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Role of atomic transverse migration in growth of diamond-like carbon films*

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The growth of diamond-like carbon (DLC) films is studied using molecular dynamics simulations. The effect of impact angle on film structure is carefully studied, which shows that the transverse migration of the incident atoms is the main channel of film relaxation. A transverse-migration-induced film relaxation model is presented to elucidate the process of film relaxation which advances the original model of subplantation. The process of DLC film growth on a rough surface is also investigated, as well as the evolution of microstructure and surface morphology of the film. A preferential-to-homogeneous growth mode and a smoothing of the film are observed, which are due to the transverse migration of the incident atoms.

Keywords: diamond-like carbon, molecular dynamics
PACC: 7115Q, 6855

1. Introduction

Diamond-like carbon (DLC) films are widely used in industry due to their superior structural and functional properties. Structurally, DLC is an amorphous solid consisting of a random carbon network without grain boundaries,[1] while DLC films are atomically smooth, continuous, compact and pin-hole free.[2] The key parameters to characterize DLC film structure are the high film density and fraction of sp^3 bonding, on which depend the excellent functional properties of the film, such as high hardness and low friction.[3]

The generally accepted subplantation model proposed by Lifshitz,[4] Davis[5] and Robertson[6] attributes densification, compressive stress and the high sp^3 fractions to shallow implantation of energetic atoms. A process of 'thermal spike' anneals the impact region to a sp^2 bonded graphite phase and reduces the density and stress. However, the model mainly deals with the atomic movement in the normal direction of the substrate, the transverse migration of the atoms is not considered, and the channels of film relaxation are not presented.

In magnetic storage devices, 1–2 nm thick diamond-like carbon films are deposited on heads and discs as protective overcoats to achieve recording densities over 152 Gbit/cm^2. DLC film provides an amorphous, continuous and atomically smooth coating to magnetic layers, which can duplicate the surface morphology of the original substrate. However, there usually exist some small bulges and pits locally on the substrate, due to the Ar^+ sputtering as a pretreatment of the samples. The effects of surface roughness on the film growth have not been investigated by molecular dynamics (MD) simulations, if the substrate is not atomically smooth.

In the present study, three-dimensional MD simulations are carried out using the reactive empirical bond order (REBO) potential for carbon–carbon interactions,[7] which is a revised form containing analytic function and an extended database relative to Brenner potential. The rest of the paper is organized as follows: Section 1 introduces the potential and model for MD simulations. The effects of impact angle on the film properties are discussed in Section 2.1, through which a transverse-migration-induced film relaxation model is brought forward. In Section 2.2, the process of DLC film growth on a rough surface is studied. Conclusions are presented in Section 3.

2. Model and method

The model for this study is similar to that for our previous study.[8] Successive impacts of 1300 atoms on diamond substrate with lateral dimensions

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of 2nm×2nm are simulated. Various impact angles are assigned by setting different values to the transverse components of the kinetic energy of incident atoms. Here, the impact angle refers to the angle between incident direction of the atom and the horizontal direction. The chemical interactions between carbon atoms are described using the reactive empirical bond order (REBO) potential with an increased C–C cutoff.[9] This potential is not based on the traditional many-body expansion of potential energy in bond lengths and angles, instead, a bond order function is used to introduce many-body effects and chemical bonding into a pair potential, which enables this potential to allow for covalent bond breaking and forming with appropriate changes in atomic hybridization.[7] The total energy U of an N-particle system is described in the form

$$U = \sum_i \sum_{j(>i)} [V^{\mathrm{R}}(r_{ij}) - b_{ij} V^{\mathrm{A}}(r_{ij})]. \tag{1}$$

The function $V^{\mathrm{R}}(r)$ and $V^{\mathrm{A}}(r)$ are pair-additive interactions that represent all interatomic repulsions and attractions, respectively, which are revised forms of the Morse-type potential

$$V^{\mathrm{R}}(r) = f^{\mathrm{c}}(r)(1 + Q/r) A \mathrm{e}^{-\alpha r}, \tag{2}$$

$$V^{\mathrm{A}}(r) = f^{\mathrm{c}}(r) \sum_{n=1,3} B_n \mathrm{e}^{-\beta_n r}. \tag{3}$$

The quantity r_{ij} is the distance between pairs of nearest-neighbour atoms i and j. The cutoff function $f^{\mathrm{c}}(r)$ limits the range of the covalent interaction. And b_{ij} is a bond order between atoms i and j, which is expected to be primarily controlled by local coordination and the atomic environment. The bond order function b_{ij} is written as

$$b_{ij} = \frac{1}{2}[b_{ij}^{\sigma-\pi} + b_{ji}^{\sigma-\pi}] + b_{ij}^{\pi}. \tag{4}$$

Values for the functions $b_{ij}^{\sigma-\pi}$ and $b_{ji}^{\sigma-\pi}$ depend on the local coordination and bond angles for atoms i and j, respectively. The function b_{ij}^{π} depends on the dihedral angle for carbon-carbon double bonds and whether a bond between atoms i and j is part of a conjugated system. The detailed formulation of REBO potential can be found in the literature.[7]

In order to simulate the process of DLC film growth on a rough surface, however, we enlarge the simulation cell to study the surface morphology evolution. To imitate surface roughness, four small hills, each composed of 230 carbon atoms with a height of 7 Å are located on a 6nm×6nm flat substrate. The modified model is schematically depicted in Fig.1. The space between hills is referred to as the valley.

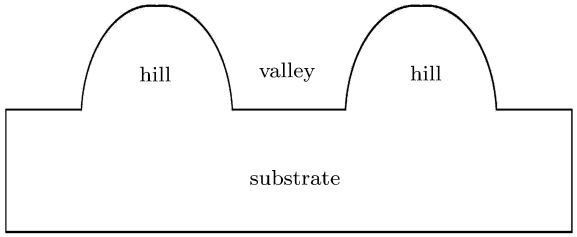


Fig.1. Model of the rough surface.

3. Results and discussion

3.1. Pathways of film relaxation

According to our previous study,[10] the behaviours of incident atoms on the surface are classified into four categories: implantation, surface freezing, transverse migration and rebounding, according to the atomic movement. The behaviours of incident atoms have an important influence on microstructure and growth mode of DLC film. However, the existing models of DLC film growth mainly deal with the atomic movement in the normal direction, with little consideration of the transverse migration of the incident atoms.

To study the role of transverse migration of incident atoms during film growth, the structures of DLC films deposited with different impact angles are analysed. In this model, besides the normal component, there are also transverse components of kinetic energy of an incident atom. Various impact angles are assigned by setting different values to the transverse components of the kinetic energy, while the magnitude of normal component is held fixed. Such structural parameters as film densities and sp^3 fractions are calculated under impact angles of 30 °, 45 °, 60 ° and 90 °. Results are shown in Fig.2. While the normal component of kinetic energy remains unchanged, both the relative density and sp^3 fraction increase markedly with increasing impact angle, both of which reach maximum values when the atoms impact the substrate in the normal direction (with impact angle of 90 °). This implies that the transverse component of the impact energy will enhance the transverse migration of the incident atoms, which will enables the

incident atoms to overcome energy barriers and settle at an energetically more favoured position. So the transverse migration of the atoms can lower the potential energy of the system, and is the main pathway of film relaxation.

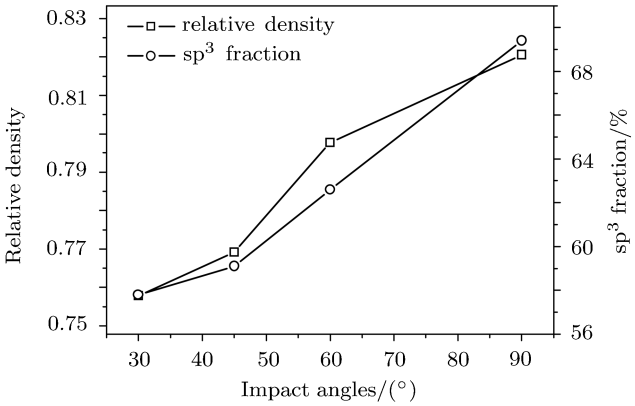


Fig.2. Effect of impact angle on film structure.

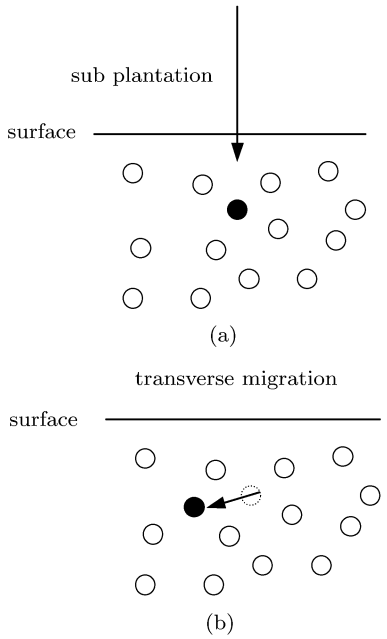


Fig.3. Schematic illustration of models of DLC film growth: (a) Subplantation model; (b) Transverse-migration-induced film relaxation model. Black disc indicates the incident atom, hollow circles show substrate atoms.

Figure 3(a) gives the subplantation model[4] of DLC film growth, where some energetic atoms are implanted into the subsurface of the film as interstitial atoms, which causes local densification, a large fraction of sp^3 bonds and structural incompatibility resulting in formation of atomic-level stress. However, this increase in local density is a metastable process, the incident atoms may also cause local melting of the substrate around the impact site. This process is schematically depicted in Fig.3(b) and a transverse-migration-induced film relaxation model is proposed. That is, the implanted atom has a transverse migration and move away from the impact region to a nearby vacancy. As a metastable phase, the sp^3 structure is readily converted to sp^2 structure which is energetically more favourable, under some disturbance, for example, the thermal excitation. The atomic implantation causes a process of 'thermal spike',[4] which provides the required energy for this transformation. So a sp^2 bonded graphite phase is formed and the local density and stress of the impact region is reduced, which also explains why sp^3 fraction and residual stress in DLC films usually vary with impact energy in a similar manner. The transverse migration of the atoms is the main channel of film relaxation. The competition between atomic implantation and transverse migration determines the growth mode and final structure of the film.

3.2. Smoothing of DLC film grown on a rough surface

From the discussions above, the transverse migration of the incident atoms can cause film relaxation, which is disadvantageous to deposition of DLC film with large sp^3 fraction. To further clarify the role of transverse migration of atoms in film growth, we study the DLC film growth on a rough surface.

Figure 4 shows atomic structures at different stages of the deposition process. Grey balls represent substrate atoms, white balls the deposited atoms. In the initial stage of deposition, the broadening and coalition of the hills are observed, which are due to the preferential growth of the film in the valley between the hills. Some incident atoms impacting the substrate at the hillside are activated to migrate to the valley. And there is small probability that the atoms incident or sputtered into a valley overcome the energy barriers caused by surface roughness to move upward to the top of the hill. As the deposition process is going on, the peak-to-valley distances are continuously reduced, until the preferential growth in the valley is no longer obvious. Finally, homogeneous growth of the film prevails. The smoothing of the film is mainly attributed to the transverse migration of surface atoms around the hills and the restricted movement of the atoms in the valley, as consequences of the atom im-

pact and the post-impact relaxation.

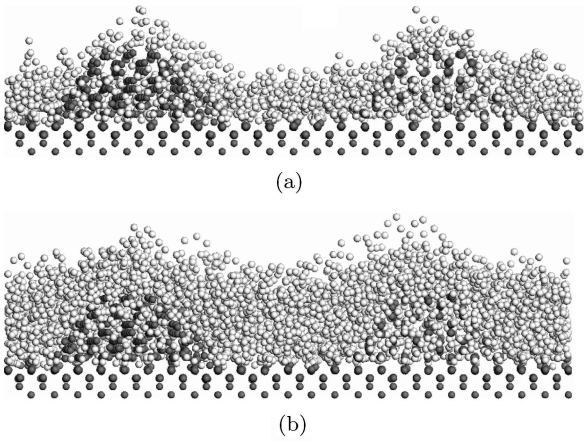


Fig.4. Atomic structures at different stages of the deposition process. (a) Atomic structure of DLC film at t = 1900 ps; (b) Atomic structure of DLC film at $t = 4300$ ps with a thickness of 1 nm. (side views).

The evolution of surface morphology and roughness is shown in Fig.5. In Fig.5(a), three curves with different height of bumps represent surface morphologies of three stages of the deposition process relative to the average surface level. Here, the dashed line shows the average position of the surfaces, which are set to 0 on purpose for all three surfaces for the convenience of comparison. The root mean square (RMS) roughness of the surface decreases from 0.24 to 0.17nm when the film thickness increases from 0.1nm to 1nm. Here the film thickness is calculated through evaluating the instantaneous average surface position. From the evolution of surface morphology and surface roughness, it is straightforward to quantitatively understand the smoothing process of DLC film growth.

The smoothing process of the DLC film can be well accounted for by the behaviour of atomic transverse migration. In Fig.6, the solid curve shows the track of a single incident atom during the deposition process on a rough surface, whose profile is depicted by the dashed curve. When the incident atom falls onto the rough hill of the surface, its trajectory deviates from the initial direction. An obvious transverse migration of the incident atom takes place, until the atom is brought to the valley of the surface and finally reaches equilibrium. Conversely, it is difficult for the incident atoms directly deposited in the valley to migrate to the top of the rough hill or settle at the hillside. This helps to clarify the preferential growth of the film in the valley in the early stage of the deposition. As the deposition goes on, however, the surface becomes smoother and the hills become lower. So it gets easier for the atoms to settle at the rough hills, more atoms are able to overcome the energy barriers and move from the valley to hills, which further smooths the surface.

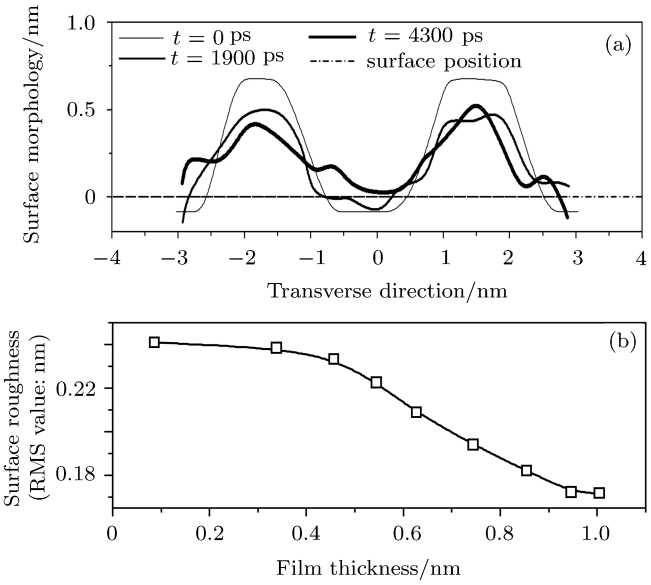


Fig.5. Evolution of (a) surface morphology (side view) and (b) surface roughness.

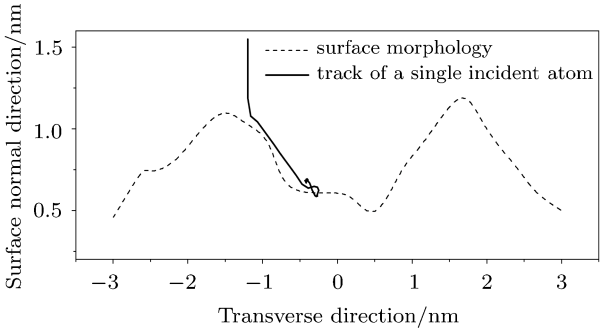


Fig.6. Track of an incident atom on rough surface (side view).

4. Conclusions

The role of atomic transverse migration in growth of diamond-like carbon films are twofold. Firstly, the transverse migration of the atoms is the main channel of film relaxation, resulting in the transformation of sp^3 structure to sp^2 structure and reduction of local density of the film. We propose a transverse-migration-induced film relaxation model based on the subplantation model. The competition between atomic implantation and transverse migration determines the growth mode and final structure of the film. Secondly, the smoothing of the film is

also attributed to the transverse migration of surface atoms around the hill and the restricted movement of the atoms in the valley, which is the consequence of the atom impact and the post-impact relaxation. This implies that DLC films can provide atomically smooth coatings and satisfy the requirements for the ultimate storage density.

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