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A Molecular Dynamics Method for Atomic Models for Amorphous Material: an Example with SiO_2

Mingzhi Gao, Jinyu Zhang, Jing Lu, Yan Wang*, Zhiping Yu
Institute of Microelectronics, Tsinghua University, Beijing, China 100084
*E-mail address: wangy46@tsinghua.edu.cn

With the scaling of MOSFET, the degradation of circuit performance caused by the interconnection network impairs signal propagation delay, power dissipation and signal integrity. Following the transition from aluminum to copper interconnects, the search for suitable low-*k* dielectrics is currently the most important and urgent step in the course of the continued miniaturization of device dimensions in the microelectronics industry. In addition to the dielectric constant, sufficient mechanical strength is a key to successful integration of the low-*k* materials. Theoretical investigations of dielectric and mechanical properties of low-*k* films would be useful for finding appropriate film component and suitable micro-structure of the film. Unfortunately, theoretical research on the property prediction of low-*k* films has been limited.

Tajima et al. [1] developed a method to create molecular models of amorphous polymers with cross-links in which the chemically possible molecular structures were generated from a given atom-group composition. They have applied this method to the molecular modeling of a typical SiOCH low-*k* film which is made by plasma enhanced chemical vapor deposition. However, their structures were too small (containing 66 atoms) to reproduce the complexity of low-k material and the first principle calculation they applied to get dielectric property was costly in time. We followed this method and found that the direct extending of their method to larger structure will confront the difficulty in structure relaxation [2], as the totally random initial structure takes no essential of bonds (like bond length and bond angle) into account and causes the molecular dynamics (MD) relaxation hard to complete. This is exactly one important motivity of current work. Besides, fullerene based insulating materials with extremely low dielectric constants and good mechanical properties were designed by Zagorodniy et al. [3]. This kind of material is, however, something away from the state-of-art low-k film.

Producing atomic structure for amorphous material by sudden increasing and decreasing simulated temperature in MD and by continuous local bonds rearrangement [4] are among the favorite methods of physicists. However, it is difficult to transplant these methods into low-k structures modeling because of the peculiarity of the material, e.g. porosity, and the effect of cross-link of atoms on the dielectric and mechanic properties. In this paper, we propose a MD based method to create amorphous atomic structure of several hundred atoms，in which dielectric constants and mechanical properties can be predicted more efficiently comparing with first principle simulation. This method is also easy to deal with the porosity and complicated cross-link of atoms in low-k material with acceptable computational cost.

It is noted that bonding-fixed (BF) potential, (i.e. the potential that needs not only the atom position but the bonds between the atoms to calculate the force on the atoms, and that never changes the bonds during the process) in MD calculation is robust and it can be used to relax the initial structures to stable ones. With a coarse but rational initial guess given, BF potential can be used to relax amorphous structure of several hundred atoms. And a further structure optimization using non-BF potential will give a more stable thus more reasonable final configuration. If the relaxation fails in this step, it suggests that it is the bonds restriction rather than things more physically meaningful makes the BF relaxed structure stable. Amorphous material is in the sub-stable state, and any artificial structures must be relaxed to rational one with the minimum energy. With polarizable potential used (e.g. shell model potential, the simplest while widely used classic potential that take polarization into account), we can get dielectric as well as mechanic properties from MD calculation. The flow chart of the process is shown in Fig.1. The BF-potential will maintain the bonding relation of the initial chemically possible structures that make it possible to study the effect of cross-link of atoms on the material properties. The BF potential offers capability to uphold the pores introduced in the initial guess that make the study of porous material possible.

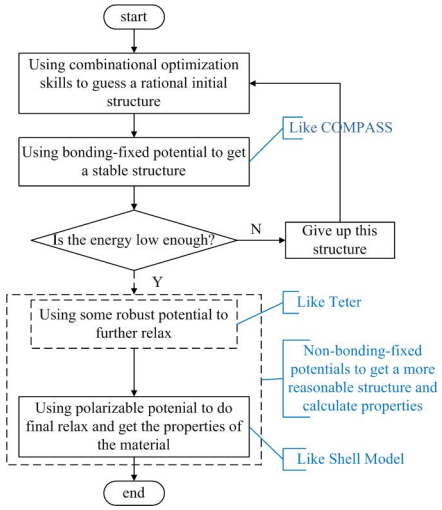

Fig.1: the process of the method for producing amorphous structure

As noted above, we found that a good initial structure is critical to produce stable result of BF relaxation, especially when the number of atoms gets large. Our process to get the initial guess is shown in Fig.2. We iterate the following process in a framework of Taboo Search and Simulated Annealing. For each structure in a sequence, we first give the bonds to the atoms and second calculate the punish functions, such as functions indicating punishment for long bonds, for unrealistic angles and torsions, for bond rings containing only a few atoms on them, etc.. —— these functions are easy to calculate and stand for some essential of the real material structure. Then the positions of the most punished atoms (and of other atoms with a smaller probability) are changed to get the next structure in the sequence. The other operations in Fig.2 are included to make Taboo Search and Simulated Annealing working. The use of combinational optimization methods offers the capability to search some good initial struture in the guess space composed of sturctures with different atom positions and bond relations. And the set of simple punish functions used here obviates the difficulty in finding a 'real' structure but

turns to focusing on providing a good start for BF relaxation and leaves the work of building a stable structure to one MD relaxation run. The way to give an initial guess of the atom positions to start this process, the rule to assign bonds to the atoms, the definition of the punish functions and the way to change the positions of atom each has effect on the result and sometimes should be modified with regard to the number of atoms. We will not give the detail here because of the limit of length.

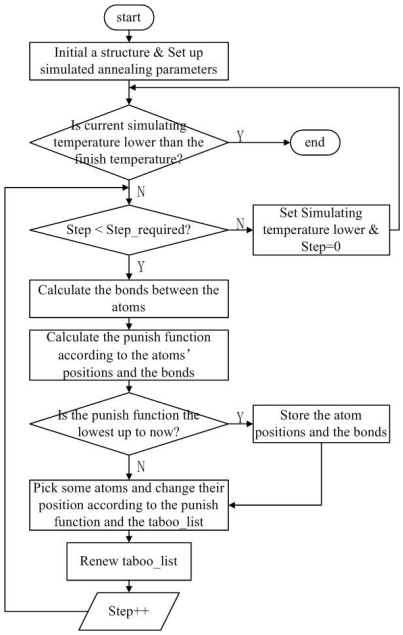

Fig.2 the flow chart of the initial guess generation process.

As a demo of this method, we applied it to SiO_2. The system contained 180 atoms in all (SiO_2-180). We produced 200 initial guesses using the process shown in Fig.2 and discussed above. Half of them passed the energy threshold after the BF potential relaxation. The threshold is The BF potential used was COMPASS [5]. And before send BF relaxed structures to the relaxation using shell model (SM) potential given by [6], we used Teter potential [7] to relax them first. The reason is that the structures relaxed after COMPASS is denser than the real material, which make the direct use of SM prone to fail and Teter potential will draw the density back to some reasonable range. Finally, 39 structures passed the SM relaxation. All these calculation was done within one week on a PC. The code used for relaxation was GULP [8]. The mechanic and dielectric properties were also calculated using SM potential.

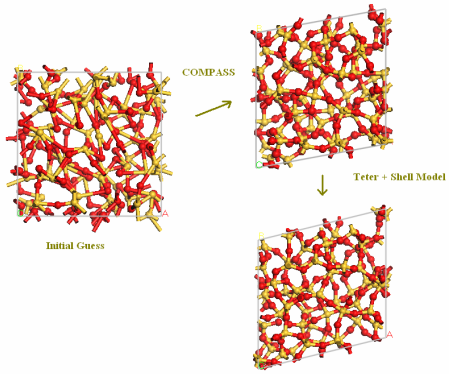

Fig.3 relaxation process of one structure of SiO_2-180: from initial guess (left) through BF relaxed structure (right-top) to the final result after non-BF relaxation (left-bottom). Here, yellow ball stands for Si atom and red one for O atom.

The resulted structures are still somewhat denser than the real amorphous SiO_2. The dielectric constant tends to be overestimated by about 1/4 by the SM potential (we checked this point in crystal SiO_2, and took it as a systematic error). The relaxation process of one structure is shown in Fig.3. The average density of the 39 structures is 2.78 g/cm^3. The average dielectric constant is 5.86 and average Young's module is 86.05 GPa. For comparing, quartz SiO_2 experimentally has density of 2.6 g/cm^3, Young's module of 93 GPa and dielectric constant of 4. Taking the overestimated density and the 1/4 magnification of dielectric into account, the result is quite reasonable .Using Clausius formula, the dielectric constant of SiO_2 of density of 2.78 is 4.4; considering 1/4 systematic error, the result is 5.5 which is close to the average calculated dielectric constant 5.86. When checking the correlation among these three properties (as shown in Fig.4), we are surprised to find there is little correlation between mechanic and dielectric properties. The non-correlation between dielectric and mechanic properties makes it possilble to find suitable low-*k* film with high hardness.

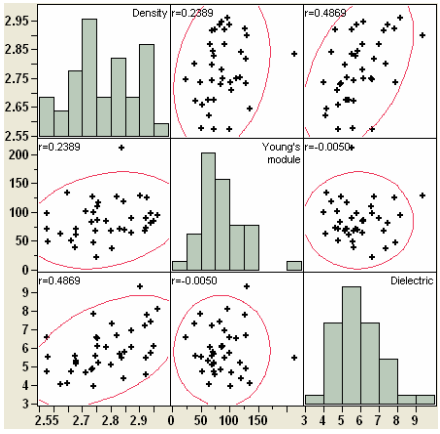

Fig.4 Correlation among density, dielectric constant and Young's module

In summary, we have proposed a new MD based method to create atomic models of several hundred atoms for studying amorphous materials. The initial network structures are generated with combinational optimization process. These initial network structures then have been submitted to the MD simulations to get the final structures by two-step relaxation. This method has been applied to the modeling of the microstructure of a SiO2-180 system. The calculated mechanic and dielectric properties from all 39 structures are consistent with the experimental results. This method is convenient to be applied to low-k material and would be useful for finding appropriate film component and suitable micro-structure of the film. The calculations on larger system i.e. SiO2-360 and on other systems are on the way.

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