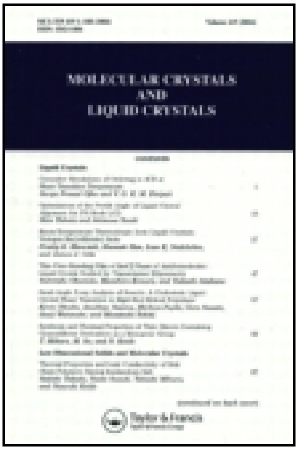

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Hierarchical assembly of nanostructured carbon foam

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HIERARCHICAL ASSEMBLY OF NANOSTRUCTURED CARBON FOAM

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This contribution addresses the unusual structural and electronic properties of carbon foam, a hypothetical new system that may form by a hierarchical self-assembly process from nanostructured graphite. Due its topological relationship to bulk forms of carbon, the postulated foam covers the structural phase space extending from hexagonal diamond to graphite. Ab initio results for the optimized structure indicate that carbon foam should be stable, structurally rigid, and metallic.

Keywords: carbon; nanostructures; foam

INTRODUCTION

During the past fifteen years, initiated by the discovery of the C_{60} "buckyball" and carbon nanotubes, a plethora of unusual nanostructures attracted the attention of carbon scientists [1]. Examples of these

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intriguing systems are other fullerenes, onions, single- and multi-wall nanotubes, and hybrid structures such as peapods. Whereas most of these sp^2-bonded systems are know to grow from carbon vapor under extreme conditions, structures like multi-wall nanocapsules and peapods may form by a hierarchical self-assembly process, involving activated bond rearrangement in ultra-disperse diamond [2] or highly defective graphite. In the following, we characterize the structural, elastic and electronic properties of carbon foam, which may be obtained by a similar hierarchical self-assembly process from nano-graphite [3] or from polymerized nanotubes [4].

MORPHOLOGY OF CARBON FOAM

Among the various form of nanostructured bulk carbon showing a combination of sp^2 and sp^3 bonds, which have been discussed in the literature [5–11], we focus on a porous structure that had been first proposed in Ref. [11]. As shown conceptually in Figure 1, this structure is based on interconnected graphite strips.

The resulting periodic 3D network, depicted in Figure 2, is structurally reminiscent of a foam. Long open channels are formed by terraces in the layered structure. These terraces consist of graphitic strips that are interconnected in a seamless manner. The primitive orthorhombic

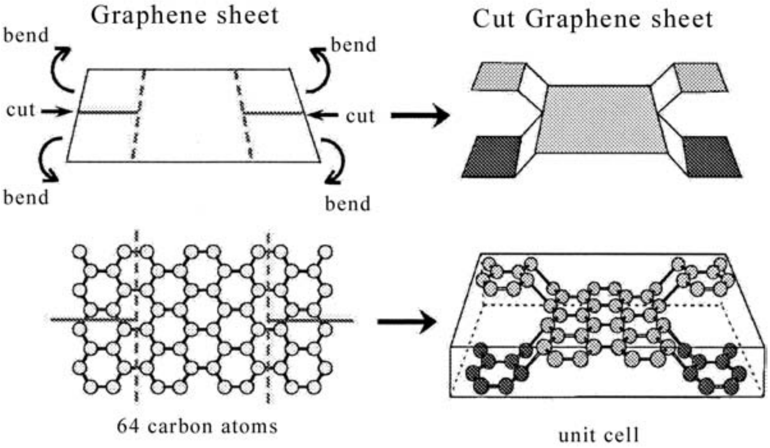

FIGURE 1 Structural description of carbon foam. Top panel: Schematic illustrating the structural relationship between carbon foam and layered graphite. Bottom panel: Conventional orthorhombic unit cell of carbon foam, holding 64 atoms.

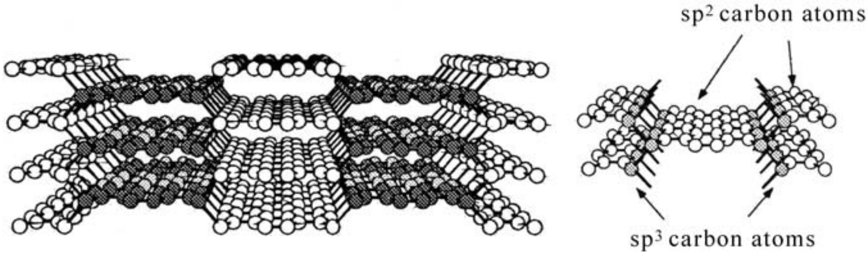

FIGURE 2 Left panel: Perspective view of the unoptimized 3D foam lattice structure, based on the 64-atom unit cell depicted in Figure 1. Right panel: use of sp^2 and sp^3 coordinated atoms in the carbon foam structure.

conventional unit cell of a particular foam structure, containing 64 atoms, is depicted in Figure 1.

The rigidity of the foam structure depends on the density of bonds in the *c* direction that connect the terraces in the *ab* plane of the initial graphene layer. By construction, these bonds are formed by connecting atoms within the graphite terraces with additional neighbors in the *c* direction, normal to the *ab* plane, thus locally converting sp^2 to sp^3 hybridized carbon atoms.

Increasing *b* yields a structure of interconnected graphite strips that eventually becomes indistinguishable from graphite as $b \to \infty$. Keeping *b* at its minimum value near 2.46 Å and reducing the terrace width in the *a* direction to zero, the structure reduces to a network of fourfold coordinated carbon atoms, namely that of hexagonal diamond or wurtzite. Increasing *a*, on the other hand, yields a structure which, in the $a \to \infty$ limit, is that of layered graphite. With the flexibility of independently adjustable values of *a* and *b*, we have a system that continuously spans the structural phase space between diamond and graphite, the most stable phases of elemental carbon.

EQUILIBRIUM STRUCTURE AND STABILITY OF CARBON FOAM

We used *ab initio* calculations within the framework of the density functional theory to optimized the geometry and to describe the structural and electronic properties of carbon foam [3]. For the system depicted in Figures 1 and 2, which contains 64 atoms in the unit cell, the optimized lattice parameters are $a_{\text{opt}} = 16.44$ Å, $b_{\text{opt}} = 9.58$ Å, and $c_{\text{opt}} = 3.28$ Å. The optimized structure is shown in Figure 3. We find the intra-layer bond lengths to be close to the graphite value of 1.42 Å, and the inter-layer distance to be only slightly smaller than the graphite value of 3.35 Å.

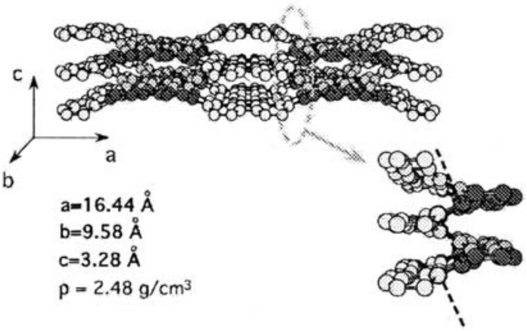

FIGURE 3 Left panel: Perspective view of the optimized 3D foam lattice structure, based on the 64-atom unit cell depicted in Figure 1. Right panel: detail of the $sp^3 - sp^2$ rehybridization during the relaxation process.

During the optimization process, depicted in Figure 3, we observe an intriguing structure relaxation especially near the sites labeled sp^3 in Figure 2. These atoms sacrifice one of their four neighbor bonds, characterizing an initial sp^3 hybridization, and bind strongly to only three neighbors with strong sp^2 bonds.

Our total energy calculations indicate that the foam is almost as stable as graphite and diamond, the most stable allotropes of carbon. We find the cohesive energy of the foam with 64 atoms per unit cell to be smaller by 0.13 eV/atom than that of graphite (or the equally stable diamond). The foam is more stable by 0.31 eV/atom than the isolated C_{60} molecule, and

	New graphic Foam	Graphite	Diamond
ρ	2.48 g/cm^3	2.27 g/cm^3	3.51 g/cm^3
C_{11} (along a axis)	9.02 Mbar	12.3 Mbar	11.29 Mbar
C_{22} (along b axis)	9.42 Mbar		
C_{33} (along c axis)	0.816 Mbar	0.34 Mbar	
Bulk modulus	0.792 Mbar	0.326 Mbar	4.69 Mbar

FIGURE 4 Summary of the elastic properties of carbon foam in comparison to those of graphite and diamond.

similarly stable as carbon nanotubes. Consequently, we expect the new carbon foam to remain stable once it is synthesized.

The above optimized structure yields a mass density of only $\rho = 2.48\,g/cm^3$. This value is nearly as low as that of graphite, $\rho = 2.27\,g/cm^3$. In spite of its low density, the foam material shows an unusually high stiffness along all three axes, as well as a large bulk modulus, as shown in Figure 4.

ELECTRONIC STRUCTURE OF CARBON FOAM

The bonding integrity throughout the structure is reflected in delocalization of the charge density in the entire structure [3]. To investigate the degree of metallic behavior, we show the band dispersion along high-symmetry lines in the primitive orthorhombic unit cell in Figure 5. We find the band dispersion within the *ab* plane, i.e. along the $\Gamma - X$ and $\Gamma - Y$ directions, to be large and comparable to the dispersion of a graphitic monolayer, reflecting the strong sp^2 bonding. Our 64-atom unit cell holds 256 valence electrons, and we find that the 128th and the 129th bands cross the Fermi level along the $\Gamma - Y$, $\Gamma - Z$, and the $Y - T$ lines. The electronic density of states of carbon foam, displayed in the right panel of Figure 5, is reminiscent of graphite, reflecting the structural similarity of the two structures. The system is metallic, with the non-vanishing value of the density of states at the Fermi level $N(E_F) = 1.0$ states/eV/spin, similar to other previously discussed sp^2 lattices [7].

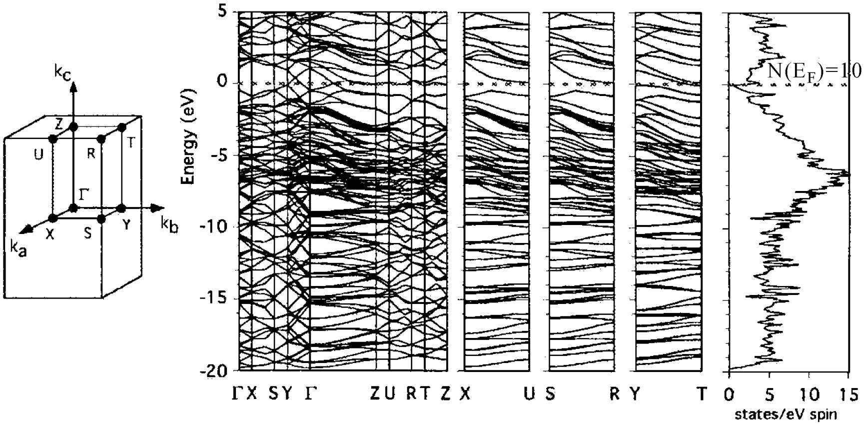

FIGURE 5 Electronic band dispersion along high-symmetry lines in the Brillouin zone of the foam structure depicted in Figure 2. The schematic drawing of the Brillouin zone shows the labeling of high-symmetry points. The corresponding density of states is shown in the right panel. The Fermi level is defined as $E = 0$.

WAYS TO SYNTHESIZE CARBON FOAM

A possible way to synthesize carbon foam may be achieved by directed assembly on a templated substrate. Recently, graphitic strips have been synthesized by hydrocarbon decompostion on stepped transition metal or metal carbide surfaces, such as Pt(557), Ni(557), or TiC(557) [12,13]. Whereas hydrocarbons, such as benzene, graphitize on the flat terraces, the more active step sites have been shown to break the graphitic bonds, thus separating the graphitic overcoating into disconnected strips. We postulate that under conditions where graphite layers still remain intact, such a separation into strips may be suppressed. Due to the stronger local bending of the still intact overlayer near the steps, the strained segments become more reactive. With more than one graphitic overlayer, the initially layered structure, reminiscent of wavy graphite, may reconnect to a foam-like structure.

An alternate way to synthesize carbon foam would involve aligned nanotubes, which may coalesce and polymerize under high pressures, at high temperature, or when exposed to a high-energy electron beam [4].

Bonding arrangements, reminiscent of those illustrated in Figure 2, also likely exist in defective graphite. In that case, however, the channels are likely to become very irregular, inducing significant strain to the lattice. We would like to emphasize that the structural motif of the carbon foam introduced here is also easily extended to other layered systems, such as boron nitride. The high porosity and accessibility of the foam structures suggests their potential for the absorption and storage of hydrogen or alkali metals for fuel cell or battery applications.

REFERENCES

[1] For recent reviews, see *Science and Application of Nanotubes*, (Eds.) by David Tomanek & Richard Enbody (Kluwer: New York, 2000); Dresselhaus, M. S., Dresselhaus, G., & Eklund, P. C. *Science of Fullerenes and Carbon Nanotubes* (Academic Press: San Diego, 1996).

[2] Young-Kyun Kwon, David Tománek, & Sumio Iijima, (1999). "Bucky-Shuttle" Memory Device: Synthetic Approach and Molecular Dynamics Simulations, *Phys. Rev. Lett.*, *82*, 1470.

[3] Koichiro Umemoto, Susumu Saito, Savas Berber, & David Tomanek, (2001). *Phys. Rev. B*, *64*, 193409.

[4] Terrones, M., Terrones, H., Bannhart, F., Charlier, J.-C., & Ajayan, P. M. (2000). *Science*, *288*, 1226.

[5] Hoffman, R., Hughbanks, T., Kertesz, M., & Bird, P. H. (1983). *J. Am. Chem. Soc.*, *105*, 4831.

[6] Liu, A. Y., Cohen, M. L., Hass, K. C., & Tamor, M. A. (1991). *Phys. Rev. B*, *43*, 6742.

[7] Liu, A. Y. & Cohen, M. L. (1992). *Phys. Rev. B*, *45*, 4579.

[8] Corkill, J. L., Liu, A. Y., & Cohen, M. L. (1992). *Phys. Rev. B*, *45*, 12746.

[9] Park, N. & Ihm, J. (2000). ***Phys. Rev. B***, ***62***, 7614.

[10] Karfunkel, H. R. & Dressler, T. (1992). ***J. Am. Chem. Phys. Lett.***, ***114***, 2285.

[11] Balaban, A. T., Klein, D. J., & Folden, C. A. (1994). ***Chem. Phys. Lett.***, ***217***, 266.

[12] Terai, M., Hasegawa, N., Okusawa, M., Otani, S., & Oshima, C. (1998). ***Appl. Surf. Sci.***, ***132***, 876.

[13] Rokuta, E., Hasegawa, Y., Itoh, A., Yamashita, K., Tanaka, T., Otani, S., & Oshima, C. (1999). ***Surf. Sci.***, ***428***, 97.