Fullerene and nanotube formation in cool terrestrial ''dusty plasmas''

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The simultaneous generation of dust during the deposition of semiconducting thin films by radio frequency plasma enhanced chemical vapor deposition has so far been regarded as a troublesome by-product. However, we present results from recent microstructural investigations of carbonaceous dust particles from a methane precursor that demonstrate that the technique may be suited to generating fullerene molecules, nanotubes, and nanoparticles. Chemical analysis reveals that these particles contain few contaminant species, and we deduce that they nucleated in the plasma, with the carbon ions possibly self-arranging through the action of coulombic forces. © *1998 American Institute of Physics.* [S0003-6951(98)03747-4]

Fullerenes were discovered in an attempt to recreate the conditions believed to exist in interstellar clouds, which arise from the cosmological phenomenon of ''dusty plasmas.''[1] The many potential uses of fullerenes and nanotubes for nanoengineered materials include a possible electronic super/semiconductor, self-aligned electron field emission tips,[2] catalyst cradles for highly selective chemical reactions,[3] and a transport medium for medical drug delivery. Hence, research into this form of carbon is of utmost scientific and industrial interest, with relatively large quantities of fullerenes and related material being produced commercially by using the carbon-arc discharge process[4] which requires extraction and purification.[5] In addition, the carbon arc is not particularly efficient nor controllable, with the conditions within the chamber varying dramatically between the discharge region and the outer walls. This is problematic if a cost-effective and industrially scaleable process is to be developed.

Dusty plasmas have also been studied by researchers involved with plasma enhanced chemical vapor deposition (PECVD) of amorphous hydrogenated silicon (*a*-Si:H) thin films.[6] When silane, for example, is used to produce large areas of *a*-Si:H for solar cells and thin-film semiconducting devices, small particles nucleate within the plasma and create local instabilities and power fluctuations.[7] These cause nonuniformity in the deposited films, and in extreme cases lead to unacceptable contamination rendering the material unusable for electronic applications.[8] This has led to a number of publications focused on understanding the formation, dynamics, and consequences of these terrestrial dusty plasmas, with regard to silicon-based PECVD dust.[9] However, the development of amorphous hydrogenated carbon (*a*-C:H)[10] devices formed from a methane precursor, for example, is still very much in its infancy, and little attention has so far been paid to the nature of carbonaceous dusty plasmas.

The *a*-C:H films routinely grown by PECVD are of interest for field emission cold cathodes[11] and tunable wide band-gap semiconductors.[12] Unlike silicon, it is carbon's ability to hybridize as sp^1, sp^2, or sp^3 bonds that makes the family of *a*-C:H films so interesting and varied. Similarly, the PECVD generated carbonaceous dust also exhibits a wide variety of structures that may be of significant interest to the fullerene community based on a cheaper and more widely available technology.

An industrial standard Plasma Technology DP800 radio frequency PECVD system was operated at 200 W with a 250 mTorr process pressure of methane gas maintained by a flow rate of 30 sccm. The chamber and electrodes were water cooled with the substrate table temperature maintained below 50 °C while the deposition ran continuously for 1 h. After completion, ~10 g of brown colored dust was collected from the floor adjacent to the chamber wall. A small quantity of this was ultrasonically dispersed in toluene and then spread on a holey carbon support film of a gold electron microscopy finder grid. The morphology and microstructure of the particles were analyzed using a JEOL 4000 EX(II) high resolution transmission electron microscope (HRTEM) operated at 400 kV with a LaB_6 filament. High resolution images were obtained at Scherzer defocus with a point-to-point resolution better than 1.7 Å. The chemical content of the identified particles was investigated using a 200 kV JEOL 2010 HRTEM equipped with nanoprobe capabilities and a light-element energy dispersive x-ray (EDX) detector.

Approximately 5% of the dispersed particles and agglomerates captured on the grid were found to consist of compact aggregates containing graphitic crystallites. These appeared to be very similar to the material reportedly obtained by arc-discharge evaporation of graphite electrodes,[13] and EDX analysis confirmed that they were predominantly carbonaceous. Such aggregates were typically 1 to 2 μm across consisting typically of the order of a thousand nanoparticles; a general view and example of which we have published previously.[14] Incorporated in such aggregates were nanotubes varying in length from 100 to 300 nm with diameters in the range of 10–30 nm and internal tube diameters of 2–5 nm, leading to walls consisting of 5–30 graphene layers. A striking example of a well developed carbon nanotube found in our sample is shown in Fig. 1. It is a multiwalled variant with a region of successively terminated internal tubes exhibiting curved graphene layers indicative of

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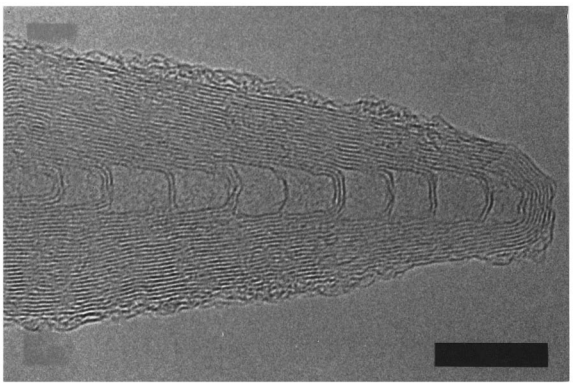

FIG. 1. High resolution transmission electron microscopy image of a carbon nanotube seen in the dust generated using a radio-frequency plasma-enhanced chemical vapor deposition system. Of particular interest is the fact that such fullerene-like structures occur in these hitherto troublesome by-products of thin-film production. Scale bar =10 nm.

fullerene-like pentagonal defects in the hexagonal network. The end caps include triple, double, and single walls as have been seen by other investigators working with arc-discharge material,[15] and the tube exhibits a degree of crystalline imperfection and turbostrata within its walls. There is also an amorphous surface region of 2 to 3 monolayers which is not an uncommon feature of these materials.[16]

It should be noted that these structures have been formed in a much less energetic process when compared to the arc-discharge process. Preliminary measurements using an electrostatic probe equipped with a compensating electrode have shown that in the conditions described, the electron temperature in the plasma was ~2.4 eV. Further work is now being performed to characterize the plasma more fully and monitor changes that occur as particles nucleate within it.

A graphitic region of an aggregate with well developed and angular nanoparticles is illustrated in Fig. 2. The arrow indicates a circular fringe of ~10 Å in diameter believed to be a single fullerene molecule. It was relatively mobile under the electron beam suggesting that it was a discrete entity isolated from the neighboring graphitic fringes, and held in the vicinity by relatively weak Van der Waals forces. We are

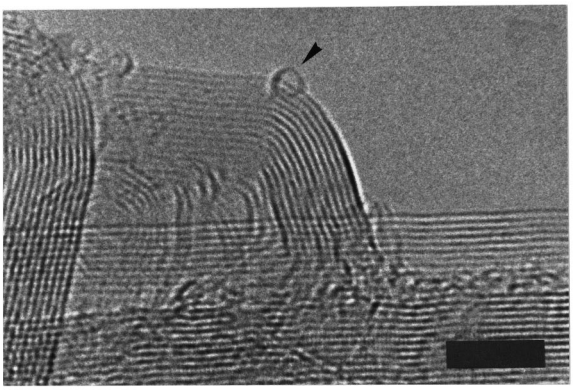

FIG. 2. An area of carbonaceous nanoparticles with a single C_{60} fullerene indicated by the arrow. This is believed to be the first occasion that visual evidence has been published showing that fullerene molecules can be generated at room temperature in a PECVD system using methane as the precursor gas. Although close examination of the fringes suggests that the electron beam was causing some damage to the molecule at the time of photographic exposure, its apparent mobility as a circular entity confirmed it was a discrete fullerene. Scale bar =5 nm.

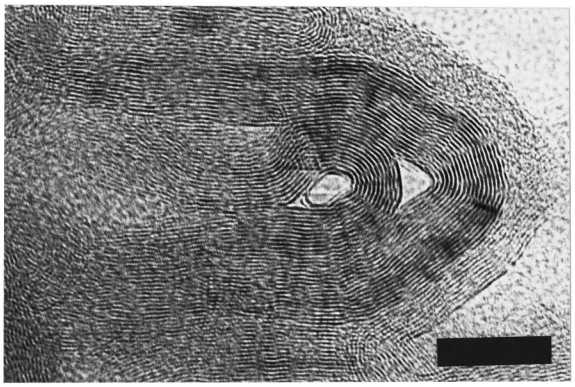

FIG. 3. A further striking example of fullerene-related material seen in the carbonaceous dust. The level of contrast exhibited by this phase object suggests that the graphene layers extend some distance perpendicular to the plane of the image. Scale bar =10 nm.

certain that this molecule did not form under the influence of the electron beam.[17] Indeed, the moderate electron-beam current density used in the HRTEM investigation of these structures had not previously been seen to create fullerene molecules elsewhere in the sample. We therefore believe that this molecule had been created during the PECVD deposition of the dust, and is the first visual evidence that we are aware of that confirms that fullerenes can be produced by this low-temperature method using a gaseous source of carbon, namely methane.

The fringes that we believe are behind the indicated fullerene in Fig. 2 form part of a large nanoparticle with curved ''onion-like'' corners and a high degree of order in the concentric graphene layers. Figure 3 illustrates another striking example of a nanoparticle containing highly curved and nested graphene layers. The high contrast in this photomicrograph suggests that the graphene layers extend perpendicular into the plane of the paper, and that the curvature may be more akin to that of a rolled-up carpet than that of the nanotube seen in Fig. 1. Hence, the conditions present during PECVD must have enabled graphene layers to both nucleate and then grow to a significant extent.

We hypothesize that these particles nucleated within the plasma, rather than on the electrodes, and that the carbon ions were forced into a hexagonal arrangement by coulombic forces which have been reported to account for macroscopic pseudocrystals generated in a similar plasma environment.[18] Being on a significantly smaller scale, this could accommodate the trigonal bonding that leads to the observed graphene layers. The net flow of gas to the cooler plasma edge would eventually allow the carbon aggregates to condense and form their final arrangement of nanotubes and nanoparticles. Further evidence that these particles nucleated in the plasma phase rather than on the electrodes of the system is provided by the observation of totally amorphous films grown on substrates placed on either electrode under these conditions.

Many particles were also found on the grid that consisted of curled amorphous fragments believed to be remnants of stress-relieved *a*-C:H film originally deposited on the upper driven electrode. These are thought to have spalled from the electrode, fallen into the plasma, and remained electrostatically levitated while being carried with the gas flow to the edge of the system. Eventually, away from the plasma

and under the influence of gravity and vortices from the gas flow, these particles fell to the chamber floor. These particles and flakes were totally amorphous in nature. It should be appreciated that the microscopy grids would probably be more efficient in the capture of these larger fragments than the compact fullerene-like aggregates and therefore a higher volume fraction of the latter could be expected.

By configuring a PECVD system for optimum dust generation in the plasma rather than by material spalling from the electrodes, it should be possible to develop an inexpensive, controlled, and reproducible technique to continuously produce large quantities of fullerene containing material. With further work, it may be feasible to improve the yield of one particular species, thereby removing the need for a secondary purification process. The findings we report in this initial investigation suggest that fullerene science and dusty plasmas have come full circle, and that the PECVD generated carbonaceous dust is itself technologically important and not just an inconvenient by-product of semiconductor thin-film processing.

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