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Atomistic simulations of diamond-like carbon growth

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ABSTRACT

Diamond-like carbon (DLC) films are composed of carbon bonds with different hybridizations, including sp^2, sp^3 and even sp^1. Understanding the atomic bonding structure is essential to understanding the properties and optimizing the process parameters of the films. Because of the limited analytical tools for characterizing the atomic bonding structure in amorphous materials, computational research at the atomistic scale could provide significant insight into the structure–property relationships in diamond-like carbon films and has been applied to understanding the various phenomena occurring during DLC film growth. The contributions of the atomistic simulations and electronic structure calculations pertain mainly to three important issues: (i) the sp^3 bond formation and stress generation mechanisms, (ii) the stress reduction mechanism by metal incorporation, and (iii) the impact angle-dependent surface smoothening/roughening mechanisms.

1. Introduction

Diamond-like carbon (DLC), commonly referred to as amorphous carbon (a-C), with a high content of sp^3 bonds, has attracted considerable attention from the scientific community since a thin film of the material was created by Aisenberg and Chabot in 1971 using an ion-beam deposition technique at room temperature [1]. DLC films exhibit properties comparable to those of diamond materials, such as a high mechanical hardness and chemical inertness. These characteristics are attributed to the covalent sp^3 bonding; a high bond strength (7.41 eV for a σ bond in diamond) allows the materials to be both mechanically hard and chemically inert. Such properties are desirable for applications where surface protection is required. With the technical availability of thin DLC film fabrication by various methods, e.g., filtered cathodic vacuum arc and mass-selected ion beam methods, DLC coatings are widely used in industry [2,3].

DLC films with a variety of properties can be generated by tuning the growth conditions, among which the ion energy E has the most critical role. An E in the range of 50–500 eV is usually used for DLC film growth [2]. The dependence of the film structure on the ion energy has been extensively studied by experiments and atomistic simulations, and it is accepted that $E = 50$–100 eV is the optimum energy range for producing a high sp^3 fraction. At relatively low energies, an sp^2-rich film is produced, while at high energies (greater than 100 eV) the sp^3 fraction also begins to decrease [3].

Although DLC films are satisfactory with respect to their superior mechanical properties (hardness = 60–120 GPa), the high residual compressive stress (6–20 GPa) can cause poor adhesion between the film and the substrate [4,5]. Therefore, buckling or even delamination (particularly with hard substrates such as glass) is often encountered [6], which hampers the performance.

Extensive effort has been devoted to understanding the mechanisms that mediate these features of DLC using atomistic simulations such as molecular dynamics (MD). Now, computational methods are becoming more important in shedding light on veiled microscopic details, thanks to the rapid development of both computational power and reliable interatomic potentials (see next section).

In this brief review, we shall focus on two aspects of DLC or hydrogen-free a-C growth: first, what previous MD or ab initio studies have to tell us about (i) the sp^3 bond formation process and the origin of intrinsic high residual compressive stress and (ii) the stress reduction upon the incorporation of a small amount of metal, and second, the origin of surface smoothening or roughening bifurcated by the impact angle.

2. Development of the empirical carbon potential

In this section, a brief history of the empirical carbon potential is introduced. Tersoff developed the general formalism of the empirical potential for a covalent system by considering Si as a representative element [7]. The formalism was soon empirically re-parameterized and applied to carbon systems in 1998 [8]. Although both C and Si are group IV materials and are able to covalently bond with themselves, their amorphous phases display clear differences in bond formation; for a-C, the sp^2 hybridized bonds are contained in the structure, while they appear only as dangling bonds in amorphous silicon (in other words, Si presents an absence of π-bonding) where an sp^3-bonded network is constructed. Thanks to the small differences in the enthalpies of sp^2 and sp^3 lattices, carbon is versatile and is able to form multiple bonds, including single, double and triple

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bonds, with itself and with other elements, while Si is unable to form multiple bonds due to weak p_π–p_π orbital overlap, the overlap modality involved in forming multiple bonds [9]. A good interatomic potential for carbon should be sensitive to such diverse and unique properties of carbon bonding, thus enabling accurate modeling of the material's chemistry and the related dynamic processes.

Based on the work of Abell [10] and Tersoff, Brenner introduced improved potentials for hydrocarbons in 1990 and 1992 [11,12]. The motivation was to empower atomic-scale dynamics simulations to resolve the issues on diamond films produced by chemical vapor deposition. Although the Abell–Tersoff approach describes C – C bond lengths and energies (including single, double and triple bond) reasonably well, the underlying assumption only takes into account nearest-neighbor interactions and can overestimate the binding energy (so-called "overbinding") for intermediate bonding configurations, e.g., bonding between a three-coordinate C atom (a radical) and a four-coordinate C atom, and favor decidedly unphysical configurations such as a five-coordinate carbon atom, i.e., the overbinding of radicals [13]. In the Brenner potential, such conjugation effects or many-body interactions were taken into account by means of the bond order function [14].

In 2002, Brenner et al. revised the potential to be suitable for extended data sets and called it the 2nd generation reactive empirical bond order (REBO) potential [15]. The REBO potential is capable of modeling chemical interactions, e.g., C – C or C – H covalent bond formation and breaking. To take into account van der Waals interactions between molecules, e.g., forces between graphite layers, the adaptive intermolecular reactive empirical bond order (AIREBO) potential was proposed by Stuart et al. in 2000 [16]. The AIREBO potential includes two additional energy terms besides the REBO energy term for covalent bonding; one is the Lennard–Jones 6–12 potential that represents the attractive van der Waals dispersion interactions for non-bonded long-range intermolecular interactions, and the other is a torsional potential for refining the relative orientations of dihedral angles coupled with single bonds.

Marks introduced the environment-dependent interaction potential (EDIP) for carbon [17]. However, the EDIP is inherently unable to reproduce the correct distances for double and triple C – C bonds [17]. Lee et al. reported the modified embedded atom method (MEAM) interatomic potential for carbon, stating that the MEAM potential is as good as the original Tersoff potential for carbon and is easily extended to various metal–carbon alloy systems [18]. However, thus far, there have been few reports that confirm its capabilities. The reactive force field (ReaxFF) developed by van Duin et al. is the most advanced potential in that it provides a proper way to handle not only the bond order approach but also charge equilibration. Consequently, it can deal with more complex systems and has described many organic and inorganic systems [19,20]. However, MD simulations of DLC film growth with ReaxFF have not yet been reported. Although there are some variants of the potentials described above, this is a functional line-up of the well-recognized empirical carbon potentials. Citation statistics indicate that the Brenner, REBO and AIREBO potentials are still in mainstream use in MD simulations of systems containing C and H [14].

3. The physical origin of the high residual compressive stress of DLC films fabricated by ion-beam methods

There are two widely accepted models used to explain the high residual compressive stress of DLC films: one is the subplantation model, and the other is the thermal spike model. In what follows, computational approaches to address this issue are briefly reviewed. Lifshitz et al. proposed the subplantation model to explain both the high sp^3 fraction and the high compressive residual stress in DLC films generated by energetic ion bombardments [21–23]. Subplantation is a shallow implantation of incident energetic atoms in the subsurface when they have sufficient energy to penetrate the target surface. If deposited at the subsurface, they would induce a local structural distortion of the existing carbon network, producing increased internal stress and densification of the film. Moreover, a tetrahedral sp^3 environment would be more likely to yield at the surface because the surface atoms are less coordinated than the bulk atoms [24–26]. The thermal spike model, however, assumes that a significant fraction of the energy from energetic ions is transferred to the local region near the impacts, causing a 'thermal spike' region or a local melting region. In such a region, carbon atoms would favor a metastable sp^3 site that is made thermodynamically stable under the high pressure and high temperature induced by the thermal spike [26–28].

Uhlmann et al. carried out the first three-dimensional MD simulation with a density-functional-based tight-binding (DFTB) method [29]. For $E > 30$ eV, the effect of subplantation increased substantially due to C incorporation and momentum transfer, while the surface was covered with a defective sp^2-rich structure due to the collision damage. Overall, a composite structure consisting of an sp^2-rich/sp^3-rich layer was developed. For $E < 30$ eV, the incoming C was deposited on the surface, and a rough, sp^2-rich film was generated. This is supportive of the subplantation model rather than the thermal spike model because the atoms in the collision damage region were significantly displaced, and as a result, a low sp^3 fraction and density were obtained.

Kaukonen and Nieminen found through MD simulations with the Tersoff potential that dense diamond-like structures were formed in an energy window of $E = 40$–70 eV, consistent with previous experimental suggestions [30]. This demonstrated that an MD approach using an empirical potential (neglecting electronic processes) is applicable to real deposition processes. The authors argued that the optimal energy window is produced by the interplay between annealing due to local heating and defect generation, both of which are generally attributed to thermal spikes at high energies.

Lee et al. reported MD results supportive of the thermal spike model [31]. The sp^3 fraction reached a peak in an energy window of $E = 50$–75 eV and then decreased at higher energies. The density and the residual stress also exhibited similar trends (Fig. 1). These

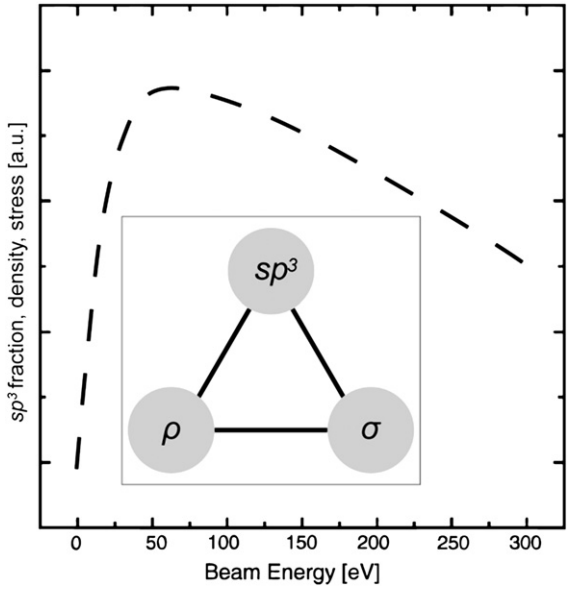

Fig. 1. Nearly identical responses of the three structural factors (the sp^3 fraction, the density ρ, and the stress σ) to the beam energy. Each response curve is collapsed to one curve, which is represented by the dashed line, adapted from Ref [31]. These three components of the DLC are closely coupled with each other; if the sp^3 fraction increases, the density ρ and the stress σ would be increased due to the $\rho \rightarrow \rho_0$ transition and the many distorted bonds involved with the subplantation, respectively (inset).