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Comparison of empirical potentials for calculating structural properties of amorphous carbon films by molecular dynamics simulation

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ABSTRACT

Amorphous carbon (a-C) films were deposited by molecular dynamics simulation using Tersoff, REBO and AIREBO potentials, respectively. The hybridization and the distributions of both bond angles and lengths as a function of the three potentials were analyzed, and the density and residual stress were calculated. Results revealed that comparing with the Tersoff and REBO potentials, the AIREBO potential gave the more reasonable values of density, hybridization ratio and residual stress. This attributed to that in AIREBO potential, the conjugation effect between the different coordinated atoms was corrected by revising the bond order term, which was responsible for the sp^3 content; while the introduction of long-range Lennard-Jones (LJ) interaction described the compressed graphite structure correctly following the rational density; in particular, both the LJ and torsion interactions were indispensable for the accurate evaluation of residual stress of a-C films. In addition, the simulation result using AIREBO potential suggested no dependence on the processing methods of atom-by-atom deposition and liquid-quenching method.

1. Introduction

Amorphous carbon (a-C) film has been widely used in the fields of automobile, aerospace, biomedicine and so on due to its superior mechanical, tribological, optical properties and chemical inertness [1–3]. Because the excellent properties of a-C film originate from its special structure composed of sp^3 and sp^2 hybridizations, the accurate evaluation for sp^3/sp^2 structures is essential for systematic exploration of its properties. However, due to the difficulties in quantitative analysis of the atomic structure by experiment, such as Raman [4], X-ray photoelectron spectroscopy [5], electron energy loss spectroscopy [6] and nuclear magnetic resonance [7], it is only possible to obtain an insufficient or a phenomenal understanding of the relationship between the structure and properties.

Molecular dynamic (MD) simulation either of *ab initio* or empirical method enables one to capture deeper insight on the structure-property relationship from atomic or electronic scale. In principle, *ab initio* MD simulation is applicable to a-C system to obtain an accurate description of the structure and properties [8,9]. However, high computational expense practically limits the application to a small system composed of less than 100 atoms. It would be too expensive to simulate the growth process of a-C film. On the other hand, the simulation with empirical potential describes the relationship between the energy and geometry with a set of relatively simple potential functions, which allows it to be applied to much larger systems than *ab initio* MD simulation. Empirical MD simulations have been successful in simulating the growth behavior of a-C film and describing the structure-property relationship. For example, Li et al. [10] carried out MD simulation of a-C film growth to investigate the structural evolution for various incident energies of carbon atoms. They revealed the “Point-Line-Net” formation process. Stuart et al. [11] simulated the a-C films with different densities and reported that the structural factors such as void volumes and coordination numbers were more useful than ring size distributions in characterizing the structure of a-C film. Ma et al. [12] studied the microscopic process underlying the friction of a-C films using MD simulation, and revealed that the excellent lubricity of a-C arose from the atomic shear induced by strain localization.

In the empirical MD simulation, the reliable description of interatomic interactions is strongly and solely dependent on the empirically interatomic potential. The selection of empirical potential is thus crucial for accurate simulation of the a-C model. It would affect the hybridized bond structure and the corresponding properties. Many empirical potential models are now available for carbon system, including Tersoff [13,14], REBO [15], AIREBO [16], Reactive Force Field

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potential [17], Environment Dependent Interaction potential [18] and Charge optimized many-body potential [19]. Among of them, Tersoff, REBO and AIREBO potentials have been more widely used to study the structural properties of a-C film [10–12,20,21], but it is yet to be obvious that how much the different potentials result in the difference in the simulated structures and which factor in the potential model mainly causes the difference in the simulated results. In the present work, we performed the same a-C film growth simulation with different empirical potentials of Tersoff [14], REBO [15] and AIREBO [16] to comparatively address the dependence of simulated result on the empirical potentials model. The density, hybridization structure, residual stress and both the bond angle and bond length distributions were analyzed. The results evidently showed that the AIREBO potential correctly handled the overbinding effect of specific bonding configurations. Furthermore, AIREBO potential led to the reasonable description of structure and properties owing to the additional long-range Lennard-Jones (LJ) and torsion interaction terms.

2. Simulation details

Classical MD simulation was used to carry out the comparative study of the empirical potentials of carbon. We compared the structural properties of a-C films prepared by the identical deposition simulation using three different interatomic potentials (Tersoff, REBO, and AIREBO potentials). Fig. 1 gave the model used in the calculations according to previous studies [20,21]. A diamond (0 0 1) single crystal with size of 20.18 × 20.18 × 25 Å^3 in x, y and z directions was served as substrate, which consisted of 29 atomic layers with 64 carbon atoms per layer and was equilibrated at 300 K for 100 ps before carbon deposition simulation. The atoms in the bottom three monolayers were fixed to mimic the bulk substrate. Temperature of the next eight layers was kept at 300 K during simulation for providing a thermal reservoir to the simulation system. Atoms of top eighteen layers were totally unconstrained to simulate the structural evolution during deposition. The incident carbon atoms were introduced at the position of 50 Å above the substrate surface at a random {x, y} position. The deposition was simulated using *NVE* ensemble implemented in the large-scale atomic/molecular massively parallel simulator (LAMMPS) code [22]. Periodic boundary conditions were applied in both the *x* and *y* directions.

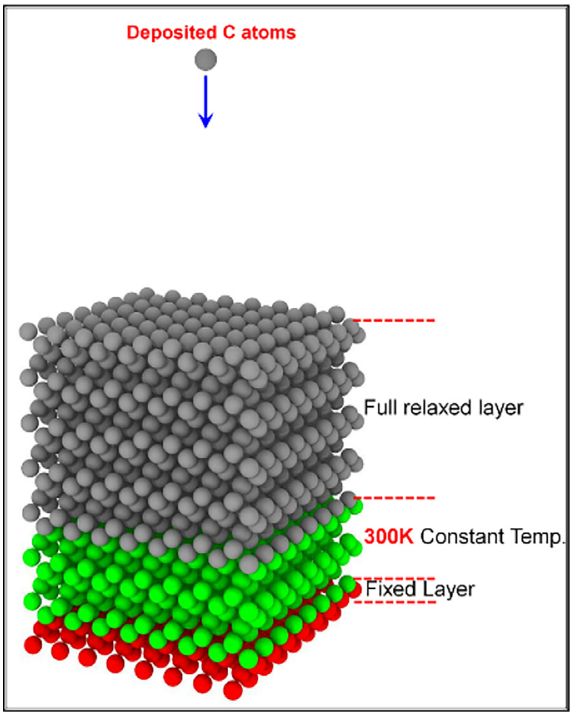

Fig. 1. Deposition model used in the calculations.

Total 1750 carbon atoms were deposited at the normal incident angle. The time step of simulation was 0.25 fs. The kinetic energy of incident carbon atoms was fixed at 70 eV/atom, that was known to be the optimum energy for a highly stressed and dense tetrahedral amorphous carbon film deposition [10]. The time interval between the sequential carbon atom depositions was 10 ps, which corresponded to an ion flux of 2.46 × 10^{28}/m^{2}s. The previous report has indicated that the time interval of 10 ps was enough for relaxing the atomic structure induced by the energetic incident carbon bombardment [10]. Diffusion or rearrangement processes were ignored in this simulation, because the event would be very rare at room temperature once the structural agitation by energetic carbon bombardment was settled down. The system temperature was rescaled to 300 K by the Berendsen method [23] after 10 ps when the atomic arrangement caused by the bombardment of the incident atoms was finished. Heat bath coupling constant was set to be 10 fs in all simulations.

3. Results and discussion

3.1. Results

Fig. 2 shows the morphologies of deposited films obtained by Tersoff, REBO and AIREBO potentials. Color of atoms represents the coordination number. The amorphous carbon films with the thickness about 36 Å is obtained for each case. Since the incident energy of carbon atoms (70 eV) is much higher than the cohesive energy of diamond (7.6–7.7 eV/atom) [21], the incident C atoms can penetrate into the diamond substrate, resulting in the intermix layer with high residual stress due to impairing the regular lattice of substrate. After intermixing, a steady state film grows with the surface transition layer.

This growth behavior is evident when analyzing the thickness dependence of film properties. Fig. 3 shows the variations of density and coordination number along the growth direction. The coordination number of carbon atoms is determined by using a cutoff value in the interatomic distance of 1.85 Å. It reveals that the a-C film can be divided into three regions: interfacial intermixing region, steady state growth region and surface transition region. The structural property gradient can be observed obviously in the intermixing region (yellow region in Fig. 3), which is caused by the intermixing with the substrate. The surface transition region (gray region in Fig. 3) exhibits a markedly deterioration of the structure and properties. In the steady state growth region with the thickness about 20 Å, the constant values for density and coordination numbers are obtained along the growth direction (light blue region in Fig. 3). The steady state growth region is used for further analysis of the structural properties of the deposited films using different interatomic potentials.

Fig. 4 shows the density, hybridization ratios of the bonds, and the residual stress of a-C films obtained by the three interatomic potentials. The biaxial stress, σ, in the film is calculated using Eqs. (1)–(3).

$$P_{IJ} = \frac{\sum_k^N m_k v_{kI} v_{kJ}}{V} + \frac{\sum_k^N r_{kI} f_{kJ}}{V} \tag{1}$$

$$P = \frac{P_{xx} + P_{yy} + P_{zz}}{3} \tag{2}$$

$$\sigma = -\frac{3}{2}P \tag{3}$$

Here, *I* and *J* take on values *x*, *y* and *z*; *k* is the atom in the domain; *N* is the number of atoms in the system; m_k is the mass of atom *k*; v_{kI} and v_{kJ} are the *I*th and *J*th components of the velocity of atom *k*; *V* is the system volume (or area in 2d); r_{kI} is the *I*th component of the position of atom *k*; f_{kJ} is the *J*th component of the force applied on atom *k*; *P* is the hydrostatic pressure; P_{xx}, P_{yy} and P_{zz} are the diagonal components of