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Thin film deposition of tetrahedral amorphous carbon: a molecular dynamics study

N.A. Marks*

School of Physics A28, The University of Sydney NSW 2006, Australia

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Abstract

Molecular dynamics simulations of carbon thin film deposition are performed using the Environment Dependent Interaction Potential. Films deposited with carbon beams in the range 1–100 eV reproduce the energy dependence of the biaxial stress, density and tetrahedral bonding fraction observed experimentally. The transition from low-density, graphite-like amorphous carbon to the high-density tetrahedral phase occurs at an energy at which impacting ions do not penetrate the surface of the film. This result is incompatible with the generally accepted subplantation explanation for the diamond-like properties, and a new model of energetic burial is deduced from the simulations. Radial distribution functions compare well with experiment, and represent a significant improvement over Tersoff and Brenner simulations which contain unphysical distances.

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1. Introduction

Tetrahedral amorphous carbon (ta-C) is an industrially useful diamond-like material prepared as a thin film using energetic ion beams [1–5]. Formation of ta-C is associated with an energy range of approximately 30–500 eV, and within this window ta-C has a tetrahedral bonding (sp^3) fraction as high as 80–85%, large compressive stresses (5–10 GPa) and a density of 3 g/cm^3. Outside of the energy window amorphous carbon (*a*-C) is found, characterized by low stress, low-density structures and a predominance of graphite-like (sp^2) bonding.

Despite over a decade of investigation into ta-C, there remains ongoing debate over the nature of the process responsible for the high sp^3 fraction. The generally accepted subplantation model [6–8] attributes densification, compressive stress and the high sp^3 fractions to shallow implantation of energetic ions, while the cylindrical thermal spike model suggests a temperature induced mobility process [9]. Other models propose a pressure-induced mechanism of sp^3 promotion arising from either compressive stress [1,10] or peening effects during energetic impact [11]. The theoretical uncertainty surrounding ta-C arises in part from experimental variability [9] associated with deposition and characterization, giving computational studies an important role. Molecular dynamics is the ideal tool for resolving the sp^3 question and other deposition issues, but modeling thin film growth is itself a formidable challenge requiring simulations with ~10^3 atoms running for ~10^6 timesteps. This computational burden has prevented the most accurate techniques such as density functional theory and non-orthogonal tight-binding from simulating film growth, and these methods have instead been applied in liquid-quench simulations at fixed density [12–16].

Empirical potentials have the computational efficiency required to model thin film growth, but typically the calculations have been limited by the transferability of the potential. Deposition simulations using the Tersoff potential [17] produced films which were neither ta-C nor a-C, having a density of 3 g/cm^3 but an sp^3 fraction less than 30%

* Tel.: +61 293518167; fax: +61 293517726.
E-mail address: nigel@physics.usyd.edu.au.

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[18,19]. Jäger and co-workers [19,20] deposited films using the Brenner potential [21] and these were found to have even lower sp^3 fractions than the Tersoff calculations, while high sp^3 content films deposited using a modified Brenner potential contained unphysical structures and distances. Similar anomalous features were observed in 100 eV orthogonal tight-binding simulations using a truncated cutoff [22]. The most successful simulations of ta-C deposition have used the Environment Dependent Interaction Potential (EDIP) [23]. These calculations [24,25] reproduce the transition from a-C to ta-C with increasing energy, anomalous distances are absent, and post-deposition implantation reproduces the energy window effect [25]. Somewhat controversially, the EDIP simulations found that films grown with beam energies of ~10 eV can have a density approaching 3 g/cm^3, an sp^3 fraction greater than 50% and a large compressive stress—all the hallmarks of ta-C. This finding has significant implications for models of ta-C formation, and brings the accuracy and applicability of EDIP deposition under close scrutiny.

In this article we report on a significant set of details of the EDIP simulations which have not been previously presented. The procedure for depositing the EDIP films is explored carefully, and issues such as nucleation of the steady-state, identification of the bulk region and subplantation characterization are addressed. Analysis of the surface and bulk regions of the simulated films are shown to agree with experiment, and impact classification provides quantitative insight into the deposition of ta-C. Additional simulations are also performed in which EDIP is modified to increase its resemblance to the Tersoff and Brenner methods, and these calculations help explain some of the limitations of these methods for the simulation of ta-C.

1.1. Film growth models

Theoretical descriptions of the ta-C formation process have sought to explain three principal properties: compressive stress, density and sp^3 fraction. Experiments show that all three quantities are maximal in the same energy window, and share the same energy dependence [2]. Other materials also show an energy window for the compressive stress (e.g. TiN [26] and SiO_2 [27]), and thus theories of stress generation have an applicability beyond the amorphous carbons. The four principle explanations for ta-C are illustrated schematically in Fig. 1, and are discussed below.

1.1.1. Subplantation

This is the generally accepted explanation for the properties of ta-C, and has been proposed variously by Lifshitz [6], Davis [7] and Robertson [8]. In this model shallow implantation of energetic species is considered to generate a density increment in the sub-surface layers of the film, leading to sp^3 promotion and compressive stress.

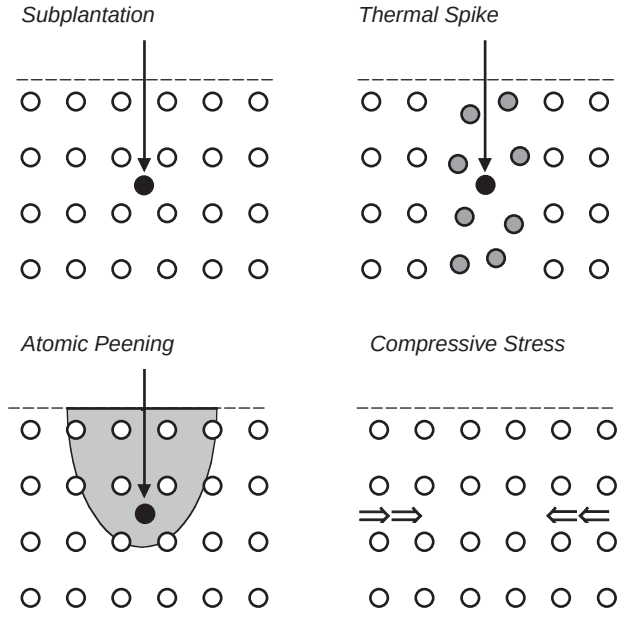

Fig. 1. Schematic illustration of popular models of ta-C thin film growth. The subplantation mechanism is attributed to Lifshitz [6], Davis [7] and Robertson [8], while the peening, thermal spike and compressive stress models are proposed by Koponen [11], Hofsäss [9] and McKenzie [10] respectively.

Experiment [28] and simulation [18,29] concur that surface penetration occurs with ions with energies greater than 30–40 eV, and thus a prediction of the subplantation model is that films with high-density, compressive stress and large sp^3 fractions should only occur above this energy.

1.1.2. Thermal spike

Hofsäss et al. [9] proposed a cylindrical thermal spike model in which the transient heating generated by ion impact leads to atomic rearrangements which favor the diamond-like properties of ta-C. Using analytic models of heat diffusion and ion implantation statistics from binary collision calculations, they predict ta-C formation between energies of 50 eV and 2 keV. This model lies in opposition to conventional understanding of energetic beam deposition where thermal spikes are considered a mechanism for annealing, leading to stress relief, reduction in density reduction and lower sp^3 fractions.

1.1.3. Compressive stress

Under high-pressure (~4 GPa) graphite will transform to diamond at room temperature and McKenzie et al. [1,10] have suggested that the compressive stress generated during film growth could be responsible for the high sp^3 phase. This model draws upon thermodynamics, and is suggestive of a threshold process, and thus the compressive stress explanation would suggest that the sp^3 fraction has a non-linear dependence on the stress. Due to experimental uncertainty it has not been possible to quantitatively determine this relationship.