

Cross-Linked Nano-onions of Carbon Nitride in the Solid Phase: Existence of a Novel $C_{48}N_{12}$ Aza-Fullerene

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We report a new fullerene-like material consisting of cross-linked nano-onions of C and N. Growth of the onion shells takes place *atom by atom* on a substrate surface and yields thin *solid* films during magnetron sputter deposition. Electron microscopy and energy loss spectroscopy show that the core shell contains up to 20 at. % N corresponding to $C_{48}N_{12}$ aza-fullerene composition. Nanoindentation of this nanostructured material gives high resilience with hardness 7 GPa, Young's modulus 37 GPa, and complete elastic recovery after loading with 0.5 mN to a depth of 75 nm. Total energy calculations show the stability of $C_{60-2n}N_{2n}$ aza-fullerenes and suggest the existence of a novel $C_{48}N_{12}$ molecule.

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Hitherto, the applications of carbon fullerenes have been limited by their weak interaction from van der Waals bonds. However, aza-fullerenes—fullerene molecules with nitrogen substituting for carbon atoms—may hold a key for the design of fullerene-like materials in solid state. From chemical synthesis it is known that $C_{59}N$ molecules are highly reactive and prone to form dimers [1]. The N incorporation gives the molecules a radical nature that provides cross-linking at C sites [1,2]. For synthetic *growth* of fullerene-like structures, this substitution of N for C is also important since it reduces the energy barrier to form pentagons [3], thus inducing the required curvature [3–5]. We find that the most stable structure of carbon-nitride networks is in the form of aza-fullerenes, which is also attributed to be the driving force behind the formation of our carbon nitride nano-onions. Growth of aza[60]fullerenes with N concentration as high as 20 at. % is possible.

This Letter shows that a new fullerene-like material can be grown by magnetron sputtering. Specifically, we employed ultrahigh vacuum (base pressure $<2 \times 10^{-7}$ Pa) unbalanced reactive sputtering of a C graphite target in an Ar/10% N_2 discharge at 0.4 Pa. The substrates were Si(001) and NaCl wafers held at temperatures between 200 and 450 °C. A negative bias voltage was applied to the substrate giving an effective ion energy of 28 eV. The growth rate was 0.4 \AA s^{-1} with an ion flux of $\sim 0.075 \text{ mA cm}^{-2}$. Plan-view and cross-sectional samples for high-resolution transmission electron microscopy (HRTEM) were prepared by the floating-off technique and ion milling, respectively. These were investigated in a Philips CM20 UT electron microscope operated at 200 kV. Spatially resolved electron energy loss spectroscopy (EELS), using the line-spectrum mode

for acquiring and processing sequences of spectra [6], was performed in a VG HB501 STEM. Elastic recoil detection analysis (ERDA) showed that the films contained only C and N (13 at. %) and no O or H in the bulk (less than the detection limit of 0.05 at. %). Nanoindentation experiments were performed in a Hysitron TriboIndenter using a cube corner diamond tip.

Figure 1 shows a plan-view HRTEM image of a film deposited at 450 °C. Lattice fringes of curved planes with a 3.5 Å separation are resolved. At the tear edges nanometer-sized features can be distinguished, composed of concentric fullerene-like shells (referred to as nano-onions). The nano-onions typically consist of seven to ten shells and their diameter is up to 7 nm. Cross-sectional images show that the onions nucleate as quasispherical features on the substrate surface, as well as on top of

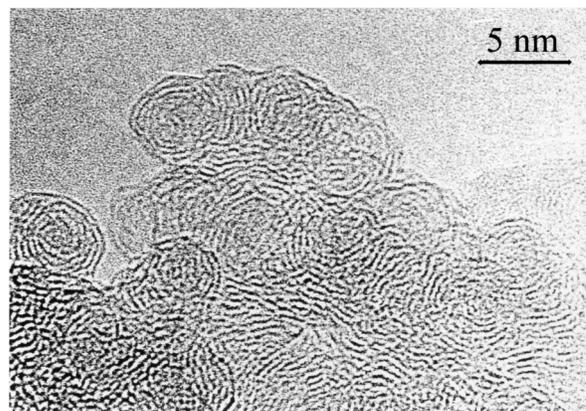


FIG. 1. Plan-view HRTEM image taken at Scherzer defocus ($\Delta f = -40 \text{ nm}$) of a 48-nm-thick fullerene-like carbon nitride film, imaged at a fracture edge.

as-grown onions by means of secondary nucleation. Depositions at substrate temperatures down to 200 °C also yielded fullerene-like films, however, with more cross-linkage from meandering shells. For comparison, depositions in pure Ar discharges, i.e., without any nitrogen incorporation, resulted in the growth of amorphous (glassy) films which contain exclusively sp^2 -bonded C films at temperatures up to 450 °C, above which crystalline graphite formation was observed.

In the spherical onions (see Fig. 1), the radii of the successive shells follow the sequence of 3.5, 7, 10.5, 14, 17.5, and 21 Å. The measured radii of the onion shells correspond to the sizes of Goldberg polyhedra [7], which consist of $60n^2$ atoms (n is an integer) with diameters $\sim nr_0$ where r_0 is the radius of a C_{60} molecule: ~ 3.5 Å.

Formation of such encapsulated polyhedra in onionlike carbon was previously known for high-energy electron-irradiated [8–10] or annealed material [10,11]. Energetic deposition conditions in arc evaporation of graphite are also known to generate fullerene-like composites. These pure carbon films contained onionlike fragments that were formed in the discharge [12,13]. However, the corresponding formation of nano-onions in carbon-based films during vapor phase deposition and requiring much less of thermal activation has not been previously reported. Thus, the magnetron sputtering process employed here (substrate temperature 200 to 450 °C, ion energy 28 eV, and ion flux 0.075 mA cm^{-2}) present a new synthesis route to such film materials. In the sputtering process C is ejected predominantly as atoms. Reactions at the graphite target surface and subsequent chemical sputtering leads to the formation of species C, Ar, and N_2 and a low fraction of C_2 , C_2N_2 , CN, and C_2N (see Ref. [14]). Thus, the growth of onions proceeds by repeated surface nucleation and growth of shells atom by atom at the substrate. As mentioned above, the N plays an active role in that substitution of N for C reduces the energy barrier to form pentagons in graphitic planes, thus promoting the growth of fullerene-like phases. The discovery of onions with a high N content and the effects of N on the reactivity of C are discussed below.

EELS line scans with a 1-nm electron probe across the nano-onions showed an overall N content in the films of 12%. This is in close agreement with the ERDA experiment that showed 13 at. % nitrogen. Figure 2 shows, however, that the N content recorded over the center part of an individual nano-onion is 13.0 ± 2.2 at. %, while it is only 8.2 ± 1.3 at. % for the outermost shells. Other nano-onions investigated gave the apparent N concentrations at the center of up to 17 at. %, whereas the perimeter concentration was ≤ 8 at. %. Because of the overlap in information from the outer and inner shells, the N content of the core shell must be higher than the measured values over the center and can amount to $\sim 20\%$. Interestingly, the N content correlates with the degree of curvature of the shells. Calculations show that N substitution decreases the energy of pentagon formation in graphite [3], whereas heptagons and other odd-member rings are energetically

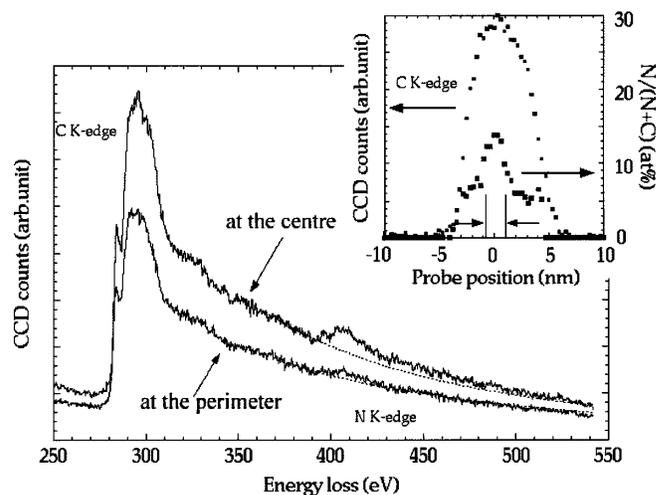


FIG. 2. EELS spectra recorded over the center and perimeter of a carbon nitride nano-onion. Inset shows C counts and relative N content recorded by a 1-nm electron probe line scan. Considering the probe broadening effect, the examined onion had a diameter of ~ 6 nm.

less favorable [2,3]. Growth of successive shells requires lower pentagon density for geometrical reasons. However, concurrent with the driving force for shell growth is the constant supply of nitrogen with a low-energy ion bombardment that promotes the formation of pentagons and effectively provides nucleation sites. This, we infer, leads to an effective maximum size of the individual nano-onions. By the same token, a variation of the process parameters may yield other fullerene-related compounds.

Based on molecular dynamics simulation [15], fullerenes and nano-onions can be expected to exhibit an extreme elasticity, but the forces between the nano-onions largely determine the overall properties of the material. As a matter of fact, cross-linking is observed to occur between aza-fullerene structures like $C_{59}N$ in the form of dimers [1]. Formation of a thin solid film of densely packed nano-onions indicates that cross-linking of fullerene fragments plays an important role in the growth. C sites adjacent to a lonely N site are strongly reactive [2], resulting in the formation of sp^3 -coordinated C [4]. This is likely to occur in the outermost shells where the N concentration is lower, thus promoting cross-linking between adjacent nano-onions. For pure carbon films, hard and elastic films could be created by arc deposition with C nanotubes and onions incident upon a substrate at high velocity. During impact, these C nanoparticles fragment and recombine at their open ends [13]. Similarly, fullerene-like C films with an sp^2 network structure with incorporated onionlike features were found [12].

In the present experiments, an sp^2/sp^3 ratio analysis on EELS K-edge could not be achieved because we are dealing with CN_x onion in which the thickness and plane orientation are varied from place to place. *In situ* scanning tunneling microscopy and local tunneling spectra from fullerene-like domains, however, revealed an increased proportion of sp^3 bonding at cross-linking or merging sites

of curved basal planes compared to graphitic domains [5]. Thus, there is experimental support for the proposed model for sp^3 cross-linking at C sites.

The presence of N in the pentagons of the polyhedral shells of the onions implies that the innermost sphere (radius ~ 3.5 Å) has the structural formula $C_{60-2n}N_{2n}$ [n -aza(60)fullerene]. Full geometry optimizations and total energy calculations were performed using the B3LYP [16,17] hybrid density functional theory (DFT) method which include a mixture of Hartree-Fock exchange with DFT. The split-valence 6-31G* basis set with polarization functions is used in all calculations. The results of these calculations show that two N atoms preferentially sit together in one hexagon as shown in Fig. 3. Let ΔE_{2n} be the total energy of $C_{60-2n}N_{2n}$ with respect to C_{60} . We find that the ground state energy of the most stable isomer of $C_{58}N_2$ has a total energy which is $\Delta E_2 = 33.253$ a.u. lower than that of C_{60} . With increasing n this energy increases close to proportionally for each pair of C that is replaced by N, i.e., ΔE_{2n} follows the linear relation $\Delta E_{2n} = n\Delta E_2$. The linearity holds up to $n = 6$, i.e., up to and including the structure $C_{48}N_{12}$ (Fig. 3) with a N content of 20% (ΔE_{12} is 5.7 times ΔE_2 in the calculations). The relation applies to $C_{60-2n}N_{2n}$ isomers for which each pentagon receives a maximum of one N and two N are separated from each other by at least two C atoms. Recently, Stafström *et al.* [18] compared B3LYP/6-31G* total energies for nitrogen in the $C_{60-2n}N_{2n}$ environment with those for substitutional nitrogen in a planar graphite structure. The calculations show a clear stabilization for each pair of N that is transferred from the planar to the curved structure up to and including the $C_{48}N_{12}$ structure. Attempts to further increase the N content in the aza(60)fullerene results in destabilization as compared to the planar structure.

Following the International Union of Pure and Applied Chemistry numbering [19] for [60]-fullerenes, the $C_{48}N_{12}$

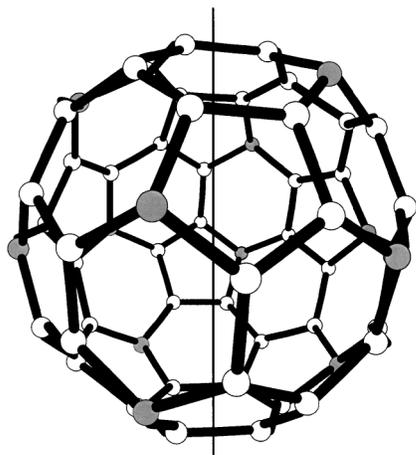


FIG. 3. Structure of the $C_{48}N_{12}$ aza-fullerene; N is shown in grey. The S_6 point group is defined by the two symmetry operations C_6 and σ_h . A solid line shows the (C_6) symmetry axis. The reflection (σ_h) is done in the plane perpendicular to this axis cutting the molecule in half.

isomer is denoted (7,12,17,23,26,29,32,35,38,44,49,54)-dodeca-aza[60- S_6]fullerene (see Fig. 3). Note that $C_{48}N_{12}$ is isoelectronic with C_{60}^{-12} and therefore corresponds to a complete filling of the h_{1u} and t_{1g} levels of C_{60} . In the reduced symmetry of the $C_{48}N_{12}$ molecule (S_6 point group), the threefold degeneracy of both these levels is lifted to two doubly degenerated levels of e_u or e_g symmetry and two single levels with a_u or a_g symmetry.

The calculated high relative stability of $C_{48}N_{12}$ indicates that it should be possible to produce fullerene-like structures during vapor phase deposition on a substrate with up to 20 at. % N corresponding to one N per five-member ring in the fullerene. Very interestingly, this result is in accordance with the measured N content in the center of a nano-onion. Previously, clusters attributed to $C_{60-2n}N_{2n}$ with N content up to and including $C_{48}N_{12}$ have been detected by mass spectrometry to form in the discharge during arc vaporization of graphite in the presence of pyrrole vapor [20]. In agreement with our calculations, molecules with $n \geq 7$ were not formed. Aza[60]fullerenes with more than one N replacing a C atom in the cage have not been synthesized by chemical means. From the general result that the N atoms are associated with the pentagons it is clear that shells with larger radii contain a smaller fraction of N. This is also seen experimentally from our EELS measurements. However, N atoms might be incorporated in positions away from the pentagons in the shells with larger radii. A simple thermodynamic argument based on the total energies would lead to a lower fraction of N in these spheres, and also a lowering of the symmetry as compared to $C_{48}N_{12}$.

Nanoindentation tests show evidence of a highly elastic material combined with an appreciable hardness. Figure 4 shows the load-displacement curves from indentations with a diamond tip into the carbon nitride film of cross-linked nano-onion microstructure compared to some well-known materials sapphire (Al_2O_3), silicon, and fused silica (amorphous SiO_2). The present carbon nitride film showed complete elastic recovery after removing a 0.5 mN load from a depth of 75 nm. For comparison, the reference hard materials all exhibited residual deformation. For a reduced load of 100 μ N (see Fig. 4 inset), also the sapphire could be seen to recover totally, however, from a much lower displacement depth of 6 nm. The hardness of the carbon nitride film was 7 GPa and the Young's modulus is 37 GPa as determined by the Oliver and Pharr model. A range of loads was used from 60 μ N to 7.5 mN corresponding to 20 nm and 450 nm maximum displacement, respectively. The film-to-substrate dominated behavior could thus be determined using the fitting procedure described in [21]. Significantly higher values for the hardness and modulus in carbon nitride can be obtained by increasing the film density and cross-linking. The film microstructure thus remains fullerene-like, however, with less defined onion features [3,4]. The carbon nitride compound thus constitutes a resilient material with good prospects for wear-protective applications. Also, the results serve as an illustration for

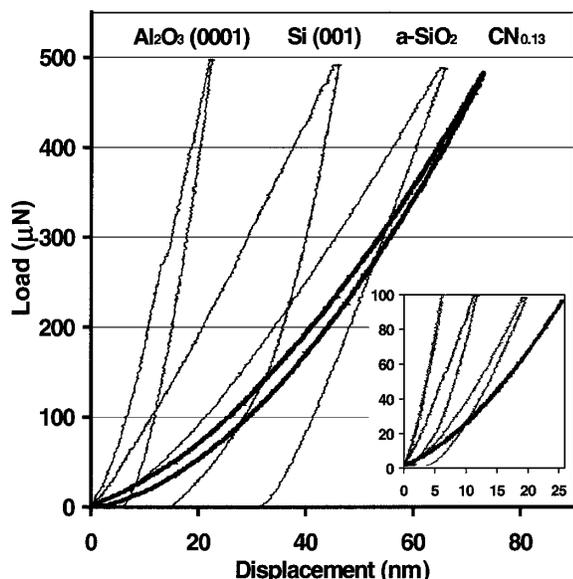


FIG. 4. Nanoindentation load-displacement curves in a 400-nm-thick carbon nitride film with cross-linked nano-onion microstructure on a Si(001) substrate compared to bulk materials of sapphire (Al_2O_3), silicon, and fused silica (amorphous SiO_2) obtained with a cube corner diamond tip and maximum load of 500 and 100 μN (inset).

the principle of how elastic materials can be designed. As a matter of fact, ultrathin (≤ 5 nm) films of CN_x are replacing diamondlike C films as a protective top coating on magnetic heads and hard disks [22]. The observation of an enhanced tendency to form pentagons in graphitic planes for the present deposition process might also be relevant for materials design of surface features with a high aspect ratio—such as nanotubes—to be employed for field emission in flat panel displays. Another proposed application is for orthopedic implants where initial results show decreased friction in human serum lubrication conditions, but also increased wetting of human blood plasma to CN_x films was observed compared to the bare surfaces [23]. Finally, the findings have impact for large-scale industrial application of fullerenes that requires low-temperature synthesis processes on a range of substrate materials such as plastics previously not devised.

In conclusion, reactive magnetron sputtering is presented as a new method to synthesize fullerene-like structures at low substrate temperatures that can constitute solid materials. Thus, thin films consisting of cross-linked carbon nitride nano-onions can be synthesized. The nano-onions form by a continuous nucleation of curved basal planes upon which successive shells are growing on the film surface. Effectively, the presence of N reduces the energy barrier to form fullerenes. Also, it increases the reactivity of C atoms in its vicinity thus providing sp^3 cross-linking sites between onions. The N content in the onions—up to 20 at. %—is the highest measured for an

aza-fullerene in the solid phase. From this observation together with total energy calculations of $\text{C}_{60-2n}\text{N}_{2n}$ aza-fullerene molecules we postulate the existence of a novel $\text{C}_{48}\text{N}_{12}$ aza-fullerene. This powerful synthesis method for generating solid phase fullerene-like materials should make them much more accessible for further study and applications.

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- [1] C. M. Brown *et al.*, J. Am. Chem. Soc. **118**, 8715 (1996).
- [2] S. Stafström, Appl. Phys. Lett. **77**, 3941 (2000).
- [3] H. Sjöström, S. Stafström, M. Boman, and J.-E. Sundgren, Phys. Rev. Lett. **75**, 1336 (1995).
- [4] N. Hellgren, M. P. Johansson, E. Broitman, L. Hultman, and J.-E. Sundgren, Phys. Rev. B **59**, 5162 (1999).
- [5] N. Lin *et al.*, Phys. Rev. B **61**, 4898 (2000).
- [6] C. Colliex *et al.*, Mikrochim. Acta **114/115**, 71 (1994).
- [7] P. W. Fowler, Chem. Phys. Lett. **131**, 444 (1986).
- [8] H. W. Kroto, Science **242**, 1139 (1988).
- [9] M. S. Zwanger and F. Banhart, Philos. Mag. B **72**, 149 (1995).
- [10] D. Ugarte, Nature (London) **359**, 707 (1992).
- [11] T. Cabioc'h, E. Thune, and M. Jaouen, Chem. Phys. Lett. **320**, 202 (2000).
- [12] I. Alexandrou *et al.*, Phys. Rev. B **60**, 10 903 (1999).
- [13] G. A. J. Amaratunga and M. Chhowalla, Nature (London) **383**, 321 (1996).
- [14] R. Kaltofen, T. Sebald, and G. Weise, Thin Solid Films **290**, 112 (1996).
- [15] R. Smith, K. Beardmore, and A. Gras-Marti, Vacuum **46**, 1195 (1995).
- [16] A. D. Becke, J. Chem. Phys. **98**, 5648 (1993).
- [17] C. Lee, W. Yang, and R. G. Parr, Phys. Rev. B **37**, 785 (1988).
- [18] S. Stafström, L. Hultman, and N. Hellgren, Chem. Phys. Lett. **340**, 227 (2001).
- [19] E. W. Godly and R. Taylor, Pure Appl. Chem. **69**, 1411 (1997).
- [20] S. Glenis, S. Cooke, X. Chen, and M. N. Labes, Chem. Mater. **6**, 1850 (1994).
- [21] A. M. Korsunsky, M. R. McGurk, S. J. Bull, and T. F. Page, Surf. Coat. Technol. **99**, 171 (1998).
- [22] C. S. Bathia *et al.*, ASME J. Tribol. **120**, 795 (1998).
- [23] E. Broitman *et al.*, Wear **248**, 55 (2000).