

# The prediction of the mechanical stiffness of the silicon based crystalline/amorphous nano-structures using molecular dynamic (MD) simulation

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## ABSTRACT

The mechanical stiffness of the silica nano-structures, including the crystalline silicon and amorphous silica, is studied using the molecular dynamics (MD) method. The MD simulation procedure is based on the linear-elastic theory, and the stiffness parameter can be acquired by the reaction forces of the sample. Moreover, we also propose a molecular structure generation algorithm for the amorphous silica, which is a low-dielectric material (SiOC:H). In the simulation of crystalline silicon, the results shows good approach to the experimental results and the size effect of the nano-structures was captured. Moreover, the simulation of amorphous silica, the trends which are indicated by the simulation results exhibit good agreements with the ones by the experiment.

**Keywords:** molecular dynamics, atomistic modeling, mechanical stiffness, amorphous material

## 1 INTRODUCTION

It is known that the mechanical characteristics of nano-scaled structure differ from the ones of bulk-scaled structures [1]. These mechanical characteristics are difficult to measure directly due to the limitation of the nano-scale experimental techniques, and the simulation method should be established to understand the trend of the size effect. One of the candidate methods is molecular dynamics (MD), which often used to describe the physical response of the nano-scaled materials.

Moreover, as feature sizes for the advanced IC continue to shrink, the semiconductor industry is focusing the technology development to minimize the intrinsic time delay for signal propagation, quantified by the resistance-capacitance (RC) delay [2][3]. The increasing demands for the electronic performance of the IC wiring have recently driven the replacement from aluminum to copper traces, and the alternative materials for SiO<sub>2</sub> film with lower dielectric constant [2][5]. Among the materials of advanced

IC backend structures, the low-k material (e.g. SiOC:H, or called Black Diamond, BD) has low mechanical stiffness, approximately 5-15 GPa. Experiments [5] show that enhancing the Young's modulus of the low-k material will increase the interfacial toughness of SiOC:H/TaN interface, which is known as the most critical interface in these structures. However, the amorphous nature of the SiOC:H film together with the porosity increases the difficulty to directly simulate its nano-scaled mechanical response. An algorithm which is capable of generating a reasonable molecular network structure of the SiOC:H based on the given concentration of basic building blocks is established.

In this paper, the one-dimensional uniaxial model based on the linear-elastic theory is used to capture the mechanical stiffness, which represents as the Young's modulus. The Young's modulus can be extracted by the reaction force of the model, the loading and its geometrical characteristics. The simulation results show that the predicted values (of both Young's moduli and densities) are higher than the value from the bulk experiments, due to the size effect and neglecting the point defect, dislocation and grain boundary.

Moreover, a novel molecular structure generating algorithm is developed for the amorphous silica. In order to qualitatively validate the generation method, the oxygen bond angle distribution (O-BAD) of the model is obtained and it will be compared to the experimental data. After the MD simulation, the comparison between the experimental and simulated results shows that the MD simulation can exhibit the trend of the mechanical characteristics with respect to the variety of the chemical composition.

## 2 THEORY

### 2.1 Molecular dynamics method

The molecular dynamics (MD) method, which is widely used in material science of IC technology, provides a theoretical and numerical framework for the many-particle problems [6]. Based on the Newton's second law of motion, the movements of the particle are described by the

coordinate variables. The interactions between the particles are described by the force fields.

## 2.2 Bar loading method

An atomistic method is established herein to predict the mechanical stiffness parameter, which is represented by the Young's modulus, of the nano-scaled structure. The nano-scaled specimens are simulated by the MD method proceeded by the energy minimization procedure.

A bar model is established as illustrated in Figure 1, where one end of the bar is fixed and the opposite end is applied a displacement. The applied displacements and reaction forces which obtained at the fixed end are used to extract the Young's modulus by the elasticity theory. Due to the small deformation assumption of elasticity [7], the total amount of the longitudinal deformation should be less than 1.0% of the total length of the specimen. Moreover, based on Saint-Venant's principle, a model with high aspect ratio ( $L/h$ ) is required to prevent boundary effects, as illustrated in Figure 1. The loading and boundary conditions are applied at the longitudinal direction. Moreover, due to the linearity assumptions, reaction force outputs are linear with the externally applied displacement. The reaction forces  $\bar{F}^i$  ( $i$  represent the  $i$ -th substeps) at the fixed end can be extracted by the energy gradient at the fixed atoms.

According to linear elasticity theory, the mechanical deformation of the uniaxially loaded bar can be represent as:  $\Delta d = FL/EA$  [7], where  $F$ ,  $E$ ,  $L$  and  $A$  represent external mechanical force, Young's modulus, initial length and initial cross section area of the specimen, respectively. Accordingly, we can obtain the Young's modulus by:

$$E = \left( \frac{\Delta F^{ij}}{\Delta d^{ij}} \right) \left( \frac{L_0}{A_{avg}} \right), \quad A_{avg} = V_0 / L_0 \quad (1)$$

where the  $V_0$  and  $L_0$  are the volume and the length at the initial stage. Clearly, the difference of the volume and the length of the molecular model between the initial and final stage should be small enough to satisfy the assumption of the linear elasticity theory.

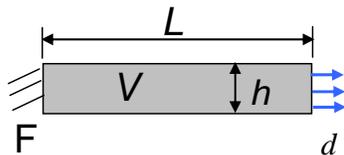


Figure 1. Illustration to bar loading model

## 2.3 Generating algorithm of amorphous/porous silica material

The amorphous/porous SiOC:H film is consisted of different basic building blocks: Q, T, D, M and void, as illustrated in Figure 2. The size of the void is assumed to be the same as the basic blocks. We further assume that only the single bond would exist between any two atoms. The generating procedure follows:

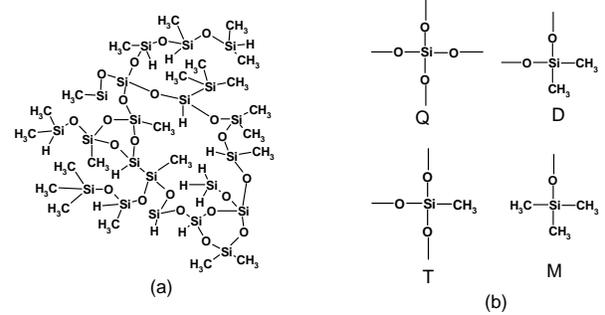


Figure 2. Chemical structure of SiOC(H). (a) is the illustration of the material. (b) is the illustration of the connection capability of the basic building blocks.

- A cubic grid is first assumed. However, for each node, two of the six connection capabilities are removed based on a fixed pattern. The distance between two nodes is approximately 0.3nm. The reason why we choose the cubic grid is that we can provide more free space for the structural relaxation step (Figure 3a).
- Based on the concentration of void which determined by the experiment, the void is randomly distributed into the framework (Figure 3b).
- When the Q is distributed into the grid, only the node with four connection capacities can be the candidate (Figure 3c).
- To distribute the T, the nodes with three must-connected links will be first satisfied. The rest of T will be randomly distributed into the nodes with more than three connection capabilities (Figure 3d).
- The distribution algorithm of D/M is similar to T, but takes two/one connections instead of three (Figure 3e).

Note that this algorithm will not guarantee the existence of the results. Therefore, a series of the iterations of procedure a) to f) with different random number (for the random distribution of void, Q, T, D and M) should be used.

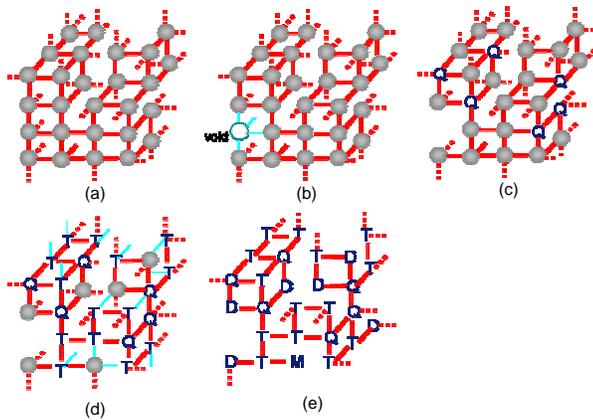


Figure 3 . Illustration of generating algorithm (a) Basic framework. (b), (c) and (d) are the distribution of void, Q, T, respectively. (e) is the obtained structure.

### 3 MD SIMULATION RESULTS AND DATA ANALYSIS

#### 3.1 Crystalline silicon results

The molecular model of pure silicon shown in Figure 4 (a) and (b) are simulated by the commercial MD solver Discover (version 2005.2)[8], and the force field between the atoms is described by the COMPASS (definition: cff91, version 2.6). All computations are performed on an i686 machine with 2.8GHz CPU. In this paper, the canonical ensemble (NVT) ensemble, which conserves the number of atoms (N), the system volume (V) and the temperature (T), is used. The Berendsen algorithm is used as the thermostat control. Moreover, no periodic boundary condition is applied to any model. The loading rate of all cases is fixed to 5.0 (m/s).

A series of sensitivity analyses is performed to examine the stability of the proposed method and to understand the geometrical effect of the nano-scaled structure. The length of the specimen is 10nm, and the cross section varies from 1.2 to 6.6 nm<sup>2</sup>. Obviously, the predicted Young's moduli vary with the cross section size. Compared to the Young's modulus of bulk silicon, the smaller cross section would present the higher value. Figure 5 indicates the trend that decreasing the cross section size results in an increase of Young's modulus.

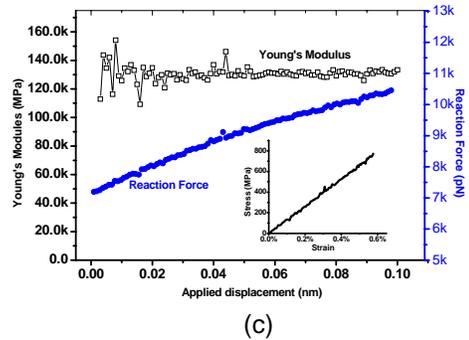
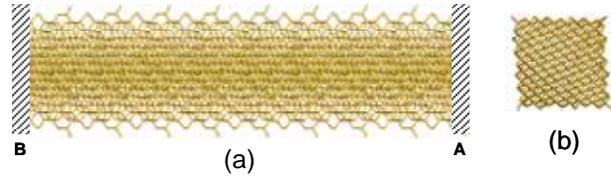


Figure 4 . (a) is the illustrated scheme of the bar type molecular mode based on the nano-scaled specimen of silicon <111>, (b) is the cross section view. The model comprises 2,688 atoms and the volume is 58.3 nm<sup>3</sup>. At 'A' section, an external displacement loading is applied in the longitudinal direction; at the 'B' section, at all degrees of freedoms is fixed. (b) is the reaction force and the predicted homogenized Young's modulus plots versus the applied external displacement.

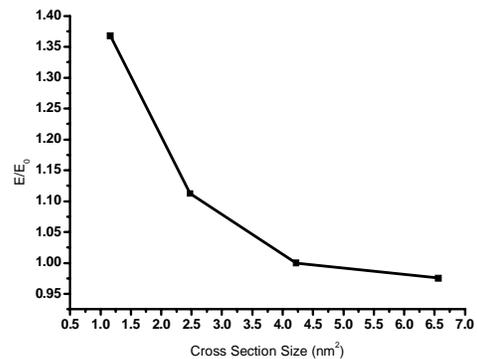


Figure 5 . Relationship between the predicted Young's modulus and the cross section size. E<sub>0</sub> is the Young's modulus of the model with cross section size equaled to 4.22 nm<sup>2</sup>.

#### 3.2 Amorphous/porous SiOC:H results

In order to verify the accuracy of the amorphous structure which generated by the proposed method, two molecules, the SiOC:H before and after UV treatment, are

used as the qualitative validation. In reference [5], the concentrations of the basic building blocks and oxygen bond angle of two molecules have been measured by nuclear magnetic resonance (NMR) and Fourier Transform infrared Spectroscopy (FTIR), respectively. The basic block concentrations are listed in the case BU and AU of Table I. Moreover, the FTIR results indicated that the SiOC:H will lose large angle Si-O-Si bond after the UV treatment. Two models, according to the experimentally obtained building block concentration, have been established by the proposed method. The bond angle distributions of these two models represent the loss of large angle oxygen bond, which is shown in Figure 6.

Table I Parametric analysis of the SiOC:H

Case	Ratio of basic building blocks					E* (GPa)	D* (g/cm <sup>3</sup> )
	Q	T	D	M	Void		
BU*	16%	44%	29%	1%	10%	16.4	1.72
AU*	21%	49%	19%	1%	10%	22.5	1.81

\*: BU and AU represent the SiOC:H molecule before and after UV treatment.

\*\*: E and D represent Young's modulus and density, respectively.

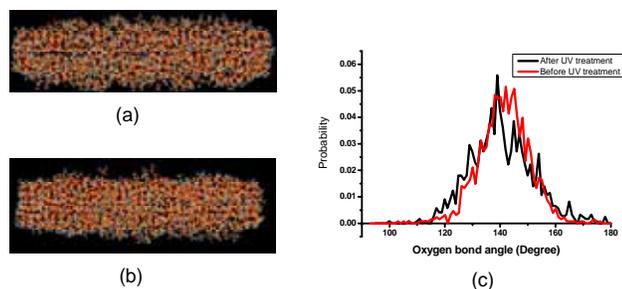


Figure 6. Qualitative validation of the obtained SiOC(H) structure by oxygen bond angle distribution (BAD). (a) and (b) represent the model before and after UV treatment (c) is the BAD plot.

The mechanical simulation results list at the case BU and AU of Table I, which follows the similar step using in the crystalline silicon. Moreover, the experiment value the Young's moduli of BU(before UV treatment) and AU(after UV treatment) are 11 and 16 GPa and densities are 1.48 and 1.52 g/cm<sup>3</sup> [5]. The simulation shows that the Young's modulus and density of AU is slightly higher than BU, and the similar trend is also found in the experiment. Note that the simulated density is defined as the ratio of atomic mass and molecule volume. Note that the molecule volume is defined as the volume which is occupied by the molecular surface with the Connolly radius of 0.1 nm. This simple case study demonstrates that the MD simulation has the capability to describe the variation of Young's modulus and density as function of chemical composition.

## 4 CONCLUSION

In this paper, the mechanical stiffness of the crystalline silicon and amorphous SiOC:H are simulated by the molecular dynamics method. The extraction of the Young's modulus is based on the classical elastic theory. The simulation results of silicon show that the mechanical stiffness is dependent upon the geometry size. Moreover, in order to simulate the amorphous nature of SiOC:H, an additional molecular structure generating algorithm is established. The oxygen bond angle distribution of the SiOC:H shows the qualitative match between the experiment and simulation. Moreover, the simulated Young's modulus and density also exhibit similar trend which discovered in the experiment.

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