiences successively bending, flattening and then buckling. Now it is even possible to tune the outer diameter and wall thickness of NPs in fabrication.\textsuperscript{15} However, up to date, the quantitative analysis of the deformation in hollow Si NPs is still absent. The present paper is aimed to illuminate the deformation mechanism in hollow Si NPs through atomistic simulations.

Figure 1 shows the schematic model of compression of a hollow Si NP with the outer radius $R$ and the wall thickness $t$. To construct hollow NPs, perfect bulk single crystalline silicon samples of diamond cubic structure are firstly generated with a lattice constant of 5.43 Å, and then all the atoms outside the region between two homocentric spherical surfaces are removed. The SW potential\textsuperscript{9} is adopted to describe the interaction between silicon atoms, which can accurately reflect both the elastic behavior and the evolution of lattice defects. To simulate the uniaxial compression, two rigid planar indenters are used to compress the hollow NP from above and below along the $z$-axis ([001] crystallographic direction). A repulsive potential is chosen to describe the interaction between the indenters and Si atoms as

$$U_i(z_i) = \begin{cases} 
K(z_i - h_T)^3 & z_i \geq h_T \\
0 & h_B < z_i < h_T \\
K(h_B - z_i)^3 & z_i \leq h_B 
\end{cases} \quad (1)$$

where $K$ is a specified constant chosen to be 20 eV/Å$^3$, $z_i$ is the $z$-coordinate of the $i$-th atom, $h_T$ and $h_B$ are the positions of the top and bottom compression planes perpendicular to the $z$-axis, respectively.

In the present study, the molecular dynamics package, LAMMPS,\textsuperscript{16} is employed for the MD simulations. An NVT ensemble with velocity-Verlet integration and a time step of 2 fs is chosen to describe the atomistic system. The Nosé-Hoover thermostat\textsuperscript{17} is adopted to maintain a constant
temperature at 300 K. Prior to compression, the carved hollow NP is firstly relaxed using the conjugate gradient method to reach a stable structure state with minimum energy, then the whole system is equilibrated at temperature 300 K for about 100 ps. Following this, to fulfill the compression, two planar indenters move simultaneously toward the nanoparticle center with a constant speed of 0.1 Å/ps. A series of atomistic simulations are conducted for NPs with \( R = 20 \) nm and \( t \) ranging from 2 to 15 nm.

To identify and track dislocation movements, we use the slip vector \(^{18}\) in simulations, which is defined as

\[
\vec{S}_i = \frac{1}{n_s} \sum_{j \neq i} n \left( \vec{X}_{ij} - \vec{X}_{ij}^0 \right),
\]

where \( n \) is the total number of the nearest neighbors to atom \( i \), \( n_s \) is the number of slipped neighbors, \( \vec{X}_{ij} \) is the vector difference of atom \( i \) and \( j \) at the current configuration, and \( \vec{X}_{ij}^0 \) is the corresponding vector at the initial unstrained reference configuration. OVITO\(^{19}\) software is utilized for visualization and image rendering.

Figure 2 presents the compressive load-depth curves for several representative NPs with the same outer radius \( (R = 20 \) nm) but different wall thickness \( t \). Each load response can be separated into elastic and plastic regimes. In the primary elastic stage, load increases smoothly as the compression depth increases for all NPs. To reach a given compression depth in the elastic stage, a larger load is required for the particles with thicker wall. At the limit of elastic deformation, there are sudden load drops for NPs, as indicated by arrows in the figure. The yielding point corresponds to the named pop-in (PI) event observed in stressed solid silicon NP\(^1\), which is attributed to the onset of plasticity in defect-free crystals. It is seen that the yielding load increases firstly and then declines as the wall thickness decreases. No clear load drop is observed for the thinnest NP \((t = 4 \) nm\), in which buckling occurs before material failure.

Based on the SW potential, we also calculate the elastic constants of single crystalline silicon in a Cartesian coordinate system with [100], [010] and [001] crystal orientations corresponding to axes 1, 2, and 3, respectively. The three independent material constants are given as \( C_{11} = 151.4 \) GPa, \( C_{12} = 76.4 \) GPa and \( C_{44} = 56.4 \) GPa. For the solid sphere with radius \( R \) compressed by two rigid planes, the anisotropic elastic contact mechanics gives the relation of load \( P \) versus penetration \( \delta \) as\(^{20}\)

\[
P = \frac{4}{3} E^* R^{1/2} \delta^{3/2},
\]
where $E^*$ is the indentation modulus depending on the indentation direction with respect to the crystalline orientation of particles. For the compression along [0 0 1] direction, the indentation modulus $E^*$ is calculated as 132.1 GPa. The theoretical prediction based on Eq. (3) is also plotted in Fig. 2. It is seen that atomistic simulation agrees well with the theoretical model, and thus gives support to our simulations.

Due to the intrinsic brittle characteristic of silicon crystals, solid Si NPs can undergo only a very small amount of plastic deformation before final fracture. To reveal the plastic deformation and failure mechanisms at atomic scale in hollow NPs, we calculate the atomic slip vectors for various NPs during deformation to characterize the inside defect evolution, and some critical representative dislocation structures are displayed.

For extra-thick-walled hollow Si NPs ($t/R \geq 0.5$), the plastic behavior is quite similar to solid NPs. Fig. 3 displays the dislocation structures of NP with $t = 12$ nm at several loading steps. An effective strain $\varepsilon$ defined by the ratio of indent depth to the outer radius of NP is used to indicate the compression process. Plastic deformation starts at strain $\varepsilon = 0.13$, and perfect dislocation loops homogeneously nucleate on a [111] plane in the region just below the contact area. In Fig. 3, the enlarged part indicates a perfect dislocation loop ($b = a/2 <01\bar{1}> = 3.84$ Å) on the [111] shuffle plane. As the load increases, the front of the dislocation loop will continue to expand on the [111] plane with $60^\circ$ character, while pure screw components will cross slip to [110] plane and then to another shuffle set [111] plane. The defects grow up and result in the slipped planes forming a V-shape structure on two [111] planes connected by a [110] plane. As $\varepsilon$ increases to 0.14, some dislocation loops expand sideling across the particle and annihilate at the outer surface, which leave permanent surface steps. Though the plastic deformation of extra-thick-walled hollow NPs is similar to that of solid NPs, the wall thickness affects the position of dislocation nucleation and the critical load to activate dislocation. As the thickness declines from 20 nm to 10 nm, the location of initial dislocation core moves from about 2.3 nm to 4.5 nm below the contact surface, and higher load is necessary to activate dislocations. The onset of plasticity is related to shear stress and can be roughly estimated by von Mises’ yield criterion. According to the contact mechanics, the maximum von Mises’ stress in solid NPs is proportional to the average pressure over the contact region and lies below the contact surface at a certain distance being linear with the contact radius. Under the same load, the extra-thick-walled NPs will generate a larger contact radius than that of solid NPs and thus a smaller average pressure. Therefore, the maximum von Mises’ stress in extra-thick-walled NPs is smaller than that of solid NPs and its position is further away from the contact surface. This might qualitatively explain that the extra-thick-walled hollow NPs exhibit higher strength and ductility than solid NPs.

![FIG. 3. Slip vector images of extra-thick-walled hollow NP with $t = 12$ nm. The enlarged part indicates a perfect dislocation loop ($b = a/2 <01\bar{1}> = 3.84$ Å) on the [111] shuffle planes. Surface atoms of the mid-section are shown in grey for easy reference.](image-url)
For mid-thick-walled hollow NPs ($0.3 \leq t/R < 0.5$), their atomic scale plastic deformation is clearly different from that of extra-thick-walled hollow NPs. Fig. 4 shows atomic defect structures inside a hollow Si NP with $t = 8$ nm. At the strain $\varepsilon = 0.17$, two perfect dislocation loops ($b = a/2<01\bar{1}>$) are formed on the $\{111\}$ shuffle planes close to the inner surface. As the compressive load increases, dislocation loops expand and the frontiers glide towards the outer surface. However, the perfect dislocation loops do not cross slip to other planes, which is different from extra-thick-walled NPs. Shortly after their nucleation, dislocations slip across the wall and annihilate at the outer surface.

For thin-walled NPs ($t/R < 0.3$), no dislocation is observed inside the particles, but the shells buckle under compression. Fig. 5 shows the buckling process of a hollow NP with $t = 2$ nm. At the strain $\varepsilon = 0.10$, the center of contact region starts to detach from the planar indenter and collapse. Careful examination shows that most part of the thin-walled hollow NP is in elastic state before buckling except the central contact region, where appears a small amorphous zone. By analyzing the variation of contact area through Delaunay triangulation, the critical point for buckling can be determined. The critical strain of hollow NPs calculated by this approach is close to the magnitude of $t/R$, which qualitatively agrees with the theoretical analysis based on the elasticity theory.\textsuperscript{22}
After buckling, the contact region bends inward to form a dimple, and the thin-walled silicon NP is easy to crush. Similar buckling and circumferential cracking have been observed in Yin et al.’s experiment for thin-walled NPs.

To quantitatively characterize the overall mechanical response of NPs, we define the effective stress as the normal stress component along the z-axis of atomic virial stress averaged over the entire volume possessing by the outer surface. Fig. 6 displays the effective stress-strain response, and the circles in this picture indicate the elastic limits. It is noticed that the effective stress always achieve its maximum value at the elastic limit, therefore we use this value as the critical stress of hollow NPs.

As we have exploited above, Si NPs will either fracture due to dislocation movement for thick-walled NPs or buckle for thin-walled NPs. To evaluate the deformability of NPs, we use the strain when dislocations cut through the particles for thick-walled NPs or buckling occurs for thin-walled NPs as the critical strain. According to this criteria, the critical strain is 0.12 for solid NPs, and 0.18 for hollow NPs with $t/R = 0.3$, which are in good agreement with the fracture strain of 0.13 for solid NP\textsuperscript{23} and 0.16 for hollow NPs with $t/R = 0.29$ in experiments.\textsuperscript{12} Owing to the intrinsic brittle nature of silicon, there is only a slight difference between the strain at elastic limit and the critical strain. The difference gets smaller as the thickness decreases.

Fig. 7 demonstrates the critical stress and the critical strain for various hollow NPs, and three regimes are distinguished according to the failure mechanisms: (I) dislocation nucleated below the...
outer surface and slipping sideling toward the opposite surface, (II) dislocation initiated from the inter surface and moving toward the outer surface, and (III) elastic buckling. It is interesting to find that both the strength and deformability increase as the thickness decreases in the region I. In the region II, the deformability improves only slightly, while the strength decreases dramatically. In the region III, both the strength and deformability will decline as the thickness decreases further. This result suggests that hollow NPs with $t/R$ around 0.5 possess much better mechanical properties in both strength and ductility.

In summary, atomistic simulations are conducted to investigate the mechanical response of hollow silicon NPs under compression. Stillinger-Weber potential is employed for better characterizing the elastic behavior and dislocation related yielding. Three distinct failure mechanisms in hollow Si NPs are uncovered depending on the thickness. The influence of wall thickness on the overall capacity of NPs to sustain external loading and deformation are quantitatively analyzed. The present investigations predict that hollow NPs with wall thickness about half of outer radius will achieve optimized strength and ductility. The obtained results are useful to tailor the mechanical properties of hollow NPs by changing their wall thickness according to practical requirement.

Supports from the National Natural Science Foundation of China (Grant Nos. 11072186 and 11272249), and computational resources from Shanghai Supercomputer Center are acknowledged.

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