Available online at www.sciencedirect.com
SCIENCE DIRECT®
Diamond and Related Materials 12 (2003) 2003–2010
DIAMOND AND RELATED MATERIALS
www.elsevier.com/locate/diamond

Atomistic simulation of energy and temperature effects in the deposition and implantation of amorphous carbon thin films

N.A. Marks*, J.M. Bell, G.K. Pearce, D.R. McKenzie, M.M.M. Bilek

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

Abstract

Molecular dynamics simulations of carbon deposition and implantation are performed using the newly developed environment dependent interaction potential. Three scenarios are considered: room temperature deposition, post-deposition implantation and high temperature substrate heating. The room temperature depositions exhibit the characteristic energy dependence observed experimentally and shows that tetrahedral amorphous carbon forms at energies well below the subplantation threshold. In agreement with the experiment, implantation results in graphitisation and stress reduction and the critical dose for maximal change are well predicted. Simulations of ex-situ and in-situ heating investigate kinetic effects and thermal stability respectively, with the latter revealing an unexpected epitaxial growth mode.

Keywords: Amorphous carbon; Molecular dynamics; Thin film deposition; Ion implantation

1. Introduction

In 1990 McKenzie and coworkers [1] first synthesized a hydrogen-free diamond-like amorphous carbon, a material which would come to be known as tetrahedral amorphous carbon or *ta*-C. It has now well established that *ta*-C is formed when the incident carbon beam falls within an energy window of 30–500 eV, with the optimal energy-dependent on the details of the deposition apparatus [1–5]. With high density and hardness, *ta*-C has found important applications in wear-resistant coatings and as a corrosion barrier in hard drives. Lower density amorphous carbon or *a*-C, is also technologically useful, and has been proposed as a heart pump component in which the high fraction of π-bonding ensures a durable yet low-friction material. Very thick *a*-C films have recently been produced [6,7] using the plasma ion immersion implantation (PIII) method [8], which combines deposition with implantation to greatly reduce compressive stress and promote the sp^2 phase.

Molecular dynamics (MD) simulations provide unique insight into deposition and implantation process, but progress has been slow due to the complexity of the carbon bond. Well-known interaction potentials such as Tersoff [9], Brenner [10] and Stillinger-Weber [11,12] perform badly in calculations of the liquid and amorphous states, finding qualitatively incorrect coordination fractions, densities and stresses [13,14]. These errors arise from an inadequate description of the crystalline state, where all three methods falsely predict graphite to have a density similar to or even greater than diamond.

We recently developed a new potential which includes non-bonded interactions and is thus able to describe graphite and other π-bonded phases. Known as the environment-dependent interaction potential or EDIP [15], this new interaction potential provides high transferability at a fraction of the cost of tight-binding methods [16–18]. Comparisons with ab initio data [13–15] show the EDIP method provides an excellent description of crystalline, amorphous and liquid states, all of which may be present during carbon thin film deposition. EDIP thus represents an important new investigative tool for the understanding of carbon thin film processes.

This paper describes three virtual experiments using EDIP in which the substrate temperature and incident energy are varied. The first set of simulations use monoenergetic carbon beams to deposit tetrahedral amorphous carbon (*ta*-C) thin films at room temperature. In an example of the insight provided by MD, it is shown that the subplantation model [19–21] (the de

*Corresponding author. Tel.: +61-9036-9085; fax: +61-2-9351-7725.
E-mail address: nigel@physics.usyd.edu.au (N.A. Marks).

0925-9635/03/$ - see front matter © 2003 Elsevier Science B.V. All rights reserved.
doi:10.1016/S0925-9635(03)00215-2

facto explanation for the tetrahedral bonding) is not supported by the simulations, with *ta*-C production observed for energies less than 10 eV. The second set of simulations considers the bi-modal energy distribution of the PIII method. High energy impacts (200–500 eV) are used to ion-beam damage a film deposited with 25 eV atoms, initiating a transformation from *ta*-C to *a*-C with increasing implantation dose. In the final simulation set, we consider the effect of elevated temperature during and after deposition. Intriguing results are found for the in-situ simulations where the elevated temperature (1000 K) is found to inhibit the amorphous phase and promote epitaxial growth of the diamond substrate.

2. Method

The films were grown using monoenergetic beams, with each film deposited onto a (001) diamond substrate with (2×1) reconstructed upper and lower surfaces. Periodic boundary conditions were applied in the x and y directions, each with a side length of 14.22 Å, and for each energy 500–1000 atoms were individually deposited onto the upper surface with normal incidence and random position in the xy-plane. The impact of each energetic atom leads to substantial heating of the substrate and film, and thus velocity rescaling wall thermostats of thickness 2 Å acted upon atoms with a lateral displacement greater than 6.11 Å from the initial position of the incident atom. These thermostats prevent recycling of energy through the boundaries and a similar thermostat applied to the substrate base removes heat, which also diffuses away in an infinite system. The motion of all atoms was followed for between 0.5 and 1 ps and rethermalisation to the substrate temperature was carried out prior to deposition of the subsequent atom. This scheme approximates the experimental situation where the time between successive impacts is in the order of a millisecond, and the simulations specifically exclude thermally activated diffusion processes, which might possibly contribute to increased surface graphitisation. However, the most important interactions occur on the sub-picosecond scale and are fully described, as in the case of room temperature deposition, electron energy loss linescan experiments [22] find no thermally activated graphitisation.

Chemical interactions were described using the environment-dependent interaction potential (EDIP) first proposed for silicon [23] and recently generalized for carbon [15]. Carbon EDIP consists of three components: a two-body pair energy, a three-body angular term and a generalized coordination. The two- and three-body terms have environment dependence controlled by the atomic coordination, which in general has a fractional value. The coordination is decomposed into spherical and aspherical terms, the latter unique to the carbon potential and vital for describing non-bonded π-interactions.

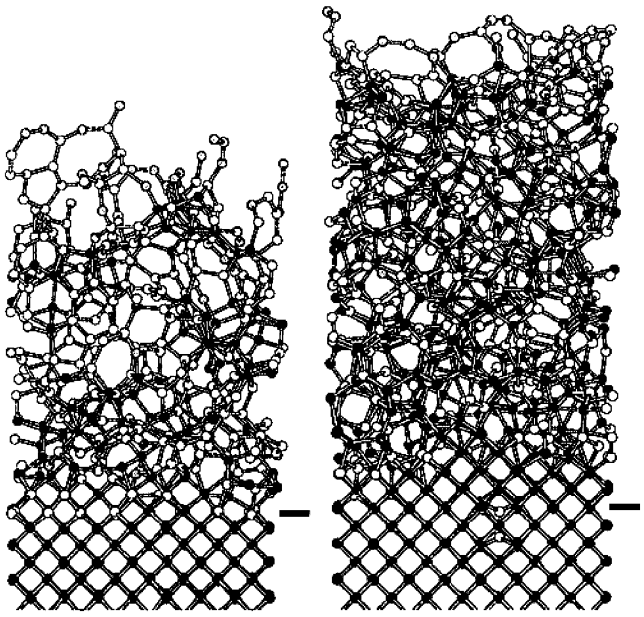

Fig. 1. Structure of amorphous carbon thin films deposited with 1 eV atoms (left) and 70 eV atoms (right). The coordination was determined by counting neighbours within 1.85 Å, with grey, white and black circles denoting atoms with two, three and four neighbours, respectively. The horizontal bar indicates the initial height of the substrate.

Nuclear stopping processes were described using the screened coulomb Ziegler–Beirsack–Littmarck (ZBL) potential [24]. Unlike fixed coordination potentials, the pair potential cannot be joined by spline fitting to the ZBL expression due to the environmental dependence. Instead, a pair of Fermi switching functions was used to interpolate between the pair and ZBL potentials. The switching functions were offset by 0.3 Å to avoid changes in concavity in the transition region.

3. Energetic deposition

Eleven films were deposited onto a 300 K substrate, using monoenergetic beams with energies of 1–100 eV. All the films were amorphous and possessed a low-density π-bonded surface, but the properties of the bulk regions varied significantly. Here the energy of the deposition beam was found to be strongly influential on important material properties such as density, sp^3 fraction and biaxial stress. Fig. 1 illustrates the dramatic changes in morphology and structure, which are driven by the beam energy. In the left panel the 1 eV beam generates a low-density film containing mostly sp^2 bonded atoms indicated by white circles, while in the film deposited with a 70 eV beam (right panel) the majority of the bulk atoms are sp^3 bonded (black circles) and the density is noticeably higher. This energy-induced