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Molecular dynamics simulation of the growth of thin films by deposition of carbon atoms and C_{60} molecules on diamond and silicon substrates

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The impact of C atoms and C_{60} molecules with ideal diamond and silicon (100) substrates and the subsequent growth of carbon films have been investigated by molecular dynamics simulations. The interatomic many-body potential proposed by Tersoff has been used. The structural and vibrational properties of the as-grown and annealed films are studied as a function of the deposition energy (in the range 1–150 eV for C atoms and 1–1000 eV for C_{60} molecules) and are compared with experimental results. Analysis of films grown from C_{60} molecules reveals a behavior with deposition energy similar to that experimentally observed. For low deposition energies (below 100 eV) fullerene cages preserve their identity, constructing low-density structures with large intermolecular holes and practically no interface with the substrate. For higher deposition energies the molecules are broken into pieces, giving as a result high-density amorphous carbon films. Although the penetration depth of molecular fragments into the substrate increases with deposition energy, the resulting interface is considerably thinner than in the case of using individual atoms as projectiles. This is in agreement with experimental evidence of a poor adherence of films obtained by accelerating $C_{60}{}^{+}$ ions on silicon substrates.

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I. INTRODUCTION

The growth of amorphous carbon films has been the subject of numerous studies, due to the interesting physical properties of these materials. In the last two decades there has been a lot of experimental work in this field using a variety of methods: chemical vapor deposition,[1] rf and dc plasma deposition,[2] the laser plasma source method,[3] sputtering techniques,[4] ion-beam deposition,[5] etc. Depending on methods, precursors, substrates, and experimental conditions, a great variety of carbon-based materials can be obtained, such as microcrystalline diamond, diamondlike carbon (DLC) films, amorphous carbon films (*a*-C), hydrogen-containing amorphous carbon films (*a*-C:H), etc. In contrast to microcrystalline diamond, where all carbon atoms are four-coordinated (sp^3 bonded), in DLC and *a*-C films there are mixtures of three- (sp^2 bonded) and four-coordinated atoms with different sp^2 to sp^3 ratios. A number of physical and technological interesting properties such as vibrational spectra, density, hardness, wear resistance, electrical resistivity, etc., can be related to this ratio.

Recently, an additional precursor has been added to the previously used ones (graphite, hydrocarbon gases, etc.); research is starting on the growth of carbon films from the deposition of ionized C_{60} fullerene molecules.[6,7] This experimental work was motivated by the hard carbon structures prepared from fullerenes under high pressures and temperatures, inducing amorphization or polymerization in microscopic dimensions.[8] However, it is not possible to grow films by a high-pressure–high-temperature method; therefore this technique was replaced by the dynamic process of deposition of fullerenes at different energies.

In recent years a number of molecular dynamics calculations have been performed to simulate the growth of amorphous carbon films by deposition of single carbon atoms on diamond and silicon substrates.[9–12] Physical properties (such as density, atomic coordination, ring statistical analysis, etc.) of the resulting films have been studied as a function of the deposition energy of the projectiles. On the other hand the impact of one fullerene molecule with graphite,[13,14] diamond,[15,16] and silicon substrates[17] has also been studied by molecular dynamics, and structural changes of the projectile and the substrate have been analyzed as a function of the deposition energy. To our knowledge, calculations simulating the growth of carbon films by the successive deposition of energetic fullerene molecules have not been reported.

In this paper we present a molecular dynamics simulation of the impact of C atoms and C_{60} molecules with ideal diamond and silicon (100) substrates and the subsequent growth of carbon films. Our aim is to achieve a better understanding of the deposition process on an atomic scale, and to study the structural and vibrational properties of the resulting films as a function of the deposition energy in order to compare with our experimental results.

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II. COMPUTATIONAL MODEL

In order to describe the interaction between C atoms and C_{60} molecules with silicon and diamond substrates, we employed the semiempirical many-body Tersoff potential,[18] using the parameters given in the literature for the C-C, C-Si, and Si-Si interactions. These parameters were obtained from a fit to the cohesive energy, lattice constant, and bulk modulus of diamond and silicon and are known to provide a good description of carbon polytypes including fullerene structures and polymerized fullerenes.[19] Therefore, it also seems adequate to describe disordered carbon films, where the carbon atoms are in different bonding environments.

The inelastic processes due to electronic excitations are not important in the energy range studied and the electronic stopping power is neglected. We also focus on neutral atoms and fullerene molecules because the true charge state is important only for the first few collisions.

The evolution of the system was followed using Verlet's molecular dynamics algorithm. The time interval of the molecular dynamics steps, Δt, was chosen in the range 0.5–0.1 fs in order to ensure atomic displacements smaller than 0.01 Å in the relaxed system after the projectile has been incorporated, in the full energy range studied.

As projectiles we used single carbon atoms and C_{60} molecules impinging perpendicularly to the substrate surface at a random location with deposition energies in the range 1–150 eV for single C atoms and 1–1000 eV for fullerenes. In the last case this energy refers to the translational kinetic energy of whole molecules generated with random orientations and vibrating with atomic velocities corresponding to a temperature of 300 K.

As substrates we employed ideal diamond and silicon (100) crystals consisting of a number of atomic layers depending on the expected penetration depth of the projectiles for each deposition energy, as will be seen later. In all cases the two bottom layers are fixed to their equilibrium positions representing a semi-infinite crystal. The remaining layers are allowed to move with full dynamics, applying periodic boundary conditions in the layer's (xy) plane.

Before deposition the substrates were allowed to relax at $T=300$ K and $P=0$ for about 1000 fs. Individual C atoms and C_{60} molecules were deposited at time intervals of 250 and 5000 fs, respectively, in order to ensure that each projectile has enough time to dissipate its energy to the substrate before the next one hits the surface. During the deposition we applied the method of Berendsen *et al.*[20] to simulate the cooling of the system, using a thermal relaxation constant $\tau_t=50\Delta t$, scaling velocities at intervals of $4\Delta t$. In order to allow complete energy transfer from the projectile to the substrate, the last ten single C atoms or the last C_{60} molecule were not included in the thermalization process.[21] This deposition procedure is analogous to that employed by Kaukonen and Nieminen[9] for the growth of diamondlike films by energetic carbon-atom beams.

After growth, the samples were allowed to relax during about 10^4 fs, previous to performing structural and dynamical studies. Structural characterization included pair radial and angular distribution functions, density profiles, bonding composition, etc. On the other hand, velocity autocorrelation functions were obtained by averaging over ten time origins, taken at intervals of 5000 fs, to study the vibrational properties of the systems. Thermal annealing (at temperatures ranging between 900 and 2200 K) was performed on some of the samples in order to study structural and vibrational changes.

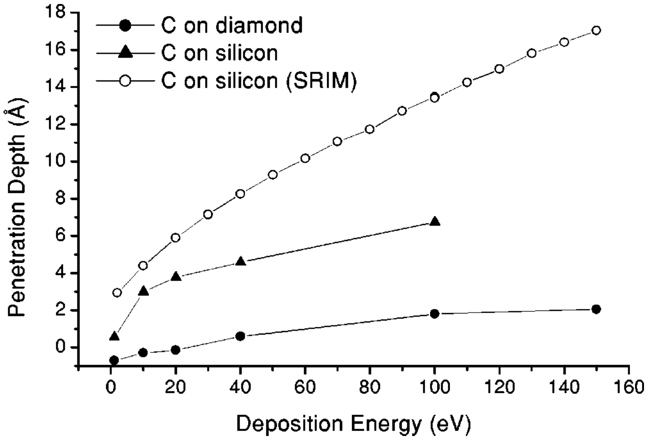

FIG. 1. Calculated mean penetration depth of individual C atoms on diamond and silicon (100) substrates as a function of the deposition energy. Results of the SRIM code (version 2003.26) for C atoms on a silicon substrate are also shown.

III. RESULTS

A. Deposition of individual carbon atoms on silicon and diamond substrates

The atoms were thrown perpendicularly to the substrate surface at a random location and followed during 2500 fs. Figure 1 shows statistical results for the penetration depth in simulations of the deposition of one carbon atom on both substrates as a function of the deposition energy (E_{dep}). It can be seen that the mean penetration depth increases proportionally to the deposition velocity. The mean penetration into silicon is of about 7 Å for 100 eV, but some atoms may penetrate up to 15 Å, giving a lower limit to the number of atomic layers that are needed to grow a film with deposition energy lower than 100 eV. For the sake of comparison, the penetration of a carbon-ion beam of different energies at normal incidence into a 10 μm silicon layer (density 2.3212 g cm^{-3}), calculated using the SRIM code version 2003.26, is also shown in Fig. 1. The deposition of individual C atoms on diamond shows a similar behavior, but in this case the penetration depth is lower, allowing higher deposition energies with a similar number of layers in the substrate. For 100 eV we found a mean penetration depth of about 2 Å with some atoms penetrating up to 5 Å.

B. Deposition of individual C_{60} molecules on silicon and diamond substrates

As in the case of single C atoms, vibrating C_{60} molecules were thrown perpendicularly to the surface, at random location with energies ranging between 1 and 1000 eV. The system is followed by molecular dynamics during about 3000 fs

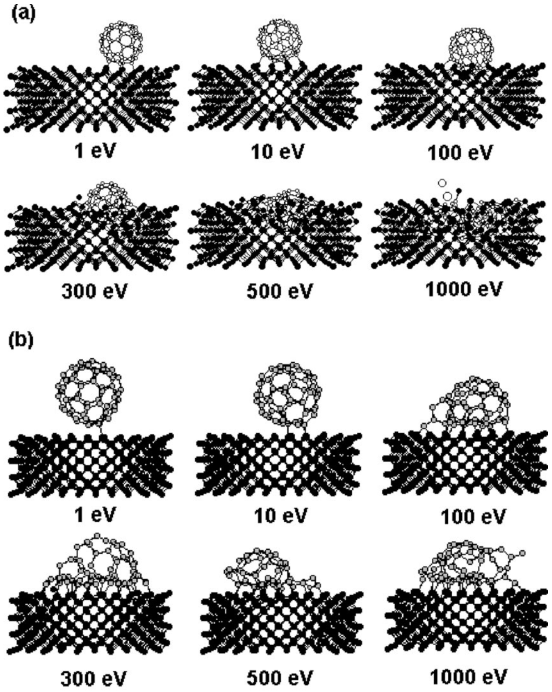

FIG. 2. Snapshots of C_{60} molecules thrown at different energies on (a) silicon (100) substrates and (b) diamond (100) substrates, after relaxation of the system.

until equilibrium is reached. Then, we can distinguish three energy regimes: (i) at low energies (under 10 eV) the molecules either bounce away or remain weakly bonded to the substrate with little distortion of the molecular geometry; (ii) at intermediate energies (up to 100 eV for diamond and 300 eV for silicon) molecules form progressively more bonds with the substrate and suffer an increasing distortion of the fullerene cage with the deposition energy; (iii) at higher energies molecules are fragmented into pieces of varying number of atoms, some of which form bonds with the substrate, while others bounce away, and the rest, mainly monatomic or diatomic fragments, can penetrate into the substrate. In the last case the penetration is definitely smaller than that for single-atom projectiles. Some of these simulations are illustrated in Figs. 2(a) and 2(b). Tight binding molecular dynamics[15] yields similar results on diamond: fragmentation of the fullerene cage occurs for energies greater than about 200 eV and, even at high energies, the substrate remains little distorted after the collision. In order to investigate if these results depend on the substrate's orientation, we have deposited C_{60} molecules on a diamond (111) surface. Figure 3 shows that the threshold energy for fragmentation of fullerenes is significantly lower on this surface: for a deposition energy of 100 eV the fullerene cage is just broken.

The aforementioned structural changes are also partially reflected in dynamical properties as the vibrational density of states calculated via the Fourier transform of the autocorrelation velocity function. It is worthwhile to point out that we only intend a qualitative description of vibrational spectra. It has been shown[19] that the upper frequencies for known carbon structures, calculated using the Tersoff potential, are appreciably higher than experimental ones: 1568, 2474, and 1928 cm^{-1} for diamond, graphite, and the C_{60} molecule, respectively, while experimental values are 1333, 1585, and 1573 cm^{-1}. Figure 4 shows results for some deposition energies over silicon substrates. It can be seen that at low energies the vibrational spectra show well-defined peaks that resemble those of free C_{60} molecules; in the high-energy regime the peak structure disappears giving rise to a broad band as could be expected from an amorphous carbon system.

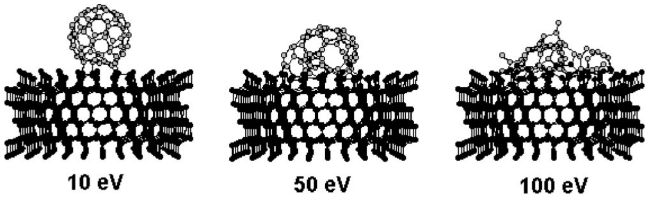

FIG. 3. Snapshots of C_{60} molecules thrown at different energies on diamond (111) substrates after relaxation of the system.

C. Film growth from single carbon atoms

Based on the results of penetration depth for individual carbon atoms, we have worked with diamond substrates consisting of 12 layers, each one containing 50 atoms, and silicon substrates of 16 layers containing 32 atoms. A total of about 1000 atoms were deposited for each energy studied.

Figure 5 shows films grown at 1, 10, and 40 eV on silicon substrates. An increment of the film density and of the interface region with deposition energy can be appreciated: while at 1 eV there is a well-defined substrate-film frontier, at 40 eV numerous carbon atoms have penetrated into the substrate, breaking the crystalline order and ejecting silicon atoms to the film. On diamond substrates there is less interpen-

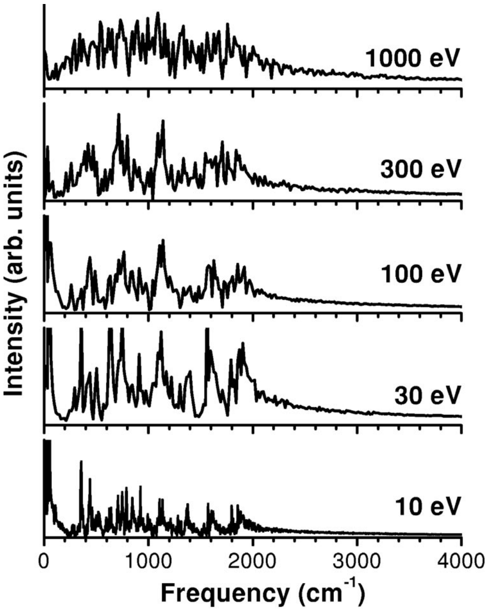

FIG. 4. Vibrational density of states for a C_{60} molecule thrown on a silicon substrate at different energies.

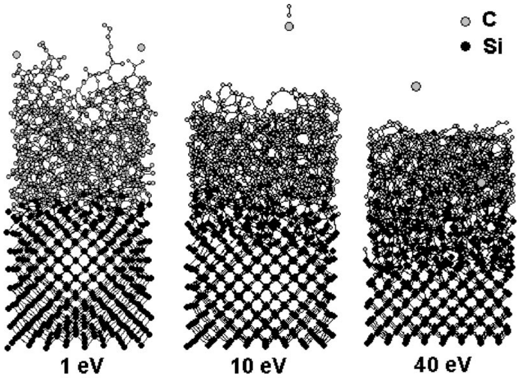

FIG. 5. Films grown by throwing individual C atoms on silicon (100) substrates. In all cases the substrates initially consisted of 16 layers each one containing 32 atoms.

etration between the substrate and the incident atoms for a given energy. Deposits performed between 1 and 150 eV show results similar to those obtained by Kaukonen and Nieminen.[13]

Figure 6 shows the density profiles for two of the films illustrated in Fig. 5; mean densities were calculated by sliding a slice in the *z* direction in small increments across the sample, discriminating atomic species. This description allows us to quantify the previous observations about the density of the films and the thickness of the Si-C interface. It is clearly seen that there is an increment in film density of about 30% and that the thickness of the interface grows from about 5 to 25 Å for films grown at 1 and 40 eV, respectively. The silicon content decreases linearly across the interface, in qualitative agreement with experimental Auger electron spectroscopy depth profile results.[5] Figure 7 summarizes density results for films grown on diamond and silicon substrates and compares them with experimental results on silicon.[22] These results agree with the ones found by Jäger and co-workers.[10,11]

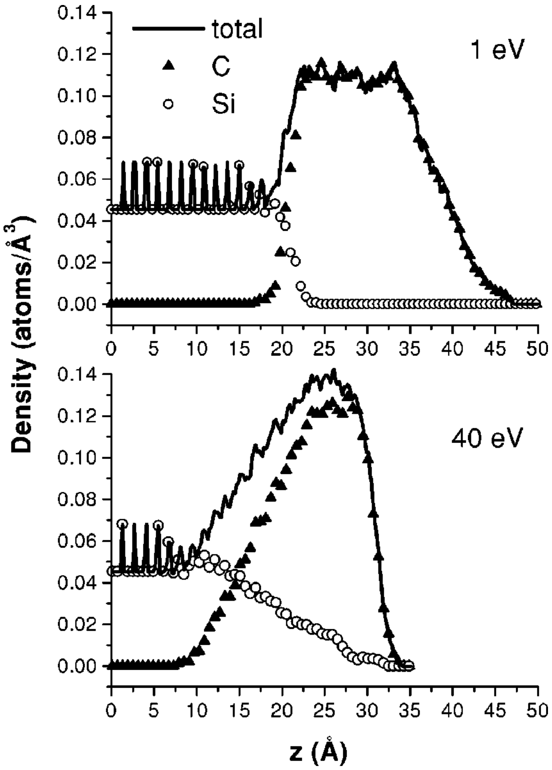

FIG. 6. Density profiles of two of the films shown in Fig. 5.

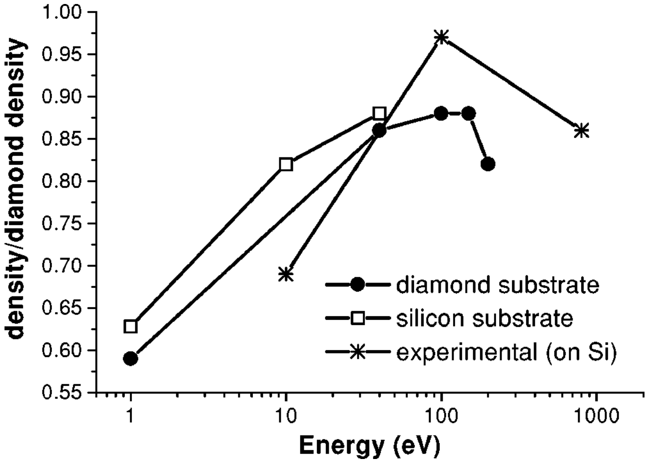

FIG. 7. Relative density of films grown by throwing individual carbon atoms on diamond and silicon (100) substrates.

Films grown on diamond substrates were thermally annealed up to 2200 K, with temperature steps of 200 K. Annealing below 1000 K does not have any significant effect on the atomic coordination of the films. Between 1000 and 1600 K there is a remarkable growth of the number of three-coordinated atoms at the expense of the number of four-coordinated atoms. This conversion process seems to saturate at 1600 K. These results are in qualitative agreement with experimentally observed graphitization of the samples upon annealing. A typical annealing procedure is illustrated in Fig. 8 for the sample grown at 40 eV. Figure 8(a) shows three snapshots of a film grown on a diamond substrate and thermally annealed at 1400 and 2200 K; it shows the sp^3 to sp^2 bonding conversion in the film, while the substrate remains unaltered. Figure 8(b) is an example of the temperature ramp used in the annealing procedures and Figure 8(c) shows the increasing conversion from sp^3 to sp^2 bonding as the annealing temperature rises up to about 1400 K; annealing at higher temperatures yields similar results. Figure 9 shows the density profile and sp^2-sp^3 content of the same as-grown and annealed film at 2200 K. It can be seen that the bonding conversion is nearly uniform all across the film.

D. Film growth from C_{60} molecules

Films were grown on silicon (100) substrates consisting of eight layers, each one containing 50 atoms. A total of about 30 molecules were deposited for each energy studied. Figure 10 shows films grown between 20 and 1000 eV on silicon substrates. Samples grown at 20 eV exhibit little distortion of the fullerene cages with large intermolecular holes, yielding very low-density films. At 100 eV the fullerene molecules still preserve their identity, but the density of the film increases and the substrate is slightly distorted. For

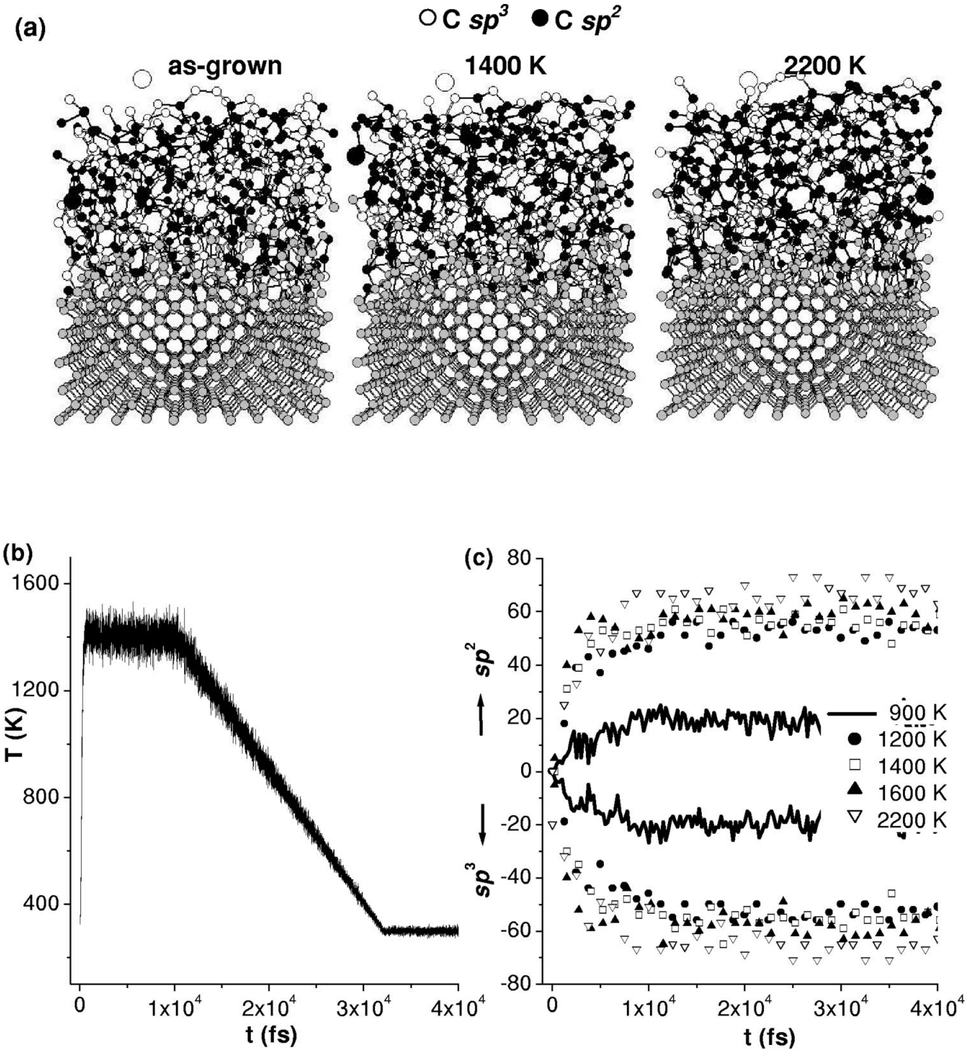

FIG. 8. (a) Snapshots of a film grown by throwing individual carbon atoms on a diamond (100) substrate at 40 eV and annealed at 1400 and 2200 K. (b) Example of the temperature ramp for the annealing treatment given to the sample grown on a diamond (100) substrate at 40 eV. All the ramps were identical to the one shown for the annealing at 1400 K. (c) Conversion from sp^3 to sp^2 bonding of the deposited carbon atoms in the film as a function of the annealing temperature.

300 eV and higher deposition energies the molecules are no longer recognizable; they have been fragmented, forming high-density films. The film density and distortion of the substrate increase with the deposition energy. It can be seen that even for high deposition energies, the interpenetration between carbon atoms arising from C_{60} disintegration and the silicon substrate is considerably smaller than in the case of using individual atoms as projectiles with the same energy per atom. This is in agreement with experimental evidence of a poor adherence of films obtained by accelerating $C_{60}{}^{+}$ ions on silicon substrates.[7] In order to compare with films grown from individual atoms, it is worthwhile to have in mind that in the present case the deposition energy refers to whole molecules; i.e., the translational kinetic energy of each atom is 60 times smaller than that of the projectile.

Mean densities across the films were calculated as described previously. Figure 11 shows density and sp^2 to sp^3 ratio vs deposition energy curves. It can be seen that for deposition energies up to 50 eV the density of the films is low, even lower than that of the van der Waals C_{60} molecular crystal, due to the fact that the fullerene cages preserve their identity, forming a porous structure with big intermolecular holes; carbon atoms in the films are mainly three-coordinated, as they are in the individual molecules. From 50 eV up to about 500 eV, the density of the films grows; for deposition energies greater than 300 eV the resulting films are denser than the the three-dimensional polymerized fullerite, about 75% of the diamond density.[23] We have not observed a maximum in the density vs energy curve, as was observed for the deposition of individual atoms on diamond (Fig. 7). The sp^2 to sp^3 ratio falls abruptly with increasing deposition energy up to 300 eV. For higher energies this ratio becomes nearly 1. This behavior is experimentally observed for energies larger than 200 eV; but calculated sp^2 to sp^3 ratio are greater than the experimental ones.[5] Similar results have been previously reported:[9–11] the Tersoff potential underestimates the sp^3 fraction in amorphous carbon films.

Pair radial distribution functions $g_{\mathrm{CC}}(r)$ were calculated in such a way that $\int_0^R g_{\mathrm{CC}}(r) 4\pi r^2 dr$ is the mean number of carbon atoms inside a sphere of radius R centered at a carbon atom. In addition, angular distribution functions, with vertices on C and Si atoms, were calculated and compared with those corresponding to undistorted fullerene molecules in order to analyze the degree of molecular distortion and/or fragmentation. Figure 12 shows the radial distribution function for films grown between 10 and 1000 eV. At low energies, $g_{\mathrm{CC}}(r)$ exhibits the peaks belonging to individual C_{60} mol-

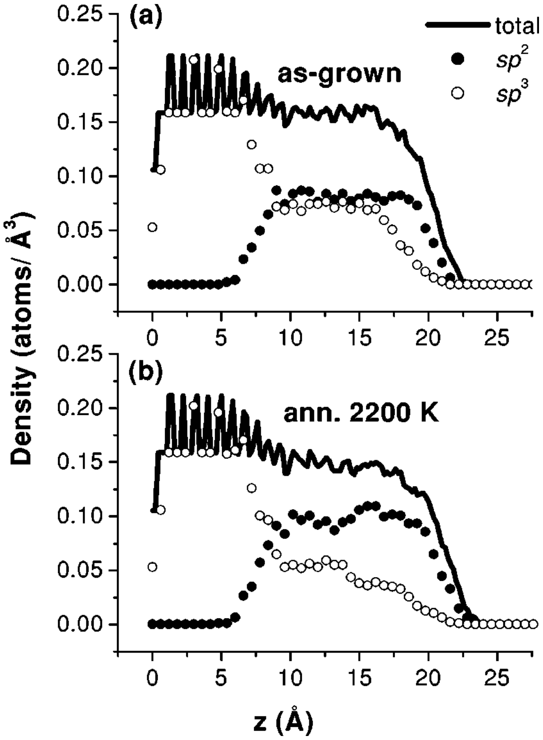

FIG. 9. Density profile discriminating sp^2- and sp^3-bonded carbon atoms for (a) the as-grown and (b) the 2200 K annealed film, grown at 40 eV on a silicon (100) substrate.

ecules; as the deposition energy increases there is a progressive broadening of the peaks until they practically disappear, leaving only the one corresponding to first neighbors. It can be seen that the intensity of the peak at 2.1 Å increases with the deposition energy from about 100 eV; this peak has been reported as a little shoulder by Kaukonen and Nieminen[9] and more extensively analyzed by Pan *et al.*[16] The appearance of a peak at 2.1 Å is an artifact of the potential: this is exactly the cutoff radius given by Tersoff's parameters. In fact, we have found that the peak position changes with the cutoff radius. In the present case this peak is evident at high densities when there is a considerable number of carbon atoms that do not have fivefold coordination.

The angular distribution functions are shown in Fig. 13; they were calculated taking angles with vertices at C and at Si atoms; in the former case we distinguish three- and four-coordinated C atoms. At low energies the great majority of C atoms are three-coordinated with bonding angles corresponding to the pentagonal (108°) and hexagonal (120°) faces of C_{60} molecules. As the energy increases the peaks are broader, the 108° peak disappears denoting the fragmentation of the fullerene cages, and four-coordinated C atoms begin to appear as vertices of angles, giving rise to a new broad peak centered at about the tetrahedral angle at 109°.

Figure 14 shows calculated vibrational spectra for films grown at several energies, together with that of pristine C_{60}. Frequencies higher than 2000 cm^{-1} could be partially attributed to the aforementioned failures of the Tersoff potential together with anharmonic effects. As was observed for individual C_{60} projectiles, we find that for energies up to about 200 eV the peak structure remains similar to that observed for pristine C_{60} and low-energy-deposited molecules; for higher energies this structure is lost, giving rise to a broad band with a continuum of frequencies that cannot be observed in the case of isolated deposition molecules, suggesting that the fullerene cages are broken upon deposition, giving rise to an amorphous material. Experimentally observed Raman spectra exhibit analogous changes for energies higher than about 300 eV.[6]

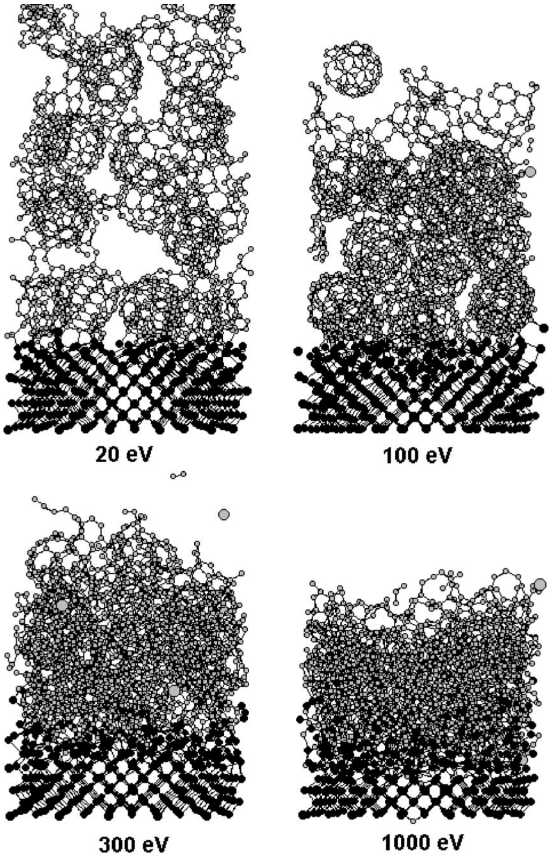

FIG. 10. Films grown by throwing C_{60} molecules on a silicon (100) substrate. In all cases the substrate consisted initially of eight layers, each one containing 50 atoms.

IV. CONCLUSIONS

The penetration depth of carbon atoms into the substrate is considerably higher for silicon than for diamond substrates, as could be expected since diamond is denser than silicon. Similar results are found with C_{60} molecules as projectiles, but in this case, we can distinguish two different effects: at low energies (up to about 300 eV) deformation of the fullerene cage is greater on diamond than on silicon substrates; however, as deposition energy increases, fragmentation of C_{60} molecules takes place at lower energies on silicon, allowing the penetration of carbon atoms into the substrate. We also found that the threshold energy for deformation and fragmentation of C_{60} projectiles is dependent on the substrate's orientation. In all simulated cases using C_{60} molecules as projectiles, there is a low penetration depth of carbon atoms into the substrate, which could be responsible

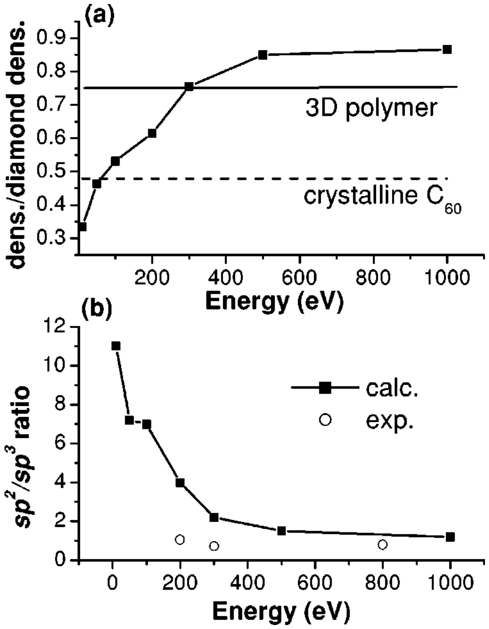

FIG. 11. (a) Relative density and (b) sp^2 to sp^3 ratio, as a function of the deposition energy for films grown by throwing C_{60} molecules on silicon (100) substrates. In (a) the density of the van der Waals C_{60} crystal and of the three-dimensional fullerite polymer are also shown for comparison.

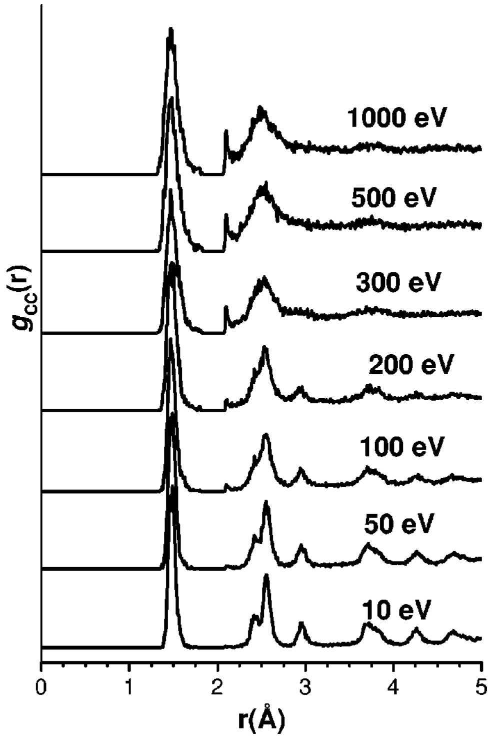

FIG. 12. Radial distribution function $g_{CC}(r)$ for films grown from C_{60} molecules deposited on silicon (100) substrates at different energies.

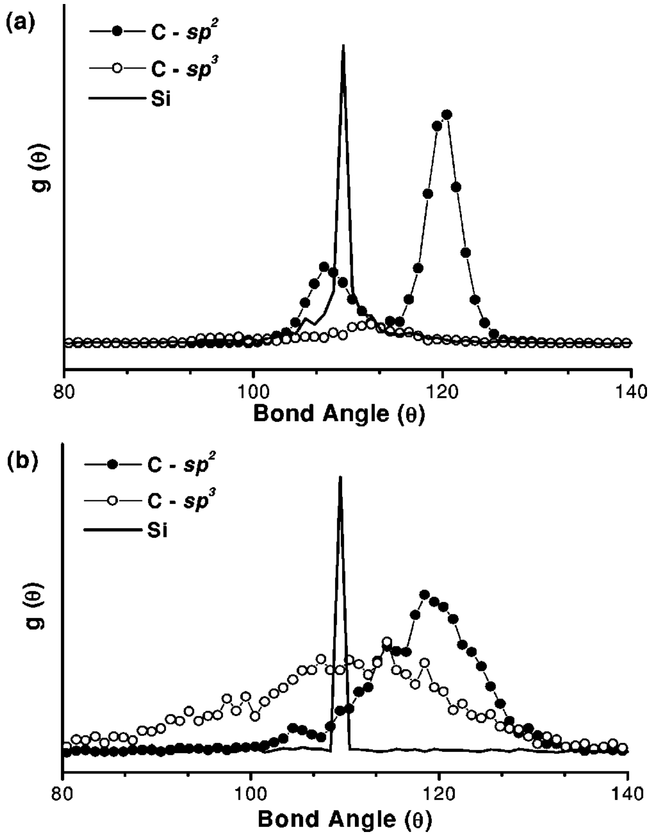

FIG. 13. Angular distribution functions calculated taking angles with vertices at sp^2 C atoms (filled circles), sp^3 C atoms (open circles), and silicon atoms (line) for films grown from C_{60} molecules deposited on silicon (100) substrates at (a) 10 and (b) 1000 eV.

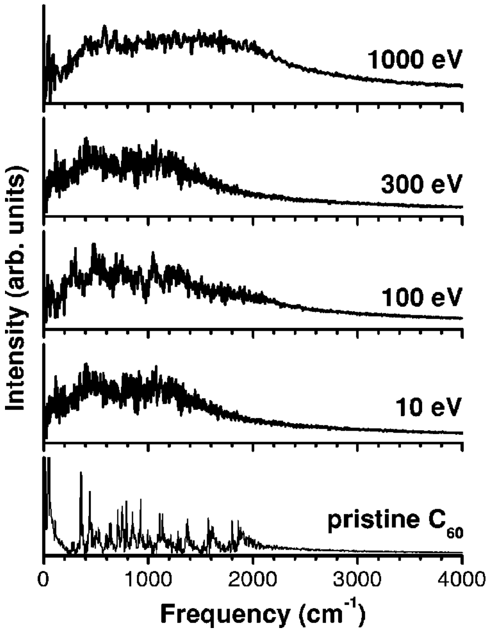

FIG. 14. Vibrational density of states for films shown in Fig. 10. The density of states calculated with the same method for a C_{60} van der Waals crystal is also shown for comparison.

for the poor adherence experimentally observed.

The density of films grown by deposition of single carbon atoms and fullerene molecules depends on deposition energy. In both cases the maximum density attained is about 85% of diamond density. In the first case there is a narrow energy range around 100 eV that maximizes density and then a slight decrease is observed for higher energies. In the case of films grown from fullerene molecules, the density increases with deposition energy up to about 400 eV and then remains practically constant.

An analysis of the structural properties of films obtained by deposition of fullerene molecules shows that molecular identity is preserved up to deposition energies of about 100 eV; for higher energies the films exhibit an increasing disorder until reaching the characteristics of amorphous carbon films resembling those obtained from individual carbon atoms. This is evidenced in the pair radial and angular distribution functions as a loss of the peaks corresponding to the fullerene molecule and the absence of long-range order. Experimentally observed Raman spectra of films grown from C_{60} ion beams lead to similar conclusions about structural properties of the films as a function of the deposition energy.

In conclusion, the use of C_{60} molecules as projectiles allows one to grow dense amorphous carbon films in a wide range of energies and it is reasonable to assume that they would have interesting tribological properties, based on hardness measurements from similar films grown by other methods. The adherence is an experimental problem to be solved. As it was proven that the penetration depth increases on going from diamond to silicon substrates, and considering the good agreement between these simulations and our previous experimental results, work is in progress to simulate the growth of films on germanium substrates and to carry out the subsequent experimental work.

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