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Effects of pore design on mechanical properties of nanoporous silicon

Nicholas Winter, Matthew Becton, Liuyang Zhang, Xianqiao Wang*

College of Engineering, University of Georgia, Athens, GA 30602, United States

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ABSTRACT

Nanoporous silicon has been emerging as a powerful building block for next-generation sensors, catalysts, transistors, and tissue scaffolds. The capability to design novel devices with desired mechanical properties is paramount to their reliability and serviceability. In order to bring further resolution to the highly variable mechanical characteristics of nanoporous silicon, here we perform molecular dynamics simulations to study the effects of ligament thickness, relative density, and pore geometry/orientation on the mechanical properties of nanoporous silicon, thereby determining its Young's modulus, ultimate strength, and toughness as well as the scaling laws versus the features of interior ligaments. Results show that pore shape and pattern dictate stress accumulation inside the designed structure, leading to the corresponding failure signature, such as stretching-dominated, bending-dominated, or stochastic failure signatures, in nanoporous silicon. The nanostructure of the material is also seen to drive or mute size effects such as “smaller is stronger” and “smaller is ductile”. This investigation provides useful insight into the behavior of nanoporous silicon and how one might leverage its promising applications.

1. Introduction

The design and fabrication of nanoporous materials are hot topics at the forefront of current materials science. With the availability of advanced nanoscopic design techniques including ion etching [1], chemical vapor deposition [2], and atomic manipulation via scanning tunneling electron microscopy [3], tailoring nanostructures to a specific design is not only possible, but the fabrication processes to achieve these nanostructures continue to increase in precision and viability. Nanopores bestow incredible characteristics upon materials such as high surface-to-volume ratios, increased catalytic power [4], high yield strength [5], and strain reversibility [6]. These properties make nanoporous materials ideal for applications in sensing [7], tissue engineering [8], fuel cell technology [9], and sequestration/filtration [10].

Nature seems to have mastered the design of nanostructured materials and devices through the iterative processes of natural selection, for example bone which is hard and strong under compressive force yet light weight due to its porous structure, spider silk with a unique combination of high tensile strength, extensibility, and flexibility that derived from peptide bonds and simple hydrogen bonds, and the diatom's intricate cell-wall, which is a mechanically superb, nanoporous structure composed of amorphous silica [11] as shown in Fig. 1(a) [12]. The pores in the diatom's cell-wall create remarkably uniform designs at the nanoscale ranging from ribs to honeycombs [11]. These designs have been shown to heavily influence the mechanical properties of the diatom's cell-wall [13] and represents the larger end of the scale for np-Si with pore sizes reaching up to ~1500 nm (Fig. 1(b)). At the smallest end of the scale is MCM-41 (Mobil Composition of Matter No. 41, a family member of np-Si materials) with nanopores as small as 2 nm Fig. 1(c) [14], which provides a realistic justification for our computational model in Section 2. Nanoporous silicon with pore size range from 2 nm to 1500 nm has been widely used in industrial applications including the connection of catalytic components such as enzymes [15], anodes in lithium ion batteries due to its high energy density [16], resistive random-access memory in computers (RRAM) [17], and scaffolding for cell encapsulation and implantation due to the well-understood saline chemistries as well as its anisotropic mechanical properties [8]. np-Si has also been emerging as a fuel in microelectromechanical systems because it is highly energetic and its rate of energy release is tunable [9], and has also shown promise as a highly-sensitive ion-selective transistor owing to its conductivity and very high surface area to volume ratio [7].

Understanding how the mechanical properties of np-Si may be altered is important for designing np-Si for the previously stated applications. For instance, one promising technique in RRAM is

* Corresponding author.
E-mail address: xqwang@uga.edu (X. Wang).

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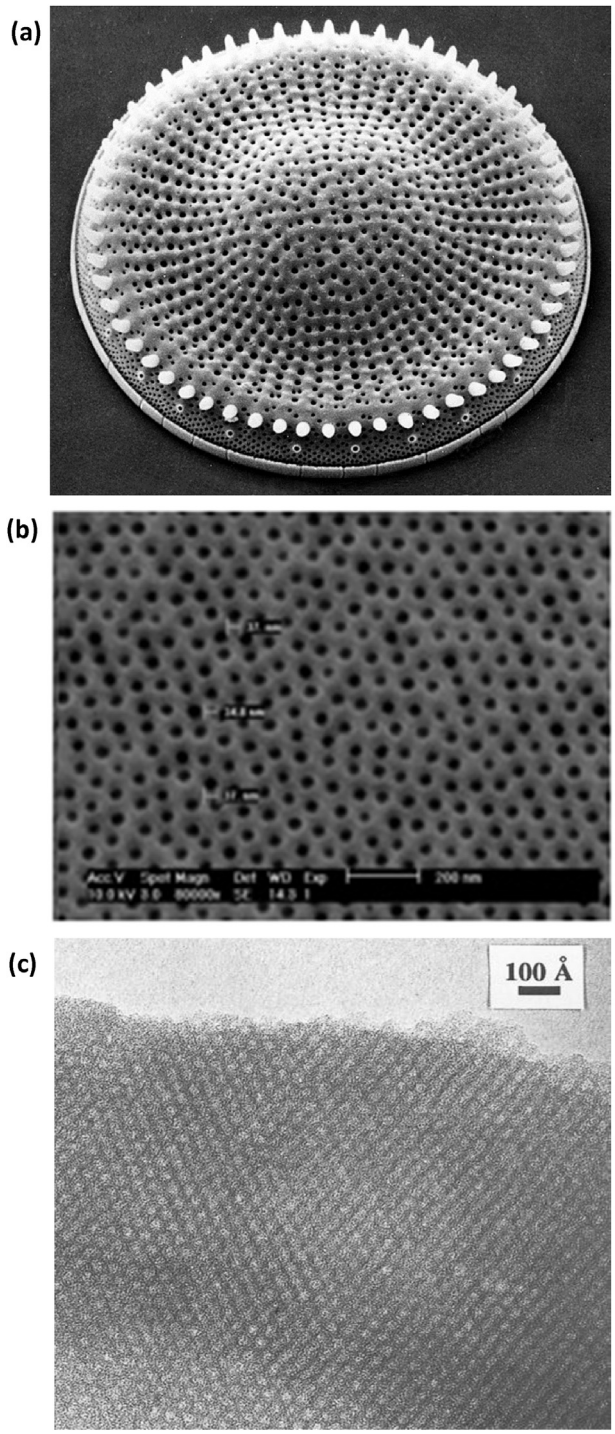

Fig. 1. (a) Structure of diatoms, showing their porous silica structure (image is reprinted from Ref. [12] with permission); (b) a TEM picture of np-Si produced via lithography (image is reprinted from Ref. [23] with permission) (c) TEM photograph of calcined np-Si known as MCM-41 (image is reprinted from Ref. [14] with permission).

electromechanical coupling using mechanical strains to induce a change in the magnetic order of a material and is a possible solution for decreasing the energy needed to store information [17]. The magnetic order of np-Si in this scenario is dependent on the absolute strain that it is experiencing and therefore the material's elastic modulus is an important design parameter for sizing the np-Si and developing np-Si that satisfies the engineering constraints. In previous studies by Garcia et al. tension studies on nanoporous silica with a rectangular mesh geometry and constant void volume between various sized models have been simulated. They found that the failure mechanism of nanoporous silica is correlated with relative density and ligament thickness and can change from crack propagation dominated failure, to failure characterized by the competition between crack propagation and shear mechanisms, and even failure fitting the criteria of ductile rupture [18,19]. Garcia et al. also claim that as ligament size is decreased the ductility of nanoporous silica increases, its elastic modulus decreases, its strength decreases, and that its toughness has a complex relationship with ligament thicknesses below 27 Å [18–20]. These studies shed light on the nature of the connection between mechanical properties of nanoporous silicon and size but by maintaining a constant void volume while changing the size of ligaments the relative density must be changed too and so the observations cannot conclude whether the cause of changes in mechanical response is due to relative density or size effects. To further these investigations, we tease apart the effects of relative density and ligament thickness to make clear how each design parameter changes the mechanical response of nanoporous silicon and we also test the effects of pore geometry on the mechanics of nanoporous silicon as well. To better understand how one might manipulate the mechanical properties of np-Si via control of its nanoporous structure, here we computationally model np-Si with various relative densities, ligament thicknesses, and pore geometries under tensile loadings and discuss the results.

2. Computational models and methods

For this work, molecular dynamics simulations based on the open-source code LAMMPS are performed in order to investigate the mechanical behavior of np-Si [21]. Through preliminary stress simulations (see Fig. S1 in the Supplemental Materials) on bulk silicon using the environmentally dependent interatomic potential (EDIP) [22], Stillinger-Weber (SW) Potential [23], and Tersoff potential [24], we found that the Stillinger-Weber potential shows the best accuracy in bulk modulus and elastic modulus with comparison of the experimental data stress-strain curves [25]. Therefore, we choose the SW potential to perform the relevant MD simulations. The details of SW potential are tabulated as follows:

$$E = \sum_i \sum_{j>i} \varphi_2(r_{ij}) + \sum_i \sum_{j\neq i} \sum_{k>j} \varphi_3\left(r_{ij}, r_{ik}, \theta_{ijk}\right) \tag{1}$$

$$\varphi_2(r_{ij}) = A_{ij}\varepsilon_{ij}\left[B_{ij}\left(\frac{\sigma_{ij}}{r_{ij}}\right)p_{ij} - \left(\frac{\sigma_{ij}}{r_{ij}}\right)q_{ij}\right]e^{\left(\frac{\sigma_{ij}}{r_{ij}-a_{ij}\sigma_{ij}}\right)} \tag{2}$$

$$\varphi_3\left(r_{ij}, r_{ik}, \theta_{ijk}\right) = \lambda_{ijk}\varepsilon_{ijk}\left[\cos\theta_{ijk} - \cos\theta_{oijk}\right]^2 e^{\left(\frac{\gamma_{ij}\sigma_{ij}}{r_{ij}-a_{ij}\sigma_{ij}}\right)} e^{\left(\frac{\gamma_{ik}\sigma_{ik}}{r_{ik}-a_{ik}\sigma_{ik}}\right)} \tag{3}$$

where φ_2 is a two-body term describing the interaction of two atoms (ex: Si_1Si_2) and φ_3 is a three-body term representing the interaction of three atoms (ex: $Si_1Si_2Si_3$). The summations in the formula are over all neighbors J and K of atom i within a cutoff distance equal to $a\times\sigma$.

Here, models with dimensions 43 nm × 43 nm × 7 nm, inspired by the thin nanoporous silicon plate shown in Fig. 1(c) [12,14,26], are used to study the mechanical properties and failure patterns of np-Si materials. In order to investigate the effect of pore patterns on the mechanical properties of np-Si, we propose three different pore