Bulk modulus of amorphous carbon and silicon-carbon multilayered films grown by molecular dynamics simulations

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Carbon and silicon-carbon amorphous multilayered films have been studied by molecular dynamics simulating the experimental growth by ion beam deposition techniques. Atomic interactions were described using the semiempirical Tersoff potential. Pure C films were grown with alternated deposition energies of 1 and 40 eV. Each mixed Si-C film was grown at single deposition energy (1 or 40 eV). For pure amorphous carbon films density, average atomic coordination, local atomic stress, and bulk modulus oscillate with deposition energy. It is found that the bulk moduli of whole samples are similar to those of high-density layers and clearly higher than the average values taken on all individual layers. For mixed Si-C multilayered films the bulk moduli of the whole samples are only lightly higher than the average values over individual layers of the different materials. A very low stress value is calculated to be present in Si layers. Thermal annealing of the films produces an average coordination and bulk modulus decrease, while density remains practically unchanged.

I. INTRODUCTION

Multilayered amorphous films cover a great variety of materials: they can be composed by a single element deposited in different conditions or by alternating sequences of two or more materials. These films can have properties very different from those of the constituent layers. Besides, there are other structural parameters, as the number of layers and their thickness, which can modify mechanical, tribological and/or electrical properties. Hence multilayered amorphous films offer a promissory research field because of the wide variety of materials that can be generated.

Amorphous carbon multilayers have also been investigated as a way of depositing thick films without excessive intrinsic stress which can limit the thickness of coatings and cause buckling or even delamination of the films from the substrate.[1,2] The introduction of a thin layer of amorphous silicon between the substrate and the film has also been assayed as a way of reducing stress in amorphous carbon materials.[3,4]

It has been experimentally observed that amorphous carbon multilayers of alternated sp^3 and sp^2 rich zones exhibit higher hardness values than those corresponding to individual layers.[5] A similar behavior was predicted time ago by Koehler's model[6] for multilayered films made from two materials with different elastic modulus.

In a previous work, the growth of multilayered amorphous carbon films by means of ion beams with alternating deposition energies has been simulated using molecular dynamics.[7] Structural analysis of the obtained films showed

the alternation of layers with different density, average coordination, and local atomic stresses. High density and average atomic coordination and compressive stress regions were associated to high deposition energies while low deposition energies gave rise to low density and coordination and tensile stress zones.

Some authors have suggested that hardness correlates roughly with bulk modulus for Groups IV, III-V, and II-VI materials.[8,9] In the present work we calculate, among other structural properties, the bulk modulus of different types of multilayered amorphous films grown by molecular dynamics simulation: amorphous carbon multilayers grown alternating deposition energies and sequences of amorphous carbon and amorphous silicon layers. As far as we know, for this last type of mixed silicon-carbon multilayered films there are no theoretical studies or numerical simulations in the literature; only electronic properties[10] and possible ways to solve adherence problems have been considered.

II. COMPUTATIONAL MODEL

The semiempirical many-body Tersoff potential[11] for atomic interactions has been used to simulate the growth of multilayered amorphous carbon and silicon structures by molecular dynamics (MD); it enables to handle a great number of atoms which is essential to model multilayered systems.[1,2,12,13]

Two sorts of multilayered films were grown on diamond (100) and silicon (100) substrates. The first type consisted of alternated carbon layers of different density and average co-

ordination number, obtained by controlling deposition energies (1 eV for low-density layers and 40 eV for high-density ones). The second type consisted of alternated amorphous carbon and amorphous silicon layers deposited at the same energy; samples generated at 1 and 40 eV were studied.

In each sample the number of atoms per layer was fitted to produce layers of approximately the same z height with periodic boundary conditions in the xy plane. Each layer was generated by throwing carbon or silicon atoms with a given kinetic energy, impinging perpendicularly to the substrate surface at a random location in the xy plane.

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. Ideal diamond (100) and silicon (100) crystals were employed as substrates. The number of (xy) crystalline planes (3 or 4 bilayers) was chosen according to the expected penetration depth of the projectiles for the deposition energy of the first amorphous layer. In every case the two bottom planes of the substrate were fixed to their equilibrium positions representing a semi-infinite crystal. The remaining atoms were allowed to move with full dynamics, applying periodic boundary conditions in the (xy) plane to a region of 3×3 unit cells. The substrates were thermalized at room temperature and zero pressure for about 1000 fs, before deposition. Then deposition process started throwing atoms at time intervals (about 200 fs) in such a way that each projectile had enough time to dissipate its energy to the system before the next atom reached the surface. System thermalization was simulated applying the method of Berendsen *et al.*,[14] with the last ten impinging atoms not included in the cooling process allowing a full dynamics energy transfer from the projectile to the substrate. During deposition process some bouncing and ejected atoms were removed from the system.

Prior to performing structural, atomic level stress, and bulk modulus studies the samples, consisting of several alternated layers, were allowed to evolve at room temperature for about 10^4 fs. Further details about the MD simulation and the procedure followed to calculate mean densities across the films and atomic stress distribution are given in Refs. 2 and 7.

Bulk modulus was calculated following a procedure similar to that described by Mathioudakis *et al.*[15] considering an isotropic compression and expansion around the equilibrium position of a material piece with periodic boundary conditions. System energy was calculated at about 40 points varying the volume at steps of 0.5%. From the resulting energy vs volume curve (fitted with a forth order polynomial) the bulk modulus at zero pressure is obtained as: $B_o = V(\partial^2 E / \partial V^2)_{V=V_o}$.

In order to obtain reference values, the bulk modulus of crystalline silicon and diamond have been calculated resulting in close agreement with experimental values. Calculated values are 100.4 and 450.1 GPa for silicon and diamond respectively; the corresponding experimental values are 102[16] and 443 GPa.[17,18]

Unlike the method used in Ref. 15 where the samples were grown by Monte Carlo simulations imposing periodic boundary conditions in three dimensions, we have simulated the multilayered films growth by MD performing a sequential deposition of atoms with periodic conditions in only two dimensions. In order to obtain a three-dimensional periodic sample the portion of the film to be analyzed is chosen cutting the sample by two planes perpendicular to the z direction and periodic boundary conditions are imposed. At this point two procedures were applied; in the first one all the atomic positions in the piece are relaxed during a certain number of MD steps and the period along z is continuously modified until the minimum energy state is reached. In the second one, the minimum energy is searched varying only the period in the z direction and then atomic positions are relaxed in order to obtain the equilibrium sample. Both procedures were applied to a few samples with similar results for the calculated bulk modulus; for this reason we decided to use the less time consuming second procedure.

The selected portions were taken in such a way that could include from a portion of one layer (typically about 10 Å height) to the whole multilayer film (more than 100 Å). All these calculations were performed at room temperature.

Thermal annealing at 2500 K (for pure amorphous C layers) and at 1500 K (for C-Si multilayers) was simulated on some of the samples in order to study possible changes in structural properties (density, coordination, etc.) and bulk modulus, and atomic stress relaxation effects. To do so, temperature was raised at a rate of 5 K/fs, the sample was maintained at the desired 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

Pure C multilayered films were grown on diamond and silicon substrates starting with a 1 eV and 40 eV layers. Films of alternated Si layers and C layers were deposited on diamond and silicon substrates at 1 eV and 40 eV starting in all cases with an amorphous silicon layer. For this last sort of multilayers several samples were grown with different layers thickness ranging from about 10 Å to 40 Å.

Figure 1 shows snapshots of multilayered amorphous carbon films deposited on diamond (a) and silicon (b) substrates with alternating deposition energies of 1 and 40 eV. Figure 2 shows snapshots of films obtained alternating amorphous C layers and amorphous Si layers deposited on silicon at 1 eV (left) and at 40 eV (right). The corresponding density profiles are shown in Figs. 3 and 4. For pure C films (Fig. 3), low- and high-density oscillations are correlated with the regions where C atoms were deposited at low (1 eV) and high (40 eV) energies, respectively. Both layer types have an average width of approximately 15 Å. Figures 4(a) and 4(b), corresponding to amorphous Si—amorphous C films deposited at 1 and 40 eV respectively, are appreciably different. Whereas in 1 eV deposits the frontiers between amorphous Si and amorphous C layers (of about 35 Å) are well defined, 40 eV deposits show large interfaces for C layers deposited on Si and small interfaces in the opposite case. This is due to the greater penetration depth of C on Si compared to that of Si on C. In Fig. 4(b) C layers exhibit a high density (about 90% of diamond density) as compared to that in Fig. 4(a) corre-
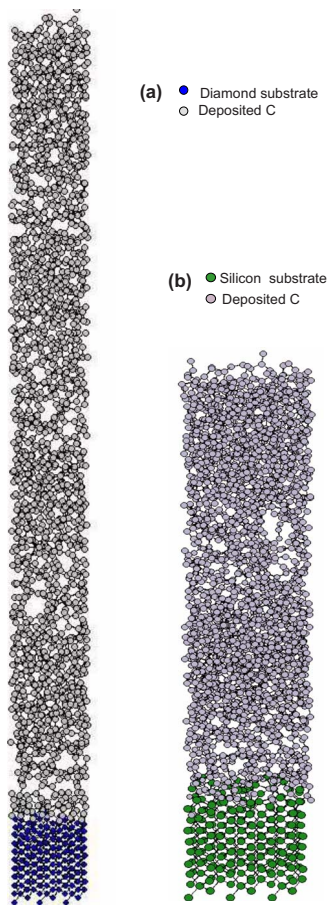
FIG. 1. (Color online) Snapshots of multilayered amorphous carbon films deposited on diamond (a) and silicon (b) substrates with alternating energies of 1 and 40 eV.

sponding to 1 eV deposits (about 60% of diamond density). Even though there is a little variation in amorphous silicon density with deposition energy, the atomic coordination analysis shows a high percentage of fivefold coordinated Si in 40 eV deposits, absent in 1 eV samples.

Calculated bulk modulus values for individual layers and for whole samples are represented in Figs. 3 and 4 by horizontal bars, defining the sample segment used for the calculation in each case. Figure 3 clearly shows that the bulk modulus of the whole sample is considerably higher than the average value over individual layers, and very close to the maximum values obtained for this sample. This behavior was observed in all amorphous C samples grown on silicon and diamond substrates. In all cases the calculated bulk modulus is smaller than that of crystalline diamond; nevertheless there is a great difference in the calculated bulk modulus values between layers deposited at 1 eV (about 200 GPa) and at 40 eV (higher than 300 GPa).

For mixed Si-C multilayers grown at 1 and 40 eV [Figs. 4(a) and 4(b)] the bulk modulus of the whole sample is only lightly higher than the average value over individual layers. In order to analyze if this result was dependent on the layers thickness, two other samples were grown at 1 eV with thinner layers of about 15 Å and 8 Å; the calculated bulk modulus for these samples showed similar results. Figures
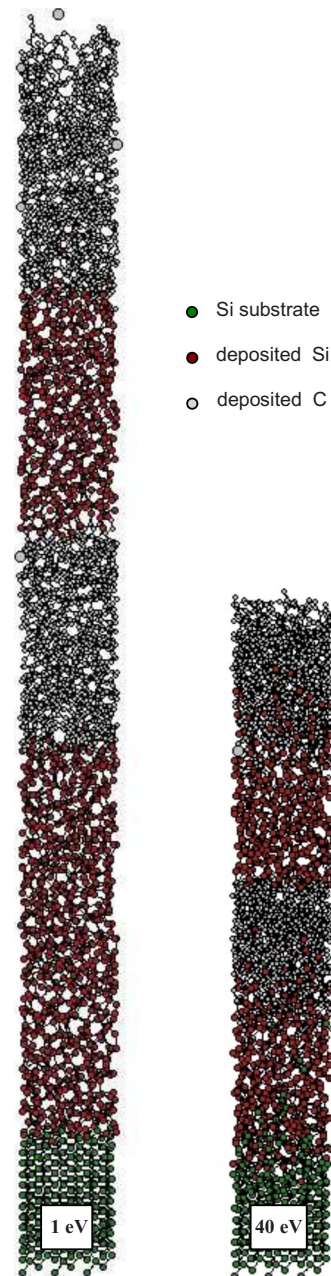

FIG. 2. (Color online) Snapshots of multilayered amorphous silicon-amorphous carbon films deposited on silicon at 1 eV (left) and at 40 eV (right).

4(a) and 4(b) also show that the bulk moduli of amorphous silicon layers grown at 1 eV are close to that of crystalline silicon, while the bulk modulus of those grown at 40 eV are about 50% higher.

In a previous paper[7] it was shown that the atomic stress distribution in multilayered carbon films was strongly correlated with deposition energy, and hence with density and average atomic coordination. Low density and sp^2 rich C layers (1 eV) are under tensile local stress while high density and sp^3 rich ones (40 eV) are under compressive local stress. The stress distribution was also calculated for mixed Si-C multilayer films. For multilayers grown at 1 eV, C layers are under tensile stress and Si layers are unstressed; this is
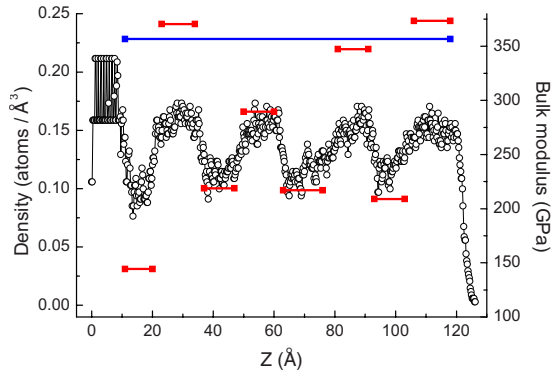
FIG. 3. (Color online) Density profiles (left scale) and bulk modulus (right scale) corresponding to the snapshot shown in Fig. 1(a). Horizontal bars define the sample segment used for bulk modulus calculations. Short bars correspond to individual layers; the long bar indicates the segment used for the whole sample. The conversion factor from [atoms/Å³] to [g/cm³] is 20.1 for carbon atoms.

shown in Fig. 5 together with the corresponding atomic density profile. For samples grown at 40 eV, C layers are under compressive stress and Si layers remain unstressed. Annealing at 1500 K reduces stress in C layers.

A strong correlation between bulk modulus, atomic coordination, and density has been found for all amorphous car-
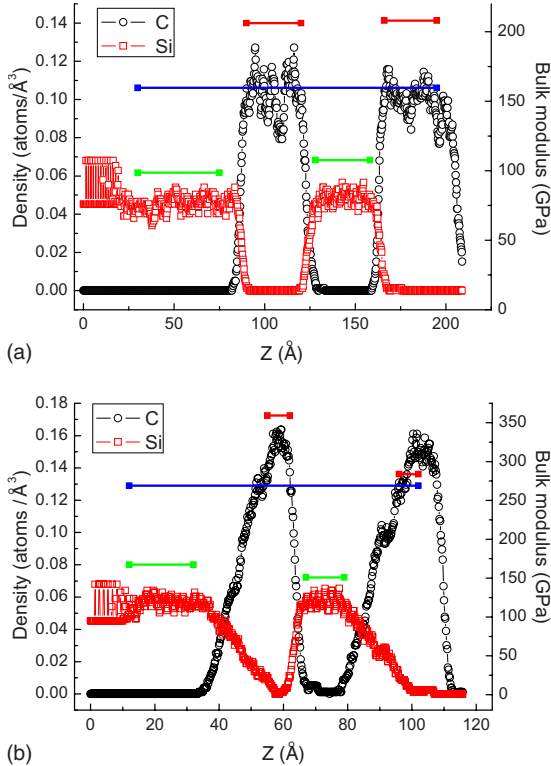

FIG. 4. (Color online) Density profiles (left scale) and bulk modulus (right scale) corresponding to the snapshots shown in Fig. 2. Horizontal bars define the sample segment used for bulk modulus calculations. (a) Amorphous silicon—amorphous carbon film grown at 1 eV; (b) amorphous silicon—amorphous carbon film grown at 40 eV. The conversion factor from [atoms/Å³] to [g/cm³] is 20.1 for carbon atoms and 46.9 for silicon atoms.
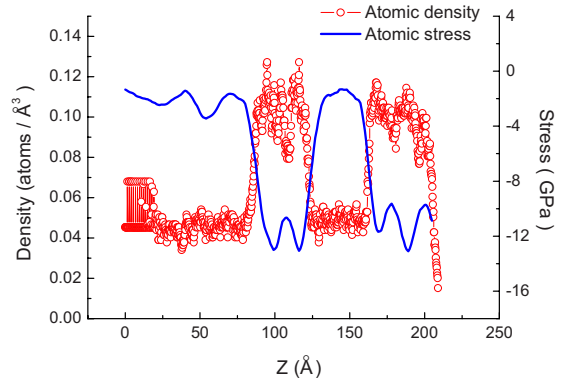

FIG. 5. (Color online) Stress distribution (right y axis) and atomic density profile (left y axis) for a mixed Si-C multilayered film deposited at 1 eV.

bon samples studied. Figure 6 shows plots of bulk modulus vs average coordination and bulk modulus vs density. It summarizes the results obtained for four different samples grown on diamond and silicon substrates alternating deposition energies of 1 and 40 eV. Bulk modulus for individual layers has been calculated selecting portions as shown in Fig. 3; a mean
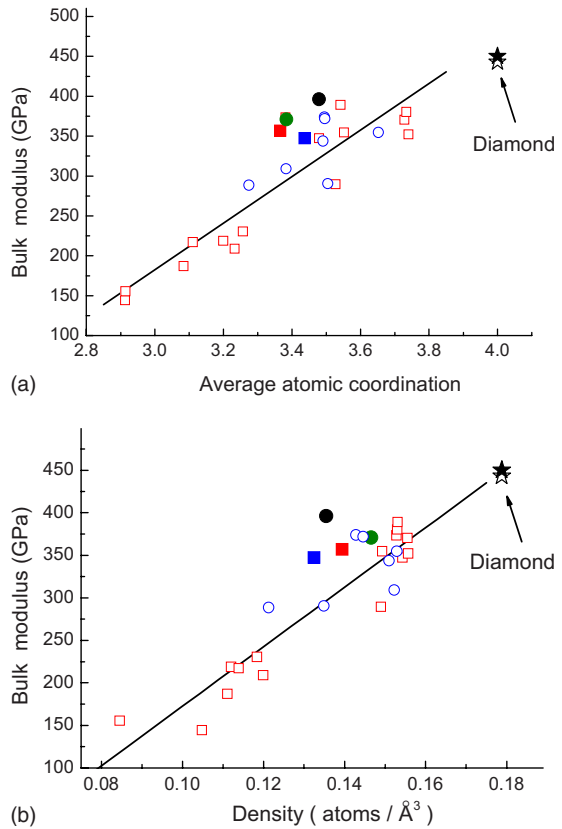

FIG. 6. (Color online) (a) Bulk modulus vs average atomic coordination; (b) bulk modulus vs density. Plotted values as empty squares (circles) correspond to different portions amorphous carbon samples grown on diamond (silicon) substrates with alternating deposition energies of 1 and 40 eV. Straight lines are fits to these values. Solid squares (circles) correspond to whole samples grown on diamond (silicon) substrates. Stars are experimental (empty) and calculated (solid) values for crystalline diamond.
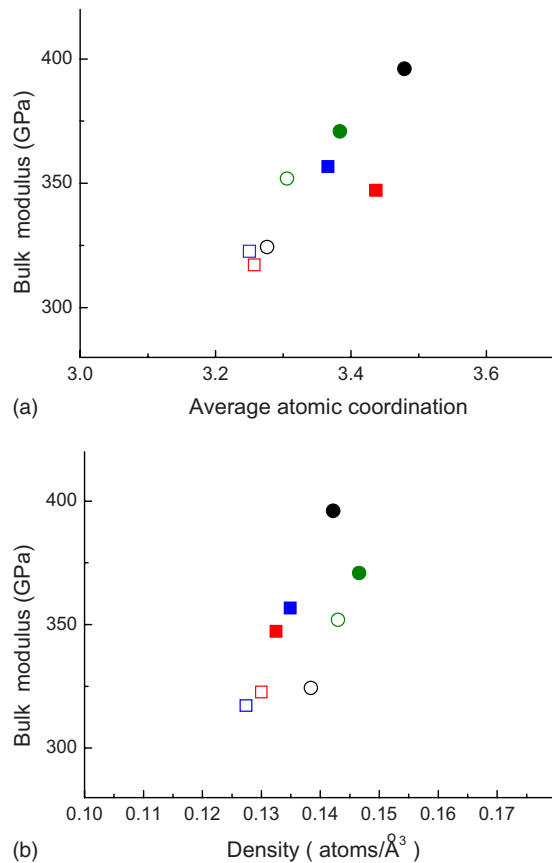
FIG. 7. (Color online) Results of annealing at 2500 K on the four samples shown in Fig. 6. (a) Bulk modulus vs average atomic coordination; (b) bulk modulus vs density. Calculated values for whole samples are plotted. Squares: samples grown on diamond substrates; circles: samples grown on silicon substrates. Solid symbols: as grown samples; open symbols: after annealing.

atomic coordination has been calculated using the same sample portions. The straight lines are fits to the values corresponding to individual layers. Figure 6(a) shows an appreciable dispersion (up to 20%) of the bulk modulus for similar average atomic coordination values; this rather large fluctuation is to be expected due to the nonhomogenous nature and the reduced size of the analyzed layers. Our results are in reasonable good agreement with Mathioudakis et al.[15] ones. However, bulk modulus values calculated in the present work are systematically higher (about 15%); this slight discrepancy could be related to the different method employed for samples generation. Calculated values for the whole samples have been added to the plots. As reference values calculated and experimental diamond parameters have also been included. It can be seen that the values for whole samples are always over the linear fit to individual layers in the bulk modulus vs average coordination plot [Fig. 6(a)] as well as in the bulk modulus *vs.* density plot [Fig. 6(b)] and are in the region of maximum bulk modulus for amorphous carbon materials (350–400 GPa). Diamond parameters are never reached and are a good extrapolation of the values calculated for individual layers in both figures.

Figure 7 shows the results of annealing performed at 2500 K on the four amorphous C multilayers presented in Fig. 6. It

can be seen that, as a general trend, average atomic coordination and bulk modulus decrease [Fig. 7(a)], while density remains practically unchanged [Fig. 7(b)]. A similar result is obtained for the annealing performed at 1500 K on mixed Si-C samples grown at 1 eV. For the sample grown at 40 eV the most remarkable result is the great number of Si atoms that change from fivefold to fourfold coordination.

IV. CONCLUSIONS

The growth of amorphous multilayered films by means of ion beams has been simulated using molecular dynamics. Pure C multilayered films were grown alternating layers deposited at 1 and 40 eV while mixed Si-C films were grown at a single energy (1 or 40 eV) alternating silicon and carbon layers.

For amorphous carbon films, density, and local atomic stresses oscillate with deposition energy; high density and compressive stress regions are associated to high deposition energies while low density and tensile stress zones correspond to low deposition energies. In the present work it has been found that bulk modulus is also correlated with deposition energy. High density and sp^3 rich layers grown at 40 eV have a high bulk modulus, close to that of diamond (75–80% of diamond bulk modulus). For low density and sp^2 rich layers grown at 1 eV bulk modulus is considerably lower (about 50% of diamond bulk modulus). Hence, bulk modulus is in close correlation with average atomic coordination and density. On the other hand, the bulk moduli of whole samples are similar to those of high-density layers and clearly higher than the average values taken on all individual layers. This result is in agreement with experimental observations and theoretical predictions as mentioned above.[5,6]

On the other hand, for mixed Si-C multilayered films the bulk moduli of the whole samples are only lightly higher than the average values over individual layers of the different materials. The same result was obtained for different layers thicknesses studied. In this case the advantage of a multilayered film with Si as one of its components should be the low stress present in Si layers (even for high-energy deposits). This should be the reason of the good adherence experimentally observed for amorphous carbon films grown on amorphous silicon layers deposited on different substrates.

Thermal annealing on amorphous carbon multilayers produces an average atomic coordination and bulk modulus decrease, while density suffers only a slight reduction. A similar result is obtained for the annealing on mixed Si-C samples; the main effect of annealing is observed for the sample grown at 40 eV where there are a great number of Si atoms that change from fivefold to fourfold coordination.

The simulation results obtained for mixed Si-C multilayers should encourage experimental work on this kind of samples; in particular it would be interesting to explore the different bulk modulus behavior as compared to pure C multilayers.

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