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International Journal of Solids and Structures 45 (2008) 3908–3917

INTERNATIONAL JOURNAL OF SOLIDS AND STRUCTURES

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Molecular dynamics simulations of ion-irradiation induced deflection of 2D graphene films

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Received 1 June 2007; received in revised form 8 November 2007
Available online 26 January 2008

Abstract

Ion-irradiation induced surface stress generation and the resulting deflection of 2D cantilever graphene films is studied using molecular dynamics (MD) simulations. The simulation results show that the free-end deflection is strongly dependent on the kinetic energy of the incident ions. At low incident energies ($\ll$10 eV), the graphene film bends towards the irradiated side (upward deflection in our simulations); a transition from bending towards the irradiated side (upward deflection) to bending away from the irradiated side (downward deflection) occurs when the incident energy is ~10 eV; the downward deflection peaks at ~50 eV. Further increases of the incident energy cause the magnitude of downward deflection to decrease. The evolution of free-end deflection with respect to the number of incidences is also dependent on the incident energy. The dependence of the deflection behavior of the graphene films on the incident energy revealed by our atomistic simulations suggests the generation of intrinsic stress of different levels in the growing films. Such behavior may be attributed to competing mechanisms of production and annihilation of interstitial- and vacancy-like defects in the growing film. Understanding the dependence of thin film deflection on the incident energy provides guidelines for controlling thin film shapes at the nanometer scale using ion-beam machining.
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Keywords: Molecular dynamics simulations; Ion-beam machining; Deflection; Interstitials; Vacancies

1. Introduction

In applications of micro-opto-mechanical systems (MOMS) and nano-electro-mechanical systems (NEMS), it is often desirable to tailor the contour shape of free-standing thin films on the nano-meter scale so as to minimize surface adhesion and friction between two mating surfaces with nanometer gaps, or to ensure uniformly directed light reflection. However, residual strains are often introduced into these thin films during

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0020-7683/$ - see front matter Published by Elsevier Ltd.
doi:10.1016/j.ijsolstr.2007.12.025

their manufacturing processes, resulting in a radius of curvature on the order of micrometers, which becomes one of the major concerns in aforementioned applications. It has recently been demonstrated (Bifano et al., 2002) that ion-beam machining can effectively incorporate a high-level residual stress to the thin films by modifying their subsurface nanostructures, thereby presenting a unique technique for nanoscale control of the contour shape of free-standing thin films. Therefore, it is both fundamentally and practically critical to uncover the underlying mechanisms responsible for curvature formation and elimination in free-standing thin films during ion irradiations. During ion bombardment, if the impacting ions do not penetrate into the substrate, the process is referred to as thin film deposition or thin film growth; whereas if the impact ions penetrate significantly into the substrate, the process is called ion irradiation. Irradiation could occur under other conditions such as in nuclear reactor structures where high energy particles (mostly neutrons but sometimes ions, too) penetrate deep into the surface of the reactor structure.

Various experimental techniques have been used to monitor stress evolution during ion bombardments (Bifano et al., 2002; Volkert, 1991; Zhu et al., 2003). Such experiments typically involve *in situ* measurement of film curvature, with which the stress in the thin film can be determined using the Stoney's equation. It was generally observed in these experiments that ion bombardment amorphizes the film surface and the steady-state stress of the films is strongly dependent on the kinetic energy of the incident ions. Volkert (1991) observed that in a silicon film upon MeV ion irradiations the compressive stress increases and peaks as the amorphous regions are formed. The compressive stress then decreases and reaches a steady-state value as amorphization continues and eventually saturates. Lee et al. (1999) observed that ion irradiations result in a decrease in the compressive stress in diamond-like carbon films, and the steady-state stress is slightly tensile. Differently, van Dillen et al. (1999) observed a transition from tensile to compressive stress in alkali-borosilicate glass samples irradiated by MeV Xe ions. For high surface mobility films, it was observed that the evolution of the residual stress typically occurs in alternating stages of compressive, tensile, and compressive growth (Abermann, 1990; Floro et al., 2001; Shull and Spaepen, 1996; Spaepen, 2000), exhibiting a rather complicated stress generation mechanism.

Motivated by these experimental observations, predicative theoretical models have been developed to study stress generation mechanisms during ion irradiations. Within the framework of elasticity, Guinan (1974) obtained a rough estimate of thermal stress induced by a single impinging ion in terms of the dissipated energy in the damage zone. It is however not straightforward to extend this model to the cases where many energetic ions sequentially impact the substrate since the existing damage regions may have a strong influence on the subsequent defect production. Based on the knock-on linear cascade theory, Windischmann (1987) predicted a square-root dependence of compressive stress on the incident ion energy. This model, however, is not applicable to cases of high incident energy. Davis (1993) and Robertson (1993) separately developed a subplantation model in which the compressive stress formation in thin films is attributed to densification of subsurface due to ion implantation. An underlying assumption of the subplantation model is that the film surface, upon ion bombardment, is overdense containing no voids. However, experimental measurements and numerical simulations indicate that films are usually under-dense. For epitaxially grown thin films on a substrate, it has been well established that the lattice-mismatch is the driving force for the thin film surface stress (Freund and Nix, 1996). Stress evolution during film growth has also been attributed to competing mechanisms between island growth and coalescence (Floro et al., 2001; Nix and Clemens, 1999). For polycrystalline films, Chason et al. (2002) developed a model of stress evolution during film growth, in which the generation of compressive stress in the films is attributed to the flow of excess atoms into grain boundaries driven by surface chemical potential due to the impinging growth flux.

Molecular dynamics (MD) simulations have been carried out to uncover the stress generation mechanisms during ion irradiations (Gibson et al., 1960; Jager and Albe, 2000; Kalyanasundaram et al., 2006; Kaukonen and Nieminen, 1992; Kaukonen and Nieminen, 2000; Kinchin and Pease, 1955; Marks et al., 1996; Muller, 1987; Zhang et al., 2003). Depending on the substrate materials and the kinetic energy of the incident ions, the generated stress can be either compressive or tensile. These MD simulations allow direct investigation of the atomic structures of the surface region impacted by energetic ions. Results of the MD simulations may provide useful insight into the atomistic mechanisms of stress generation. For example, for only a few ion bombardments, Gibson et al. (1960) observed that the damaged configuration primarily consists of interstitial–vacancy pairs, i.e., the Frenkel defects. Muller (1987) found that ion-irradiated nickel films contain a

large fraction of voids, which account for the overall tensile stress in the film. Marks et al. (1996) observed that the amorphous graphene structures consist of ring structures of different sizes, and established a relationship between the kinetic energy of incident ions and the steady-state stress. Recently, Zhang et al. (2003) performed 3D MD simulations of ion irradiation of an initially perfect diamond lattice. In addition to the establishment of a relationship between the kinetic energy of incident ions and the steady-state stress, they developed a theoretical model in which the compressive stress formation is attributed to the competing mechanisms between Frenkel defect production and annihilation. The evolution of surface stress upon ion irradiations was studied using MD simulation by Kalyanasundaram et al. (2006) for a silicon substrate bombarded by argon ions. They found that, upon medium-energy ion bombardment, the induced stress is initially tensile, but it becomes compressive with further bombardment and gradually saturates. Such a transition from tensile to compressive stresses is different from the experimental observations during thin film growth, where film stress evolves from compressive to tensile, and back to compressive (Abermann, 1990; Floro et al., 2001; Shull and Spaepen, 1996; Spaepen, 2000). The discrepancy in the stress evolution phenomena suggests different active stress generation mechanisms in the numerical models and experiments.

The aforementioned MD studies were unexceptionally focused on the calculations of the intrinsic stress without explicitly determining the curvature of the thin films. This is largely due to the prohibitively high computational costs for numerical simulations of 3D curvature formation. In the present study, we adopt a 2D model consisting of a thin graphene film of one monolayer thick, irradiated by energetic carbon neutrals (termed "ions" by convention). The structural simplicity of the 2D model significantly reduces the computational cost, thus allowing not only direct observations of the defects produced during ion irradiations, but also monitoring of the evolution of the deflection profile of the film during ion bombardments. The measured deflection of the thin films can then be used to determine the stress state of the growing thin films.

The rest of the paper is organized as follows: Section 2 presents numerical models and methodologies adopted in the present simulations; Section 3 reports simulation results, including the relationship between the free-end deflection and the kinetic energy of the incident ions, and the deflection evolution during ion irradiation. Section 4 presents the atomic structures of the grown films and their implications to the overall stress state. Possible mechanisms responsible for the generation of the intrinsic stress are proposed. Discussions and concluding remarks are given in Section 5.

2. Models and methodologies

Our numerical model consists of a perfect 2D graphene film of one monolayer thick irradiated by energetic carbon neutrals, as shown in Fig. 1. The motion of the atoms in the ensemble is confined to the plane of the film, thereby significantly reducing the computational cost. Compared to the previous 3D MD simulations, this 2D model allows us to simulate much larger cells, therefore enabling direct monitoring of the evolution of thin film deformation during ion bombardments. Apart from its computational convenience, single graphene sheet has recently been identified as a novel material that may have promising applications (Bunch et al.,

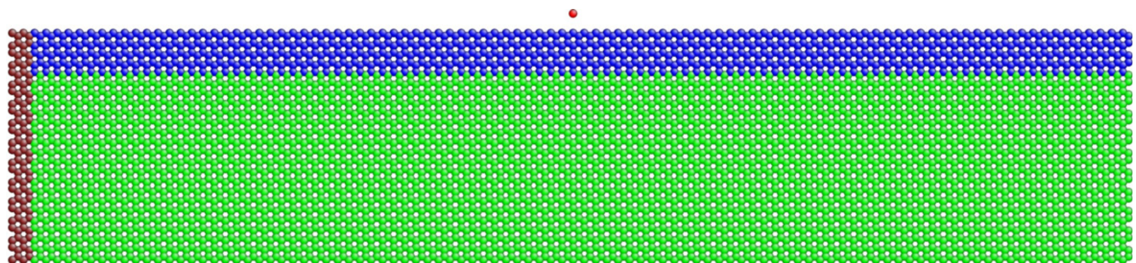

Fig. 1. A 2D graphene film fixed at one end and free at the other. Several layers of atoms on the left end (plum-color) are held fixed; those "green" atoms are coupled to an external bath of 100 K, and those "blue" atoms are completely free. Carbon neutrals (red) are sequentially deposited onto the top surface of the film with normal incidence and randomly chosen locations. The kinetic energy of the incident carbon neutrals ranges from 1 eV to 100 eV. (For interpretation of color mentioned in this figure the reader is referred to the web version of the article.)

2007; Stankovich et al., 2006). Ion-beam machining presents a unique surface modification technique to create defects on its edges, which promotes covalent bond formation between the graphene sheet and its surrounding matrix.

The bond-order Tersoff–Brenner potential (Brenner, 1990) is adopted to describe the carbon–carbon interactions:

$$\phi = \sum_{i} \sum_{j>i} f_{c}(r_{ij})[V^{R}(r_{ij}) + b_{ij}V^{A}(r_{ij})], \tag{1}$$

where ϕ is the total potential energy of the atomic system, r_{ij} is the distance between atoms i and j, V^{R} and $V^{A}$are the pair-wise repulsive and attractive interactions, respectively, b_{ij} is a bond-order function that has a complicated dependence on the bond angles and bond lengths involving atoms i and j, and f_{c} is a cutoff function of the interaction potential that decreases to zero when r_{ij} is larger than 2.0 Å. This potential has been popularly used for the study of hydrocarbon systems since it can appropriately describe both bond breaking and bond forming.

The initial perfect graphene film consists of ~4800 carbon atoms with 12 hexagonal layers. Prior to deposition, the graphene film is quasi-statically relaxed to its minimum energy configuration using the limited memory BFGS geometry optimization algorithm (Gilbert and Nocedal, 1993). To mimic a cantilever beam configuration, several layers of atoms at the left end are held fixed (plum-color); atoms within 10 hexagonal layers from the bottom (green) are coupled to an external bath of 100 K by employing the method developed by Berendsen et al. (1984); the remaining atoms (blue) are completely free and evolve according to Newton's equations of motion without any constraints. We also apply periodic boundary conditions in both directions in the plane of the 2D graphene film. The dimensions of the periodic cell are sufficiently larger than the dimensions of the film to ensure vanishing interactions between the opposite edges. So imposing the in-plane periodic boundary conditions is solely a choice of computational convenience for accommodating gas-phase carbons that are sputtered from one edge and travel to the other (these gas-phase carbons need to be manually removed when they travel to the boundaries of the computational box if the in-plane periodic boundary conditions are otherwise not applied). Energetic carbon neutrals are then sequentially deposited onto the top surface of the graphene film with normal incidence and randomly chosen locations. In addition, we also performed simulations with different seeds of random number generators in determining the randomized depositing locations, and we observed negligible differences in our simulation results. For each simulation, the incident energy of the impacting ions is kept constant. A number of simulations have been performed in which the incident energy of the impacting carbons ranges from 1 eV to 100 eV. Between two consecutive depositions, the system is thermostated with a relaxation time of approximately ~2.5 ps. A total of 1000 carbon neutrals are deposited to ensure appreciable free-end deflection of the graphene films.

3. Simulation results

MD simulations of ion-beam depositions are performed at eight levels of incident energies: 1, 10, 20, 30, 40, 50, 70 and 100 eV, respectively. It was observed that surface sputtering occasionally occurs during depositions. The higher the incident energy, the more frequent the occurrence of sputtering. When sputtering occurs, the net number of atoms incorporated into the film is less than the carbon atoms that are actually deposited.

Upon deposition, the graphene film bends either towards the irradiated side (upward) or away from the irradiated side (downward). The deflection of its free end is strongly dependent on the incident energy. Fig. 2 shows the maximum free-end deflection normalized by the height of the original graphene film as a function of the incident energy. Negative deflection in the figure represents upward bending, while positive deflection represents downward bending. At 1 eV, the film bends upward, the corresponding configuration is shown in Fig. 3(a). A transition from upward to downward deflection occurs at around 10 eV at which the film is nearly flat (see Fig. 3(b)). When the incident energy is higher than the transition energy, the graphene film bends downward, as shown in Fig. 3(c) and (d). The free-end downward deflection reaches a peak at around 50 eV (see Fig. 3(c)). Further increase in the incident energy causes a decrease in the free-end deflection, as shown in Fig. 2.

Fig. 4 shows the evolution of the free-end deflection of the graphene films as ions are being deposited at different incident energies. Three typical evolution phenomena are observed. At low incident energies

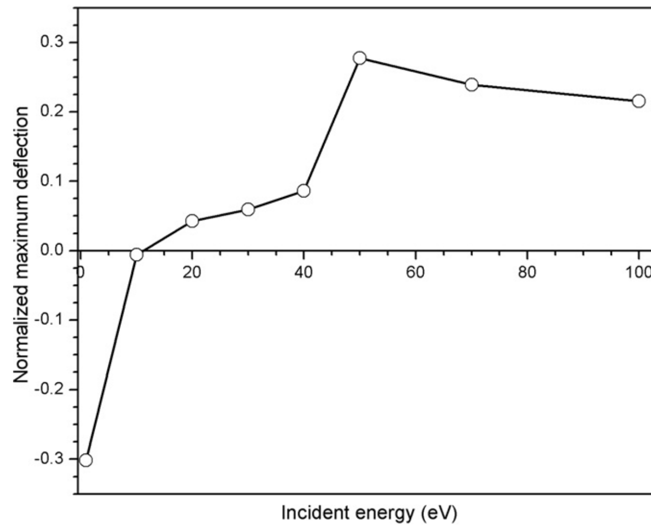

Fig. 2. The free-end deflection of the cantilever graphene film normalized by the height of the original graphene film as a function of the incident energy. At 1 eV, the film bends towards irradiated side (upward), characterized by a negative deflection. The film at other incident energies bends away from the irradiated side (downward), characterized by a positive deflection. The downward deflection peaks at 50 eV beyond which it monotonically decreases.

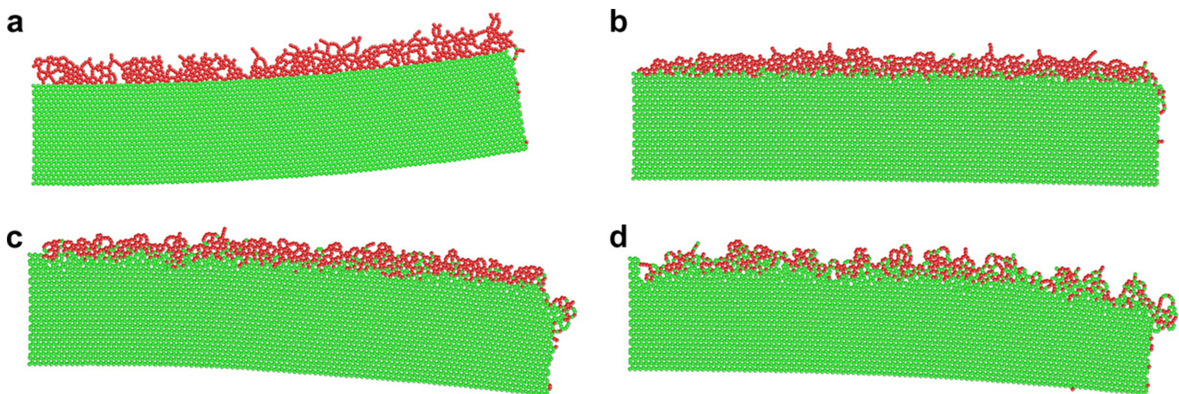

Fig. 3. Atomic configurations of the bent films at different incident energies. (a) 1 eV impact; (b) 30 eV impact; (c) 50 eV impact; (d) 100 eV impact.

(1 eV), the film always bends upward, while at high incident energies (>50 eV), the film always bends downward. At moderate incident energies, however, the film initially bends upward upon a small number of incidences. As ion bombardment continues, a transition from upward to downward deflection occurs. As an example, the configurational evolution for 30 eV irradiation is shown in Fig. 5.

4. Atomic structures and stress generation mechanisms

The deflection of the graphene films is a result of the intrinsic stress generated in the grown films during ion irradiation. From an energetic point of view, excessive strain energy stored in the growing films is dynamically reduced at the expense of bending of the originally stress-free substrate. From mechanics point of view, the grown film can be viewed as a highly stressed surface layer and the originally stress-free substrate glued together at the interface as a bi-material beam. To relieve the excessive stress, the deposited surface layer on top has a tendency to expand (for compressively stressed layer) or shrink (for surface layer in tension)

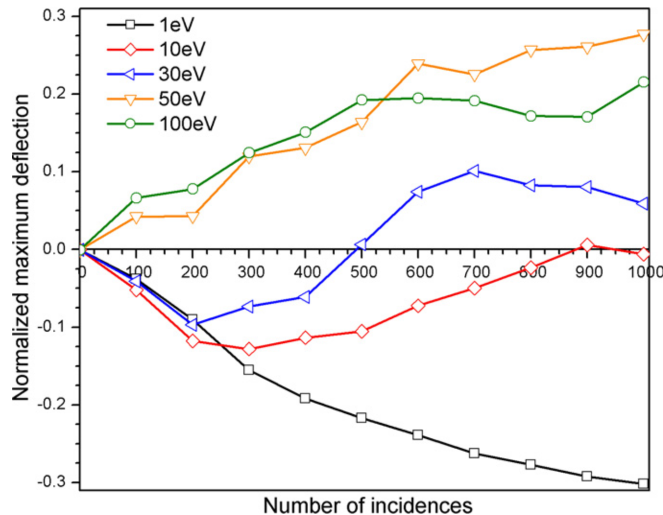

Fig. 4. Evolution of the free-end deflection as a function of the number of incidences. Three typical evolution phenomena are observed. At low (1 eV) or high (>50 eV) incident energies, the film bends always either upward or downward. At moderate incident energies, a transition from upward to downward bending occurs as ions are being deposited.

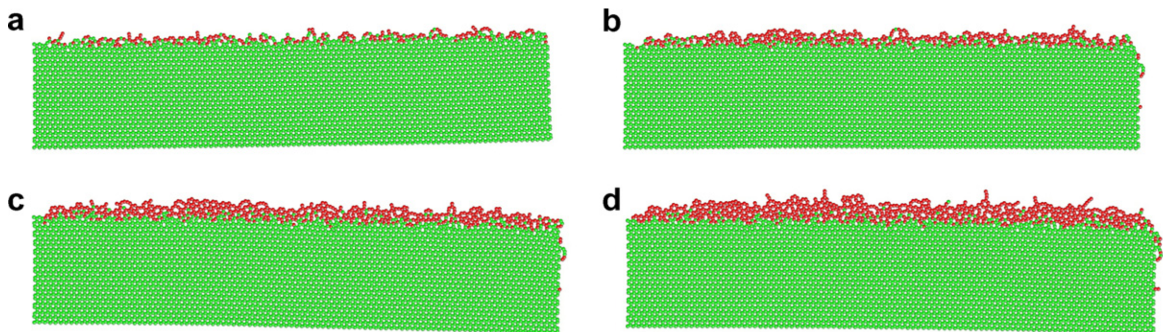

Fig. 5. Configurational evolution of the films irradiated by 30 eV carbon neutrals. A transition from upward to downward deflection is clearly seen. (a) 250 incidences; (b) 500 incidences; (c) 750 incidences; (d) 1000 incidences.

in length. The net effect of this tendency of the surface layer to change its dimension on the bi-material beam is to cause it to bend upward (for surface layer in tension) or downward (for surface layer in compression).

From an atomistic point of view, the intrinsic stress generated in the grown films can be attributed to the incorporation of defects during ion irradiation. The distribution of such defects determines the surface forces responsible for bending of the film. For a better understanding of the deformation of the films, the characteristic atomic structures of the grown films should be examined.

Several features of atomic structures are observed in the deposited surface layer (see Fig. 6), which may shed lights into the stress generation mechanisms in the grown films. In Fig. 6, as in previous figures, the ‘‘red’’ atoms are the incident ions deposited during bombardment whereas the ‘‘green’’ atoms are the ones from the original perfect lattice. Fig. 6 shows that, with increasing incident energy, the mixing between the newly deposited atoms and the atoms from the substrate progressively increases. Note that in a perfect graphene lattice all rings are 6-sided (hexagon). As incident ions are deposited onto the surface, the growing surface layer typically contains ring structures of different number of sides. In an overdense region, rings with less than 6 sides (e.g., pentagons or even squares) are present, while in an under-dense region, rings with greater than 6 sides are present. A ring structure with fewer than 6 sides can be regarded as an interstitial-like defect (or free-area-shortage), while a ring structure with more than 6 sides is equivalent to a vacancy-like defect (or

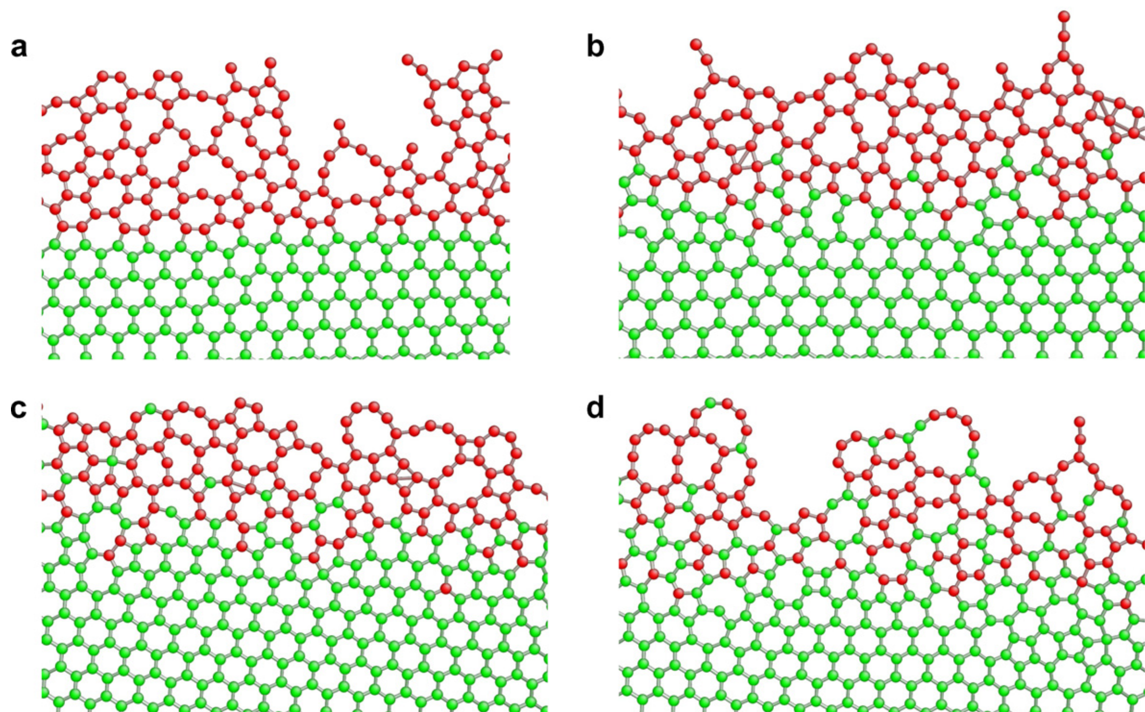

Fig. 6. Atomic structures of the grown films at different incident energies. (a) 1 eV impact; (b) 30 eV impact; (c) 50 eV impact; (d) 100 eV impact.

free-area-excess). Atoms in the vicinity of the interstitials are in compression, while those in the vicinity of the vacancies are in tension. The overall stress of the grown films is a function of the relative densities of these two defects.

Besides the ring structures, free surface (or increased surface area) created by ion irradiation can be regarded as another type of defects, which have the same effect as vacancies. It is observed that different incident energies give rise to different extent of surface irregularities of the grown films, which characterize the area of the free surface of the grown films. It is apparent that the films grown by 1 eV ion irradiation (Figs. 3 and 6(a)) and 100 eV ion irradiation (Figs. 3 and 6(d)) have relatively larger free surface area compared with those grown by 30 eV (Figs. 3 and 6(b)) and 50 eV (Figs. 3 and 6(c)) impact.

The production of ring structures and free surfaces is a consequence of the dynamics of the incident ions and their interactions with the surface of the growing films. Our simulation results clearly demonstrate that the incident ions do not sub-plant below the surface of the growing films, even for high-energy impact. The observed mixture between deposited atoms and those originally in the substrate is primarily due to a "caving-in" mechanism (Marks et al., 1996), i.e., the energetic ions break C–C bonds, pushing the substrate atoms in the lateral direction. This observation seems to invalidate the previously proposed subplantation model. During bombardment by 1 eV ions, the incident energy is insufficient to break the C–C bonds, thus the incident ions simply attach themselves to the surface by forming bonds with atoms to which they approach. During impact by higher-energy ions (greater than 10 eV in the present simulations), the incident energy is sufficient to break the C–C bonds (the bonding energy is 4.93 eV). As a result, local displacement spikes (Kinchin and Pease, 1955) are formed. Dynamic bond reconstruction associated with the displacement spikes often results in converting a large ring on the surface of the growing film into smaller rings, thus modifying the local stress from tensile to compressive.

In addition to breaking bonds, the excessive kinetic energy of high energy ions is transmitted to the local lattice in the form of concentrated lattice vibration upon impact, forming thermal spikes (Kaukonen and Nieminen, 2000). Such thermal spikes promote local atomic relaxation. Careful examinations of the simulated impact sequences at different incident energies reveal that the relaxation primarily involves bond reconstruction in the lateral direction. Within the thermal spikes, smaller rings in pre-stressed regions tend to be

converted to six-sided or larger rings, or simply form free surfaces. Another dynamic process during bond reconstruction is the annihilation of interstitials and vacancies to form 6-sided rings. Both processes modify the local stress from compressive to neutral or tensile. With increasing incident energy, the size of relaxed domain increases, and relaxation becomes more efficient.

The competition between defect generation due to displacement spikes and relaxation due to thermal spikes governs the overall stress state of the grown films, and hence the free-end deflection. At low incident energy, only thermal spikes are active. As a result, very few interstitials are produced, and the overall stress is tensile. When the incident energy is greater than a critical value enough to break C–C bonds, the overall stress is compressive since the effect of interstitials prevails. At very high incident energy, relaxation due to thermal spikes becomes more effective, thus the magnitude of compressive stress is reduced.

It could be argued that bond reconstruction due to competing effects of displacement spikes and thermal spikes is also the fundamental causes for the stress evolution in the graphene films observed during ion irradiation. When the impact energy is low, the stacking process creates substantially more vacancies than interstitials during deposition, thus the overall stress is always tensile, giving rise to the monotonic increase in the upward free-end deflection of the graphene film. When the impact energy is sufficiently large to break the C–C bonds, interstitials, vacancies, and free surface are produced within the displacement and thermal spikes. At the intermediate energy level, the effect of free surface upon impact may be considerable at the initial stage since the original surface was disrupted. On the other hand, the effect of interstitials produced by the displacement spikes at the early stage of irradiation may be insufficient to compete with the effect of the free surface because of their small number. Therefore the overall stress in the grown surface layer is tensile. However, as ion bombardment continues, the free surface gradually reaches a saturated level; but the number of interstitials created within the grown films continues to increase with the number of impact ions. At a critical number of incidences, the effect of interstitials in the grown films may overtake that of the free surface, giving rise to a transition from tensile to compressive stress in the grown film. Such transitional evolution of thin film stress should be present within a range of incident energy levels, as indicated by our simulation results in Fig. 4 where the range seems to be from 10 eV to a level slightly below 50 eV. With an impact energy higher than 50 eV, however, the density of interstitials created per ion impact due to displacement spikes may be so high that their effect may always prevail over that of free surfaces and relaxation induced by thermal spikes. In that case, the overall stress is always compressive regardless of the number of incidences.

5. Discussions and conclusions

In the present work, 2D MD simulations are performed to investigate the deformation of a cantilever graphene film under irradiations with energetic carbon neutrals. The simulations show that both the direction and the magnitude of the free-end deflection are governed by the kinetic energy of the incident ions. Specifically, at low-energy impact, the graphene film bends upward. A transition from upward to downward bending occurs when bombarded with 10 eV ions. Beyond the transition energy, the downward free-end deflection increases with increasing incident energy, and reaches a peak at 50 eV. Further increase the incident energy leads to a decrease in the downward free-end deflection. The incident energy also plays a critical role in the evolution of the free-end deflection with respect to the number of incidences. With low- or high-energy impact, the free-end deflection remains either upward or downward throughout the entire impact process. But with intermediate-energy impact, a transition from upward to downward defection occurs as number of impact incidences increases.

The observed bending of the graphene films upon ion irradiations is due to the stress generated in the grown films. The atomic structures obtained from the MD simulations provide valuable insights into the stress generation mechanisms in the grown films. We proposed that the intrinsic stress built in the grown films can be attributed to the competing mechanisms of production of interstitials in the displacement spikes and the subsequent relaxation in the thermal spikes. The evolution of the free-end deflection can also be understood as the competing mechanism between interstitials and vacancies/free surfaces.

Observations from our numerical simulations invalidate the subplantation model. While our recently developed model (Zhang et al., 2003) accounts for the competing mechanism of Frenkel defect production and recombination, it is unable to explain the generation of tensile stress, corresponding to the upward bending

of graphene film in the present study. To understand the deformation of the films for a full spectrum of kinetic energy of the incident ions, the densities of the interstitials and vacancies need to be considered separately, rather than in the form of Frenkel pairs.

In addition to obtain the fundamental understanding of the underlying deformation mechanisms of free-standing thin films upon ion irradiations, the present study on the structural deformation of graphene films provides a theoretical basis for tailoring thin film shapes at nanoscale using ion-beam machining. It should be noted that other deposition conditions, such as incident angle, the substrate temperature, etc. may also influence the generation of the intrinsic stress and hence the deformation of the films. Studies of such effects are current underway.

Acknowledgement

S. Zhang gratefully acknowledges the support from the NSF Grant under Award No. CMMI 0600661; K.J. Hsia gratefully acknowledges the support of NSF Grant No. CMS 04-09683.

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