

Molecular-Dynamics Study of the Fundamental Processes Involved in Subplantation of Diamondlike Carbon

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Molecular-dynamics simulations of diamondlike carbon film growth from carbon atoms with kinetic energies between 10 and 100 eV are performed. The interatomic forces are calculated by means of an efficient density-functional based tight-binding scheme. The results show that surface processes are dominant for deposition below 30 eV, while subsurface processes govern the structure formation for higher energies. The mechanisms leading to a composite structure of these films characterized by a deep sp^3 rich dense layer below a defective surface layer are revealed. [S0031-9007(98)06671-X]

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Low energy (~ 1 –1000 eV) carbon containing species have been widely used for carbon film deposition following Aisenberg and Chabot [1]. The crucial role of the ion energy in tuning the properties of the evolving films between those of graphite (sp^2 bonding) and diamond (sp^3 bonding) was demonstrated [2–17]. An energy window exists in which the amorphous carbon films have a predominant tetrahedral configuration corresponding to an sp^3 fraction exceeding 80% [2–4], denoted as tetrahedral amorphous carbon (ta-C) or diamondlike carbon (DLC). The unique properties and the variety of the different diamondlike carbon films have led to considerable efforts in developing models to understand the deposition processes and the related structure and properties [18–22]. Lifshitz *et al.* proposed a subplantation model suggesting that the deposition by hyperthermal species is a shallow implantation process. This has been supported by experimental findings and simulations [7,9,18,22]. The incorporation of carbon species into subsurface layers and the associated internal stresses is claimed to be the dominant mechanism forming a dense diamondlike phase. Several semiquantitative descriptions were suggested which tried to explain some of the experimental data [19–21,23]. Few molecular dynamics (MD) studies approached the buildup of stress in the DLC films [15,24–26]. Because of the difficulties in studying experimentally or by calculations the elementary processes responsible for the evolution of DLC films, the mechanisms of sp^3 formation and sp^2 suppression are still under debate. The field was recently reviewed by several authors [3,27–30]. This Letter describes the first three-dimensional MD work which follows the details of the evolution of DLC films under bombardment. A carbon target is subjected to collisions of C atoms with energies between 10 and 100 eV. In contrast to previous MD growth simulations, which rely on empirical many-body potentials [24–26], in this study a density-functional based tight-binding (DFTB) method as a *first principle* approach is applied for the calculation of the interatomic forces [31]. The DFTB

is much more efficient in terms of computer time than real *ab initio* MD methods (e.g., Car-Parinello). It is known to be successful in predicting ground state geometries and physical properties of different carbon systems [32,33] and allows one to treat the problems addressed in this Letter. Our simulations first show (in accord with a host of experimental data) that, below a critical energy, surface processes dominate and lead to the formation of rough and vacancy-rich sp^2 films. Above a critical energy the C species start to penetrate to subsurface layers, where they are incorporated on interstitial sites. Further bombardment initiates the interstitial-rich region to form a predominantly sp^3 bonded matrix below a porous sp^2 -rich surface layer.

Restricted by the present capabilities of computers, we direct the ion trajectories to an a-C surface and study the changes due to a C fluence equivalent to one monolayer ($\sim 2 \times 10^{15}$ C/cm²). The a-C surface model is constructed from a three-dimensional 128-atomic bulk supercell (69% sp^3 , 3.0 g cm⁻³) which was generated previously by simulated cooling from a liquid state to room temperature [32]. Doubling the size in one dimension and applying periodic boundary conditions in the other two dimensions lead to a model with two surfaces. The broken σ bonds on the lower surface are saturated by hydrogen atoms which are held fixed together with the carbon atoms within a layer of 5 Å thickness from the bottom of the slab. This results in a 193-atomic slab with 130 movable atoms, a thickness of 15 Å, and a surface areal of 10×10 Å. After equilibration at 1800 K for 1 ps and subsequent cooling to 0 K, the free surface has relaxed to graphitic features as well as sp bonded chains, and the sp^3 content in the volume has decreased to 56% [see Fig. 1(a)]. This structure is stable during a repeated equilibration at 3500 K and subsequent cooling. As reported from experiment [2,34], π bonded features are present on the topmost surface layers of a-C [2,34]. In the interior of the model we observe sp^2 clusters within an sp^3 matrix in accord with previous DFTB simulations [32]. The model resembles

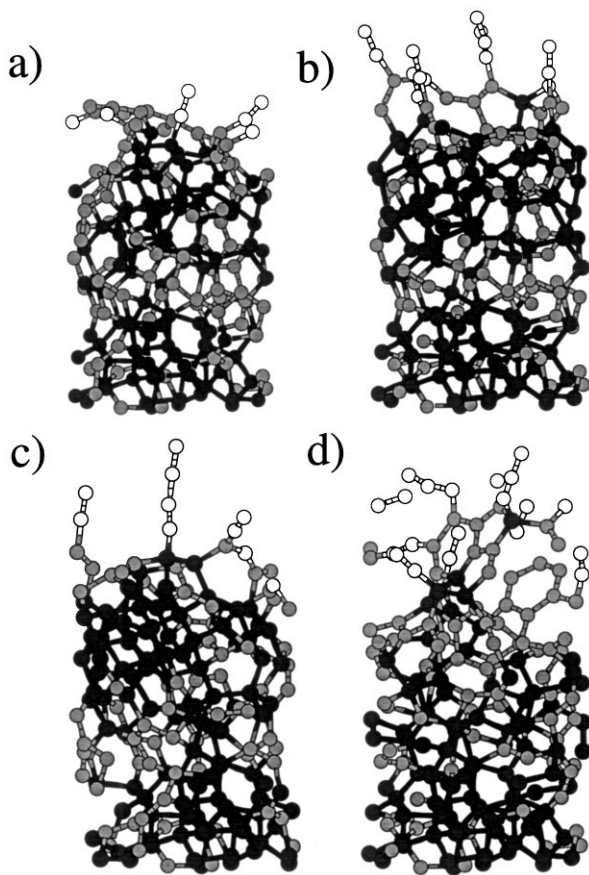


FIG. 1. Structure of the surface slab. (a) Original relaxed surface slab, (b) surface after 10 events with 20 eV, (c) surface after 18 events with 40 eV, and (d) surface after 17 events with 80 eV. sp^3 atoms: black; sp^2 atoms: grey; sp atoms: white.

a -C films with similar sp^3 fractions deposited using 30 eV C ions [8]. This substrate is subjected to C atom collisions at varying impact energy (for convention, referred to as ions). We consider each individual ion trajectory at a time. The starting and final temperatures of the slab are set to zero, since no further bond rearrangements at 300 K are observed. This allows a comparison of the minimum energy structures before and after collision by excluding the random effects of thermal vibrations. Statistics is gained by considering isoenergetic trajectories to a set of randomly distributed impact points. The ion impact affects processes on three different time scales [18,22,35]: (i) a collision stage involving penetration, energy loss, and generation of ballistic displacements ($\sim 10^{-13}$ sec), (ii) a thermalization stage, in which the excess energy is dissipated and the local structure relaxes ($\sim 10^{-12}$ sec), (iii) a long-term relaxation stage in which temperature activated processes may occur ($> 10^{-10}$ sec). The MD calculations performed in this paper reflect the effect of the first two stages, in correspondence to low temperature experiments ($T < 150^\circ\text{C}$) for which no significant thermal migration occurs [3,6,7]. During the first ballistic phase of each trajectory with a duration of about 100 fs, no temperature rescaling is applied. The second (thermalization) phase

of a trajectory implies the coupling to a heat bath, the temperature of which is gradually decreased to zero over a time of 1 ps. The time for computing one complete ion trajectory is 120 hours on an HP 9000/735 workstation.

We first address the penetration of individual incoming carbon species considering eight independent ion trajectories per energy. The maximum penetration depth and the depth of the final occupation site increase with energy although the spread is large compared to the depth itself. Subplantation, i.e., penetration through the surface layer, starts to be substantial at energies of about 40 eV, when ions are incorporated underneath the graphitic surface layer. For 100 eV, the average deposition depth is -4 \AA . Even at 10 eV atoms get incorporated into the surface layer, especially by penetration into hollow regions exposed by the rough surface. These results are in accord with the surface analysis and atomic-force microscopy (AFM) data of Lifshitz *et al.* [7,18] which show that subplantation occurs for $E > 30$ eV while surface processes dominate for $E < 30$ eV. In a previous Stillinger-Weber MD study, Marks *et al.* [26] did not observe any penetration for carbon ions deposited on a two-dimensional substrate which consists of six-membered rings of carbon atoms studying energies up to 70 eV. An important effect of ion collisions is damage caused by energy transfer into the network. This energy is distributed into lattice heating and permanent (within the time scale considered in the simulation) lattice distortion, revealing itself in an increase of potential energy. At ion energies below 60 eV most of the energy deposition goes into bond breaking within the surface layer. For $E > 70$ eV, deep displacements occur which allow for rearrangements of the network and release part of the lattice distortion.

In a second part of the simulations, we address the phase evolution and the detailed structure of the evolving film upon successive bombardment by energetic C species at selected ion energies. The surface is fully cooled and relaxed after each impact event according to the procedure described above. The succeeding trajectory is being carried out to this relaxed system. For the 20, 40, and 80 eV collision sequences, a series of 10, 18, and 17 atoms, respectively, has been collided with the surface, the latter two corresponding to a fluence of $\sim 1.9 \times 10^{15} \text{ C/cm}^2$. Because of the still high computational cost, we are unable to study the full evolution of a DLC matrix on a graphitic target, which would require 1000 subsequent trajectories (10^{17} C/cm^2), and rather concentrate on the relative changes imposed by an incremental deposition on a target representing an intermediate a -C film. The nature of the topmost layers alters under the bombardment. Figures 1(a)–1(d) show the structure of the C matrix before and after the deposition sequences. At 20 eV, mostly surface effects are observed. Subsurface processes start to play an increasing role at 40 eV. The most obvious effects are seen in the 80 eV series. In Figures 2(a)–2(c), we show the changes of the sp^3 fraction and mass density compared to the original surface versus the depth

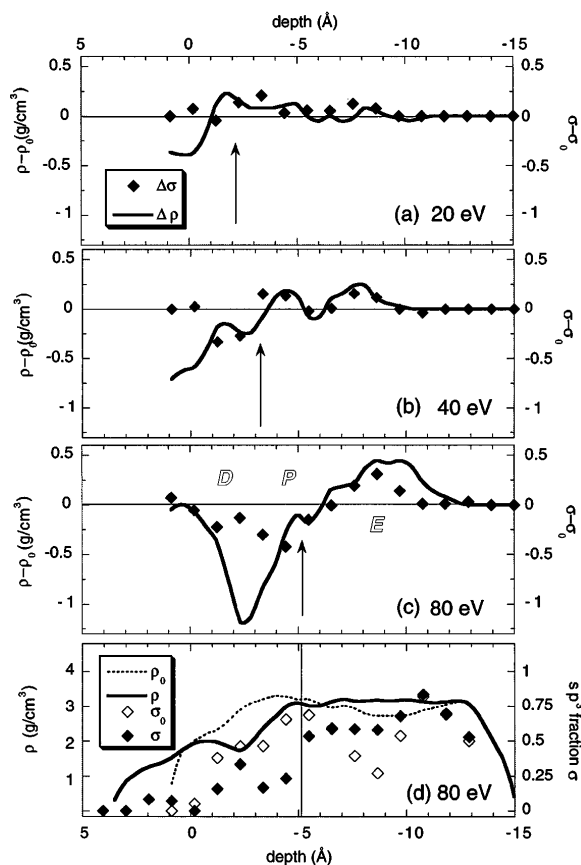


FIG. 2. Depth profile of changes in sp^3 content σ and mass density ρ after collision sequences at (a) 20, (b) 40, and (c) 80 eV with respect to the original structure. The arrows mark the average penetration depth of the ions within the sequence. Viewgraph (d) shows mass density and sp^3 fraction profile for the structure before (ρ_0, σ_0) and after (ρ, σ) the 80 eV collision sequence.

coordinate for all three series. Both sp^3 fraction and mass density profile are sampled in intervals of 0.52 \AA over horizontal slices with a thickness of 1.04 and 2.08 \AA , respectively. Figure 2(d) shows the absolute density and sp^3 fraction profile of the 80 eV structure. The arrows mark the average penetration depth of the ions of the sequence. The energetic C bombardment forms a low density, sp^2 -rich defective surface layer (D), the thickness of which scales with the ion range. In this layer, both the density and the sp^3 fraction of the C film are lower than in the starting structure. Below this defective surface layer we observe an sp^3 enriched layer (E) in which both the density and the sp^3 fraction are larger than in the initial target. Davis *et al.* [36] indeed observed this layered structure in a very recent experimental study reporting a conversion from sp^2 to sp^3 at the average depth of ion penetration. Considering the trends going from 20 through 40 to 80 eV, the changes observed in the bombarded target are statistically significant. They are also stable with respect to longer equilibration periods. A careful analysis of the data for the 80 eV sequence reveals the processes leading to the formation of layers D

and E . The distribution of the displaced atoms within the sequence shows a wide maximum within the damaged region D . Examining the distributions of displacements directed into the film and to the surface, we find a broad overlap region, but also a separation of their average origin. The average outward displacements originate in a depth of -4.8 \AA , while the average inward displacements are created at -5.0 \AA . The collision cascades at 80 eV have a mean displacement increment of 0.4 \AA directed into the target. This behavior is expected from momentum transfer considerations, and therefore is not sensitive to the statistics. The combination of displacements back to the surface with voids left by atoms knocked into the film creates the porous, low density region D . The deeper layer P is characterized by incorporated projectiles and by a dominant fraction of relocations directed into the target. This increases the local density and sp^3 fraction in the deeper region E underneath the level of average penetration P . Since the dominant part of the displacements in the deeper layer is directed forward into the film and most of the backward displacements occur close to the surface, one must get densification and compression at the deeper layer, and tensile stress at the surface layer. This composite layered structure is inevitable in a subplantation process. In a successive deposition the layer E expands internally while the sp^2 porous layer on top remains intact. While deposition at $E > 30 \text{ eV}$ was shown to be a subplantation process characterized by internal growth, this is not the case for $E < 30 \text{ eV}$. Our calculations indicate the formation of a rough surface under these conditions [see Fig. 1(b)]. Indeed, AFM data by Lifshitz *et al.* [7,9,37] show that the surface roughness of DLC films increases upon decreasing the energy below 30 eV.

Two basic mechanisms have been proposed [3,29] to be responsible for the initiation of the sp^3 bonding: (i) the high pressure high temperature associated with the “thermal spike” [15,21,28] and (ii) the incorporation of C in subsurface positions causing densification and associated stress [18–20]. The details of the DLC film growth are readily explained in terms of a densification process which occurs by the combined effect of the incorporation of the C projectiles in subsurface positions, the according momentum transfer, and compressive stress at the end of their track. It is much more difficult to explain our findings by the thermal spike quenching since the number of displacements (the deposited energy) is larger in region D where the sp^3 bonding and the density are small.

The suppression of the sp^3 bonding and the stress relief at higher ion energies or higher substrate temperatures cannot be directly treated by our MD calculations. The present results, however, indicate that the collision damage forms a porous, sp^2 -rich surface region and weakly bonded species (interstitials). Both effects increase in magnitude with energy. The competition between the damage (leading to radiation enhanced diffusion) and the densification explains the recent results of Lifshitz *et al.* [3,10] of a slow decrease of the sp^3 fraction with energy

between 600 eV and 20 keV. The thermal migration of the weakly bonded species also explains the formation of sp^2 bonded, low density films for depositions at substrate temperatures exceeding 150 °C [3,6,7].

The high computational cost keeps the deposition sequences short ($\sim 1-2 \times 10^{15}$ C/cm⁻²) which can suggest the main mechanisms of structure evolution rather than describe real film growth. Thermally assisted long-term relaxations are not included. These issues should be addressed by a combination of MD and analytical methods. For a more detailed description of the present work, the reader is referred to Ref. [38] and to a future publication [39].

Molecular dynamics calculations of DLC deposition from energetic C ions based on a DFTB scheme have been used to describe the fine details of the growth process. Our results are in very good accord with the experimental data. The simulations first show that for $E > 30$ eV the deposition is substantially a subplantation process, where the C species penetrate and occupy subsurface positions. The evolving layer has a composite structure: A defective, low density sp^2 -rich surface layer is formed, below which a dense, sp^3 -rich layer is developing. The defective layer is formed due to the collision damage while the sp^3 -rich deeper layer is a result of the combined effect of incorporation of C projectiles and the momentum transfer to C atoms at the end of the incorporated C profile. For $E < 30$ eV rough, sp^2 -rich films are evolving via surface incorporation of C in preferred sites.

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