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Amorphous carbon multilayered films studied by molecular dynamics simulations

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Amorphous carbon multilayered films have been studied by molecular dynamic simulations. Samples were grown on diamond and silicon substrates, alternating deposition energies of 1 and 40 eV; atomic interactions were described by the semiemperical Tersoff potential. Structural analysis of the obtained films shows that the film density and sp^3/sp^2 ratio oscillate with deposition energy. The alternation of layers with different local atomic stresses is also observed. High density sp^3-rich profiles and compressive stress are associated with high deposition energy regions, whereas low density sp^3 poor profiles and tensile stress are associated with low deposition energy ones. The grown films are thermally stable in the bulk under simulated annealing at 2500 K; appreciable changes, similar to those observed in monolayer films, occur mainly on the last superficial layer.

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I. INTRODUCTION

Amorphous carbon films have been the center of a great number of studies because of their multiple applications. The structure and properties of these materials have been extensively analyzed.[1,2] However, from the point of view of their technological applications, some problems are still being considered such as adherence, which is related to high intrinsic stress. It has been suggested that a multilayered structure could be a solution to this issue. The idea is that rich sp^2-bonded layers intercalated between sp^3-abundant ones would act as buffers, releasing the high stress known to be present in *ta*-C.[3] On the other hand, it has been experimentally observed that amorphous carbon thin films composed by sequential sp^3- and sp^2-rich layers exhibit higher hardness values than those consisting of a single sp^3 or sp^2 layer; it has also been noticed that hardness grows as the bilayer thickness decreases in the range 50–10 nm.[4] This behavior was predicted time ago by Koehler's model[5] for multilayered films made from two materials with different elastic modulus and a few nanometers thick per layer.

On one hand, multilayered films have promising electronic properties in electron field emission; it has been found that field emission of tetrahedral amorphous carbon (*ta*-C) films depends on the number of layers, layer thickness, and sp^3 content of each layer and, hence, field emission could be modified by controlling these parameters.[6]

In previous research, thin amorphous carbon films have been experimentally obtained by ion beam deposition[2,7,8] and then studied by molecular dynamics simulations.[9,10] Atomic carbon and fullerene molecules have been used as precursor projectiles. In some cases, a poor adherence of the films to the substrate has been observed especially in the cases of fullerenes thrown on silicon substrates or any precursor deposited on germanium; this poor adherence, causing buckling or even delamination of some films from the substrate, was partially attributed to the high stress generated as a consequence of the deposition procedure. Numerical simulations have evidenced that some physical properties such as density, sp^2/sp^3 ratio, etc., of films grown on different substrates are strongly dependent on deposition energy, in reasonable agreement with experimental observations.

In the present work, a molecular dynamics simulation of the growth of multilayered amorphous carbon thin films is presented. The aim of this calculation is to model the experimental ion beam deposition procedure, where different layers are obtained by controlling the deposition energy. Structural properties of the resulting samples (density, stress distribution, coordination, etc.), as well as the effects of thermal annealing on stress relaxation, are reported. Although there exist in the literature calculations about these systems using a similar interaction potential, there are remarkable differences in the films generation.[3] In particular, their theoretical approach is based on Monte Carlo simulations, and different layers are generated starting from separated cells of crystalline carbon at diamond and graphite densities.

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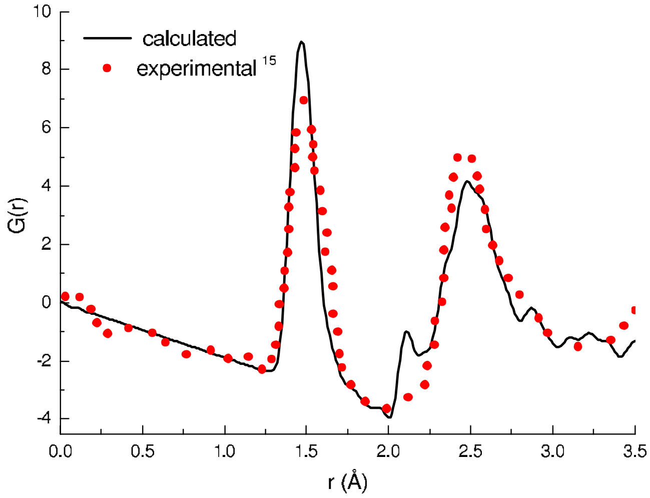

FIG. 1. (Color online) Reduced radial distribution function calculated for a monolayer film deposited at 40 eV: $G(r)=4\pi r[\rho(r)\text{-}\rho_0]$, where $\rho(r)$ is the density of atoms centers at a distance r from an atom, averaged over the system, and ρ_0 is the mean density. Experimental results by Gilkes *et al.* (see Ref. 15)

II. COMPUTATIONAL MODEL

The growth of multilayered amorphous carbon structures was simulated by molecular dynamics (MD) using the semi-empirical many-body Tersoff potential for atomic interactions.[11] This potential, which has been extensively used, provides a good description of carbon and carbon-silicon polytypes including fullerene and amorphous structures.[9–12] Despite the limitations of a semiempirical potential as compared to *ab initio* methods, it enables to handle a great number of atoms, which is essential to simulate multilayered systems.

Each layer was generated by deposition of carbon atoms with a given kinetic energy since it was proven in previous papers that structural properties such as density and sp^2/sp^3 ratio in each layer strongly depend on deposition energy.[2,7–10]

C atoms were used as projectiles, impinging perpendicularly to the substrate surface at a random location. Monolayer films deposited at 1 and 40 eV, and multilayered films deposited alternating these two different deposition energies (1 and 40 eV) were studied. Energies were chosen in order to produce amorphous carbon layers with an appreciable density and sp^2/sp^3 ratio difference, according to previous simulations. The evolution of the system was followed using Verlet's algorithm; the time interval between molecular dynamics steps, Δt, was 0.5 fs for the 1 eV deposits and 0.2 fs for the 40 eV deposits. These Δt values were chosen in order to ensure atomic displacements smaller than 0.01 Å in the relaxed system after the projectile has been incorporated at both energies studied.

As substrates, ideal diamond and silicon (100) crystals were employed. The number of (xy) crystalline planes was chosen according to the expected penetration depth of the projectiles for the deposition energy of the first amorphous carbon layer (see Ref. 9). In every case, the two bottom planes of the substrate were fixed to their equilibrium positions, representing a semi-infinite crystal. The remaining at-

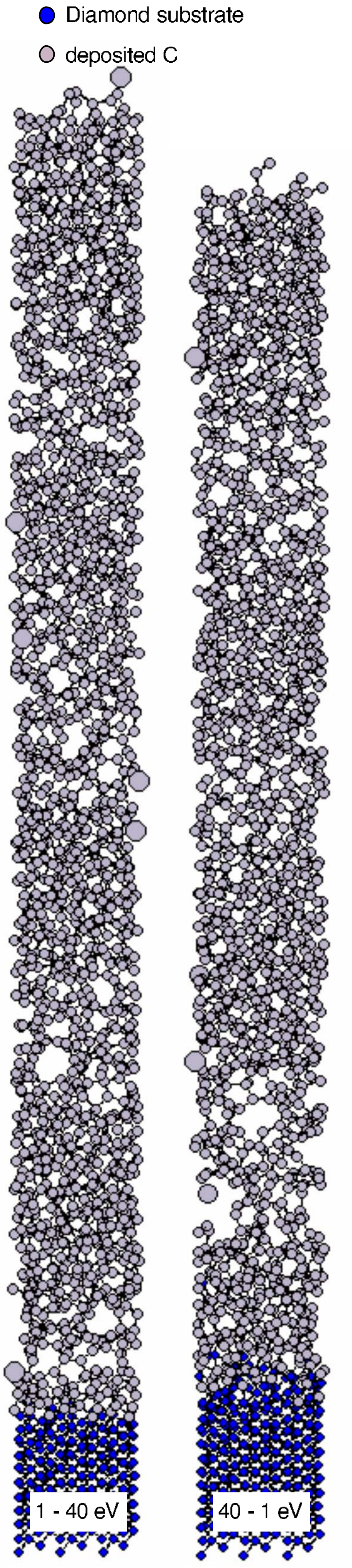

FIG. 2. (Color online) Snapshots of multilayered carbon films grown on diamond with alternating deposition energies of 1 and 40 eV. Starting with 1 eV (left) and starting with 40 eV (right).

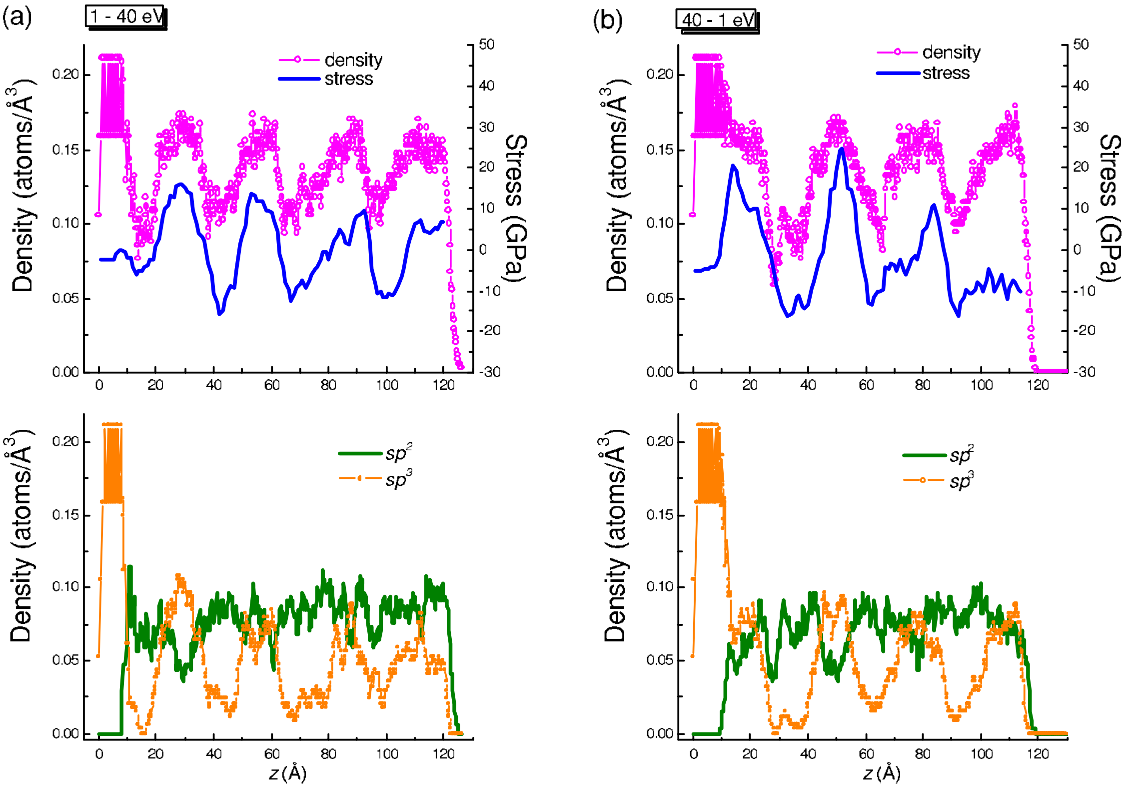

FIG. 3. (Color online) Density and atomic stress profiles corresponding to snapshots shown in Fig. 1 (up); density profile discriminating sp^2- and sp^3-bonded carbon atoms (down). (a) Starting with 1 eV, (b) starting with 40 eV.

oms were allowed to move with full dynamics, applying periodic boundary conditions in the (xy) plane consisting of 3×3 unit cells.

Before deposition, the substrates were allowed to relax at a temperature of 300 K and zero pressure for about 1000 fs. Each 1 eV layer, containing 200 atoms, was generated by throwing one atom with this kinetic energy every 250 fs (500 MD steps). Each 40 eV layer, containing 250 atoms, was generated by throwing one atom every 200 fs (1000 MD steps). In this way, differences in density and penetration depth associated to the deposition energy were compensated and, hence, both layer types resulted with approximately the same width. In both cases, each projectile had enough time to dissipate its energy to the system before the next atom hits the surface. The aim is to simulate experimental conditions of ion beam methods concerning the independence of deposition events.

During deposition, system cooling was simulated by applying the method of Berendsen *et al.*[13] using a thermal relaxation time constant $\tau_T = 4\ \Delta t$. In order to allow a complete energy transfer from the projectile to the substrate, the last ten impinging C atoms were not included in the thermalization process.

After the growth of several alternated layers at 1 and 40 eV, the samples were allowed to relax for about 10^4 fs prior to performing structural and atomic level stress studies. Structural characterization included density profiles from the substrate up to the film surface and coordination of the atoms inside the film. Mean densities across the films were calculated by sliding a slice in small increments along the z direction, discriminating atomic species (in the case of silicon substrates) and coordination number of the atoms. In a similar way, the distribution of stresses across the films were computed, averaging individual atomic stresses inside a slice of 3 Å displaced at increments of 1 Å in the vertical direction.

The calculation of local stresses was done within the empirical formalism for a-C networks given in detail in Ref. 14. The atomic stresses (σ_i) were computed from the local energies by considering an atomic compression (tension) of the system: $\sigma_i = -dE_i / d\ \ln(V/V_0)$, where V_0 is the system equilibrium volume, V is the volume after an isotropic compression (tension), and E_i is the energy of atom i. Dividing σ_i by the atomic volume Ω_i (computed as the Voronoi's volume around each atom) converts it into units of pressure $p_i \approx \sigma_i / \Omega_i$. Voronoi's volumes were calculated using a numerical procedure consisting of the construction of successive onion shells around each atom using a grid with an elemental volume of 8×10^{-3} Å^3.

The aim of this calculation is to model the experimental ion beam deposition procedure, where energetic impinging atoms produce local heating and are quenched in a metastable position. In this way, amorphous carbon is grown far from equilibrium with appreciable atomic stress and different coordination numbers, bond lengths, and angles. Therefore, in the simulated grown films, all of these features should be present.

Thermal annealing at 2500 K was simulated on some of the samples in order to study possible structural changes and relaxation effects. To do so, the temperature was raised at a

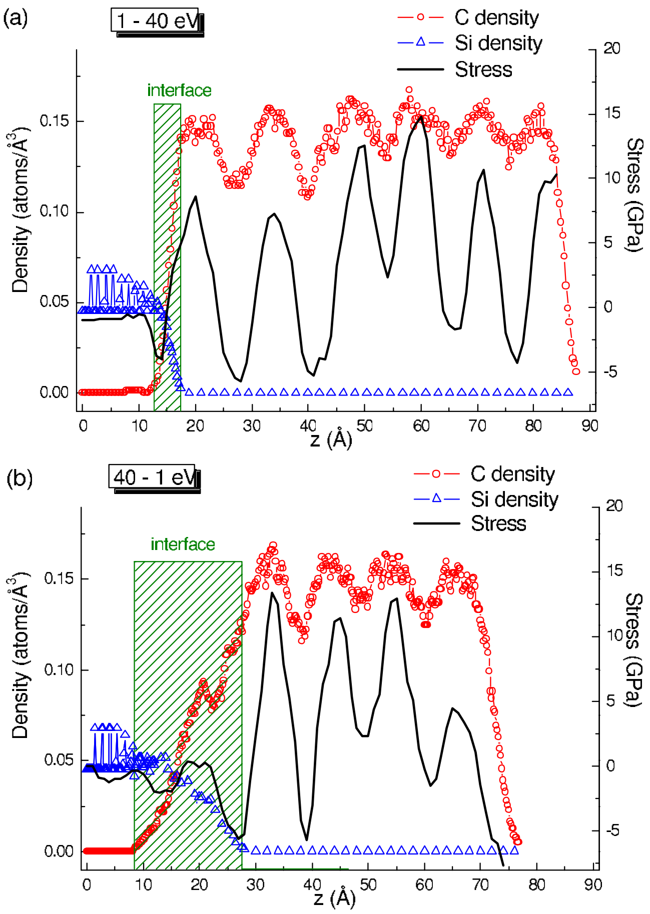

FIG. 4. (Color online) Density and atomic stress profiles of multilayered carbon films grown on silicon substrates. Interface regions are marked as shadowed zones. (a) Starting with 1 eV, (b) starting with 40 eV.

rate of 5 K/fs up to 2500 K; the sample was maintained at this temperature during approximately 2500 fs until no significant structural difference was found and then slowly cooled down to room temperature at 0.25 K/fs.

III. RESULTS

Structural analysis of monolayer films confirms previous results concerning density, sp^2/sp^3 ratio, coordination, and angular and radial distribution function.[9] Figure 1 shows the reduced radial distribution function obtained from a film deposited on a diamond substrate at 40 eV, together with the experimental results by Gilkes.[15] As mentioned in a previous paper,[9] the small peak at 2.1 Å is an artifact of the potential linked to the cutoff radius for C-C interactions. The mean density of this film (ρ_0) is about 0.15 atoms/Å^3 and the sp^2/sp^3 ratio is close to 1. The great majority of the atoms inside the film are three and four coordinated: there is only 3% of two-coordinated atoms (mainly on the film surface) and 2.5% of five-coordinated atoms (mainly in the substrate-film interface); as the film thickness increases, these percentages decrease.

Figure 2 shows snapshots of multilayered films deposited on diamond substrates with deposition energies of 1 and 40 eV where different density regions can be clearly distinguished. The corresponding density and atomic stress profiles of films deposited on diamond are shown in Fig. 3(a): low and high density oscillations are correlated with the regions where atoms were deposited at low (1 eV) and high (40 eV) energies, respectively. Both layer types have an average width of approximately 15 Å. There are no abrupt frontiers between these regions as a consequence of the growing procedure, especially going from low to high deposition energy: the penetration of the first high energy atoms jumping into the previous low energy (and low density) deposited layer generates a transition region, where density increases gradually. In the opposite case, a transition region slightly sharper is observed and would be associated to the refilling of the rough surface on top of the last high energy layer. The oscillatory behavior present in density profiles is also observed in the average atomic stresses. It can be observed that atoms belonging to high density regions are under compressive (positive) stress, while atoms belonging to low density regions are under tensile (negative) stress with compressive and tensile stresses reaching similar absolute values.

Analysis of coordination shows that the density of sp^2-coordinated atoms remains practically constant across the film after the first high density region, while the density of sp^3-coordinated atoms reaches maxima at high energy deposited regions (density ratio $sp^3/sp^2 \approx 1$) and falls at low energy deposited regions ($sp^3/sp^2 \approx 1/4$). This effect can be clearly appreciated in Fig. 3(b).

Samples grown at the same deposition energies but starting with 40 eV exhibit a similar behavior, beginning with a high density region and compressive stress, as was to be expected [Figs. 3(c) and 3(d)]. Only a slight difference is observed in the stress profile: during the first two oscillations, compressive stress reaches higher values than tensile stress, probably due to the higher stress generated in the interface when atoms are deposited at 40 eV compared to the previous case, where the first layer was deposited at 1 eV with scarce penetration in the diamond substrate.

Growth of multilayered carbon films has been also simulated on silicon substrates using both deposition energy sequences studied on diamonds (1–40 and 40–1 eV). On this substrate, several layers have been grown, having an average width of about 8 Å. The overall results are similar to those on diamond, but two differences are noticeable by inspection of Fig. 4: (i) the silicon-carbon interface width strongly depends on the deposition energy sequence; (ii) the amplitudes of density and stress oscillations are smaller since the thinness of the layers does not allow to reach the final corresponding values for each energy. This fact has been verified by growing another sample with only two carbon bilayers (of about 15 Å thickness per layer) in the 1–40 eV sequence on a silicon substrate. In this case, density and stress oscillations were similar to those observed on diamond. The corresponding snapshot and density and stress profiles are shown in Fig. 5.

Some of these features have been previously reported by Mathioudakis *et al.*[3] However, they have observed sharper transition regions between layers surely due to the way used to generate their samples. On the other hand, they have

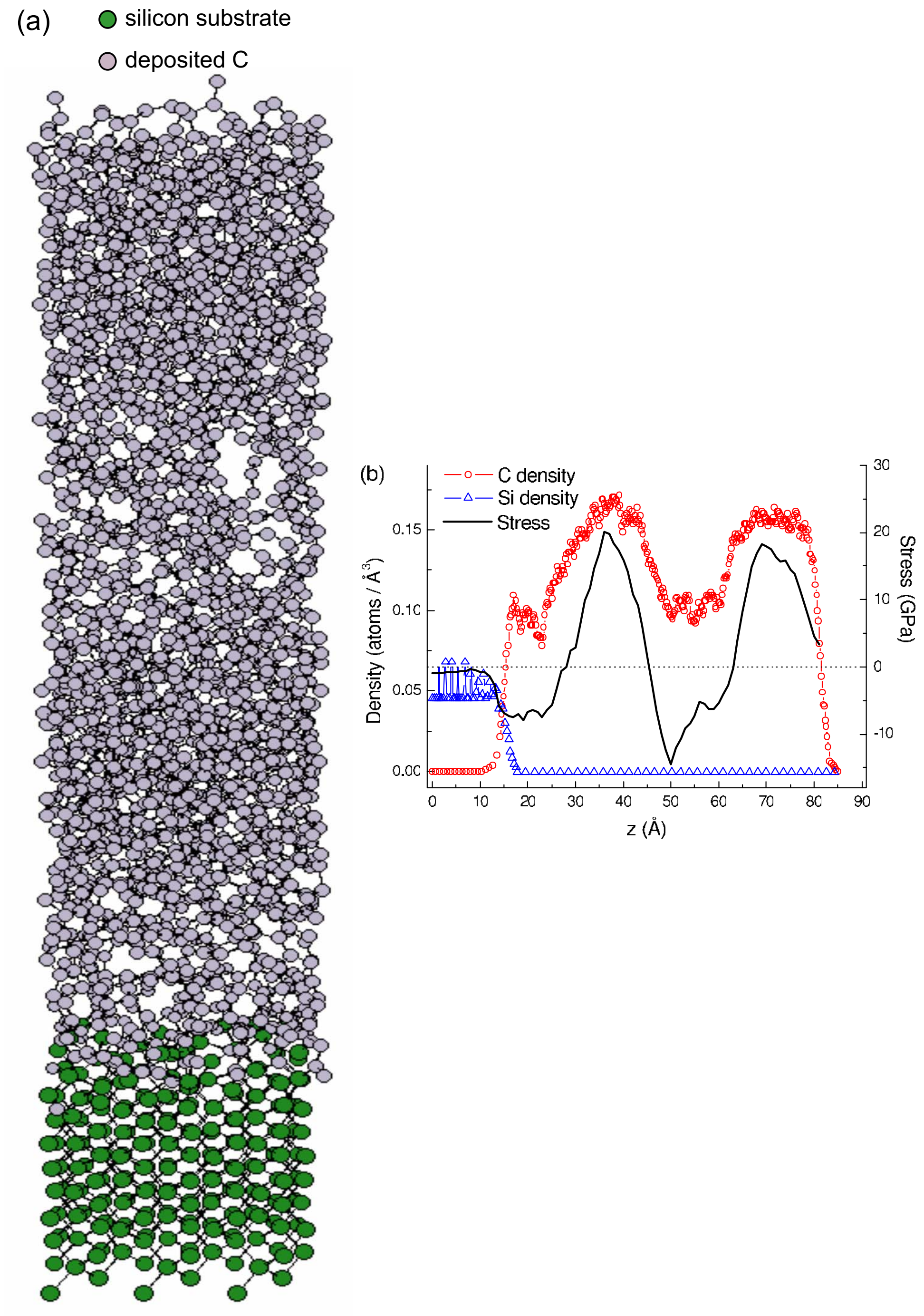

FIG. 5. (Color online) (a) Snapshot of a multilayered carbon film grown on silicon with alternating deposition energies of 1 and 40 eV. (b) Density and atomic stress profiles corresponding to the snapshot shown in (a).

found higher tensile than compressive stress values, but they have pointed out that tensile (compressive) stress is overestimated (underestimated) in their calculations because of the use of a unique mean value of Voronoi´s volume for both sp^2 and sp^3 sites, while in the present work, an individual volume Ω_i has been calculated around each atom i.

All samples were annealed up to 2500 K in order to study stress relaxation and density and coordination changes. Overall results show that appreciable changes, similar to those observed in monolayer films,[9] occur mainly on the last superficial layer. An example is illustrated in Fig. 6, where density and stress profiles are displayed for an as-grown and annealed sample deposited on diamond using the 1–40 eV sequence. Figure 6(b) shows an increment in the density of sp^2 carbon atoms at expenses of a noticeable reduction in the density of sp^3 ones in the last layer. This bonding conversion process gives rise to a sample expansion and, as Fig. 6(a) shows, a change from compressive to tensile stress in the superficial layer. In the bulk, only a slight relaxation occurs via a minor stress reduction, and an appreciable shift in the frontier between layers is not observed either in the density or in the stress plot. In monolayer systems, there is a bonding

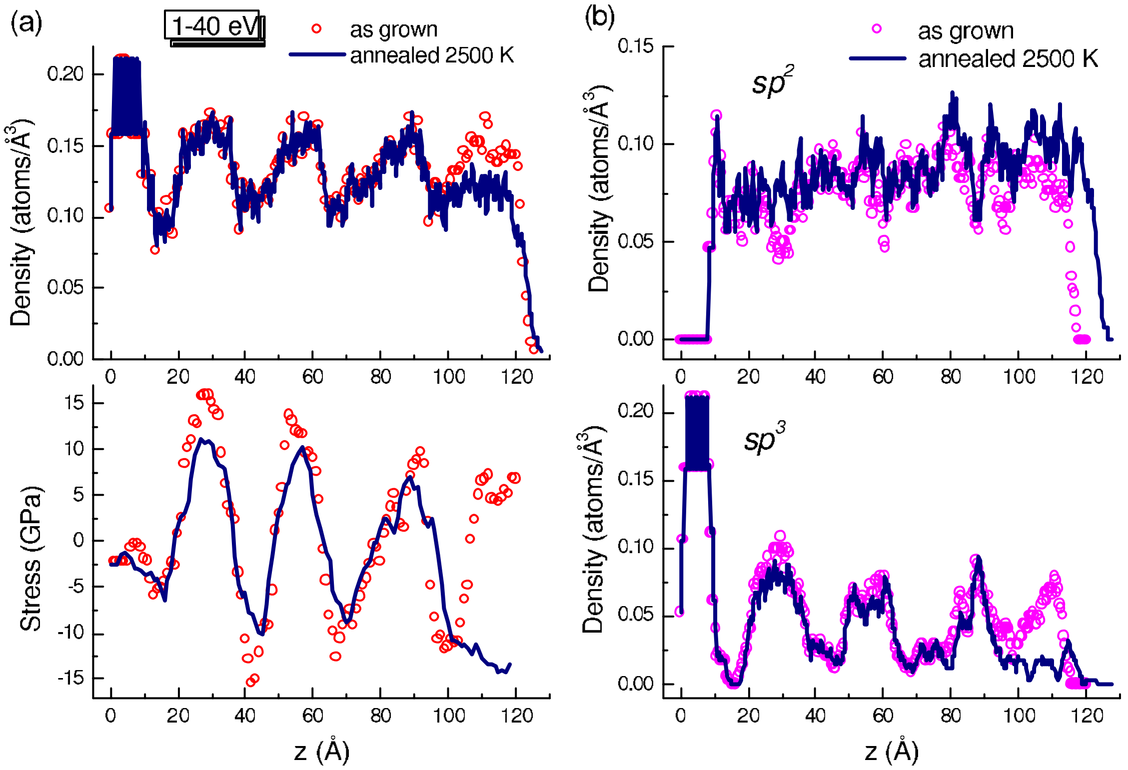

FIG. 6. (Color online) Results of annealing at 2500 K on a sample grown on diamond with alternating deposition energies of 1 and 40 eV, starting with 1 eV. (a) Density and stress profiles of the as-grown and annealed sample, (b) density profile discriminating *sp*^{2}- and *sp*^{3}-bonded carbon atoms.

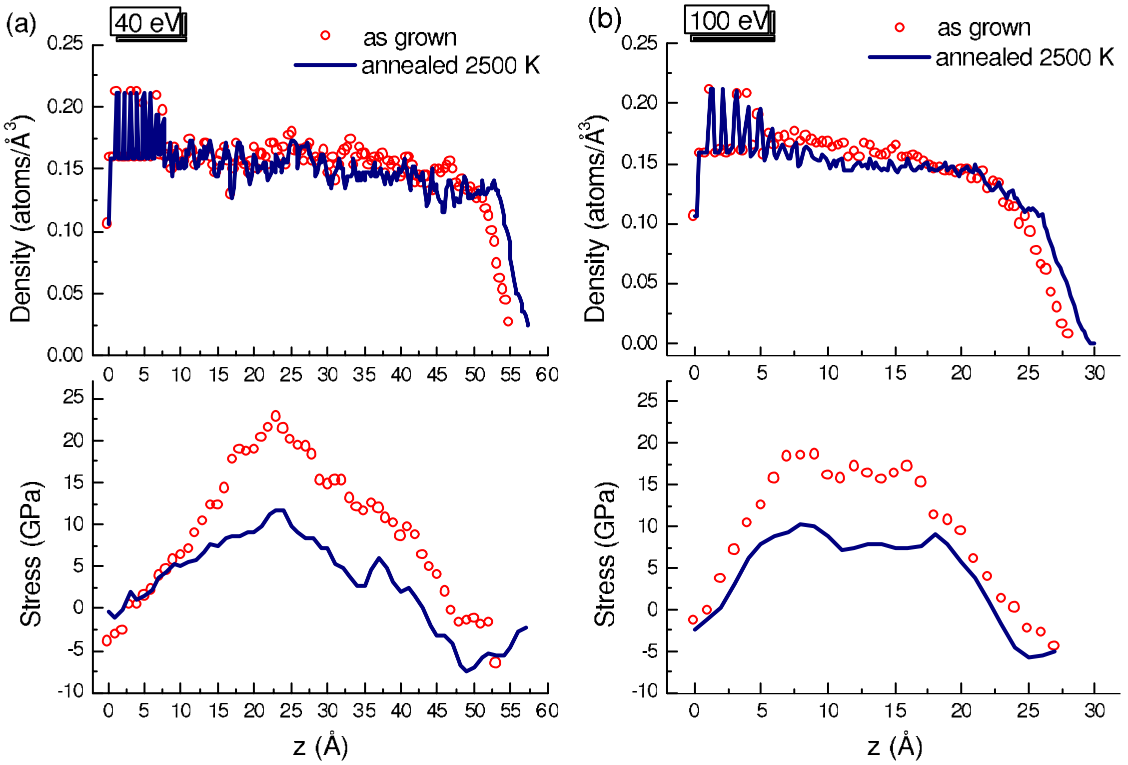

FIG. 7. (Color online) Density and stress profiles corresponding to as grown and annealed monolayered films deposited at (a) 40 and (b) 100 eV.

conversion and stress reduction along the entire sample whatever the film width, similar to that observed in the last layer of multilayer systems. For comparison, the behavior of monolayered films is illustrated in Fig. 7. It is clear that annealing changes in multilayer systems are considerably smaller than those in monolayer ones, suggesting a greater thermal stability of multilayer systems. It has been reported that the sp^3 to sp^2 conversion and stress reduction, in particular, under thermal annealing, are accompanied by a decrease in hardness.[4,16] In this sense, multilayered films, due to their thermal stability, would preserve hardness even under annealing or other thermal treatments.[3,17]

IV. CONCLUSIONS

The growth of multilayered amorphous carbon films by means of ion beams with alternating deposition energies has been simulated using molecular dynamics. Structural analysis of the obtained films shows the alternation of layers with different local atomic stresses; compressive stress regions are associated to high deposition energies and tensile stress zones to low deposition energies. Film density oscillates also with deposition energy due to the oscillation of the sp^3 bonded atoms density since the sp^2 atoms density remains approximately constant across the film. In high density layers, sp^3 content is of about 50%, corresponding to high-hardness films experimentally obtained, while in low density regions, this content falls to about 20%. These values are in the range of those experimentally obtained in multilayered films grown by rf magnetron sputtering.[3]

Thermal annealing of multilayered films shows that appreciable changes, similar to those observed in monolayer films, occur mainly on the last superficial layer. In the bulk sp^3/sp^2 ratio, density, and atomic stress oscillations remain practically unchanged, suggesting that multilayered films would preserve hardness properties under thermal treatments.

These results show that the experimental ion beam deposition technique would allow obtaining multilayered films with different sp^3/sp^2 ratio, density, and atomic stress distribution by controlling deposition energy. It would be interesting to explore the influence of the layer's thickness and the number of layers on mechanical and electronic properties.

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[1] Y. Lifshitz, in *Tetrahedral Amorphous Carbon (ta-C)*, Proceedings of the International School of Physics "Enrico Fermi" Course CXXXV, edited by A. Paoletti and A. Tucciarone (IQS, Amsterdam, 1997); N. A. Marks, D. R. McKenzie, B. A. Pailthorpe, M. Bernasconi, and M. Parrinello, Phys. Rev. B **54**, 9703 (1996); K. Kohary and S. Kugler, *ibid.* **63**, 193404 (2001).

[2] H. Huck, E. B. Halac, M. Reinoso, and A. G. Dall'Asén, in *Recent Research Developments in Physics*, 1st ed., edited by S. G. Pandalai (Transworld Research Network, Kelara, 2004), Vol. 5, Ch. 9, p. 217.

[3] C. Mathioudakis, P. C. Kelires, Y. Panagiotatos, P. Patsalas, C. Charitidis, and S. Logothetidis, Phys. Rev. B **65**, 205203 (2002).

[4] S. Logothetidis, S. Kassavetis, C. Charitidis, Y. Panagiotatos, and A. Laskarakis, Carbon **42**, 1133 (2004).

[5] J. S. Koehler, Phys. Rev. B **2**, 547 (1970).

[6] J. P. Zhao, Z. Y. Chen, X. Wang, and T. S. Shi, J. Appl. Phys. **87**, 8098 (2000).

[7] R. S. Brusa, A. Somoza, H. Huck, N. Tiengo, G. P. Karwasz, A. Zecca, M. Reinoso, and E. B. Halac, Appl. Surf. Sci. **150**, 202 (1999).

[8] H. Huck, E. B. Halac, M. Reinoso, A. G. Dall'Asén, A. Somoza, W. Deng, R. S. Brusa, G. P. Karwasz, and A. Zecca, Appl. Surf. Sci. **211**, 379 (2003).

[9] E. B. Halac, M. Reinoso, A. G. Dall'Asén, and E. Burgos, Phys. Rev. B **71**, 115431 (2005).

[10] E. B. Halac, A. G. Dall'Asén, E. Burgos, and M. Reinoso, Phys. Rev. B **74**, 174104 (2006).

[11] J. Tersoff, Phys. Rev. B **39**, 5566 (1989); Phys. Rev. Lett. **61**, 2879 (1988).

[12] H.-P. Kaukonen and R. M. Nieminen, Phys. Rev. Lett. **68**, 620 (1992); E. B. Halac, E. Burgos, and H. Bonadeo, Phys. Rev. B **65**, 125202 (2002).

[13] H. J. C. Berendsen, J. P. M. Postma, W. van Gunsteren, A. DiNola, and J. R. Haak, J. Chem. Phys. **81**, 3684 (1984).

[14] P. C. Kelires, Phys. Rev. B **62**, 15686 (2000); P. C. Kelires, Physica B (Amsterdam) **296**, 156 (2001); P. C. Kelires, Diamond Relat. Mater. **10**, 139 (2001).

[15] K. W. R. Gilkes, P. H. Gaskell, and J. Robertson, Phys. Rev. B **51**, 12303 (1995); N. A. Marks, D. R. McKenzie, B. A. Pailthorpe, M. Bernasconi, and M. Parrinello, *ibid.* **54**, 9703 (1996).

[16] P. C. Kelires, Phys. Rev. B **47**, 1829 (1993).

[17] D. G. McCulloch, J. L. Peng, D. R. McKenzie, S. P. Lau, D. Sheeja, and B. K. Tay, Phys. Rev. B **70**, 085406 (2004).