



# Structural characterization of amorphous materials applied to low-k organosilicate materials



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## ABSTRACT

We present a methodology to create computational atomistic-level models of porous amorphous materials, in particular, an organosilicate structure for ultra-low dielectric constant (ULK) materials known as “SiCOH.” The method combines the ability to satisfy geometric and chemical constraints with subsequent molecular dynamics (MD) techniques as a way to capture the complexities of the porous and amorphous nature of these materials. The motivation for studying ULK materials arises from a desire to understand the origin of the material's weak mechanical properties. The first step towards understanding how these materials might behave under processing conditions that are intended to improve their mechanical properties is to develop a suitable computational model of the material and hence is the focus of this paper. We define the atomic-scale topology of ULK materials that have been produced by chemical vapor deposition-like experimental techniques. Specifically, we have developed a method of defining the initial atom configurations and interactions, as well as a method to rearrange these starting configurations into relaxed structures. The main advantage of our described approach is the ability of our structure generation method to maintain a random distribution of relevant structural motifs throughout the structure, without relying on large unit cells and periodic boundaries to approximate the behavior of this complex material. The minimization of the different models was accomplished using replica exchange molecular dynamics (REMD). Following the generation of the ‘equilibrium’ configurations that result from REMD for a ULK material of a pre-specified composition, we demonstrate that its structural properties, including bonding topology, porosity and pore size distribution are similar to experimentally used ULK materials.

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## 1. Introduction

The consistent drive within the semiconductor industries to make faster devices with concomitant incremental reductions in their dimensions is a well-known phenomenon captured in Moore's Law [1]. One of the current roadblocks limiting further device shrinkage involves the back-end interconnect structures of the devices. These interconnect structures are composed of compact copper wiring, insulated by an ultra-low dielectric constant (ULK) material. Smaller dimensions cause an increase in capacitive crosstalk between adjacent copper wires, which has led to a need for an insulating material with a lower dielectric constant [2–4].

Efforts to find a suitable ULK material have, so far, focused on creating organosilicate glasses, or porous films of amorphous SiCOH, to replace the traditional dielectric insulator, SiO<sub>2</sub>. Introducing porosity into a material decreases its dielectric constant, and by adding carbon

to the SiO<sub>2</sub>, the porosity is increased by replacing Si–O cross-linking. This also maintains the compatibility of SiO<sub>2</sub> with the rest of the device [2–4]. Increasing porosity in these films creates a new problem, however, in that it inevitably weakens the mechanical integrity of the material. The carbon content, while it lowers the dielectric constant, also weakens the material by creating defects in the Si–O bond network [3,4].

In order to understand how the introduction of carbon into the Si–O network affects the structure and behavior of the material using molecular simulation techniques, it is necessary to have an appropriate atomic-level model for a given ULK material candidate. This model has two key components: a suitable intermolecular force field to describe the interactions between atoms in the system and a suitably accurate representation of the structure of the material. The latter is, at this point, the more difficult task, and is the focus of this paper. Such a model would make it possible to examine how different bonding topologies affect the material's properties, establishing a link between composition and properties. It would also allow us to observe how the material might respond to processing treatments that are under consideration to maintain mechanical integrity without pore collapse.

The first step in studying a ULK material using atomic-scale techniques, like molecular dynamics (MD), involves establishing a starting

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configuration for all the atoms in the system. This presents a challenge for this particular class of films, as the material's structure is a tunable composition of silicon, carbon, oxygen and hydrogen atoms arranged in a disordered amorphous configuration representative of a chemical vapor deposited (CVD) film, as described by experimental studies [5].

CVD-type films are believed to incorporate a large number of possible structural motifs, as shown in Fig. 1. Developing a model of CVD-type films is therefore inherently complicated because so many different bonded entities need to be incorporated into the system in a manner that is both random, and one which maintains appropriate ratios of structural units, as described by experimental Fourier Transform Infrared Spectroscopy data [5].

Film porosity also plays a fundamental role in determining the dielectric and mechanical properties of ULK films. It is therefore important that any computational representation of SiCOH materials addresses this issue, but this can be challenging. It is inaccurate on this length scale to assume that any unoccupied space contributes to porosity, since this definition does not guarantee that the volume in question is *accessible* by another atom. Nor does it indicate whether or not the volume could be located experimentally, as is typically the case with nano-scale pores. Examination of several sets of experimental porosity data for SiCOH systems [5–11] suggests that the smallest porous volume that could reasonably be measured experimentally is  $\sim 0.5 \text{ nm}^3$ . This essentially provides a cut-off for the minimum volume necessary to be counted as “porous volume” within the atomic-scale simulations. The porosity-finding algorithm must then search on both a fine enough scale to locate all the porous spaces, but on a large enough scale to discount any pores smaller than can be seen experimentally.

The final challenge in developing an accurate molecular-scale representation for SiCOH materials involves finding a method capable of relaxing the material from its initially assigned configuration towards one that approaches a global minimum for the system of atoms. Traditional molecular dynamics approaches are unsuitable for this relaxation because of computational limitations that make simulations infeasible for more than a few tens of nanoseconds for the large system sizes that are needed to reasonably represent amorphous materials (here  $\sim 6000$  atoms).

In this paper, we demonstrate an algorithm to generate a SiCOH structure that tackles all the challenges noted above. The algorithm incorporates all of the possible structural moieties observed in CVD films listed in Fig. 1, which is based off of structural data obtained from experimental studies of these films [5,6]. It incorporates appropriate porosities and pore sizes into our SiCOH model to determine how chemical changes to the structure will affect the mechanical behavior of the film. For this task, we will describe a unique method to calculate the simulated porosity and pore size distribution in order to verify that the included porous spaces have the correct scale and abundance. Porosity information found with this method can be

compared with experiment, while also capturing all of the nuances available as a result of an atomic-scale study. Finally, we will discuss relaxation of this film using replica exchange molecular dynamics (REMD) as a means to explore the available configurational space more effectively than traditional MD. As will be described in the methodology section, REMD [12,13] allows the material to rearrange to an energetically relaxed configuration that has sampled a larger subset of phase space than is accessible to traditional MD. The benefit of using REMD, instead of a simple energy minimization routine used in prior work in the literature, is that it provides the system with a protocol in which the material can sample a wider range of available structural configurations.

Following this process for deriving a SiCOH model structure, we performed a traditional MD-based compression measurement to estimate the elastic (mechanical) properties of the modeled film. This was to ensure that the modeled mechanical behavior was on par with experimental findings for a film of a similar nature. The dielectric constant was also verified using our previously described polarizability correlation method [14].

While this method is described for the development of a SiCOH-type structure, the underlying rule-based principles can be generalized to describe *any* amorphous porous structure. As the semiconductor industries explore other materials to redress the mechanical weakness of SiCOH materials, this method will remain equally viable as a route to produce an atomic-scale model of potential candidate materials.

## 2. Previous work

### 2.1. Studies modeling SiCOH materials

Many computational studies have attempted to model SiCOH materials at the atomic scale [15–25]. The study, conducted by Tajima et al. [15,16], created a set of theoretical SiCOH structures and compared the properties of these structures to experimental data on structure, Young's modulus, and dielectric constant. To generate possible structures, they used three types of Si-based starting units to describe the material:  $\text{RR}'\text{SiO}_2$ ,  $\text{RSiO}_3$ , and  $\text{SiO}_4$ , where R and R' represent either H or  $\text{CH}_3$ . They determined a ratio of these units that satisfied experimental atomic composition data, placed the various pieces at random throughout a repeating box, and linked these units together *via* oxygen bonds. The resulting unit cells were treated using standard energy minimization techniques and then used as the input for MD simulations where they were allowed to relax further. The study generated approximately 500 structures, from which they chose the two structures that appeared to provide the best match to experiment for further studies.

Tajima et al. calculated the Young's moduli of the samples from the change in the mean lattice constants over just 20 ps of constant-pressure MD simulations under different external stresses between 0 and 1 GPa. The dielectric constants of the samples were calculated

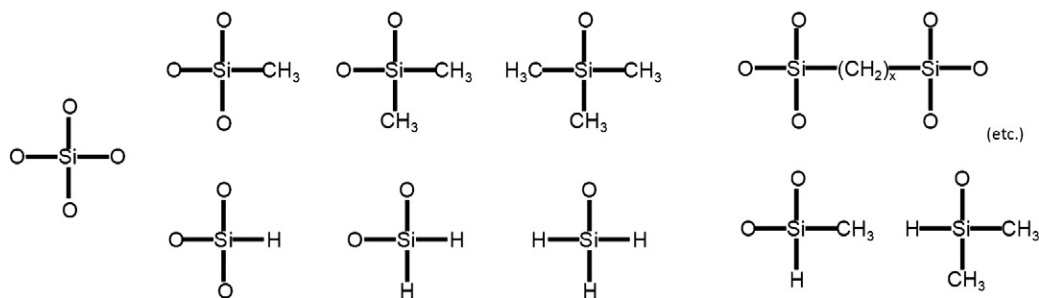


Fig. 1. Catalog of different structural entities that can occur during experimental CVD processes using standard organosilane precursors. Assuming that silicon always forms four bonds, any combination of silicon with oxygen, hydrogen, a terminal  $\text{CH}_3$  group, or a linking  $\text{CH}_2$  group is possible.

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