Molecular Dynamics Study of Orientation-dependent Tensile Properties of Si Nanowires with Native Oxide: Surface Stress and Surface Energy Effects

Sina Zare Pakzad, Mohammad Nasr Esfahani, and B. Erdem Alaca, *Member, IEEE*

***Abstract*— Molecular dynamics (MD) simulations are employed to investigate the influence of native oxide layer on the mechanical properties of Si nanowires (NWs) through analyzing surface stress and surface energy effect. This work studies the tensile response of Si NWs along <100> and <110> crystal orientations. MD results are compared with the traditional core-shell model on the estimation of the modulus of elasticity of Si NWs with a native oxide layer. Density functional theory (DFT) methods are used to verify MD results on the surface energy calculations. Surface stress and surface elastic constants are studied for native oxide surface using MD simulations and compared with unreconstructed surfaces. In this work, the role of native oxide is addressed to understand the difference between experimental and computational findings on the modulus of elasticity of Si NWs.**

I. Introduction

In the multi-disciplinary world of nanotechnology, materials based on nanometer-sized structures have attracted a great deal of interest in various fields. Nanowires are one of the most important one-dimensional (1-D) nanostructures introducing unique mechanical, electrical, and optical properties with their highly anisotropic geometry as well as finite size effects. There is a strong size dependency in the mechanical properties of NWs [1]. However, due to lack of detailed investigation of surface and interface effects on mechanical properties of Si NWs, analyzing the surface related constants effect on elastic behavior of Si NWs needs further examinations of crystal orientations as well as native oxide effects. In this study, we examine native oxide effect on the mechanical behavior of Si NWs by performing tensile tests using MD simulations while the native oxide has proven to have an amorphous crystal structure [2]. Surface effect is studied by surface energy estimations of unreconstructed {100} and {110} Si surfaces using both MD and DFT methods. Furthermore, surface energy, surface stress and surface elasticity parameters are calculated for unreconstructed Si surfaces and native oxide surface using MD simulations.

II. Simulation Methods

A. Nanowire Tensile Simulation using MD

In MD simulations, the Tersoff Munetoh potential [3] is used to describe interatomic potentials for Si-Si and Si-O interactions. The Tersoff potential is an empirical function composed of two-body terms depending on the local environments. This work studies the mechanical behavior of Si NWs with two different surface configurations including unreconstructed surface and native oxide. NWs with native oxide will be indicated as $aSiO_2$-Si NWs in the remainder.

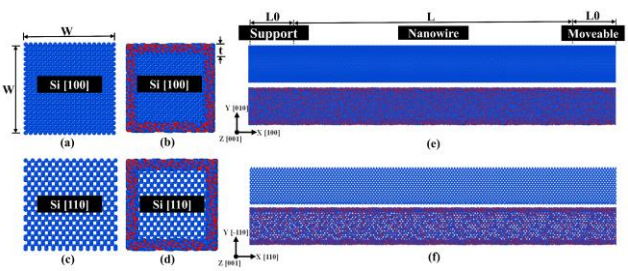


Figure 1: The initial configuration of NWs. The models in this figure are nanowire of width (W) of 5 nm and oxide thickness (t) of 0.5 nm for a) unreconstructed Si <100>, b) $aSiO_2$-Si <100>, c) unreconstructed Si <110>, d) $aSiO_2$-Si <110> and, geometry of a NW length of L and Si orientation of NW of e) <100> and f) <110>. Si atoms are colored with blue and oxygens are in red.

The initial atomic configurations of NWs along <100> and <110> crystal orientations are shown in Fig. 1. The NW width (w) and oxide layer thickness (t) are selected as 5 nm and 0.5 nm, respectively. NW length (L) of 1000 nm is considered for both crystal orientations having 250 nm on each side of the NW length denoted as support and movable regions (L_0) as shown in Fig. 1e, Fig. 1f. LAMMPS code is used for MD calculations considering non-periodic boundary conditions along all directions. NWs are first quasi-statically relaxed to a local minimum configuration through the conjugate gradient method. Then, all NWs are relaxed at a temperature of 1.0 K for 120 ps with a time step of 1 fs using a canonical NVT ensemble (Nose-Hoover thermostat). To mitigate the shock wave from the high loading rate, constant velocities that vary linearly from zero at the fixed end to a maximum of 1.0 Å/ps at the free end of the NW as well as a constant velocity value of 1.0 Å/ps for the moveable region are applied to the atoms along the x-directions as shown in Fig. 1e and Fig. 1f.

Sina Zare Pakzad is with the Department of Mechanical Engineering, Koç University, Istanbul, 34450, Turkey
(e-mail: szarepakzad18@ku.edu.tr).

Mohammad Nasr Esfahani is with the Department of Electronic Engineering, University of York, YO10 5DD, UK.
(e-mail: mohammad.nasresfahani@york.ac.uk).

B. Erdem Alaca is with the Department of Mechanical Engineering and Surface Science and Technology Research Center (KUYTAM), Koç University, Istanbul, 34450, Turkey (corresponding author to provide phone: 90-212-338-1727; fax: 90-212-338-1548; e-mail: ealaca@ku.edu.tr).

B. Modulus of elasticity using core-shell

The core-shell model is often used for studying the surface effect on modulus of elasticity of NWs [4]. This model describes the NW as a combination of core and surface regions with distinct moduli of elasticity for the core (E_0) and the surface (E_s). For a NW with diameter of D and a finite surface layer thickness of r_s under tensile loading, the effective modulus of elasticity, E_{eff}, of the NW is given by [5],

$$E_{eff} = E_0 [(1 + 4(E_s/E_0) - 1)(r_s/D - (r_s)^2/D^2)]. \quad (1)$$

Modulus of elasticity for the core and shell parts of $aSiO_2$-Si NWs is estimated by performing tensile simulation on bulk structure of Si with <100> and <110> crystal orientations and bulk structure of $aSiO_2$ using the Tersoff-Munetoh potential by applying periodic boundary conditions along all directions. Core-shell model is applied using the modulus of elasticity of the bulk Si as E_0 and modulus of elasticity of shell oxide as E_s and the results are used for estimation of the effective modulus of elasticity for the Si NW with native oxide (E_{eff}).

C. Surface Energy using MD

Surface energy, γ is the energy variation per unit area due to the surface creation and it is defined as the difference in the energy of the system with and without free surface [6]. MD simulations were performed using the Tersoff-Munetoh potential to estimate the surface energies of Si and $aSiO_2$ models. The unrelaxed and relaxed surface energies are denoted as γ_u and γ_r, respectively and are determined using (2) and (3), respectively,

$$\gamma_u = (E_{u,slab} - N \times E_{bulk}) / (2 \times A) \quad (2)$$

$$\gamma_r = ((E_{r,slab} - N \times E_{bulk}) / (A)) - \gamma_u \quad (3)$$

where A and N represent the surface area of the slab and number of atoms, respectively and E_u, E_r, and E_{bulk} are the energies of the unrelaxed slab, the relaxed slab, and the bulk, respectively [7]. To calculate the surface energy of unreconstructed (100) and (110) Si surfaces, a film model with periodic boundary conditions applied in x and y directions but not in the z direction is used which provides an infinite size film model with limited thickness (L_z) as shown in Fig. 2a and Fig. 2b, respectively. In order to define the free surfaces, thin film models are built with crystal orientations of (x, y, z) = ([100], [010], [001]) and (x, y, z) = ([-110], [001], [110]) for unreconstructed (100) and (110) Si surfaces, respectively. The simulation boxes are set as 8 times of the lattice constant of Si while for calculation of bulk energy values, same atomic systems with all periodic B.C.s are used. The evaluation area (A) is made up of two surfaces that face each other, where the film must be enough thick to prevent interface of these two free surfaces. The models associated with Si (100) and Si (110) have 4224 and 8448 atoms with an overall size of 4.35 nm × 4.35 nm × 4.35 nm and 6.15 nm × 4.35 nm × 6.15 nm, respectively. The surface area for the (100) and (110) models are evaluated as 37.8 nm^2 and 53.5 nm^2, respectively.

The surface energy associated with the amorphous SiO_2 structure, as native oxide in Si NWs, is studied by defining a film $aSiO_2$ structure as shown in Fig. 2c while for bulk energy calculation similar to Si models, periodic B.C.s were applied in all directions. The $aSiO_2$ film model consists of 11616 atoms (3872 Si and 7744 O atoms) with an overall size of 5.7 nm × 5.7 nm × 5.8 nm. The area for the free surface of $aSiO_2$ model is evaluated as 65 nm^2. Considering the amorphous nature of native oxide, 20 $aSiO_2$ were built with similar dimensions as discussed before keeping the stoichiometric ratio between Si and O atoms (1:2) while having different distribution of the atoms on the surfaces. For proper statistical treatment, the average values of 20 simulations were reported here.

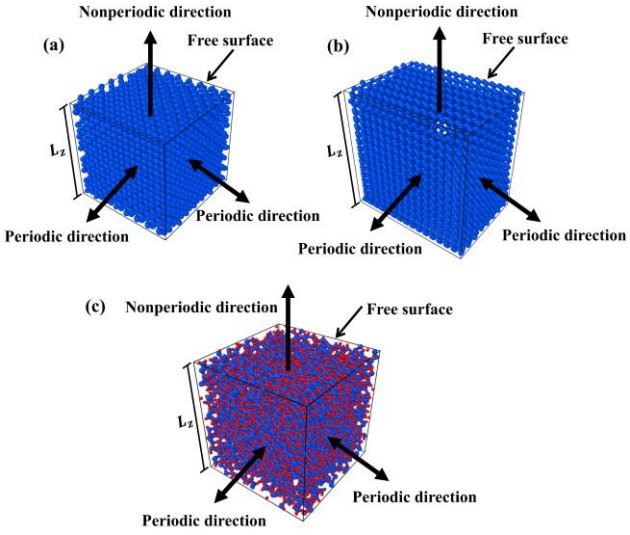


Figure 2: Surface models with non-periodic boundary conditions in z-directions for a) Si (100), b) Si (110) and c) $aSiO_2$ used for the calculation of surface-related parameters (Blue atoms correspond to Si and red ones represent oxygen atoms).

After the creation of surfaces, the systems are well-relaxed by the conjugated gradient method and the differences between bulk and film energies are used for surface energy calculations.

D. Surface Energy using DFT

For the verification of orientation dependent surface energy values DFT approach is used. The Vienna Ab Initio Simulation Package (VASP) was used to simulate the Si surfaces with (100) and (110) orientations. The project augmented wave (PAW) potential was employed to describe the interaction between the valence and the core electrons. The Perdew, Burke, and Ernzerhof (PBE) functional within the generalized gradient approximation (GGA) was applied in all calculations. Plane waves were included to a cutoff of 400 eV. The Methfessel-Paxton scheme order 1 was used with a smearing of 0.05 eV to determine the particle occupancies during the geometry optimization. The electronic and ionic optimization criteria were 10^{-5} eV and 10^{-2} eV.$Å^{-1}$, respectively and the conjugate gradient technique was adopted for the geometry optimizations. Si has an Fd3m structure, and the bulk Si structure was calculated within a diamond cubic cell using a 17×17×17 Monkhorst-Pack k-point mesh. Our calculated Si lattice constant was 5.431 Å and the Si (100) and (110) surfaces were investigated by simulating the periodic p(3×3)

supercells. Vacuum of 15Å, in the z direction was added to avoid the interaction between the neighboring cells. Four atomic layers were considered for the slabs, and the surface area of the supercells were 260.3 Å^2 and 190.1 Å^2 for the (100) and (110) surfaces, respectively. The relaxed and unrelaxed surface energies were calculated using (1) and (2). A 7×7×1 Monkhorst-Pack k-point grid was used in all surfaces to sample the Brillouin zone.

E. Surface Elastic Constants using MD

Surface elastic constants (d_{ijkl}) as an important surface parameter can be calculated using the method recommended by Ref. [6], where d_{ijkl} is defined as second-order derivative of surface energy with respect to the strain under plane-stress condition, which represents the variation in elastic constants due to the surface creation. Elastic constants for bulk (C_{ij}^{bulk}) and film (C_{ij}^{film}) models could be calculated using MD simulations while for the bulk model, the elastic constants should be defined under plane-stress condition ($C_{ij}^{bulk,plane}$) using the definitions in (4), (5) and (6)

$$C_{11}^{(bulk,plane)} = C_{11} - (C_{13})^2 / C_{33}, \quad (4)$$

$$C_{22}^{(bulk,plane)} = C_{22} - (C_{12})^2 / C_{33}, \quad (5)$$

$$C_{12}^{(bulk,plane)} = C_{12} - (C_{12}C_{13}) / C_{33}. \quad (6)$$

The relationship between the plane-stress elastic constants of the bulk and film models with the surface elastic constants is represented in (7).

$$C_{ijkl}^{(film,plane)} = C_{ijkl}^{(bulk,plane)} - (2/L_z) \times d_{ijkl}. \quad (7)$$

This method is applied to nano-scale thin films in quasistatic states with no temperature effect, which are shown in Fig. 2a and Fig. 2b denoted as unreconstructed Si surfaces and in Fig. 2c denoted as native oxide surface. The Tersoff-Munetoh potential is used for all MD calculations and to obtain elastic constants, small strains in different directions are applied to the simulation box and the variation of the energy is measured.

F. Surface Stress using MD

Surface stress is defined as the generated stress due to the surface creation being equal to the variation in the total surface energy per unit area with respect to the strain. By assuming the film thickness of L_z, the surface stress components denoted as f_{ij} are formulated as shown in (8) where η represents the averaged strain due to the relaxation.

$$f_{ij}(\eta) = f_{ij}^{(film)}(\eta) - f_{ij}^{(bulk)}(\eta). \quad (8)$$

Bulk surface stress must be estimated separately by the bulk model and surface stress for the film model can be defined by using the stress tensor definition as shown in (9):

$$f_{ij}^{(film)}(\eta) = \sigma_{ij}^{(film)}(\eta) \times L_z/2. \quad (9)$$

This method is applied to thin films of unreconstructed Si with (100) and (110) surfaces, shown in Fig. 2a and Fig. 2b, respectively, and $aSiO_2$ model represented in Fig. 2c where f_{11} and f_{22} are calculated using (9). The Tersoff-Munetoh potential was used for interatomic potential.

III. Results

A. Modulus of Elasticity

The stress-strain curves for unreconstructed Si NWs and $aSiO_2$-Si NWs are shown in Fig. 4. The stress-strain relation is essentially linear in elastic regime for all NWs and the modulus of elasticity can be directly evaluated in such elastic region. The modulus of elasticity estimation for <100> Si NWs exhibits a change from 115.6 GPa to 82.7 GPa for unreconstructed NW and NW with native oxide, respectively. Similar examination for <110> Si NWs, shows the modulus drop from 189.8 GPa to 130.5 for unreconstructed NW and NW with native oxide, respectively.

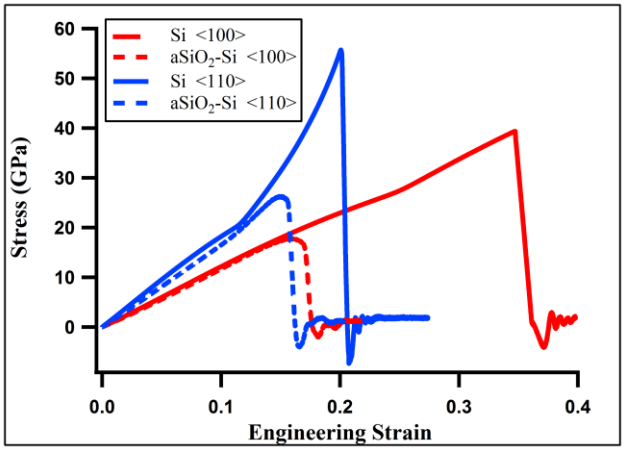


Figure 3: Stress-strain curves for tensile of unreconstructed Si and Si NWs with native oxide along <100> and <110> crystal orientations.

Such decrease in modulus of elasticity is due to the presence of native oxide layer. Those results for Si NWs with native oxide are much closer to the experimental observations [1] compared to unreconstructed Si NWs mostly modeled previously. Estimation of the modulus of elasticity for bulk silicon with <100> and <100> crystal orientations reveals moduli values of 87.4 GPa and 133.1 GPa, respectively, while for the bulk structure of $aSiO_2$, the modulus of elasticity value is predicted as 59.4 GPa. Using core-shell model and considering of the modulus of elasticity of the bulk Si as E_0 and modulus of elasticity of bulk $aSiO_2$ as E_s, the effective modulus of elasticity for $aSiO_2$-Si NWs are calculated as summarized in Table 1 and compared with MD simulations.

TABLE I. Effective Modulus of Elasticity Estimations of Si NWs with Native Oxide Using Tensile MD Simulation and Core-Shell Model.

Nanowire	Modulus of Elasticity: E_{eff} (GPa)	
	MD Simulation	*Core-shell Model*
$aSiO_2$-Si<100>	82.7	77.5
$aSiO_2$-Si<110>	130.5	106.6

B. Surface Energy Constants

After studying the elastic behavior, the surface features for unreconstructed surfaces and native oxide are investigated. The predicted surface energies of unreconstructed Si surfaces and $aSiO_2$ structures are summarized in Table 2.

The unrelaxed surface energies for unreconstructed (100)-Si using MD, and DFT method results in 2.29 J/m^2, and 2.20 J/m^2, respectively where the relaxed energies are reduced to 2.21 J/m^2 and 2.15 J/m^2, respectively. For unreconstructed (110)-Si surface the unrelaxed surface energies are estimated as 1.57 and 1.76 J/m^2 and the relaxed surface energies are calculated as 1.45 and 1.73 J/m^2. Calculated surface energies for unreconstructed Si surfaces are in good agreement with previous MD and DFT based estimations for unreconstructed (100) and (110) Si surfaces [6], [8]. Results exhibit the surface energy of 2.19 ± 0.2 J/m^2 for a SiO_2, which is also close to the range of surface energy calculations of crystalline SiO_2 structures [9]. Surface energy constants calculated for unreconstructed surfaces using both MD and DFT methods verifies the lower surface energy in (110)-Si surface compared to (100)-Si.

TABLE II. SURFACE ENERGY, SURFACE STRESS AND SURFACE ELASTIC CONSTANT FOR ATOMIC STRUCTURES USING MD. THE VALUE INSIDE PARANTHESES SHOWS THE DFT ESTIMATION.

Surface Constants	Atomic Structures		
	Si (100)	***Si (110)***	***aSiO₂***
γ_r (J/m^2)	2.21 (2.15)	1.45 (1.73)	2.19 ± 0.2
d_{11}(N/m)	–8.77	+3.4	–22.1 ±1.3
d_{22}(N/m)	–8.77	–15.1	–22.1 ±1.3
f_{11}(N/m)	–0.88	–1.57	+1.11 ± 0.10
f_{22}(N/m)	–0.88	–0.95	+0.91 ± 0.09

C. Surface Elastic Constants

Using the film models with limited thicknesses as shown in Fig. 2 for unreconstructed Si and $aSiO_2$ surfaces, the elastic constants are obtained for film structures. Also, it is obvious that the bulk models are with periodic definition in every direction without any dependence on the thickness. To calculate surface elastic constants, (7) is used with the associated film thickness of L_z, where for free surface of (100)-Si the surface elastic constants are evaluated as d_{11}= d_{22} = –8.77 N/m while for (110)-Si surface, surface elastic constants are estimated as d_{11}= +3.4 N/m and d_{22}= –15.1 N/m, respectively. The findings are in close agreement with the Tersoff-T3 and SW potentials reported in previous studies [4], [6], [10]. For the native oxide model, the calculations show the surface elastic constants of d_{11}= d_{22}= –22.1± 1.3 N/m. The results are summarized in Table 2.

D. Surface Stress Constants

As shown in Table 2, for unreconstructed (100) Si surface, compressive in plane stresses of $f_{11} = f_{22} = –0.88$ N/m are obtained using Tersoff-Munetoh potential while for unreconstructed (110) Si, the surface stresses of $f_{11} = –1.57$ N/m and $f_{22} = –0.95$ N/m are computed. The calculated surface stresses of unreconstructed Si surfaces are in close agreement with the values obtained using the Tersoff-T3 by authors in [6]. For $aSiO_2$ structure, the averaged values for the surface stress were estimated as $f_{11} = +1.11 \pm 0.10$ N/m and $f_{22} = +0.91 \pm 0.09$ N/m while the results are averaged over 20 repetitions of calculations on native oxide surfaces.

The decrease in modulus of elasticity for $aSiO_2$-Si NWs exhibit the crucial impact of native oxide in understanding of the elastic properties of Si NWs where the role of free surfaces combined with the presence of the amorphous oxide layer around the Si crystal. The predicted surface stress and surface elastic constants in this study reveals the need for detailed investigations on the surface effect in the mechanical behavior of Si NWs. Differences observed in calculated constants for unreconstructed Si and $aSiO_2$ surfaces suggest the importance of correct selection of such parameters for potential usage in other studies.

IV. CONCLUSION

The modulus of elasticity due to the presence of native oxide for Si NWs is calculated using MD simulations. Results are compared with the effective modulus of elasticity estimated through a core-shell model. Lack of reliability of the core-shell model, as an analytical calculation, is demonstrated, where the surface parameters necessitate to be implemented into analytical models. Those surface parameters including the surface energy, surface elasticity and surface stress have been calculated for Si and $aSiO_2$ surfaces. This work provides a guideline for the analysis of the size and orientation-dependent mechanical properties of Si NWs.

REFERENCES

[1] M. Nasr Esfahani and B. E. Alaca, "A Review on Size-Dependent Mechanical Properties of Nanowires," *Adv. Eng. Mater.*, vol. 1900192, pp. 1–23, 2019.

[2] H. G. Steinrück *et al.*, "Nanoscale structure of Si/SiO_2/organics interfaces," *ACS Nano*, vol. 8, no. 12, pp. 12676–12681, 2014.

[3] S. Munetoh, T. Motooka, K. Moriguchi, and A. Shintani, "Interatomic potential for Si-O systems using Tersoff parameterization," *Comput. Mater. Sci.*, vol. 39, no. 2, pp. 334–339, Apr. 2007.

[4] R. E. Miller and V. B. Shenoy, "Size-dependent elastic properties of nanosized structural elements," *Nanotechnology*, vol. 11, no. 3, pp. 139–147, 2000.

[5] C. Q. Chen, Y. Shi, Y. S. Zhang, J. Zhu, and Y. J. Yan, "Size dependence of Young's modulus in ZnO nanowires," *Phys. Rev. Lett.*, vol. 96, no. 7, pp. 1–4, 2006.

[6] S. Izumi, S. Hara, T. Kumagai, and S. Sakai, "A method for calculating surface stress and surface elastic constants by molecular dynamics: Application to the surface of crystal and amorphous silicon," *Thin Solid Films*, vol. 467, no. 1–2, pp. 253–260, 2004.

[7] M. J. Ungerer, D. Santos-Carballal, A. Cadi-Essadek, C. G. C. E. Van Sittert, and N. H. De Leeuw, "Interaction of H2O with the Platinum Pt (001), (011), and (111) Surfaces: A Density Functional Theory Study with Long-Range Dispersion Corrections," *J. Phys. Chem. C*, 2019.

[8] W. Xu and W. K. Kim, "Molecular dynamics simulation of the uniaxial tensile test of silicon nanowires using the MEAM potential," *Mech. Mater.*, vol. 137, no. May, p. 103140, 2019.

[9] Y. K. Shchipalov, "Surface energy of crystalline and vitreous silica," *Glas. Ceram. (English Transl. Steklo i Keramika)*, vol. 57, no. 11–12, pp. 374–377, 2000.

[10] H. Nejat Pishkenari and S. Rezaei, "Characterization of silicon surface elastic constants based on different interatomic potentials," *Thin Solid Films*, vol. 626, pp. 104–109, 2017.