

Carbon films obtained from fullerenes deposited on germanium: Experimental and simulated results

E. B. Halac

*Departamento de Física, Comisión Nacional de Energía Atómica, Avda. General Paz 1499,
(1650) Gral. San Martín, Pcia. Buenos Aires, Argentina*
and *Escuela de Ciencia y Tecnología, Universidad Nacional de San Martín, Martín de Irigoyen 3100 (1650) San Martín,
Pcia. Buenos Aires, Argentina*

A. G. Dall'Asén and E. Burgos

*Departamento de Física, Comisión Nacional de Energía Atómica, Avda. General Paz 1499,
(B1650) Gral. San Martín, Pcia. Buenos Aires, Argentina*
and *CONICET, Rivadavia 1917, (1033) Buenos Aires, Argentina*

M. Reinoso

CONICET, Rivadavia 1917, (1033) Buenos Aires, Argentina;
*Escuela de Ciencia y Tecnología, Universidad Nacional de San Martín, Martín de Irigoyen 3100 (1650) San Martín,
Pcia. Buenos Aires, Argentina;*
and *Departamento de Física, Comisión Nacional de Energía Atómica, Avda. General Paz 1499,
(B1650) Gral. San Martín, Pcia. Buenos Aires, Argentina*

(Received 22 June 2006; revised manuscript received 18 August 2006; published 6 November 2006)

In this work, carbon thin films have been experimentally produced by accelerating C_{60} ions on germanium substrates at different deposition energies (from 50–1000 eV). Adherence and chemical composition have been studied in order to characterize the obtained material. On the other hand, molecular dynamics simulations have been used to investigate the microscopic processes of the growth of carbon thin films obtained from the collision of C_{60} molecules on germanium substrates. The Tersoff potential has been employed to describe the atomic interactions. Some properties of the films have been studied as a function of the deposition energy (from 10–1000 eV): interface thickness, density profile from the substrate up to the film surface, etc. Experimental and simulated results have been correlated to those obtained on silicon by similar methods. The results show that the structural and dynamical properties of the films depend on deposition energy, as it was observed on silicon substrates. For the studied energies, the simulated interface thickness is larger in germanium substrates than in silicon ones. However, experimentally observed adherence is poorer on germanium substrates.

DOI: [10.1103/PhysRevB.74.174104](https://doi.org/10.1103/PhysRevB.74.174104)

PACS number(s): 61.48.+c, 83.10.Rs, 68.55.-a, 68.35.Gy

I. INTRODUCTION

The deposition of hard carbon-based materials has been extensively studied due to their technological usefulness. Previous works have demonstrated that high pressures induce polymerization or amorphization of solid C_{60} .¹ The idea of our method is to replace the high pressure and high temperature by a dynamic process of deposition of fullerenes with different energies, inducing covalent bonds between carbon atoms of neighboring C_{60} molecules, forming films with different short range organization depending on the ion beam energy. We have deposited carbon thin films from a C_{60} ion beam on silicon wafers and we have characterized them.^{2–4} We have also studied, by molecular dynamics (MD) simulations, the impact of C_{60} molecules on ideal diamond and silicon (100) substrates and the subsequent growth of carbon films. Simulated results on silicon agreed with experimental ones.⁵ In particular, the low penetration depth of carbon atoms into the substrate when using C_{60} molecules as projectiles could be responsible for the experimentally observed poor adherence to the substrate.⁶

It was proven that penetration depth increases going from diamond to silicon substrates,⁵ as expected taking into ac-

count that the volume per atom is greater for silicon. Germanium structure suggests that we could obtain still more penetration on this substrate. This motivated us to grow carbon films on Ge substrates in order to solve adherence problems and to simulate this process by molecular dynamics to achieve a better understanding of experimental results in an atomic scale.

In this work we present the characterization of carbon thin films experimentally obtained by accelerating a C_{60} ion beam on germanium (100) substrates at deposition energies (E_{dep}) from 50–1000 eV. We also present MD simulations of the growth of carbon films from C_{60} molecules on ideal germanium (100) substrates at different E_{dep} (from 10–1000 eV). The experimental and calculated results were compared with those obtained for films produced on diamond and silicon substrates.

II. EXPERIMENTAL

Fullerene powder (99.9% C_{60}) is degassed at 200 °C during several hours in order to eliminate oxygen. Thereafter, the fullerenes are sublimated at about 600 °C and an electron discharge is established between a hot filament and an anode,

producing C_{60}^+ . These ions are extracted from the discharge region and accelerated, in a first stage, to an electrode in order to separate the discharge zone from the deposition region. Finally, the ions are accelerated to the substrate by another negative extraction potential,⁷ with deposition energies ranging from 50 to 1000 eV.

Mirror polished germanium (100) wafers were used as substrates. The wafers were chemically cleaned with acetone in an ultrasonic bath for 5 min before the deposition process.

The surface morphology of the obtained material was observed by optical microscopy and some of the samples were characterized by x-ray photoelectron spectroscopy (XPS) in order to study chemical composition. XPS measurements were carried out using the Mg K_{α} line ($h\nu=1253.6$ eV) as incident radiation. The spectrometer was calibrated considering that the binding energy of the Au $4f_{7/2}$ peak was at 84 eV with respect to the Fermi level. High resolution XPS spectra (pass energy=20 eV) of C 1s, Ge 3d, and O 1s were registered from the as-grown samples and after sequential applications of sputtering with Ar^+ bombardment (4 kV, $5 \mu A/cm^2$). The spectra were fitted by Gaussians functions in order to identify the elements on the film surface.

III. COMPUTATIONAL MODEL

Verlet's molecular dynamics algorithm with semiempirical many-body Tersoff potential⁸ has been used to describe the interactions between C_{60} molecules and germanium substrates. Parameters given in the literature have been used for C-C and Ge-Ge interactions. C-Ge parameters have been interpolated as indicated in Ref. 8.

In order to avoid Ge-Ge bonds in an hypothetical CGe compound with zinc-blende (ZB) structure, the parameters defining the cut-off function for this interaction were initially reduced from $R=2.8$ Å, $S=3.1$ Å, to the values $R=2.7$ Å, $S=2.9$ Å. The dimensionless parameter χ_{C-Ge} not supplied by Tersoff was fixed at 0.986, chosen to fit the heat of formation of the mixed ZB-CGe alloy, estimated from *ab initio* calculations⁹⁻¹¹ to be of about 0.2 eV/atom.

In this way the potential allows the formation of a CGe compound with ZB structure in a relative minimum energy, though the most stable situation corresponds to phase segregation. An amorphous C-Ge material containing bonds similar to those of ZB is expected to be present in the interface as a result of the described experimental procedure, especially for the higher deposition energies.

Taking into account the relative arbitrariness in the definition of the cut-off parameters, small variations around initial values were allowed after deposition in order to analyze its effect: no significant structural changes were observed.

As projectiles we used single carbon atoms and C_{60} molecules thrown perpendicularly to the substrate surface at a random location with deposition energies (E_{dep}) in the range 1–100 eV for single C atoms and 10–1000 eV for fullerenes. In the case of molecules, E_{dep} 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.

Ideal Ge(100) crystals were employed as substrates. The number of atomic layers, each one containing 50 atoms, de-

pends on E_{dep} , ranging from 12 to 20. The two bottom layers were fixed to the equilibrium position representing a semi-infinite crystal; the remaining layers were allowed to move with full dynamics, applying periodic boundary conditions in the layer's (xy) plane. Before deposition of the molecules, the substrates were relaxed at $T=300$ K and $P=0$ for about 1000 fs. C_{60} molecules were deposited at time intervals of 5000 fs, in order to ensure that each projectile has enough time to dissipate its energy to the substrate before the next one hits the surface. The method of Berendsen¹² was applied in order to simulate the cooling of the system. For further details see Ref. 5. We have analyzed structural and dynamical properties as a function of the deposition energy: interface thickness, coordination of the atoms inside the film, density profile from the substrate up to the film surface, vibrational density of states, and pair radial and angular distribution functions.

Mean densities across the films were calculated by sliding a slice in small increments along the z direction, discriminating atomic species. Angular distribution functions were calculated taking angles between bonds with Ge and C atoms as vertices and discriminating by atomic coordination.

Thermal annealings at 1500 and 2500 K were performed on some of the samples in order to study structural changes. Temperature was raised at a rate of 5 K per fs, samples were allowed to thermalize during 10 ps at the chosen annealing temperature, and then they were cooled at a rate of 0.1 K per fs up to 300 K.

IV. RESULTS

Samples of about 0.1–0.2 μm thickness were deposited on Ge(100) wafers. Qualitative optical inspection indicates that the surface of the films is homogeneous. However, a few hours after the end of the deposition process, some parts of the film begin to detach from the substrate, indicating poor adherence. Figure 1 shows a micrograph of the film surface, where delamination by buckling can be appreciated. This result disagrees with the improvement in adherence expected from the increasing of the penetration depth going from Si to Ge. A probable cause for this behavior is suggested by MD simulation results which will be discussed later in this section.

Chemical composition of the films was analyzed by XPS. Oxygen contamination was observed on the surface, but it disappears after a few sequential applications of sputtering with Ar^+ . Figure 2 shows XPS results for the C 1s signal from a film deposited at 1000 eV. The best fitting was achieved with two peaks centered at (283.8 ± 0.1) eV and (284.6 ± 0.1) eV, which are attributed to C-Ge and C-C contributions, respectively.¹³ These results evidence the presence of C-Ge bonds in the substrate-film interface.¹⁴ There are not many theoretical publications about C-Ge materials. One of the reasons for this is that germanium carbide is not a natural material. However, the aforementioned XPS results have shown the presence of C-Ge bonds, which prompted the simulations presented in this work with the aim of achieving a deeper understanding of the growth of these films in an atomic scale. Therefore, this study could provide a theoretic-

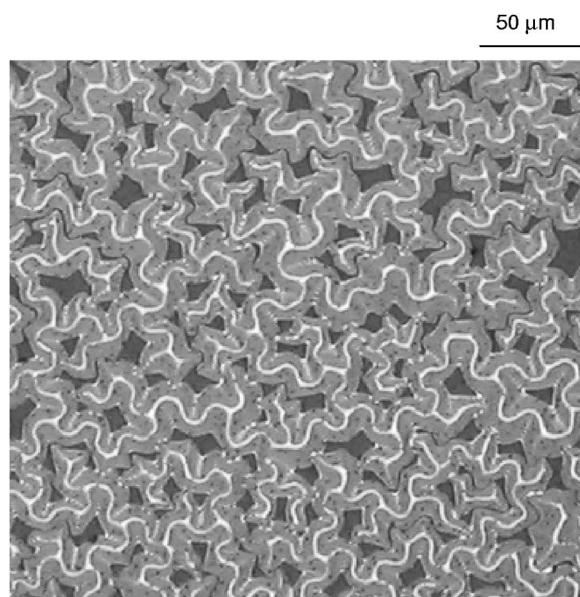


FIG. 1. Micrograph of delamination produced by buckling, observed in the surface of a sample deposited on Ge at 200 eV (100X).

cal explanation of the experimentally observed poor adherence.

Molecular dynamics (MD) calculations were carried out to simulate the growth of carbon films from C_{60} molecules thrown on Ge substrates. In order to decide the number of Ge layers to be used in each simulation, penetration of single C atoms was analyzed. Figure 3 shows statistical results of the mean penetration depth of C atoms on Ge as a function of E_{dep} ; results of C atoms on Si and diamond substrates are also included for comparison. It can be seen that all of them show a similar behavior: the mean penetration depth is approximately proportional to the deposition velocity. On the other hand, the penetration depth increases going from diamond to germanium.

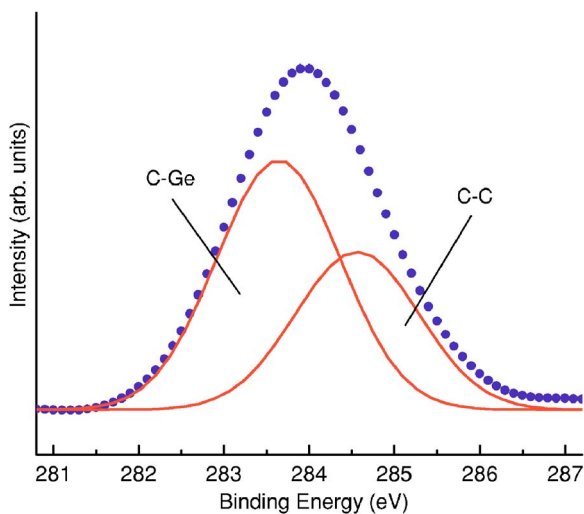


FIG. 2. (Color online) XPS spectra for the C 1s signals from samples deposited on Ge at 1000 eV: experimental data (dots), fitting curves (solid lines).

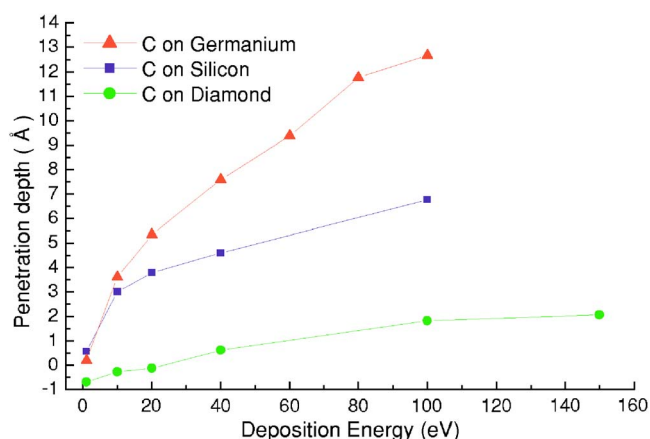


FIG. 3. (Color online) Calculated mean penetration depth of individual C atoms in Ge(100) substrates as a function of the deposition energy. Results calculated on diamond and silicon substrates are also shown.

The impact of individual C_{60} fullerenes on Ge substrates was simulated by throwing vibrating molecules perpendicularly to the surface. For each deposition energy in the range 10–1000 eV, statistical behavior was studied by generating the projectiles with different orientations and impinging the surface at random location. Figure 4 shows illustrative snapshots for three E_{dep} , together with those previously obtained on silicon and diamond for the sake of comparison. Three different behaviors can be distinguished: at low E_{dep} , the molecules either bounce away or remain weakly bonded to the substrate with little distortion of the molecular geometry; at intermediate E_{dep} , molecules form progressively more bonds with the substrate and suffer an increasing distortion of the fullerene cage; and at high E_{dep} , molecules are fragmented. This behavior is common to all substrates, but distortion and fragmentation start at different E_{dep} values for each one. In the case of Ge, at low E_{dep} there are statistically more bounces than the observed ones on Si and diamond, probably because C-Ge bonding affinity is the lowest one. Besides, for E_{dep} higher than 500 eV, mean penetration depth of fragmented molecules is considerably higher on Ge than on the other substrates, as illustrated in Fig. 4. This behavior is in agreement with results shown in Fig. 3 about penetration of individual C atoms.

Figure 5 shows films grown on Ge substrates together with previous results on Si.⁵ For Ge substrates, samples grown up to 10 eV exhibit little distortion of the fullerene cages and large intermolecular holes, yielding very inhomogeneous and low density films, nevertheless they are denser than those grown on Si. For 200 eV and higher deposition energies, the molecules are no longer recognizable: they have been fragmented forming high density films. The film density and the distortion of the Ge substrates increase with deposition energy. This behavior is similar to that observed on Si substrates.

Figure 6(a) shows density profiles corresponding to the snapshots of Fig. 5 on Ge. The density of these films increases together with the increasing E_{dep} , from about 0.08 to 0.14 atoms/Å³ for 10 and 1000 eV, respectively. These values are similar to those corresponding to samples deposited

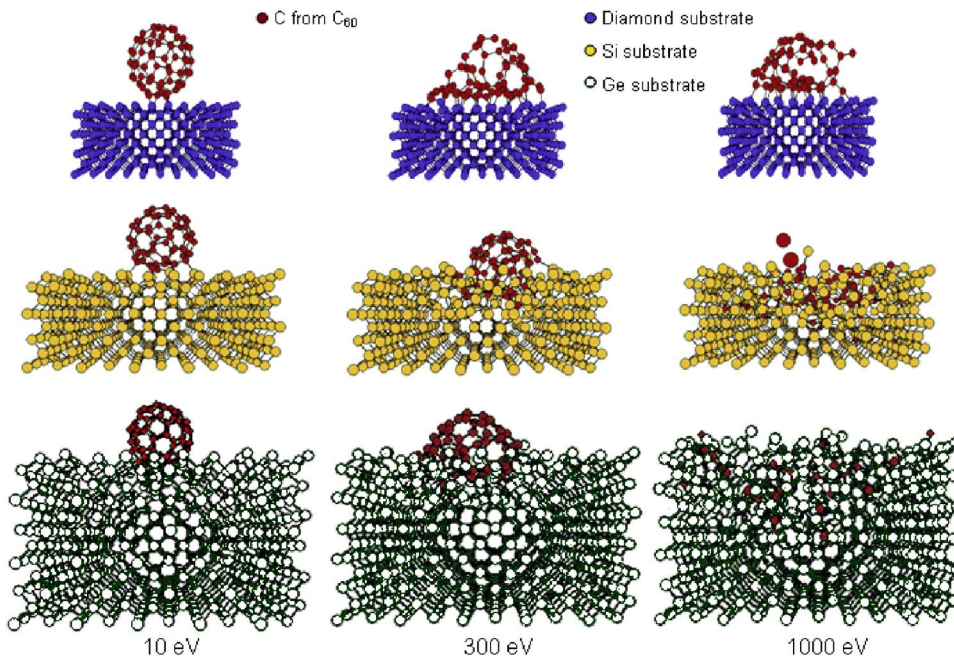


FIG. 4. (Color online) Snapshots of a C₆₀ molecule thrown on diamond (100), Si(100), and Ge(100) substrates.

on Si substrates for the same E_{dep} . As a reference, the higher value of density is comparable to the corresponding for diamond ($0.176 \text{ atoms}/\text{\AA}^3$). For the sample grown at 10 eV, it has to be stressed that the aforementioned value corresponds to the average density. The observed inhomogeneity can be attributed to the size of the analyzed area.

Figure 6(b) shows the interface thickness of films deposited on Ge, estimated from density profiles, together with previous results on Si.⁵ The interface thickness is defined as the film region where C and Ge (or Si) densities are not null. It can be seen that for E_{dep} higher than 500 eV, the thickness

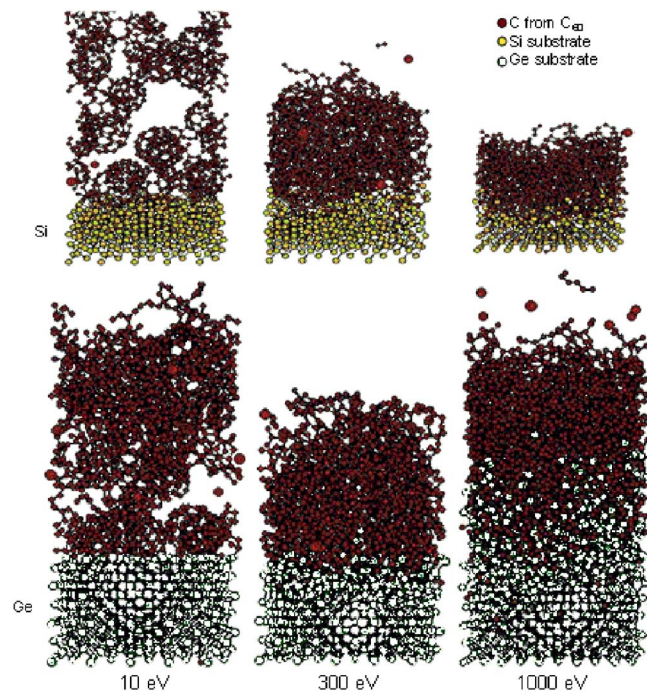


FIG. 5. (Color online) Films grown throwing C₆₀ molecules at 10, 300, and 1000 eV on Si(100) and Ge(100) substrates.

of the interface is considerably larger on Ge: not only because atomic C penetrates more on Ge (Fig. 3), but also because Ge atoms are sputtered from the substrate up to the film (Fig. 5). This result would suggest the possibility of a better adherence of the films on Ge than on Si substrates. However, as it was mentioned before, the experimentally observed adherence on Ge was even poorer than that on Si.

The coordination of C and Ge atoms in the interface and film regions was analyzed for different E_{dep} . For low E_{dep} , C atoms are mainly three-coordinated, as they are in the fullerene cage. As E_{dep} grows, the number of four-coordinated C atoms progressively increases: sp^3/sp^2 ratio is of about 0.7 at 1000 eV. On the other hand, Ge atoms are essentially four-coordinated; nevertheless, there is an increasing number of atoms with coordination five and six, as E_{dep} increases. It is noticeable that for $E_{\text{dep}}=1000 \text{ eV}$, the number of Ge atoms along the interface with coordination four, five, and six are approximately in the ratio 5:3:1. This high percentage of five- and six-coordinated Ge atoms reveals an interface far from equilibrium, which is probably the cause of the observed low adherence and film delamination (see Fig. 1). In order to study a possible rearrangement of atoms that releases stresses in the system, some samples were annealed at 1500 and 2500 K. As described in Ref. 5, 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 bonding conversion process that seems to saturate at 1600 K in the case of C₆₀ deposited on Si substrates. In the present case, a gradually convergent conversion process is observed to continue at least up to 2500 K. For C atoms there is essentially a conversion from four- to three-coordination. This graphitization process has been experimentally observed and calculated in theoretical simulations.^{15,16} For Ge atoms, the number of four-coordinated atoms grows at the expense of six- and higher coordinated atoms, whereas the number of five-coordinated atoms remains practically unchanged. Some of these results

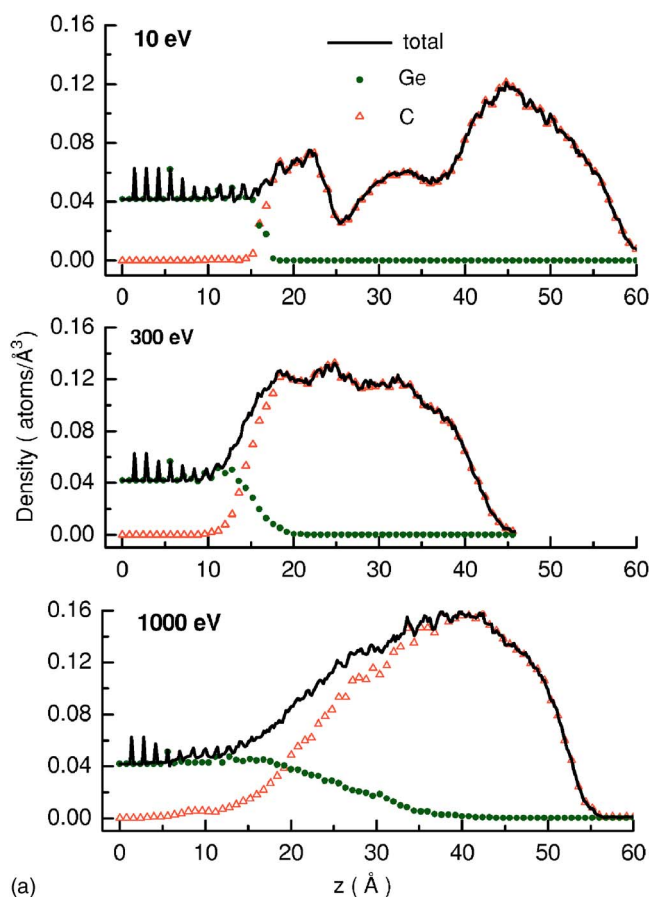


FIG. 6. (Color online) (a) Density profiles of films deposited on Ge(100); (b) interface thickness as a function of E_{dep} .

are summarized in Figs. 7 and 8, for samples grown at 1000 eV.

Structural changes as a function of E_{dep} are also reflected in radial and angular distribution functions and in velocity autocorrelation functions. As an example of these changes, Fig. 9 shows angular distribution functions for samples grown at 10 and 1000 eV. Results for Si substrates are also shown for comparison. At low E_{dep} , the great majority of C atoms are three-coordinated with angles corresponding to

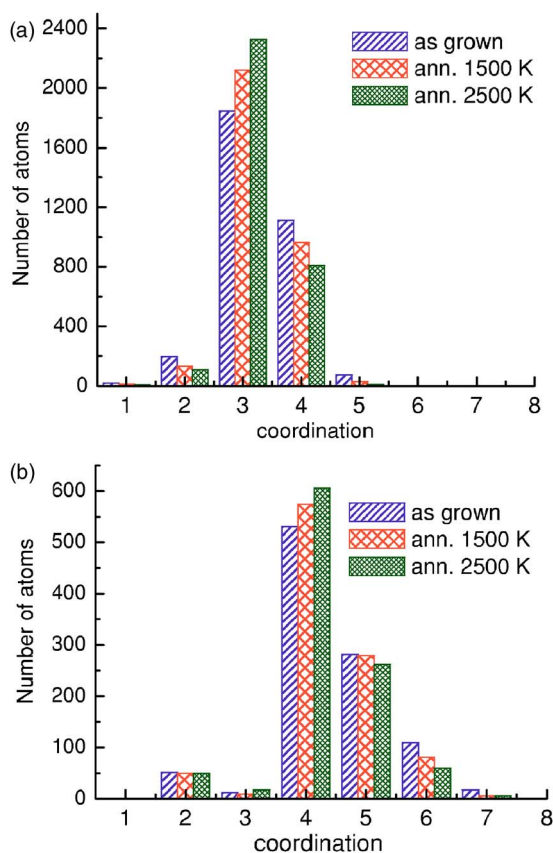


FIG. 7. (Color online) Number of n -coordinated atoms in as-grown and thermal annealed film: (a) carbon atoms; (b) germanium atoms.

hexagonal (120°) and pentagonal (108°) faces of C_{60} molecules. These peaks are more clearly observed on Si substrates, where the majority of C_{60} molecules preserve their identity in the film, as can be appreciated in Fig. 5. At high energy, the peaks are broader and approximately centered at hexagonal and tetrahedral (109°) angles for both substrates, denoting the presence of amorphous carbon films. Similarly, C-C pair radial distribution functions are comparable at high energies, but broader peaks are observed for films grown on Ge substrates at low energies.

V. CONCLUSIONS

Experimental and simulations studies of carbon thin films deposited on Ge(100) substrates were carried out.

It was proven that it is possible to deposit carbon films from C_{60} ion beams on Ge substrates. Besides, XPS spectra for the C 1s signals evidence the existence of C-Ge bonds.

MD simulations show a noticeable increase of the atomic penetration depth (for E_{dep} higher than c.a. 500 eV) and of the interface thickness going from Si to Ge substrates. However, experimentally obtained films on Ge present very low adherence to the substrate for all E_{dep} , similar or even lower than that observed on Si substrates.

MD calculations results suggest that the observed poor adherence could be attributed to the internal stress of the

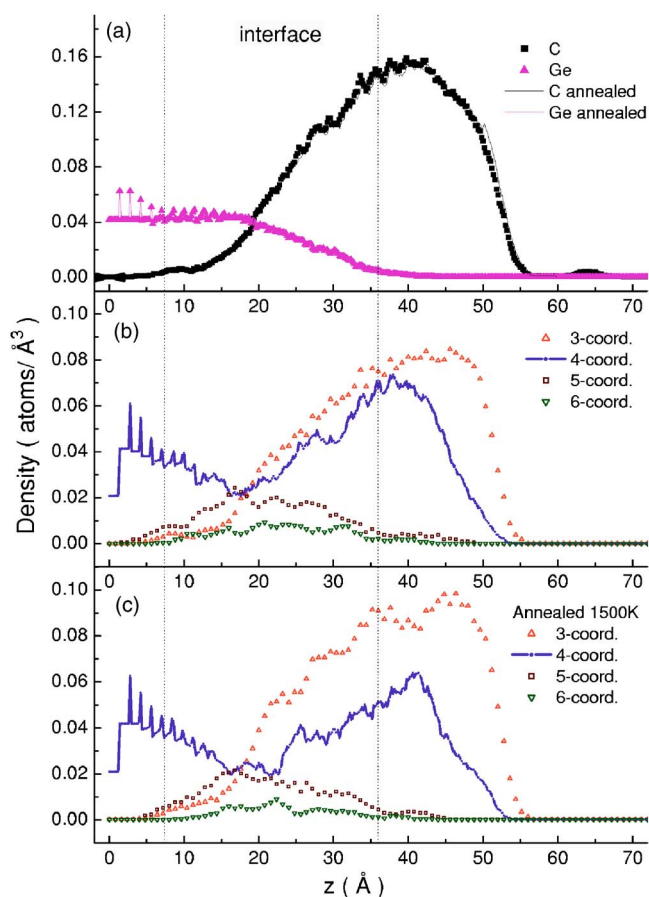


FIG. 8. (Color online) Density profiles of a film deposited at 1000 eV discriminating: (a) atomic species for as-grown and annealed (1500 K) films; (b) three-, four-, five-, six-coordination for as-grown films; (c) three-, four-, five-, and six-coordination for annealed films (1500 K).

material, essentially in the interface. In fact, in this region a high number of five- and six-coordinated atoms, especially Ge, are present. Under these anomalous conditions the atoms are weakly bonded. After thermal annealing, Ge atoms with six- and higher coordination release stress but the high number of five-coordinated Ge atoms remains practically unchanged. In fact, the experimental deposition process generates a far from equilibrium system. This kind of system hardly reaches a complete relaxation after an annealing

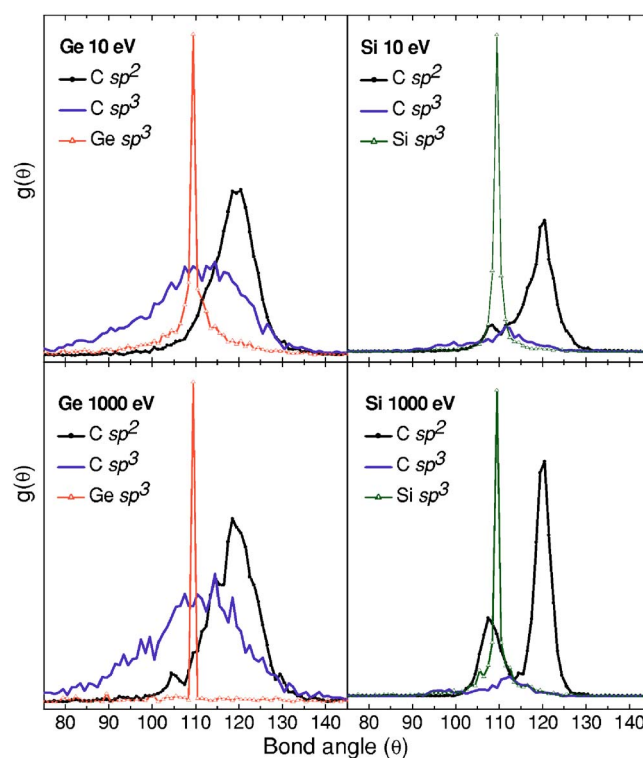


FIG. 9. (Color online) Angular distribution functions calculated taking angles with vertices at sp^2 C atoms, sp^3 C atoms, and Ge or Si atoms for films grown from C_{60} molecules deposited on Ge(100) and Si(100) substrates at 10 and 1000 eV.

process, as suggested by numerical simulations.

In conclusion, although XPS and MD simulations results show the presence of a rich C-Ge interface, the films present weak adherence to the substrate, which could be associated to a high number of overcoordinated Ge atoms in the interface.

ACKNOWLEDGMENTS

We would like to thank Cristina Oviedo and Flavio Conde for XPS measurements, and Horacio Ceva and Roberto De Luca for technical assistance with the computer system. This work was partially supported by SECyT Grant No. PICT 12-06979 and CONICET Grant PIP N $^\circ$ 02546.

¹S. M. Bennington, N. Kitamura, M. G. Cain, M. H. Lewis, and M. Arai, *Physica B* **263**, 632 (1999); M. Núñez-Regueiro, P. Monceau, and J. L. Hodeau, *Nature (London)* **355**, 237 (1992); A. M. Rao, P. Zhou, K. Wang, G. T. Hager, J. M. Holden, Y. Wang, W. T. Lee, X. Bi, P. C. Eklund, D. S. Cornett, M. A. Duncan, and I. J. Amster, *Science* **259**, 955 (1993); R. Moret, P. Launois, T. Wagberg, and B. Sundqvist, *Eur. Phys. J. B* **15**, 253 (2000); V. D. Blank, V. M. Levin, V. M. Prokhorov, S. G. Buga, G. A. Dubitskii, and N. R. Serebryanaya, *JETP Lett.* **87**, 741 (1998).
²H. Huck, E. B. Halac, M. Reinoso, and A. G. Dall'Asén, *Diamond Relat. Mater.* **11**, 964 (2002).

³H. 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).
⁴A. G. Dall'Asén, M. Verdier, H. Huck, E. B. Halac, and M. Reinoso (unpublished).
⁵E. B. Halac, M. Reinoso, A. G. Dall'Asén, and E. Burgos, *Phys. Rev. B* **71**, 115431 (2005).
⁶A. G. Dall'Asén, E. B. Halac, H. Huck, and M. Reinoso, *V Meeting on Diamond, Amorphous Carbon, Nanotubes and Related*

- Materials*, Río de Janeiro, Brazil, 2003.
- ⁷H. Huck, E. B. Halac, M. Reinoso, and A. G. Dall'Asén, in *Recent Res. Devel. Physcis*, edited by S. G. Pandalai (Transworld Research Network, Kerala, 2004), Vol. 5, Chap. 9, p. 217.
- ⁸J. Tersoff, *Phys. Rev. B* **39**, R5566 (1989); J. Tersoff, *Phys. Rev. Lett.* **61**, 2879 (1988).
- ⁹O. F. Sankey, A. A. Demkov, W. T. Petuskey, and P. F. McMillan, *Modell. Simul. Mater. Sci. Eng.* **1**, 741 (1993).
- ¹⁰P. C. Kelires, *Phys. Rev. Lett.* **75**, 1114 (1995).
- ¹¹P. C. Kelires, *Phys. Rev. B* **60**, 10837 (1999).
- ¹²H. J. C. Berendsen, J. P. M. Postma, W. van Gunsteren, A. Di-Nola, and J. R. Haak, *J. Chem. Phys.* **81**, 3684 (1984).
- ¹³T. Bruce, I. Bello, L. J. Huang, W. M. Lau, M. High, V. Strnad, and P. Panchhi, *J. Appl. Phys.* **76**, 552 (1994); C. Q. Hu, W. T. Zheng, B. Zheng, J. J. Li, Z. S. Jin, X. M. Bai, H. W. Tian, Q. Jiang, X. Y. Wang, J. Q. Zhu, S. H. Meng, X. D. He, and J. C. Han, *Vacuum* **77**, 63 (2004).
- ¹⁴M. Diani, L. Kubler, L. Simon, D. Aubel, I. Matko, and B. Chenevier, *Phys. Rev. B* **67**, 125316 (2003).
- ¹⁵R. Gago, M. Vinnichenko, H. U. Jäger, A. Yu. Belov, I. Jiménez, N. Huang, H. Sun, and M. F. Maitz, *Phys. Rev. B* **72**, 014120 (2005).
- ¹⁶P. C. Kelires, *Phys. Rev. B* **47**, 1829 (1993).