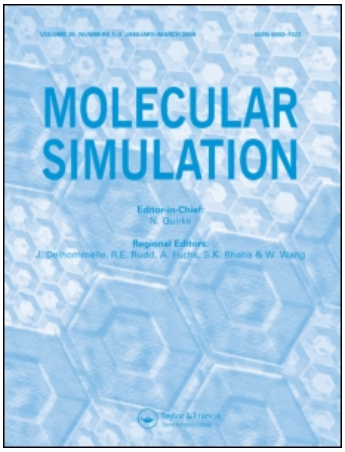

Molecular Simulation
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713644482

The importance of rare events in thin film deposition: a molecular dynamics study of tetrahedral amorphous carbon

N. A. Marks[a]; M. F. Cover[a]; C. Kocer[ab]
[a] School of Physics, University of Sydney, Sydney, NSW, Australia [b] National Institute for Materials Science, Ibaraki, Japan

To cite this Article Marks, N. A. , Cover, M. F. and Kocer, C.(2006) 'The importance of rare events in thin film deposition: a molecular dynamics study of tetrahedral amorphous carbon', Molecular Simulation, 32: 15, 1271 — 1277
To link to this Article: DOI: 10.1080/08927020601052906
URL: http://dx.doi.org/10.1080/08927020601052906

Molecular Simulation, Vol. 32, No. 15, 30 December 2006, 1271–1277

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The importance of rare events in thin film deposition: a molecular dynamics study of tetrahedral amorphous carbon

N. A. MARKS†*, M. F. COVER† and C. KOCER†‡

†School of Physics, University of Sydney, Sydney, NSW 2006, Australia
‡National Institute for Materials Science, 1-1 Namiki Tsukuba, Ibaraki 305-0044, Japan

(Received July 2006; in final form October 2006)

The transition of diamond-like materials from an sp^3 to sp^2 rich state is of particular interest because of the desirable properties of tetrahedral amorphous carbon (*ta*-C). Previous works indicate that infrequent processes may dominate this transition, but simulation of these processes presents significant difficulties, since the infrequent processes are activated on the millisecond scale. In this molecular dynamics study the environment dependent interaction potential is used to simulate the thin film deposition of *ta*-C. Infrequent processes occurring between energetic impacts were activated on the picosecond scale using elevated temperatures. The simulations reveal an abrupt transition in which the *ta*-C films transform into graphite-like sheets. A similar transformation, albeit at much higher temperatures, is also observed when the films are heated without energetic impacts. These results are found to be in good agreement with published experimental data.

Keywords: Molecular dynamics; Tetrahedral amorphous carbon; Infrequent events; Thin film deposition

1. Introduction

Tetrahedral amorphous carbon (ta-C) is a technologically useful form of diamond-like carbon [1,2]. Properties such as chemical inertness, optical transparency and high hardness have seen this material employed as a protective film on razors, tool bits and computer hard drives [3]. The useful characteristics of ta-C are associated with the high fraction of sp^3 bonds, which can be as high as 85%. The related graphite-like material known as amorphous carbon (a-C), is largely sp^2 bonded, and with only $\sim$20% sp^3 atoms possesses significantly different material properties.

Thin films of ta-C are produced experimentally using a variety of apparatus that are essentially based on the principle of ion implantation. Energetic ions are transported to a substrate, where the resulting atomic bonds are strongly affected by the ion energy, substrate temperature and deposition rate. In order to grow thin films of ta-C with a high percentage of sp^3 bonds, the ion energies should be in the range 30–1000 eV. In addition, the temperature of the film during deposition should not exceed $\sim$500 K, since above this point a sharp transition to an sp^2-rich phase is observed [4–6]. When the film is heated after deposition, a much higher temperature (1000–1400 K) is required to induce the same transition [7,8].

While the origin and nature of the energy-dependence has been extensively discussed in the literature, the same is not true for the role of temperature. This in part reflects the difficulty in determining the appropriate theoretical framework in which to discuss the role of temperature, particularly in conjunction with energetic impact processes. In this context, molecular dynamics (MD) simulation has an important role to play, since by elucidating the relevant atomic processes, new insight into the formation and phase behaviour can be determined. The difficulty for MD however lies in the well-known problem of timescale: practical MD simulations of energetic impact are restricted to the nanosecond scale, while a ta-C deposition experiment runs for periods spanning seconds to hours.

Existing MD simulations of ta-C further complicate the understanding of temperature effects, with initial Tersoff simulations [9,10] showing that substrate temperatures as high as 800 K induce no change in sp^3 fraction, while recent calculations using a modified Brenner potential found an sp^3 transition around 400 K [11,12]. In our initial exploratory simulations using the environment dependent

*Corresponding author. Email: nigel@physics.usyd.edu.au

Molecular Simulation
ISSN 0892-7022 print/ISSN 1029-0435 online © 2006 Taylor & Francis
http://www.tandf.co.uk/journals
DOI: 10.1080/08927020601052906

Table 1. Material properties from EDIP simulations of ta-C thin-film deposition using traditional MD techniques in which infrequent events are not considered. Across a range of substrate temperatures and ion energies the density and sp^3 fraction of the films are virtually unchanged. Simulations denoted by an asterisk used a longer thermal spike lifetime.

T_{sub} (K)	25 eV		40 eV		70 eV	
	ρ (g/cc)	$\%sp^3$	ρ (g/cc)	$\%sp^3$	ρ (g/cc)	$\%sp^3$
300					3.0	54.8
400	3.0	58.0	3.0	61.7	3.0	55.9
400	3.1*	57.2*				
500	3.1	60.8				
800	3.0*	58.8*	3.0	57.0	2.9	53.1

interaction potential (EDIP) [13], we used standard techniques [14] and reproduced the essence of the Tersoff result. As shown in table 1, varying simulation inputs such as substrate temperature, thermal spike lifetime and impact energy produced no effect of significance, with a near constant density and sp^3 fraction in each instance.

This initially discouraging result motivated the present study and prompted us to consider more closely the role of infrequent (or activated) processes which are traditionally ignored in MD simulations. As we outlined in a recent letter [15], when elevated temperatures are used to stimulate infrequent processes then the agreement between experiment and simulation becomes very good indeed. In this manuscript we elaborate on the methodology and rationale behind the elevated-temperature approach, and report new results illustrating the insight provided by MD simulation. We present simulations of both *in situ* heating (i.e. elevated temperatures during deposition) and *ex situ* heating (i.e. annealing of existing ta-C). Taken together, these two sets of virtual experiments show how infrequent events predict horizontal and vertical graphitic sheeting as seen in deposition experiments, and explain why the transition temperature is significantly higher for post-deposition annealing.

2. Methodology

The key ingredient in our simulations of *in situ* heating is the activation of infrequent processes which occur between each energetic impact. It has well-known that the carbon species arrive individually at the surface, producing a short-lived thermal spike measuring $\sim 1\,\text{nm}^2$ in cross-section and of approximately one picosecond duration. Most MD simulations (including our own first attempts) ignore the period of ~ 1 ms which separates successive impacts. The first suggestion that activation of rare events might occur during this period came from the experimental data of Koskinen *et al.* [4] who showed that increasing the deposition rate increased the critical temperature at which the $sp^3 \rightarrow sp^2$ transition occurred. However, their insights were not widely taken up within the amorphous carbon community, and it was only in our recent work that such effects were included in an MD simulation.

In this work elevated temperature is the tool by which the infrequent events are activated. According to the Arrhenius relationship, the frequency with which an infrequent event occurs is given by

$$f = A \exp[-E/kT] \tag{1}$$

where f is the frequency of the process, E is the energy barrier, A is the attempt frequency, T is the temperature and k is Boltzmann's constant. For a given process with energy barrier E, the frequency thus increases enormously as T increases, and it is this acceleration factor which is taken advantage of in the present work. The traditional difficulty in adopting such an approach is that the acceleration (or boost) factor varies with the value of the barrier E, and thus the relative reaction rates in the higher temperature system differ significantly from those in the lower temperature system. For such systems sophisticated schemes [16] are appropriate and even essential. In the case of ta-C deposition, however, the experimental data clearly shows a very abrupt transition, suggestive of a dominant critical process which becomes activated when sufficient time and/or temperature is available. This allows a more straightforward approach in which elevated temperatures can activate the infrequent events in a statistically meaningful manner.

As an illustration of our approach, we consider some typical experimental values in which the period between successive local impacts is 1 ms, and the critical transition occurs at 450 K. Assuming an attempt frequency for carbon of $A = 10^{14}$ Hz [1], equation (1) yields an energy barrier E of 1.0 eV. However, if such a process is to be activated on the timescale of an MD calculation (say once in 1 ps), then the frequency of the process must increase to 10^{12} Hz, and the temperature should be 2500 K. In this way the number of infrequent events between successive impacts is the same in the MD simulation and the laboratory experiment. There is one crucial point to note: it is critical that the melting point of the material be significantly above the elevated temperature, and that the number of "attempts" during the activation period be substantially greater than unity. For ta-C these criteria are satisfied comfortably, with the picosecond activation period sufficient for 100 oscillations, and the melting point of ta-C in the vicinity of 3500 K [17].

All of the MD simulations in this work are performed using the EDIP method which has been successively applied in a variety of amorphous carbon contexts. Indeed, its apparent failure seen in table 1 contrasted with previous experience. The simulations of *in situ* heating involved simulations of thin-film deposition in which energetic carbon species were introduced individually onto a pre-existing substrate. The combination of energetic impact, crystalline substrates and elevated temperatures has previously been found to cause substrate epitaxy [18],

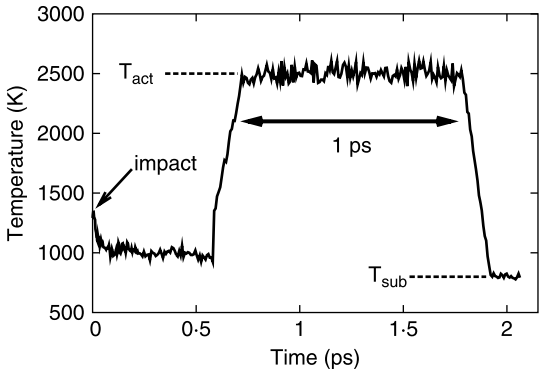

Figure 1. Representative temperature profile for an individual impact in an *in situ* simulation. Shown here is the system temperature as a function of time for a 70 eV impact with $T_{sub} = 800$ K and $T_{act} = 2500$ K.

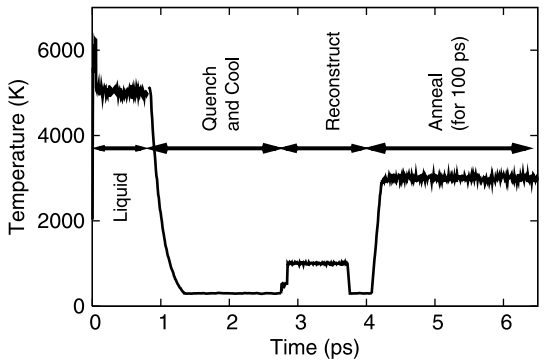

Figure 2. Temperature profile for an *ex situ* simulation in which annealing is performed at 3000 K. Key stages are indicated by the arrows: melting at 5000 K forms a liquid, followed by rapid quenching to "freeze-in" the amorphous structure. Heating to 1000 K aids surface reconstruction once the periodic boundary condition is removed in the z-direction. Most of the 100 ps annealing stage is not shown.

and so a ta-C structure from an existing deposition simulation was used as the substrate. Using an incident energy of 70 eV, a total of 500 carbon atoms were individually deposited onto the substrate. The substrate temperature at the start of each impact spanned 300, 500 and 800 K, and for each substrate temperature the elevated (or activation) temperature varied between 1000 and 2500 K. In the initial stage of each *in situ* heating cycle, the simulation is characterized by an impact (thermal spike), after which the temperature of the system returns to the substrate temperature (T_{sub}) by means of wall thermostats. Once the thermal spike has subsided (somewhat less than 1 ps), the system temperature is ramped up to the activation temperature (T_{act}). The entire system is held at the activation temperature for 1 ps, after which the system is returned to the substrate temperature prior to the subsequent impact. A representative temperature profile illustrating this simulation process is illustrated in figure 1. Note that this cycle is repeated for each and every atom: the only procedural difference between consecutive impacts is the randomly chosen (x, y) position of the newly introduced atom.

For the MD simulations of *ex situ* heating a different simulation strategy was adopted, as here the aim is to have a large ta-C structure with no substrate effects. To construct such a structure, liquid quenching [19] was used to generate a 1500-atom cell of 3.0 g/cc ta-C in which xyz-periodic boundary conditions were applied. We have previously shown [20] that the sp^3 vs density relationship for liquid quenching is the same as atom-by-atom deposition but involves far less computational cost. Liquid quenching is naturally of no use when the individual deposition phenomena are themselves of interest, but it is particularly suitable for quickly generating large ta-C samples.

Having generated the ta-C sample by first forming a liquid, and then rapidly cooling to form the amorphous solid, the periodicity of the network in the z-direction was broken to create free upper and lower surfaces. These surfaces are essential in that they permit atomic relaxation during annealing and represent an important correspondence with experiment where surface-relaxation also occurs. The cleaved amorphous surfaces are assisted in their "surface reconstruction" by heating for 1 ps at 1000 K which quickly results in a plateau in the potential energy of the system when plotted as a function of time. The final model is thus a ta-C thin film with no substrate and periodic boundary conditions only in the horizontal plane. This model is then annealed at predefined temperatures for 100 ps. The full temperature profile of the *ex situ* process (including the commencement of a 3000 K anneal) is illustrated in figure 2.

3. Results

The central result of the simulations with *in situ* heating is summarised by the ball-and-stick view in figure 3, and the temperature-dependence data shown in figure 4. When the activation temperature is below 1500 K (figure 3(b)), the effect of the elevated temperature between each impact is negligible. The 500 additional atoms simply generate more ta-C, just as in the earlier simulations of table 1. Around 1500 K, minor surface processes are activated which result in horizontal sheeting at the surface (figure 3(c)), but the growing film is still ta-C. However, a most dramatic change in morphology occurs around 1750 K in which the sp^3 fraction begins to fall rapidly, and a large fraction of the deposited atoms adopt sp^2 configurations. At still higher activation temperatures (figure 3d), the transformation to a highly ordered graphite-like material is complete. This trend from ta-C to vertically-oriented graphite with increasing activation temperature is observed for all three values of T_{sub}, and occurs at the same critical temperature (figure 4). The unimportance of the background temperature during the thermal spike phase confirms that it is indeed the activation of the infrequent events which drives the change from ta-C into sp^2-rich material.

One of the significant aspects of figures 3 and 4 is the degree to which it explains and reproduces experimental

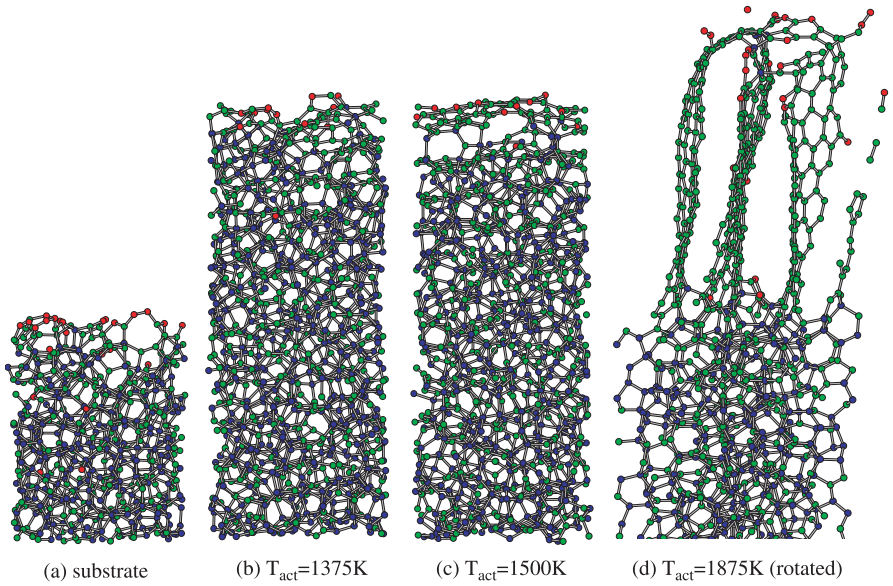

Figure 3. Ball-and-stick images of an *in situ* heated carbon film showing the effect of the activation temperature on deposition. The film was grown using 500 impacts at 70 eV using a substrate temperature of $T_{sub} = 800$ K. Atoms with two, three and four neighbours (i.e. sp, sp^2, sp^3) are coloured red, green, and blue respectively. (a) ta-C substrate prior to the start of film growth, (b) for $T_{act} = 1375$ K ta-C growth is observed, (c) for $T_{act} = 1500$ K the formation of a horizontal graphite-like layer is observed above the ta-C, (d) for $T_{act} = 1875$ K vertically orientated graphite-like sheets form; in this case the structure has been rotated to highlight the orientation of the sheets.

data. As figure 4 shows, the abrupt nature of the simulated transition corresponds very well to experimental data from Chhowalla *et al.* [5] in which the transition to sp^2 material occurs at 450 K. Other experiments [4,6] show similarly sharp transitions. Regarding the comparison in figure 4 between simulation and experiment, we note the use of multiplicative scaling which accounts for both the slightly lower fraction of ta-C within EDIP (60% sp^3 vs 85% for experiment), and the difference in time between impacts (1 ms in experiment vs 1 ps in MD).

The vertically-oriented graphitic-sheets also correspond closely with experiment, and in fact help to explain transmission electron microscopy (TEM) data which was previously not well understood. TEM analysis above the transition temperature had previously shown [5,21] the presence of (0002) reflections indicative of small graphitic regions. Furthermore, the orientation of these reflections was such that the plane of the graphite-like sheets lay perpendicular to the surface. However, this experimental data was puzzling as it appeared to suggest that low energies (< 100 eV) and low temperatures (450 K) were sufficient to drive ta-C into the thermodynamically favoured graphite phase without requiring high temperature and/or pressure. The simulations thus make two important contributions: firstly they reinforce the experimental finding that vertically-oriented graphite regions appear above the transition temperature. The second contribution is more fundamental, as the simulations provide an elegant interpretation of the energetic processes which drive the various phase transformations. In order to utilise information obtained from the *ex situ* simulations, we postpone a discussion of these insights until after presenting all of our simulation results.

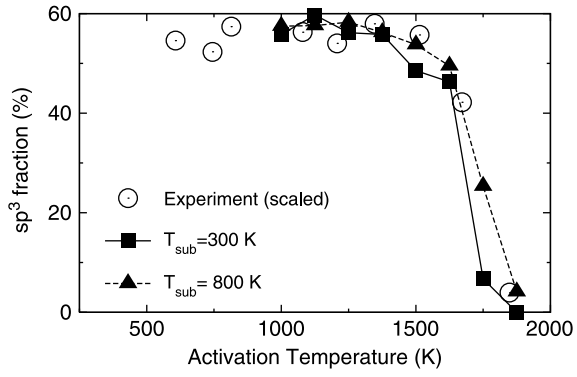

Figure 4. Tetrahedral (sp^3) bonding in ta-C EDIP simulations of *in situ* heating. Squares and triangles indicate 70 eV deposition simulations using substrate temperatures of 300 and 800 K respectively. White circles indicate experimental data from Chhowalla *et al.* [5] which is scaled as discussed in the text.

While the vertical graphitic sheets visually dominate figure 3, the surface horizontal sheeting which appears at $T_{act} = 1500$ K and above is a significant experimental detail. It is well-known experimentally [22,23] that the surface of ta-C reconstructs into such horizontally ordered graphite-like material, but prior to this work this effect had not been reproduced by simulation. It is interesting to speculate on whether ta-C would have a surface graphitic layer if deposited below room temperature. Given that the 1500 K onset for horizontal ordering is not significantly less than the 1750 K transition for vertical orientation, it is not unreasonable to suppose that liquid-nitrogen deposition (for example), might yield a material which does not have ordered sp^2 sites at the surface.

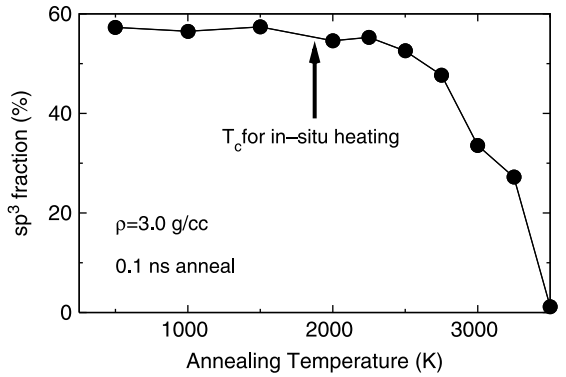

Figure 5. Tetrahedral (sp^3) bonding of a ta-C slab after 100 ps of *ex situ* annealing. The 3.0 g/cc slab was generated by liquid quenching, and the sp^3 data shown was computed using only the central section of the slab. Consistent with experiment, the simulations show that a much higher temperature is required to induce sp^2 material as compared to *in situ* heating.

In addition to the visual insights taken from figure 3, it is constructive to analyse the critical temperature (T_c) of the simulation in figure 4. If the simulated transition temperature ($T_c = 1750$ K) is substituted into equation (1) an energy barrier of 0.7 eV is obtained. While the transition temperature is less than our original estimate of 2500 K, the energy barrier itself compares well with experimental estimates obtained from the elastic moduli and sp^3 fraction; 0.57 eV [9] and 0.65 eV [4], respectively. Considering processes at room temperature, the 0.7 eV energy barrier corresponds to the activation of the dominant process on average once every 14 ms; this correlates well with the fact that room temperature experiments only produce ta-C films. This also explains why the transition temperature is dependent on the deposition rate; raising the deposition rate decreases the available time between impacts, and thus a larger temperature is required to activate the dominant process.

The results of the *ex situ* heating simulations are presented in figure 5, which shows the effect of long-term annealing on the average sp^3 fraction in the centre of the slab. As with the *in situ* case, high temperatures enable a transformation from ta-C into a graphite-like material. The crucial difference however is that the temperatures required are much higher, and the timescale is much longer. As indicated by the arrow, the *in situ* simulations of energetic deposition required only 1 ps at 1875 K to activate the dominant process. In contrast, the *ex situ* system retained its ta-C structure even when heating for one-hundred times longer. This simulation finding that *ex situ* heating significantly increases the temperature stability of ta-C corresponds very well with experiments [7,8] where a similar effect is observed.

The time evolution of the annealed system is shown in ball-and-stick view in figure 6, and illustrates an interesting microstructure which develops throughout the transformation. Below 2000 K the effect of 100 ps of annealing is minor, while at approximately 2500 K the structure begins to develop horizontal surface layers of graphite and the bulk sp^3 fraction slightly decreases. At 3000 K the surface exhibits multiple graphitic layers, and the sp^3 fraction in the bulk falls markedly. As the temperature reaches 3500 K (close to the melting point of ta-C), major structural change occurs in which the bulk of the material transforms into vertical graphite-like sheets.

We note that when interpreting the results of figures 5 and 6 it is important to remember that longer times allow the system to move closer to the thermodynamic limit. For example, running the 3000 K simulation for another 100 ps will allow further graphitic in-growth, with the eventual result that the surface layers will progressively exfoliate and shed graphitic sheets. Similarly, vastly longer simulation times will move the transition to sp^2 material to a slightly lower temperature. We also note that heating experiments involving carbon implantation [24] have observed a sharp juncture between vertically and horizontally ordered graphitic sheets, similar to those seen in figure 6(d).

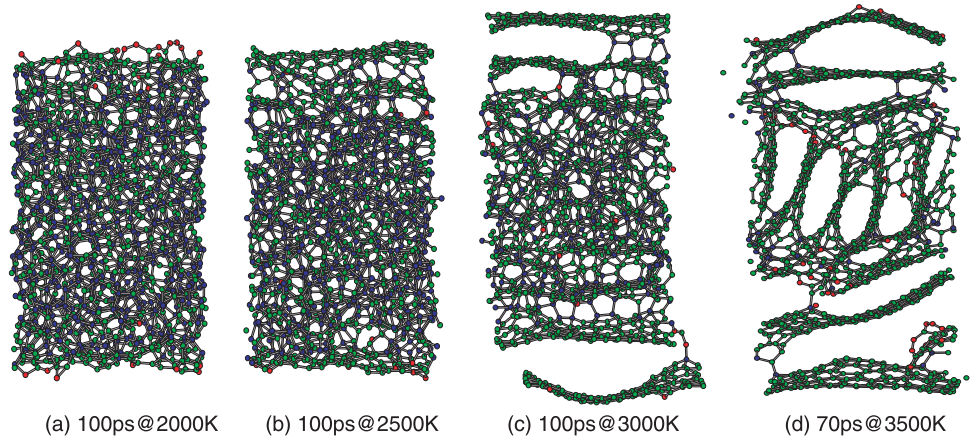

Figure 6. Ball-and-stick images of a 3.0 g/cc ta-C slab (generated through liquid quenching), after 100 ps of *ex situ* annealing. Atom colours follow the same scheme as figure 3. (a) $T = 2000$ K no change is observed in the slab, (b) $T = 2500$ K the initial stages of the formation of graphite-like horizontal layers, (c) $T = 3000$ K the formation of multiple horizontal graphite-like layers, and the exfoliation of the most upper and lower layers, (d) $T = 3500$ K the bulk of the slab is transformed into vertically and horizontally orientated graphite-like sheets.

4. Discussion and conclusion

Taken in combination, the *in situ* and *ex situ* simulations provide significant insight into the physical processes occurring during the deposition of ta-C. The simulations show that the transition of the structural change observed in ta-C films is dependent not only on a dominant process that is thermally activated, but also on the energetic impact. This is particularly apparent upon comparing the temperatures at which graphitic ordering (both horizontal and vertical) occurs in the two kinds of simulation. In the absence of energetic impact horizontal sheeting doesn't appear until 2500 K, as compared to 1500 K for *in situ* heating. Similarly, the vertically oriented structures seen after annealing at 3500 K occur at around 1875 K during deposition. This significant difference reflects the very different kinetics of the two situations: while the thermodynamics is the same, the additional mobility provided by the energetic impact assists the phase change. Related to this effect is the experimental result that increasing the ion energy (from 90 to 130 eV) decreases the transition temperature [5].

In addition to kinetic effects, the fact that energetic deposition involves the addition of new atoms (as opposed to the structural rearrangement of existing atoms as per a typical phase change) allows for the possibility of *stable growth modes*. Detailed atom-by-atom analysis of the deposition process reveals that the vertically-oriented graphitic sheets represent a particular stable growth mode. Other growth modes/configurations also are possible (e.g. amorphous or amorphous + horizontal layering), but once the vertical sheets are present this extinguishes all other growth modes. In the event of interstitial atoms lodging between graphitic sheets, subsequent atoms clear out the inter-layer spacing, thus maintaining the ordered structure. We thus find an explanation for the puzzling behaviour noted earlier: it is not just thermodynamics (or even kinetics) that explains the graphitic regions, but rather the accumulated effect of successive additions to the system in conjunction with activated events.

One question which we have yet to answer is precisely what is the critical activated process which enables the phase transformation. To answer this question will require considerable diligence and cunning, as the amorphous network does not contain easily recognised and well-defined local minima as occur in crystals and on surfaces. Other future (and ongoing) work includes increasing the duration of the high-temperature activation, varying the ion energy, and studying the effect of different initial substrates.

In summary, we have performed MD simulations in which elevated temperature is used in a controlled manner to access infrequent events which would otherwise be overlooked. We find that the capture of this infrequent process dramatically improves the agreement between simulation and experiment and leads to important new insights into the formation process in ta-C. This method opens up a wide range of new possibilities in carbon simulations, and should be particularly useful for ta-C simulations relating to hard-disk manufacture [3], where the understanding of all relevant processes is paramount.

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