

The chemical-mechanical relationship of the SiOC(H) dielectric film

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Abstract

We propose an atomic simulation techniques to understand the chemical-mechanical relationship of amorphous/porous silica based low-dielectric (low-k) material (SiOC(H)). The mechanical stiffness of the low-k material is a critical issue for the reliability performance of the IC backend structures. Due to the amorphous nature of the low-k material which has till now unknown molecular structure, a novel algorithm is required to generate the molecular structure. The molecular dynamics (MD) method is used as the simulation tool. Moreover, to understand the variation of the mechanical stiffness and density by the chemical configuration, sensitivity analyses have been performed. A fitting equation based on homogenization theory is established to represent the MD simulation results. The trends which are indicated by the simulation results exhibit good agreements with experiments from literature. Moreover, the simulation results indicate that the slight variation of the chemical configuration can induce significant change of the mechanical stiffness (over 80%) but not the density.

1. Introduction

As feature sizes for the advanced IC continue to shrink, the semiconductor industry is focusing the technology to minimize the intrinsic time delay for signal propagation, quantified by the resistance-capacitance (RC) delay. [1-2] The increasing demands for the electronic performance of the IC wiring have recently driven the replacement from aluminum trace to copper trace, and the alternative materials for SiO₂ film with lower dielectric constant [3]. These new low-k materials can be classified by silsesquioxane based material, silica based material, organic polymers and amorphous carbon. In the silica based matrix material, the attempt to reduce the k value can be obtained by two aspects. One can to replace oxygen by the carbon, hydrogen (organosilicate glass, OSG), or by fluorine (fluorinated silica glass, FSG). Generating the porosity within the material is another efficient approach.

The silicon oxide based low-k materials (SiOC(H), also called black diamond, illustrated in Fig. 1(a)) are preferred by industry because the fabricating processes of this materials exhibits high IC compatibility and high yielding rate. The k value can be reduced in two ways: either chemically by replacing oxygen by the methyl groups or H, OH, or physically by generating porosity within the material [3]. The different Si atoms are indicated with the usual denomination related to the number of O atoms linked to them: mono (M), di (D), tri (T) and quadri (Q) –functional group. The remaining links are of the type Si-R, where R is the –CH₃, O and OH functional group [4]. In addition, when functional group is replaced by a silanol group, it is indicated with OH as superscript. The Fig. 1b illustrates the groups of Q, T, D and M.

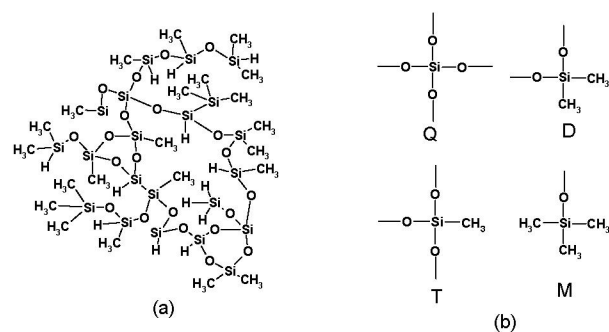


Fig. 1 . Illustration of the chemical structure of SiOC(H). (a) is the illustration of the material. (b) is the illustration of the connection capability of the basic building blocks

Among the materials of advanced IC backend structures, the low-k material has low mechanical stiffness, approximately 5-15 GPa. Experiments [4] 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. Among all the

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enhancement methods, the ultraviolet (UV) curing is preferred because the SiOC(H) film can perform the enhancement of the mechanical strength without much loss of the dielectric characteristic. However, the relationship between the chemical composition, porosity and mechanical properties remained unclear, and a trial-and-error design method is still common practice in the design/fabrication of the low-k material in the industry. Therefore, in this study, an atomic modeling method is developed, which is capable to analyze amorphous silica based material with porosity, to systematically study relation between mechanical characteristics of the SiOC(H) low-k film and its chemical structure.

Theoretically, the amorphous nature of the SiOC(H) film together with the porosity increases the difficulty to directly simulate its nano-scaled mechanical response. Due to the amorphous nature, the atomic structure can be hardly defined. The void in the SiOC(H) molecule occurs randomly, and the size of the void should be also carefully considered. According the literature, the complicate molecule (like SiOC(H) film) can be modeled when the accurate atomic structures and the potential functions are available. Yuan et al.[5-6] have stated that one can model the long chain complicate dsDNA molecule and metal after the proper atomic structures and the potential functions are obtained, no matter using the analytical solution, finite element method or the molecular dynamics. Falk and Langer [7] have applied the 12-6 Lennard-Jones potential function to describe viscoplastic deformation in amorphous solids.

In this paper, an algorithm which is capable of generating a reasonable molecular structure based on the given concentration of basic building blocks (i.e. Q, T, D, M and void). A series of simulations will be performed to understand the sensitivity of the mechanical stiffness and density with respect to the variation of the concentration of building blocks. Moreover, the fitting function based on homogenization theory is applied to understand the mechanical behavior of SiOC(H). Two sets of experimental results, the SiOC(H) film before and after UV curing, are used to validate the accuracy of the fitting function.

2. Theory

a. Molecular dynamics method

From the quantum mechanics point of view, matters have dual natures: particle and wave. However, while the geometry of the system is large enough, the wave nature of individual components becomes un-apparent and the system becomes determined. The molecular dynamics (MD), which is widely used in IC technology, is a treatment for the many-particle problems, and a determined response is prescribed. This method assumes the atom(s) as solid spheres; their movement is described by coordinate variables. The interactions between the particles are described by the potential functions, also called force fields. When the wave nature of the particle will be ignored or considered implicitly by the potential functions, MD exhibits high efficiency in the simulation

of the nano-scaled molecules. The following paragraphs will introduce the basic theory of MD, potential function, time integration scheme, boundary/initial conditions and limitation of MD.

Theoretically, MD is based on the Newton's second law of motion,

$$\vec{F}_i = m_i \vec{a}_i \quad (1)$$

for each particle i in a system constituted by N particles. In Eq. (1), m_i is the mass of particle i , $\vec{a}_i = d^2 \vec{r}_i / dt^2$ is its acceleration, and \vec{F}_i is the force acting on the particle. Therefore, MD is a deterministic technique: given an initial set of positions and velocities, the subsequent time evolution can be determined.

The interaction force between particles, which is required in Eq. (1), can be defined by the potential functions or force fields:

$$\vec{F}_i = -\frac{\partial}{\partial \vec{r}_i} U(\vec{r}_1, \dots, \vec{r}_N) \quad (2)$$

where U is the potential function and $\vec{r}_k, k = 1 \dots N$ is the atomic coordinate.

b. 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 with an additional energy minimization procedure.

A bar model is established as illustrated in Fig. 2, 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 [9], 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 [9], a model with high aspect ratio (L/h) is required to prevent boundary effects, as illustrated in Fig. 2. 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 \vec{F}^i (i represent the i -th substeps) at the fixed end) can be extracted either by the force of the pseudo-spring of the anchor point (illustrated in Fig. 3) or the energy gradient of the fixed atoms.

According to linear elasticity theory, the mechanical deformation of the uniaxially loaded bar can be represent as: $\Delta d = FL/EA$ [9], where F , E , L and A represent external mechanical force, Young's modulus, initial

length and initial cross section area of the specimen, respectively.

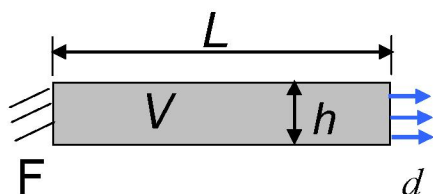


Fig. 2. Illustration to bar loading model

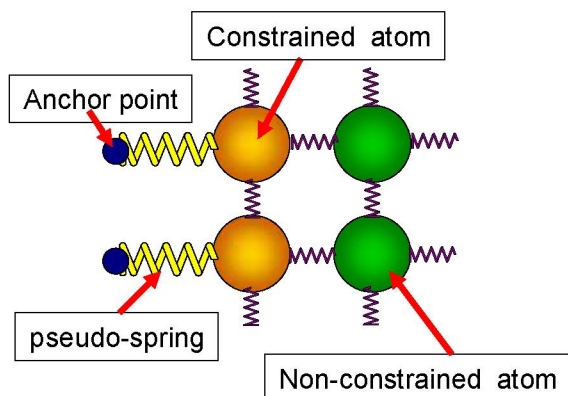


Fig. 3. Illustration scheme of the constrained atoms

3. Atomistic Model of SiOC(H)

The building blocks (Fig. 1b), Q, T, D and M, represent Si atoms having four, three, two and one capabilities to connect to other basic blocks, respectively. The size of the void is assumed to be the same as the basic blocks, and no basic group can connect to this. In the molecular modeling of the SiOC(H) film, we further assume that only the single bond would exist between any two basic groups. Moreover, the composition of the low-k film is assumed to follow the four basic blocks (Q, T, D and M). Considering the basic building blocks with silanol group and methyl group, like $-\text{OH}$ of T^{OH} and $-\text{CH}_3$ of T, both of them can not provide the connection capability to the other basic building blocks and they have the similar atomic mass. From the mechanical point of view, the transferring of the force will be terminated at the methyl or silanol group; therefore, the blocks with methyl and silanol group will be mechanically similar. Hence, the concentrations of the basic building blocks with silanol group (e.g. T^{OH} and D^{OH}) are merged into the ones with methyl groups (e.g. T, D).

In practice, SiOC(H) films with thickness ranging from 200 to 700 nm were deposited by Chemical Vapour Deposition (CVD) at 350°C . Trimethylsilane and O_2 were used as precursor and gas for film deposition [4]. Due to the similarity of the fabrication process between SiOC(H) and SiO_2 , we assume that the connection catalogue of SiOC(H) and SiO_2 are similar. Therefore, these basic blocks are assumed to be distributed onto a three

dimensional, where each node has a maximum of 4 connection capabilities. As shown in Fig. 4a, the framework will define where the building block can or can not be located. The building blocks (including the void, Q, T, D and M) will randomly distribute into the framework (Fig. 4a) and the connection between blocks will be established (Fig. 4b). However, most atoms shown in Fig. 4a are not in the equilibrium state because a cubic framework is used. The geometrical optimization procedure [10] is used to minimize the atomic potential energy of the connection catalogue.

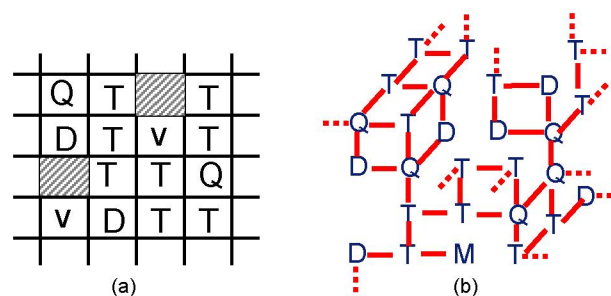


Fig. 4. Illustration of generating algorithm (a) Two-dimensional illustration of the framework and locating of the basic building block. (b) Illustration to the obtained topology of amorphous SiOC(H) molecule

4. MD simulation results and data analysis

4.1. MD simulation parameters

In order to prevent boundary effects, the length and cross section size of both cases are chosen as approximately 10nm and 6.5 nm^2 after the structural relaxation; the number of basic building blocks is 1,224. Both the cases of SiOC(H) molecule before and after UV treatment are simulated by the commercial MD solver Discover (version 2005.2) [10], and the force fields between the atoms are described by COMPASS (definition: cff91, version 2.6) [10]. Both computations are performed on an i686 machine with 2.8GHz CPU and CPU time for each case is approximately 270,500 seconds. 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. Moreover, no periodic boundary condition is applied to any model.

4.2. Parametric analysis on the case of before/after UV treatment

In order to verify the accuracy of the proposed method, two SiOC(H) models, A1 (shown in Fig. 6) and A2, having similar chemical composition as the SiOC(H) before and after UV treatment, have been generated. demonstrates the side view and cross sectional view of model A1, where the dark yellow, red, grey and white spheres represent, respectively, the silicon, oxygen, carbon and hydrogen atom. The simulation results list at the case A1 and A2 of Table I. The simulation shows that

the Young's modulus and density of A2 (after UV treatment) is slightly higher than A1 (before UV treatment), and the similar trend is also found in the experiment [4]. 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. 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.

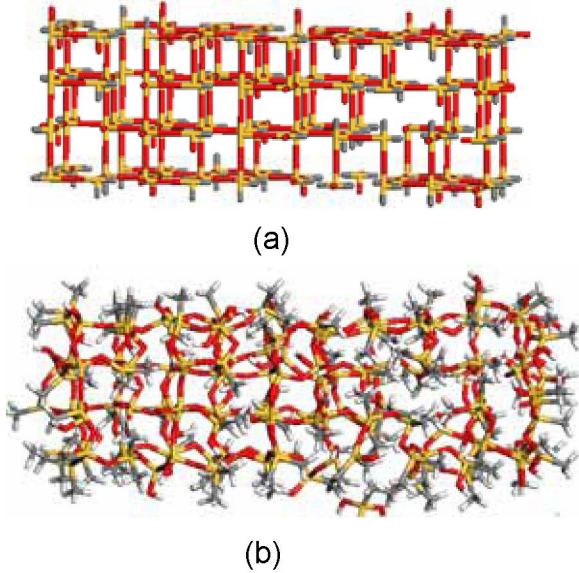


Fig. 5. (a) A generated approximate topology of SiOC(H) film. (b) the SiOC(H) film after minimization

4.3. Parametric analysis

Three series of parametric analyses are conducted as listed in Table I: the chemical composition in the B series are similar to A1 and A2; the models C1, C2 and C3 emphasize the effect of Q, T and D, respectively; the D series comprises the extreme cases (e.g. SiO₂ and air). The molecular model generating method, geometrical size and loading/boundary conditions of the B and C series and model D1 follow the same procedure of models A1 and A2. The model D1 (SiO₂) is established by the conventional silicon oxide single lattice rather than the proposed generating algorithm, but the geometry and boundary/loading conditions of model D1 is the same as the other cases. For the model D2(air), both the Young's modulus and density of D2 (air) are assumed as zero, and no computational effort is required. The simulation results of the test cases are listed in Table I, and shown in Fig. 7.

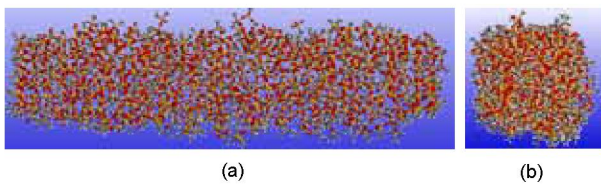


Fig. 6. The molecular model A1. (a) side view, (b) cross section view.

Considering the B series, the simulated Young's moduli and densities are similar because the concentration of basic building blocks are similar. The simulated Young's moduli for the C series exhibit large variation, but the density are similar. Therefore, the Young's modulus is highly dependent upon the chemical composition but the density is not.

Table I Parametric analysis of the SiOC(H)

Case	Ratio of basic building blocks			Young's modulus (GPa)	Density (g/cm ³)
	Q	T	D		
A1	16%	44%	29%	13.41	1.91
A2	21%	49%	19%	9.35	1.96
B1	21%	39%	29%	6.92	1.88
B2	31%	29%	29%	11.68	1.97
B3	15%	45%	16%	7.52	1.92
C1	70%	25%	6.0%	26.80	2.69
C2	22%	68%	9.4%	16.39	2.13
C3	11%	19%	69%	3.48	1.69

4.3. Data management

In order to understand how the concentration of Q, T, D and void impact the Young's modulus and density, A response function, $f_{E,density} = c_0 + c_Q r_Q + c_T r_T + c_D r_D + c_{void} r_{void}$, is used to obtain the sensitivity of the parametric analysis. For simplification, the ratio of M is merged into D because the ratio of M is relatively small compared to the rest. The coefficients of the response function are normalized by c_Q , and the results are shown in Fig. 8. The sensitivity shows that the basic building blocks of Q and T will positively influence the Young's modulus and density. Increasing the porosity will decrease both Young's modulus and density. Varying the ratio of D will not significantly influence the simulation result.

Moreover, a rather simple fitting function based on homogenization theory is used to describe the numerical results. We denote Young's moduli and densities of 100% Q, T, D are $E_Q, E_T, E_D, \rho_Q, \rho_T$ and ρ_D , respectively. Hence two fitting functions for Young's modulus and density can be written as:

$$E = E_Q r_Q + E_T r_T + E_D r_D \quad (3a)$$

$$\rho = \rho_Q r_Q + \rho_T r_T + \rho_D r_D \quad (3b)$$

The coefficients can be obtained by the least square method. Considering the detail experimental data on SiOC(H) molecule before and after UV treatment, the concentrations of basic building blocks are listed in Table II, and following the simulation results (obtained by the fitting equations (3a) and (3b)) and the experimental results. Table II indicated that the MD simulation

(represented by the fitting equation) can not provide the quantitative prediction for the SiOC(H) molecule. However, MD can simulate the increasing trend of the Young's modulus and density after the UV treatment within acceptable accuracy. Thus, our work shows that MD provides a tool to perform material design, albeit in a qualitative way. Note that the proposed simulation procedure did not consider the complex fabrication process but includes individual chemical concentration as the input.

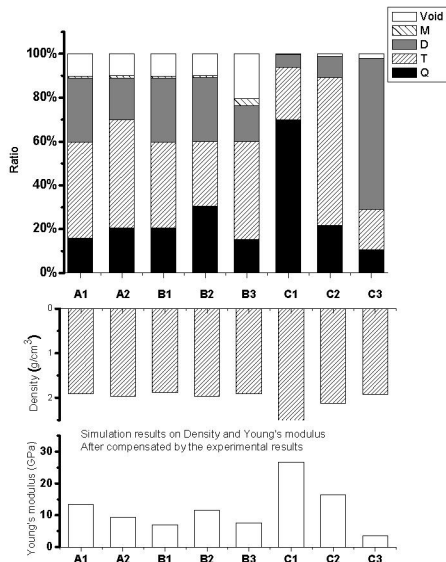


Fig. 7. The plots of concentration of basic blocks, density and Young's modulus (from upper panel to lower panel)

Table II Experimental validation on predicted trend

SiOC(H)		BU*	AU*
Concentration**	Q	15.70%	21.70%
	T	47.40%	49.70%
	D	29.80%	20.50%
By Fitting function	E (GPa)	9.87	12.43
	D (g/cm ³)	1.99	2.02
By Experiment	E*** (GPa)	11±1	16±1
	D**** (g/cm ³)	1.48	1.52

*: BU and AU represent the SiOC(H) molecule before and after UV treatment

** : obtained by nuclear magnetic resonance (NMR)

***: obtained by nano indenter

****: obtained by X-ray reflectivity (XRR)

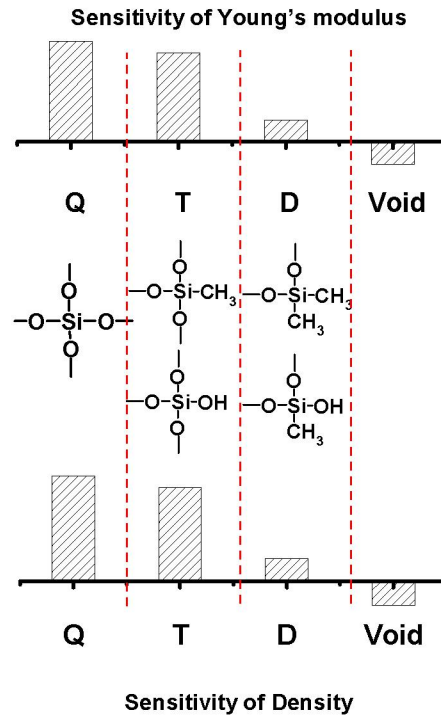


Fig. 8. The sensitivity of Young's modulus and density

Considering the magnitude of the Young's modulus density listed in Table II, the values calculated by MD are several times higher than the experimental results. Possible reasons are:

- No enough defect types are modeled, including dislocations and grain boundaries;
- Size effect: due to the fact that the surface atom may not fulfill the requirement of the octet rule, the surface atoms are often charged. This phenomenon can induce higher mechanical stiffness. Note that the surface charge is considered in the MD simulation ;
- Void collapse: the void presented in the molecular topology might collapse by the structure minimization step. After the minimization step, the void will remain 1/3 to 1/4 compared to the original topology. Therefore, the porosity of the models is much smaller than the one in reality.

However, as the size of each model listed in Table I is controlled and the porosity of SiOC(H) is approximately 10% in the reality, the qualitative trend can be validated by the experimental results.

5. Conclusions

A series of molecular modeling method is presented to simulate the amorphous low-k especially SiOC(H) material. The simulation procedure comprises three steps:

- generation of amorphous molecular model,

- parametric study by molecular dynamics (MD) method and
- data analysis.

Based on the chemical composition of the basic building blocks (Q, T, D, M) and the void, the chemical topologies are obtained and the structural minimization procedure is then performed to obtain the an approximate molecular structure. A series of parametric studies is performed to understand the sensitivity of Young's modulus and density while varying the chemical concentration. Moreover, a simple fitting function based on the homogenization theory is then applied to acquire the Young's modulus and density as functions of concentration of the basic building blocks. The experimental validation shows that the proposed method can qualitatively represent the trend. Moreover, the simulation results indicate that the slight variation of the chemical configuration can induce significant change of the mechanical stiffness (over 80%) but not the density. However, in order to achieve higher quantitative accuracy, the molecular model should be improved by increasing the geometry size, including defects of realistic size and improve method for including the porosity.

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