Thin Solid Films 552 (2014) 136–140

Contents lists available at ScienceDirect

Thin Solid Films

journal homepage: www.elsevier.com/locate/tsf

Molecular dynamics simulation for the influence of incident angles of energetic carbon atoms on the structure and properties of diamond-like carbon films

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ARTICLE INFO

Article history:
Received 14 May 2013
Received in revised form 26 November 2013
Accepted 6 December 2013
Available online 14 December 2013

Keywords:
Diamond-like carbon
Residual stress
Incident angles
Molecular dynamics simulation

ABSTRACT

The influence of incident angles of energetic carbon atoms (0–60°) on the structure and properties of diamond-like carbon (DLC) films was investigated by the molecular dynamics simulation using a Tersoff interatomic potential. The present simulation revealed that as the incident angles increased from 0 to 60°, the surface roughness of DLC films increased and the more porous structure was generated. Along the growth direction of DLC films, the whole system could be divided into four regions including substrate region, transition region, stable region and surface region except the case at the incident angle of 60°. When the incident angle was 45°, the residual stress was significantly reduced by 12% with little deterioration of mechanical behavior. The further structure analysis using both the bond angles and bond length distributions indicated that the compressive stress reduction mainly resulted from the relaxation of highly distorted C–C bond length.

1. Introduction

Owning to high hardness, low coefficient of friction, superior optical property, chemical inertness and good biocompatibility, diamond-like carbon (DLC) films are not only widely used as a protective coating in the industrial fields of cutting tools, molds, data storage and so on [1,2], but also considered as a strong candidate for the biomedical applications such as heart valves [3,4], vascular stent [5] and artificial joint [6]. However, the high level of residual compressive stress that is dominated by the distorted atomic bond structure in DLC films deteriorates the adhesive strength between the film and the substrate, which leads to the failure of coated surface.

Many efforts have been made to reduce the residual stress by controlling the substrate bias during deposition [7], fabricating the multilayer nano-structure [8,9], incorporating third elements into carbon matrix [10,11] and post-annealing process [12]. However, most of the previous works focused on the DLC films with normal incidence of carbon ions, the effect of incident angles on the structure and properties was not given enough attention. Although Liu et al. [13] have revealed that the microscopic structure of the deposited DLC films was influenced seriously by the incident angles of energetic carbon ions, the fundamental understanding of this microstructure and properties evolution from the viewpoint of atomic scale is still unclear due to the limited experimental characterization. Molecular dynamics simulation (MD) has been proved to be an effective method for deeper insight of the atomic bond structure and properties of DLC films in atomic scale. By MD simulation, the variations of structure and properties with the kinetic energy of deposited carbon atoms [14–16], the energy of the carrier gas ions such as Ar^+ [17], hydrogen content [18] or growth species [19,20] have been studied. Joe et al. [21] recently reported the growth of amorphous carbon films by the grazing incidence of energetic carbon atoms and the origin of the rough surface growth under grazing incidences was clarified by the impact-induced uphill transport of the surface atoms. Neyts et al. [22] clarified the influence of the impact angles on the sticking coefficients of several radical species on amorphous carbon surface. But the evolutions of structure and properties with the incident angles are still not fully understood yet.

In the present work, we performed a classical MD simulation to deposit the DLC films with grazing incidence of energetic carbon atoms, the structure and properties evolution were systematically investigated. The dependence of mechanical properties on the incident angles, the distribution of residual stress, the bond length and bond angle distributions were mainly focused. Structural analysis of the films revealed that the grazing incidence of carbon atoms could relax the bond length distortion, which played a key role in the reduction of residual compressive stress.

2. Computational strategy

In order to simulate the deposition of DLC films by MD simulation, the three-body empirical potential Tersoff was chosen to describe the

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0040-6090/$ – see front matter
http://dx.doi.org/10.1016/j.tsf.2013.12.012

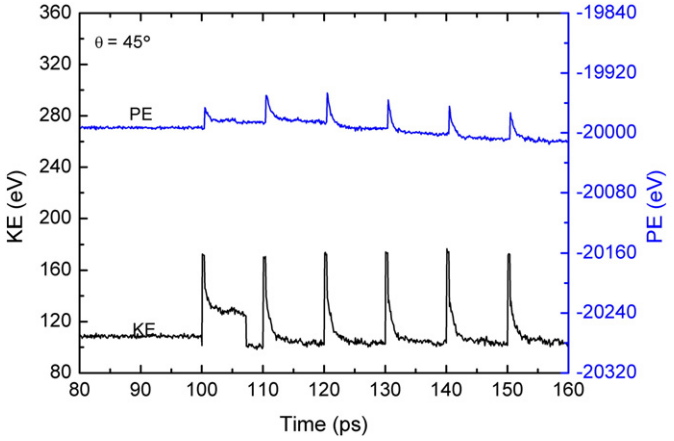

Fig. 1. Energetic variation during the deposition process when the incident angle is 45°.

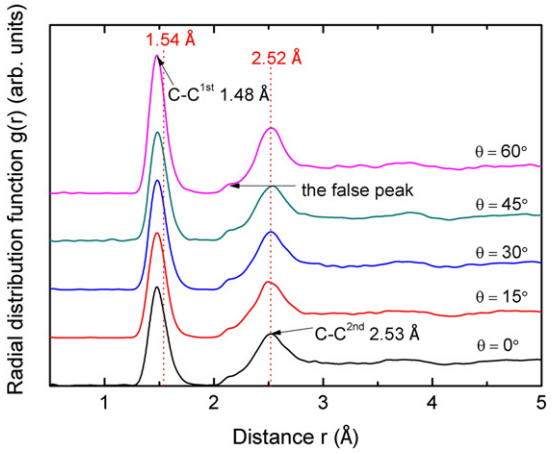

Fig. 3. RDF of DLC films with the different incident angles of carbon atoms.

interaction between the deposited carbon atoms and the diamond substrate [23]. Even if the calculated results have revealed the limit of Tersoff potential where the π bonding is not adequately considered [24–26], it is still demonstrated to be an effective potential for carbon-based system.

The diamond (001) single crystal of 25.2210 × 25.2210 ×24.0758 $Å^3$ in the *x*, *y* and *z* directions was used as substrate, which contained 2800 carbon atoms with 100 atoms per layer and was equilibrated at 300 K for 100 ps before deposition. The incident carbon atoms were introduced at the position of 10 nm above the substrate surface at a random {x, y} position. The positions of atoms in the bottom two layers were frozen to mimic the bulk substrate, while all the other atoms were unconstrained. The kinetic energy of incident carbon atoms was fixed at 70 eV/atom, because it was the optimum energy for a highly stressed and dense DLC film deposition [27]. The impacts of 2000 carbon atoms were simulated and the incident angles of carbon atoms, θ, were varied from 0 to 60°. The periodic boundary conditions were applied in *x* and *y* directions and the time step was fixed at 1 fs.

The time interval between two sequential deposited carbon atoms was 10 ps, which induced an impracticable ion flux of 1.57 × $10^{27}/m^2s$. The changes in kinetic energy (KE) and potential energy (PE) during the deposition process are illustrated in Fig. 1. It indicates that the time interval of 10 ps is enough for relaxing the atomic structure and diminishing the unrealistic effect of high carbon flux on the deposition process. However, it should be noted that a number of processes such as diffusion or rearrangement processes occur on much longer time scales. They are neglected in the simulation due to the required computation time. The substrate temperature was rescaled to 300 K by the Berendsen method [28] after the atomic rearrangement caused by the bombardment of incident atom was finished.

3. Results and discussion

Fig. 2 shows the final morphologies of DLC films at the incident angles of 0–60°, where colors represent the different coordination numbers. All the deposited films show the typical amorphous feature which will be described later by the radial distribution functions (RDF). At the normal incidence (Fig. 2a), the deposited film shows the dense structure with a smooth surface [27]. With the increase of incident angle from 0 to 60°, the surface roughness of DLC films increases and more porous structure is generated, implying the change of mechanical properties. In addition, Fig. 2d–e shows the emergence of a bump-like surface structure, which is in good agreement with the MD calculation results [21]. Because the fixed incident energy of 70 eV/atom is much higher than the cohesive energy of diamond (7.6–7.7 eV/atom), the incident atoms can penetrate into the diamond lattice and intermix with the substrate atoms. Therefore, a significant intermixing layer between the film and the substrate can be observed for each case (Fig. 2).

The RDF spectra of DLC films are shown in Fig. 3, in which the red dotted lines represent the positions of the 1st nearest neighbor (1.54 Å) and the 2nd nearest neighbor (2.52 Å) of crystalline diamond, respectively. First of all, the RDF spectra reveal that all the films are amorphous with the characters of long-range disorder and short-

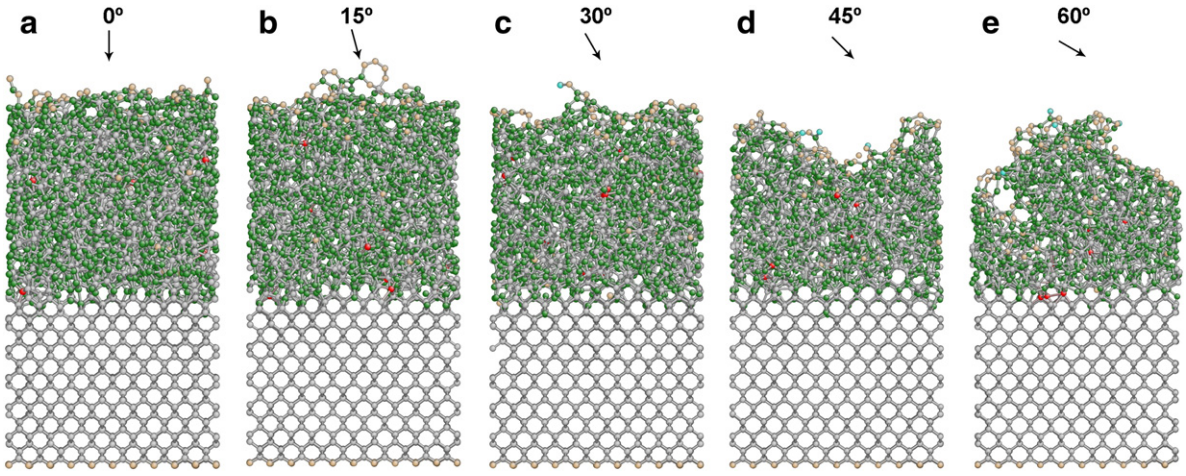

Fig. 2. Snapshots of the films at the incident angles of (a) θ = 0°, (b) θ = 15°, (c) θ = 30°, (d) θ = 45° and (e) θ = 60°, where blue, yellow, green, gray and red colors represent the different coordination numbers of 1, 2, 3, 4 and 5, respectively.