

Simulating temperature effects in the growth of tetrahedral amorphous carbon: The importance of infrequent events

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This thin-film deposition study of tetrahedral amorphous carbon shows that including infrequent processes on the millisecond scale substantially improves the accuracy of molecular dynamics simulations. Elevated temperature between energetic impacts is used to activate processes which are typically ignored. In agreement with experiment, the simulations show an abrupt transition in which diamondlike carbon transforms into vertically oriented graphitic sheets. The simulations also highlight the importance of infrequent events in combination with energetic impact. In the absence of the latter, the transition temperature is significantly higher, in good correlation with experiment. © 2006 American Institute of Physics. [DOI: 10.1063/1.2358116]

Molecular dynamics (MD) is a powerful tool for investigating processes at the atomic scale, but the need to explicitly follow atomic vibrations restricts full MD calculations to at best the nanosecond scale. To allow MD to describe infrequent events and access experimental time scales, various techniques have been proposed such as hyperdynamics¹ and temperature accelerated dynamics.² However, such methods are generally unsuited for amorphous materials due to the disordered topology which mitigates against finding a suitably small set of local minima. In this letter, we extend standard MD techniques in order to describe the physical vapor deposition of tetrahedral amorphous carbon (ta-C), an important diamondlike material.^{3,4} We show that pulsing with elevated temperatures between atomic impacts stimulates infrequent events which occur on the millisecond scale. Using this method, we reproduce and interpret key experimental data involving *in situ*^{5–7} and *ex situ*^{8,9} heating of ta-C. This success demonstrates that controlled high-temperature pulsing is a useful technique for understanding amorphous materials deposited from physical vapor sources.

Experimental preparation of ta-C involves energetic beams in which carbon species arrive individually at the surface and induce local melting (a thermal spike). This spike lasts for less than 1 ps (Ref. 10) and can be well described by MD. However, the typical ta-C growth rate of around 1 nm/s implies a gap of about 1 ms between individual impacts, and processes on this time scale are neglected in traditional MD. To access these infrequent processes, we employ the Arrhenius relationship

$$f = A \exp[-E/kT], \quad (1)$$

which describes the frequency f with which a process having energy barrier E and attempt frequency A will be surmounted at a given temperature T . The difficulty for rare-event simulations is that elevated temperatures alter the balance between competing processes. In this study we are aided by experimental data of *in situ* heating which reveal an abrupt transition from ta-C to graphitelike material at around 150 °C.^{5–7} This suggests that a dominant (but unknown) process is activated by the temperature of the substrate, a conclusion reached by Koskinen *et al.*⁵ who found that the tran-

sition temperature increases with deposition rate. In this work, we use elevated temperature to trigger this dominant process with a similar frequency on a per impact basis. To determine the elevated temperature, we assume that the dominant process is activated once during the millisecond gap between impacts ($f=10^3$ Hz), and applying Eq. (1) with $T=450$ K and $A=10^{14}$ Hz (Ref. 3) yields $E=1.0$ eV. In our simulations we heat the system to the elevated activation temperature (T_{act}) for 1 ps, during which our goal is a single activated event. Applying Eq. (1) with $E=1.0$ eV and $f=10^{12}$ Hz, we find $T_{\text{act}}=2500$ K. We stress the order of magnitude nature of this argument—the crucial point is that T_{act} is neither too high (i.e., above the melting point) nor is the simulation time too short (1 ps permits around 100 vibrations).

The environment dependent interaction potential¹¹ (EDIP) is used to perform film growth simulations in which 500 carbon atoms are deposited with an energy of 70 eV. To avoid ion-beam homoepitaxy,¹² the substrate is an existing ta-C thin film. The simulation substrate temperature (T_{sub}) is 300, 500, or 800 K, and the activation temperature spans 1000–2500 K. The simulation procedure for describing each individual impact mostly follows standard methods.¹³ The key difference is that when the thermal spike is complete, the system is heated to T_{act} and held at this temperature for 1 ps before returning to T_{sub} for rethermalization and the subsequent impact. It is during this period of elevated temperature that infrequent events are activated.

Representative results for $T_{\text{act}} < 2000$ K are shown in Figs. 1 and 2. For activation temperatures up to 1500 K, the simulated deposition process produces only ta-C, indicating that the dominant process is not being activated. However, as T_{act} approaches 1750 K, an abrupt transition occurs in which the sp^3 fraction falls rapidly to zero and major morphological changes occur. By $T_{\text{act}}=1875$ K, the deposited film is entirely sp^2 bonded and the structure consists of vertically oriented graphitelike sheets [Figs. 1(c) and 1(d)]. This behavior is observed for all three values of T_{sub} , demonstrating that the substrate temperature during the thermal spike does not influence the transformation. While we do not discuss here the results for $T_{\text{act}}=2000$ –2500 K, over this range additional processes are activated which destroy the ta-C substrate.

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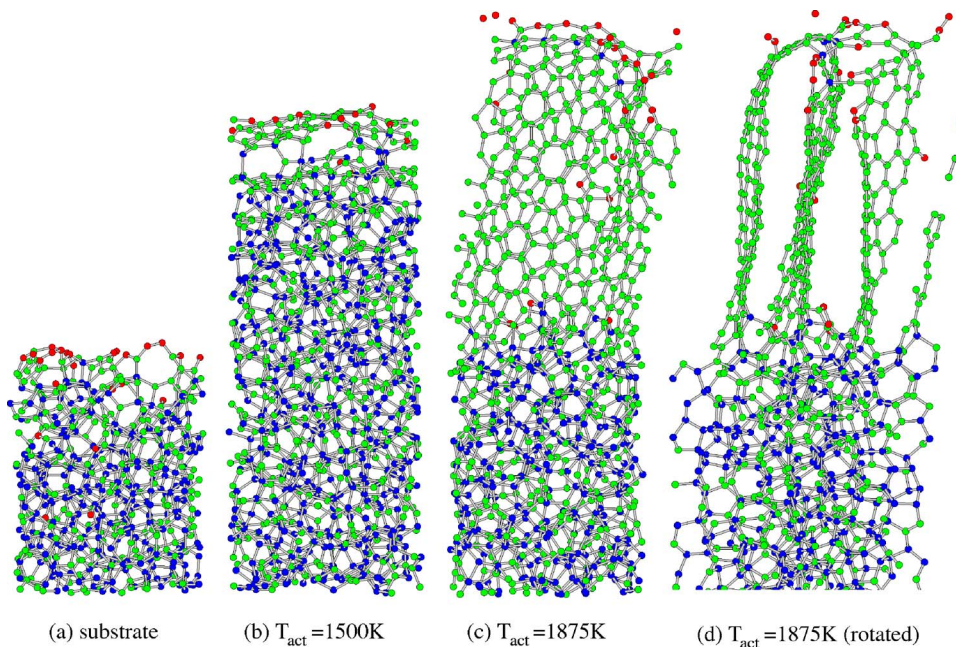


FIG. 1. (Color online) Ball-and-stick view showing the effect of activation temperature on carbon films grown using five-hundred 70 eV impacts and $T_{sub}=800\text{K}$. Atoms with two, three, and four neighbors are colored red, green, and blue, respectively. (a) ta-C film used as the substrate for the activation studies. The ta-C film is attached to a diamond base (not shown). (b) Simulations using $T_{act}=1500\text{K}$ result in the further growth of ta-C. (c) Simulations using $T_{act}=1875\text{K}$ produce graphitelike sheeting due to activation of rare events. (d) Rotated view of (c) to highlight the graphitelike sheets.

The transformation at $T_{act}=1750\text{K}$ from ta-C to a highly ordered sp^2 material is in striking agreement with experiment. As the scaled experimental data in Fig. 2 show, the simulations reproduce very well the abrupt nature of the transformation between ta-C and sp^2 -rich material. Furthermore, electron diffraction studies of ta-C (Ref. 6) and hydrogenated ta-C (Ref. 14) observe (0002) reflections above the transition temperature, indicating graphitelike layering. Fringes in high-resolution transmission electron microscopy¹⁵ also support this conclusion. The horizontal surface layering in Fig. 1(b) indicates another success of the temperature-pulsing method. Experiments indicate horizontal graphitic sheeting on the surface of ta-C thin-films,^{16,17} but previous simulations have not predicted these structures. For completeness, we note that in experiments, the graphitelike regions exist in small, uncorrelated domains. The extended structure in the present simulations is a consequence of the system being sufficiently small for collective ordering to occur.

Application of Eq. (1) with $f=10^{12}\text{Hz}$ reveals that the transition at $T_{act}=1750\text{K}$ corresponds to an energy barrier of 0.7 eV, of similar magnitude but slightly lower than our original estimate of 1.0 eV. Barrier values of 0.57 and 0.65 eV have also been obtained from experiments measuring the elastic moduli¹⁹ and sp^3 fractions,⁵ respectively. At 300 K this 0.7 eV barrier is surmounted on average only once every 14 ms, which explains why experiments at room temperature produce ta-C. However, when these processes are activated (either by substrate heating in experiment or temperature pulsing in simulation), a transition to sp^2 -rich material occurs. In this context, the deposition-rate experiments by Koskinen *et al.*⁵ are naturally understood: Increasing the deposition rate reduces the time between impacts which raises the transition temperature. The long time scale of the activated processes also explains the absence of an sp^3 transition in high-temperature picosecond-scale simulations¹⁹ using the Tersoff potential.²⁰ Surprisingly, recent picosecond-scale simulations by Jäger and Belov²¹ using a Brenner potential²² find an $sp^3 \rightarrow sp^2$ transition around 400 K. While their simulations describe well sp^2 clustering, the ta-C net-

works contain a spike in the radial distribution function, suggesting shortcomings in the barriers for bond making and breaking.

We also performed annealing simulations with EDIP to understand *ex situ* experiments in which as-deposited ta-C converts to sp^2 -rich phases at temperatures of order of 800 °C (Ref. 8) and 1200 °C (Ref. 9). Freestanding ta-C slabs containing 1500 atoms and with periodicity only in the xy directions were created to avoid in-growth from the substrate.¹² The slabs are formed by first generating an xyz -periodic ta-C sample by liquid quenching^{10,18} at 3.0 g/cm³ and then breaking periodicity in the z direction. Heating to 1000 K for 1 ps allows for surface reconstruction, followed by thermalization at 300 K. The entire slab is then heated for 100 ps.

The fraction of sp^3 sites in the bulk region of the slab after 100 ps of annealing is shown as solid circles in Fig. 2.

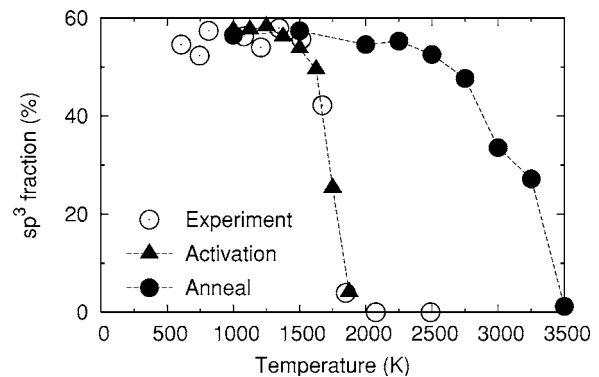


FIG. 2. Tetrahedral (sp^3) bonding in ta-C EDIP simulations of *in situ* and *ex situ* heating. Triangles indicate 70 eV deposition simulations at $T_{sub}=800\text{K}$ for which 1 ps temperature pulsing is applied between impacts (Fig. 1). Solid circles indicate EDIP simulations for the 100 ps annealing of a 3.0 g/cm³ ta-C slab. The horizontal axis indicates the activation and annealing temperatures for the triangles and solid circles, respectively. White circles indicate scaled experimental data (Ref. 6) of *in situ* heating. The scaling accounts for (i) the slightly lower sp^3 fraction of ta-C with EDIP (Ref. 18) and (ii) the temperature-induced acceleration of the infrequent events.

In agreement with experiments,^{8,9} the threshold for transforming ta-C into sp^2 -rich material is much higher when the heating is applied to as-deposited structures and energetic impact is not involved. The difference between the deposition and annealing simulations is more significant than it first appears, as the deposition simulation is held at T_{act} for just 1 ps, while the annealing lasts for 100 ps. Annealing up to 2250 K produces negligible effects, but at 2500 K the onset of horizontal surface graphitization is observed and the bulk sp^3 fraction begins to fall. By 3000 K, multiple graphitic layers are present, and the bulk region is highly sp^2 amorphous carbon. At 3500 K (close to the ta-C melting point), a major structural change occurs in which the bulk region transforms into vertically oriented graphitic sheets.

The combination of EDIP data for pulsing and annealing mirrors the *in situ* and *ex situ* experiments and provides new insights into the importance of rare events. The sharp transition in the *in situ* experiments is revealed to be controlled not only by the thermal activation of the dominant process but also by the energetic impact. The annealing simulations show that elevated temperatures generate horizontal graphitization and a progressive exfoliation in which graphite sheets are shed from the surface. Horizontal graphitization is also present in the deposition simulations, but here the activation temperature is much lower due to surface mobility from the energetic species. Furthermore, detailed simulation analysis shows that the vertically oriented graphite sheets represent a very stable growth mode in which sputtering is reduced and incoming energetic species knock out atoms situated between the graphite sheets. Chhowalla *et al.*⁶ observed an increase in the growth rate above the transition temperature, an effect which is explained here by the lower density of the graphitelike film and the increased stability of the growth mode. Considering briefly these insights from a theoretical perspective, we note that subplantation models proposed by Lifshitz *et al.*²³ and Robertson²⁴ contain some elements of the new understanding presented here. However, none of the models predicts either the temperature-driven transition or the highly ordered nature of the sp^2 sites. In both cases, the key missing ingredient is the role of infrequent events between impacts.

Looking to the future, this temperature-pulsing method will enable simulation studies of important temperature-dependent processes such as the role of ion energy,⁶ the mechanism for stress relief,²⁵ and the origin of surface roughness.^{26,27} Furthermore, this work is an important step towards the simulation of ultrathin coatings as used in hard disks.²⁸ We note, however, that the study of carbon on non-carbon substrates requires the development of new multi-component potentials.

In this study we have performed molecular dynamics simulations in which controlled high-temperature pulsing is

used to activate rare events. The method is applied to the material ta-C for which the experimental literature lacks a comprehensive picture of temperature effects. The achievements of the simulations in this study are threefold: (1) they bridge the time scale and thus describe this system accurately, (2) they are consistent with the various (and disparate) pieces of experimental information, and (3) they provide a coherent understanding of the physical processes and their time scale. Beyond the study of ta-C, this approach of temperature pulsing provides a useful tool for simulation studies of amorphous materials. Even when an abrupt transition is not present, temperature pulsing is a safeguard when rare events have the potential to render a simulation invalid.

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