Carbon Superatom Thin Films

Andrew Canning,[1,2] Giulia Galli,[2] and Jeongnim Kim[3,*]

[1]*Cray Research, PSE, EPFL, 1015 Lausanne, Switzerland*
[2]*Institut Romand de Recherche Numérique en Physique des Matériaux (IRRMA), IN-Ecublens, 1015 Lausanne, Switzerland*
[3]*Department of Physics, The Ohio State University, Columbus, Ohio 43210*

We report on quantum molecular dynamics simulations of C_{28} deposition on a semiconducting surface. Our results show that under certain deposition conditions C_{28}'s act as building blocks on a nanometer scale to form a thin film of nearly defect-free molecules. The C_{28}'s behave as carbon superatoms, with the majority of them being threefold or fourfold coordinated, similar to carbon atoms in amorphous systems. The microscopic structure of the deposited film supports recent suggestions about the stability of a new form of carbon, the hyperdiamond solid.   [S0031-9007(97)03357-7]

In recent years, significant knowledge has been acquired on fullerene solids, with studies concentrating mainly on pure and doped van der Waals bonded C_{60} crystals [1]. Much less is known about solids composed of smaller fullerenes, which could form covalently bonded fullerites with novel properties.

Of all the small fullerenes, C_{28} is the most studied [2–7]: This molecule is believed to be the smallest fullerene created in the photofragmentation [2] of C_{60} by loss of C_2, and is also produced in considerable amounts in the laser vaporization of graphite [3]. Kroto [4] proposed that the isolated C_{28} cluster is a fullerene cage, chemically very reactive, with four preferred active sites (*A* sites). The existence of solid forms of C_{28} has been conjectured by Guo *et al.* [3], who proposed that it should be possible to stabilize an arrangement of the fullerene cages in a diamond lattice, with the molecules bonded together at *A* sites. However, such a material, usually referred to as hyperdiamond [6,7], has not yet been synthesized, and the possible growth and stability of C_{28} solids remain, at present, open questions.

Recently, low energy deposition experiments of small fullerenes ($C_n, n = 20–32$) [8–10] have been performed, suggesting that thin films can be formed, which retain the bonding properties of the incident clusters. It has been proposed that this memory effect [8] could permit the synthesis of diamondlike materials, since small cages contain sp^3-like sites, with a dangling bond. However, the interpretation of Raman and electron energy loss spectra is controversial [9,10] and inconclusive about whether the deposited films contain small fullerene cages or a diamondlike network.

We have addressed the issue of the formation of small fullerene solids by performing quantum molecular dynamics (MD) simulations of the deposition process of C_{28} cages on a nonmetallic substrate, corresponding to the early stages of the growth of a disordered thin film. This is the first quantum simulation of a deposition process involving complex units such as fullerene cages. Here we present an analysis of the deposition process; we discuss

the microscopic structural properties of the deposited film and relate them to recent experimental findings [3,8–10] and to theoretical propositions on the reactivity of the C_{28} molecule [4,5,7].

In our calculations, we adopted a tight-binding (TB) model [11] in the context of a linear scaling method [O(N)] [12–15], with a semiempirical Hamiltonian which has been successfully used to study a variety of carbon systems [12]. We chose a TB picture rather than a classical potential since the high reactivity [4,5,7] of C_{28} clusters and their ability to form covalent bonds call for a quantum mechanical treatment of the interactions. We adopted an O(N) method because of the large supercells needed in the simulation of the deposition process: The favorable scaling with system size of the algorithm, together with its efficient implementation on a massively parallel computer [15], allowed us to perform quantum simulations of an unprecedented size, with cells of up to 4472 atoms, for about 70 ps.

Before performing the deposition simulation, we investigated, by using semiempirical and first-principles approaches, the structure and bonding of the C_{28} monomer, dimer and hyperdiamond (see Table I), in order to have a clear understanding of the properties of simple C_{28} systems. These calculations also allowed us to test the validity of our O(N)-TB model [16] for the description of C_{28} systems. The agreement between *ab initio* results within the local density approximation (LDA) of density functional theory and O(N)-TB results is extremely good.

In our computer experiment [16], we projected 78 fullerenes onto a diamond substrate, of which 50 remained to form a film (see Fig. 1). We used diamond since it is the simplest semiconducting surface that can be simulated in a tight-binding context, and we would expect similar results if we had used Si—exhibiting reconstructions with bonding characteristics similar to those of diamond—as in real experiments [8]. The substrate used in our simulations consisted of 12 C layers with 256 atoms per layer with periodic boundary conditions in the *x* and *y* (horizontal) directions, and a

TABLE I. Comparison between properties of the C_{28} monomer (M) and dimer (D) and of the hyperdiamond solid (Hyp.) obtained from first-principles LDA and semiempirical $O(N)$ calculations (see text). The C_{28} monomer is composed of 12 pentagons and 4 hexagons; we denote atoms at an apex where three pentagons meet as A sites, atoms on the hexagons as B sites if bonded to A sites, and C sites otherwise. The C_{28} molecule has 12 A-B, 24 B-C and 6 C-C bonds. Stable configurations of the C_{28} dimer are formed by two C_{28} molecules connected by only a single bond [17] of length R_{eq}. We considered three cases involving A and C atoms as bonding sites, since these are the most reactive sites (see text and Refs. [4,6,7]). The cohesive energy of the dimer is $E_{coh} = (E^D - 2E^M)$, where E^D and E^M are the total energies of D and M, respectively. The LDA calculations for M and D were carried out within the pseudopotential-plane-wave formalism [18,19], using a kinetic energy cutoff of 30 to 44 Ry (to check for convergence) and supercells of dimensions $(15.9 \text{ Å})^3$ and $(15.9 \text{ Å} \times 15.9 \text{ Å} \times 23.8 \text{ Å})$ for M and D, respectively. Ionic positions of both M and D were fully optimized, and the equilibrium rotational configuration of D was the same for both $O(N)$-TB and LDA calculations. The LDA results for Hyp. are taken from Ref. [7], where only the relative position of the C_{28}'s was optimized. In the $O(N)$-TB calculation for Hyp. both the lattice constant and the atomic positions were optimized; we obtained almost identical results when using supercells with 8 and 64 C_{28}'s and the Γ point.

C_{28} monomer	$O(N)$-TB	LDA
A-B bond length (Å)	1.44–1.46	1.42–1.45
B-C bond length (Å)	1.40–1.44	1.40–1.44
C-C bond length (Å)	1.47–1.55	1.46–1.57
C_{28} dimer	$O(N)$-TB	LDA
A-A bonded R_{eq} (Å)	1.54	1.51
A-C bonded R_{eq} (Å)	1.46	1.51
C-C bonded R_{eq} (Å)	1.50	1.53
A-A bonded E_{coh} (eV)	3.02	3.15
A-C bonded E_{coh} (eV)	2.13	2.48
C-C bonded E_{coh} (eV)	2.24	2.48
Hyperdiamond	$O(N)$-TB	LDA
Lattice constant (Å)	15.85	15.78
E_{coh} (eV)	0.65	0.74
C_{28}-C_{28} bond length (Å)	1.52	1.54

(2×1) reconstructed (111) surface on the upper and lower side. The deposition was performed by sending down 14 separate showers of C_{28} clusters: The initial configuration of each shower was prepared by choosing molecules randomly distributed in space and noninteracting with each other and with the surface. They were also chosen to have random orientations. The number of fullerenes belonging to each shower varied from 4 to 8. With a series of test runs (involving the study of fullerene-fullerene and fullerene-surface impacts as a function of energy), we determined the range of incident kinetic energies (20–40 eV) for which the fullerenes had the highest sticking probability without breaking up. We then projected each shower, one after the other, vertically downwards onto the surface, with each molecule having an initial kinetic energy randomly distributed within this range of energies. In this way, we tried to mimic some

of the features of low-energy neutral-cluster beam deposition (LECBD) experiments [8]. The bottom three layers of the substrate were held fixed, and the next three layers were connected to a thermostat [20] at room temperature to prevent the substrate heating up [21] under the fullerene impacts. After each shower of fullerenes, the whole system was equilibrated by monitoring the variation in time of the number of bonds as well as the bond lengths.

At the end of the deposition process, 24 fullerenes were bonded directly to the substrate, with the majority of them sticking to the surface during the first 3–4 showers. The arrangement of the first monolayer of C_{28}'s on the surface is random, with no preferential bonding sites [see Fig. 2(a)]. As expected from the large number of dangling bonds in the cluster, C_{28}'s easily attach to the diamond substrate, the average number of bonds with the surface being about three per fullerene. These can be classified as strong covalent bonds: their formation can cause the bonds between the fourfold coordinated atoms of the first and second surface bilayer to break. This locally destroys the (2×1) Pandey chain reconstruction, returning the surface geometry to an ideal (111) configuration (de-reconstruction). Nevertheless, the formation of bonds between the substrate and C_{28}'s does not induce modifications of their molecular topology. This is at variance to what was observed for C_{60} on a diamond (111) surface [22], where impacts leading to covalent bonds between the C_{60} and the surface would necessarily induce the formation of defects in the cage [22].

On the time scale of our simulation we did not observe any diffusion of the C_{28}'s on the surface. Most importantly, when heating the system after the deposition was completed, no diffusion was observed before reaching the temperature regime where cages started to break up. Therefore, we expect that the bonds between the fullerenes and the surface are strong enough to hamper rearrangements and diffusion. Consequently, the system is unlikely to undergo a disorder-to-order transition such as the one observed experimentally in the case of C_{60} on some semiconducting substrates [23]. Indeed, for C_{60}, van der Waals interactions between the molecules and the substrate play a crucial role in allowing cluster diffusion and the subsequent disorder-to-order transition.

On top of the first monolayer, a second portion of the system (26 fullerenes) was identified, which was again very inhomogeneous. In this portion of the system, during the deposition process, we observed the formation of three-dimensional islands with some polymerlike structures, where C_{28}'s were preferentially bonded to each other with two single bonds [see Figs. 2(b) and 2(c)]. This is suggestive of either a Stranski-Krastanov or a Volmer-Weber growth process [24]. However, our simulation cannot clearly establish a growth process mechanism since larger cell sizes and longer simulation times would be needed. After equilibration at room temperature, the film was heated to verify its thermal stability. During the heating procedure, we observed oscillations of the polymerlike
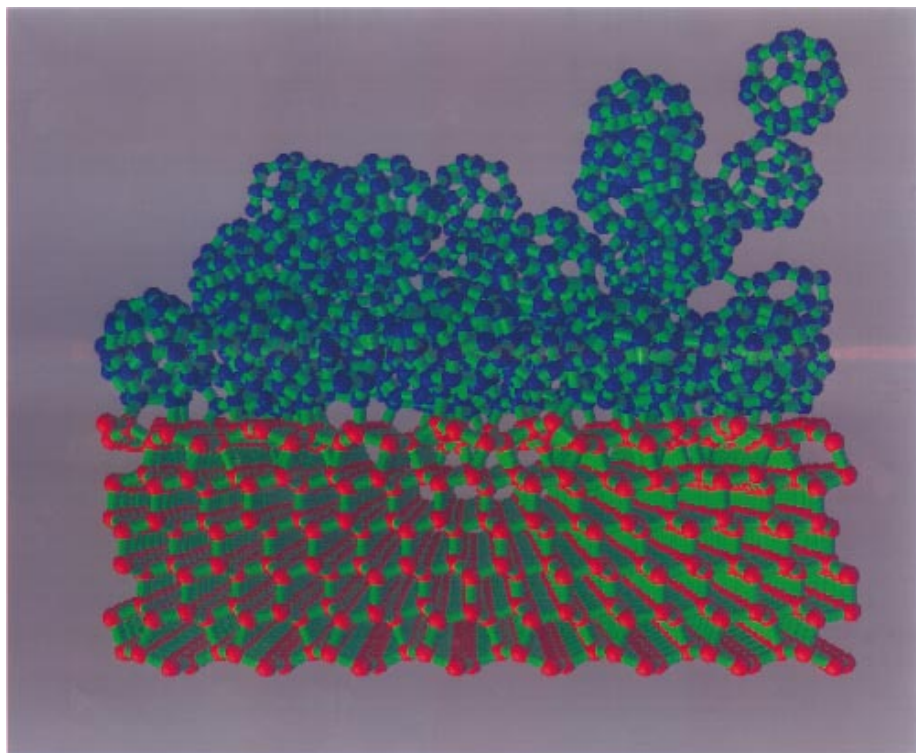
FIG. 1(color). A snapshot of the full system (4472 atoms) at the end of the MD deposition simulation showing the undamaged C_{28} cages. Red and blue spheres represent atoms belonging to the surface and to the fullerenes, respectively. Bonds between surface atoms and between fullerene atoms are represented as light and dark green, respectively. Note the numerous bonds between the fullerene and the first surface layer causing the local de-reconstruction of sections of the Pandey chains. In the deposited film the cages are slightly distorted: The maximum and minimum ratio between the principal moments of inertia of the clusters are 1.3 and 1.1, respectively, and the variations of the maximum and minimum distance within a cluster are 1.54–1.65 and 1.30–1.40 Å, respectively.

structures with no major structural change. Our results indicate that the film is stable up to about 1000 K.

The whole system at the end of the deposition process at room temperature is shown in Fig. 1. The thin film is characterized by fullerenes which retained their topology, with small distortions with respect to the original shapes. The particle density of the film is very low ($\simeq 1$ g cm^{-3}, compared to the diamond and graphite densities of 3.52 and 2.27 g cm^{-3}, respectively), consistent with the measured value of 0.8 ± 0.2 g cm^{-3} for small fullerene films obtained by LECBD [8].

We found that the total particle-particle correlation function of the deposited film has two main peaks corresponding to first- and second-neighbor distances. Each of these peaks is split. The first double peak is at 1.42 and 1.53 Å: These distances correspond to the two different intrafullerene bond lengths (see table). The longer distance (1.53 Å) also corresponds to the interfullerene bond length, as indicated by the correlation function of the sites involved in intermolecular bonds, which has its first peak centered at 1.52 Å. Most fullerenes are threefold (3f) and fourfold (4f) coordinated, although some twofold and fivefold cages were also observed. This predominance of 3f and 4f molecules indicates that the C_{28} cluster has bonding properties similar to those of C atoms in amorphous systems, which usually contain a mixture of sp^2 and sp^3 sites [25]. We found that A sites have the highest probability (0.37) to form bonds, giving rise to hyperdiamondlike configurations. They are then followed by C (0.11) and B (0.04) sites, in order of decreasing probability. Our results are in agreement with the proposition of Kroto [4] that C_{28} should behave as a carbon superatom with four preferred active sites and with several studies [5,7] on the reactivity

of the C_{28} cluster. Furthermore, our findings support the proposition of Guo *et al.* [3] that C_{28} solids in a hyperdiamond structure are stable. We note that the structural properties of the film deposited in our simulation are remarkably similar to those of a disordered system obtained by subsequent collisions of C_{28}'s, mimicking the gas phase deposition of the clusters [17].

The proportion of $4f$ atoms and thus of proper sp^3 sites is low (10%) in the deposited film. Experimentally, from analyses of Raman spectra, it has been suggested [8] that films obtained by depositing small fullerenes might be composed of small graphitic islands embedded in a diamondlike matrix. We do not find any evidence of such structures in our deposition energy regime. However, we note that the computed vibrational spectra (both within LDA and TB) of free C_{28} cages [26] are consistent with the Raman spectra derived from experimental data on small fullerene films. Neither type of spectra exhibit prominent peaks corresponding to graphite Raman active modes (the maximum vibrational frequency for the fullerene cages is 1471 and 1464 cm^{-1}, when computed using a TB and an LDA picture, respectively [26]), and both spectra show peaks centered around 600 and 1200 cm^{-1}. This indicates that the experimentally measured Raman spectra might show direct evidence for the presence of cages in the film, consistent with the observed memory effects.

In conclusion, we have shown that in a given energy range small fullerenes can be assembled on a semiconducting surface to form the first layers of a thin film where the C_{28}'s constitute the building blocks acting as carbon superatoms. Our results indicate that covalently bonded fullerite materials of small cages can be assembled, and point towards the possibility of synthesizing novel, new
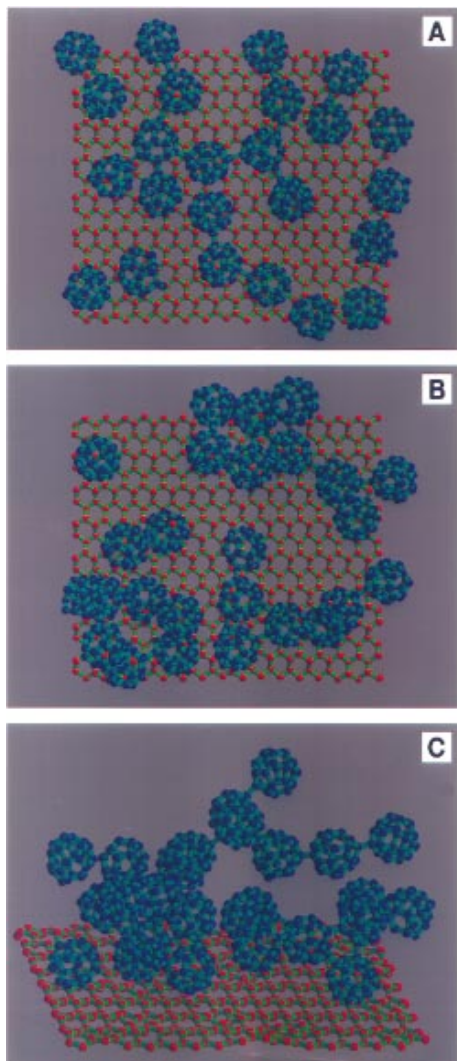
FIG. 2(color). Sections of the system displayed in Fig. 1 (color scheme as defined in Fig. 1 caption). (A) Top view of the top layer of the substrate showing only the fullerenes directly bonded to the surface: Note the random positions of the fullerenes. (B) top and (C) side view of the top layer of the substrate showing only the fullerenes which are *not* bonded to the surface: The tendency of the fullerenes to form islands and polymer type structures is clearly visible.

thin films. Our simulations also help clarify the structure of disordered films obtained experimentally by small fullerene deposition. We finally note that our calculations have been made possible by the use of $O(N)$ methods which, for certain types of systems, allow one to perform TB-MD simulations on supercells of several thousand atoms for tens of picoseconds.

*Present address: National Renewable Energy Laboratory, Golden, CO 80401.

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