JOURNAL OF MATERIALS SCIENCE 30 (1995) 4787–4792

A new technique for fullerene onion formation

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We present an original technique for growing large fullerene onions: carbon-ion implantation at high temperature into copper substrates. Used for carbon film growth (diamond or turbostratic carbon), this method is based on the immiscibility of carbon into copper and can produce an important density of giant carbon onions with size up to some micrometres which is the largest size observed up to now. We characterize these giant fullerenes by TEM, HRTEM and for the first time with AFM. On the basis of both experimental and numerical results we propose a mechanism of formation of the carbon onions during the implantation process.

1. Introduction

Since the experimental discovery of C_{60} [1], and more generally of the hollow closed cages carbon species [2], some other regular forms of carbon having curved planes (nanotubes, carbon onions) have been a subject of interest. If the studies concerning the synthesis and the properties of nanotubes of carbon are numerous, only a few focus on the so called "fullerene onions". In spite of their production with the Ebbesen and Ajayan technique, as used for nanotube synthesis [3], their properties are not well known up to now. This kind of giant fullerenes was first observed by Iijima and coworkers with high resolution transmission electron microscopy (HRTEM) [4]. Later, Ugarte [5, 6] was able to produce fullerene onion growth by an intense electron irradiation of soot particles in a transmission electron microscope (TEM). This kind of synthesis is spectacular since the onion formation is directly imaged on the screen of the microscope. Unfortunately, such a technique cannot be applied to a macroscopic synthesis of carbon onions, a step that it will be necessary to reach in order to know, with some experimental evidence, their physical properties. Furthermore the size of these objects is not the same from one experiment to the other; many onions with the same number of spherical layers cannot be isolated for further characterizations.

We present here a technique used for carbon thin film growth that could become an interesting method of studying fullerene onions. The technique we describe below was originally developed for the synthesis of single crystalline diamond thin films. It is based on two ideas: carbon and copper are immiscible, diamond and copper have a very close lattice constant and a close unit cell (f.c.c.). During a carbon-ion implantation into a hot copper substrate, the implanted carbon atoms will diffuse toward the surface and segregate. The copper substrate can act as a mould during out-diffusion of carbon atoms and one can expect an heteroepitaxial growth of a single crystalline diamond thin film on the copper substrate. The basic phenomena that take place in these experiments are not known but are of great interest since single crystalline diamond thin film, turbostratic carbon thin film, more or less crystallized, and now fullerene onions can be obtained by such a method [7–10].

2. Experimental procedure

We have performed 120 keV carbon ion implantations into polycrystalline copper substrates at high dose (5×10^{17} cm^{-2}) and high temperatures ($700\,^\circ\mathrm{C} \leqslant T \leqslant 1000\,^\circ\mathrm{C}$) with various fluxes ($0.95 \times 10^{13}$ cm^{-2} s^{-1} $\leqslant$ flux $\leqslant 3.3 \times 10^{13}$ cm$^{-2} \times$ s^{-1}) in order to characterize the microstructure of the surface layer formed by this process and to study the influence of the flux and the temperature. The copper substrates (2.8 mm in diameter) were first mechanically polished (diamond paste 0.25 μm), annealed in vacuum (10^{-4} Pa) at 980 °C for 6 h to produce grain growth (~200 μm) and then positioned on a little furnace in the implantor (see Fig. 1). A cryogenic vacuum better than 10^{-5} Pa is obtained during the temperatures rises and the carbon ion implantations. After the experiments we characterized the thin surface layers TEM, HRTEM and atomic force microscopy (AFM).

3. Results and discussion

Fig. 2 gives a typical example of a bright field TEM plane view observation showing numerous micrograins which are often circular, embedded in a uniform surface layer. The microstructure of the uniform layer (here turbostratic carbon layer) has been the subject of some previous studies [7–10] and we focus here on the circular micrograins formation. The images of HRTEM obtained on these micrograins exhibit circular planes of carbon. As shown in Fig. 3 where a micrograin with about 80 circular planes can be seen, a giant fullerene onion has been formed. The

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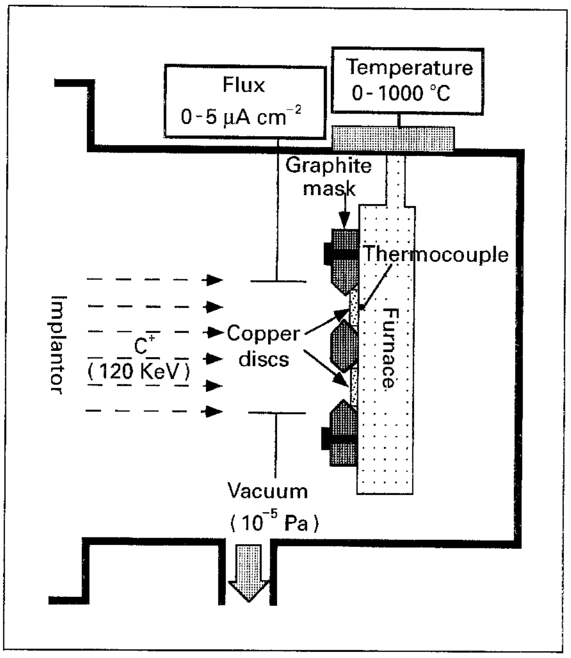

Figure 1 Experimental equipment for the carbon-ion implantations into hot copper substrates. The same energy (120 keV) and doses (5×10^{17} cm^{-2}) have been chosen for all the experiments.

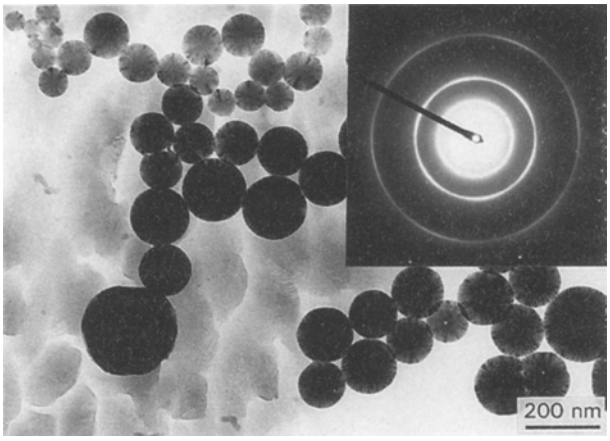

Figure 2 Plan view TEM micrograph (bright field) and its corresponding electron diffraction pattern of a carbon layer formed by a carbon-ion implantation into copper at 800 °C with a flux = 1.8×10^{13} cm^{-2} s^{-1}. A uniform carbon layer (turbostratic carbon) coexists with spherical micrograins (fullerene onions).

calculated interlayer distance is 0.343 nm calculated by the selected area electron diffraction and by the direct imaging of the planes by HRTEM. The spherical nature of these objects has been deduced from tilting experiments in TEM. The circular shape of the micrograins and the electron diffraction pattern remains unchanged when we tilt the samples (Fig. 4(a) and (b)). We can note that amorphous carbon is present between the two onions and that no interpenetration occurs between them. The three-dimensional form has been confirmed by some cross-sectional TEM observations of the copper surface as shown in Fig. 5 where an approximately spherical micrograin embedded in the uniform carbon layer can be seen.

The spherical form and the very important size of the micrograins (the majority of them have a diameter larger than 50 nm) allow us to observe them unambiguously by AFM. The images obtained by AFM confirm the presence of the micrograins on the surface of the copper substrate. Fig. 6 gives an example of a copper surface area where an important density of carbon onions is observed. Some micrograins larger than 1 μm are identified on the images on all the samples we study by AFM. Such an important size has never been observed for fullerene onions to our knowledge. TEM and AFM studies show that isolated onions as well as coagulation of many of them occur on the copper surface after all the experiments we performed. We can note here that the variations from area to area of the density of the onions seems to be not related to the copper substrate. The same variations occur on copper grains exhibiting different crystallographic orientations. The agglomeration of many onions appears randomly and is not especially located above a copper grain boundary. In parallel to these high temperature carbon ion implantations into copper, we perform room temperature implantations with the same parameters. Some further annealings at 700 and 900 °C have been carried out and characterized. Only a uniform layer of polycrystalline graphite has been synthesized and no onions were detected. These experiments indicate that, even at high temperature, the irradiation effects are necessary for the creation of the onions.

Some assumptions can be made after these observations on the way these onions are formed. During implantation at an elevated temperature, the implanted carbon atoms diffuse toward the surface driven by the chemical gradient force. Without carbon segregation in the volume of the copper substrate, the isolated carbon atoms reach the copper surface one after one. Especially at the beginning of the implantation, when no carbon aggregates are formed on the substrate, the carbon atoms will reach the surface, randomly dispersed. There they will segregate to form a carbon monolayer. As the C–Cu bonds are very weak [9, 10], C–C bonds are formed without any memory of the crystallographic orientation of the copper substrate. This means that no epitaxy occurs between the carbon monolayer and the substrate. This assumption is supported by the fact that no relationships exist between the copper and the uniform layer orientations [9, 10]. Furthermore, the uniform layer at the end of the experiments is a layer of turbostratic graphite (the basal planes of the hexagons of the graphite phase are parallel to the surface and randomly oriented around the c-axis of the graphite unit cell). The surface segregation thus allows the formation of planes of carbon with many carbon hexagons randomly oriented. As a consequence, some pentagons will be formed in these layers. In vacuum, we know that the presence of pentagons imposes a curvature of the carbon layer [2], but an adhesion force between the carbon layer and the copper surface exists. Thus some important stresses will be created in a flat carbon layer containing pentagons or heptagons. Here we can note that a curvature and a further closure of this layer will eliminate these stresses and also the dangling bonds. Thus the presence of these pentagons

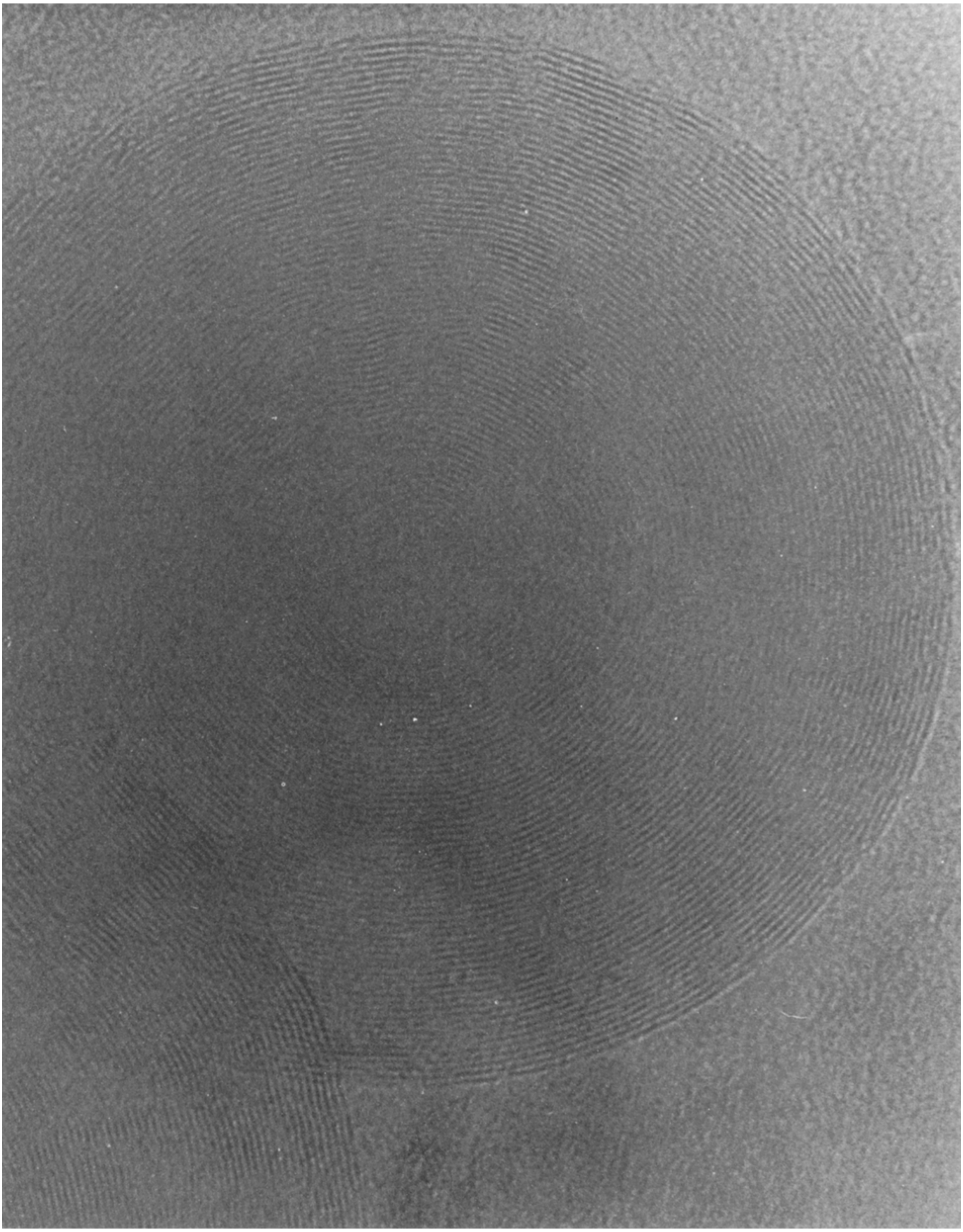

Figure 3 HRTEM image of a spherical carbon onion synthesized by carbon-ion implantation into copper at 800 °C with a flux $= 1.8 \times 10^{13}\ \mathrm{cm}^{-2}\,\mathrm{s}^{-1}$. The distance between the spherical layers is 0.343 nm.

will act as a driving force for the curvature. If this force is larger than the adhesion force a curvature will appear. The bonding between the carbon layer and the copper surface is very low and one can assume that the curvature happens under the experimental conditions. Once the curvature exists, as other carbon atoms still arrive by out-diffusion and surface diffusion, a closure will occur to eliminate the dangling bonds. These assumptions need further confirmation and it will be interesting to perform some carbon-ion implantations at high temperature with a low controlled dose on a very flat surface of copper. Some characterizations using AFM, STM or TEM will then provide new information. All the micrograins we studied were not

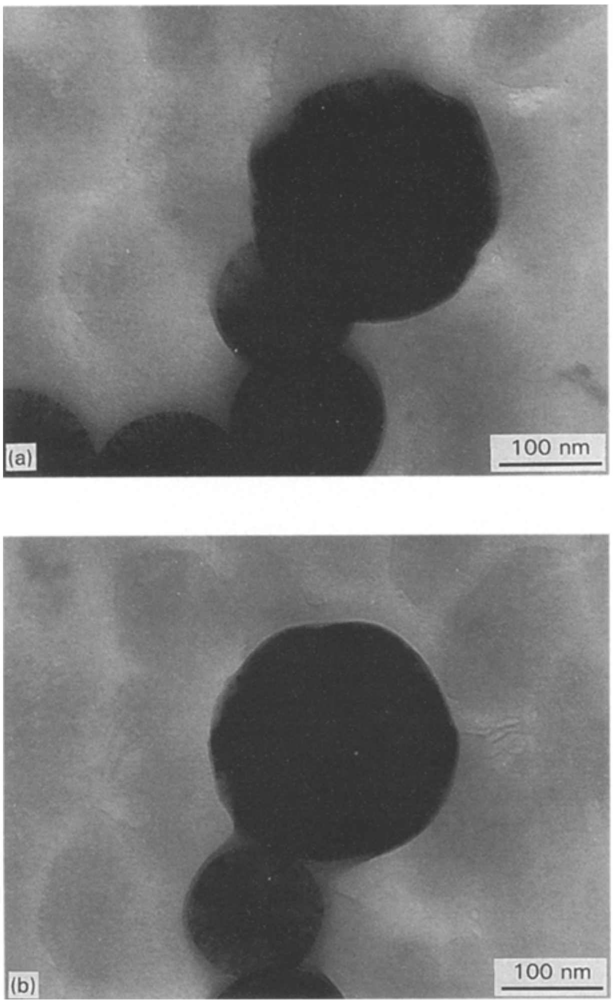

Figure 4 Plan view TEM micrograph (bright field) of a carbon layer formed by a carbon-ion implantation into copper at 800 °C with a flux $= 1.8 \times 10^{13}\ \mathrm{cm}^{-2}\,\mathrm{s}^{-1}$ with two different tilt positions in the TEM (a) $x = 0°$, $y = 0°$ (b) $x = 45°$, $y = 0°$.

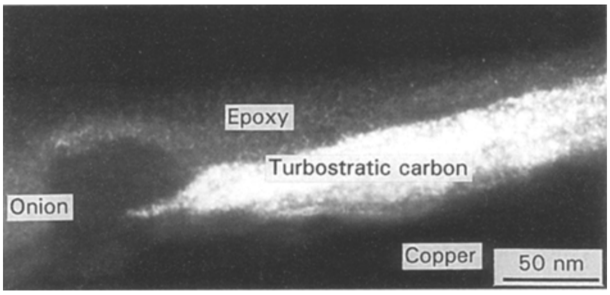

Figure 5 Cross-sectional TEM micrograph (dark field) of a carbon layer formed by carbon-ion implantation at 900 °C with a flux $= 3.3 \times 10^{13}\ \mathrm{cm}^{-2}\,\mathrm{s}^{-1}$. A spherical micrograin embedded in the turbostratic carbon layer can be clearly observed.

as spherical as those we can see in Fig. 2 or 3. Some negative curvatures, that can be attributed to some heptagons formation in the first closed cage, are visible in some micrograins. Unfortunately, as the size of the onions is in general larger than 50 nm, the thickness at the centre of the onions is too great for a clear identification of the first carbon planes by HRTEM.

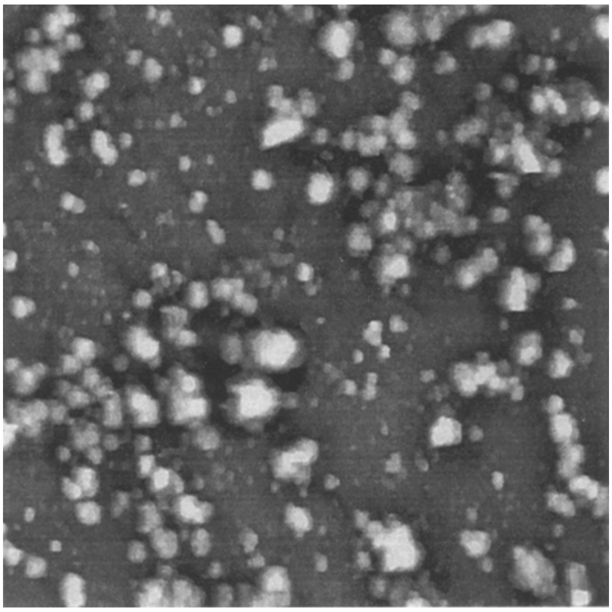

Figure 6 AFM image (size: 15 × 15 μm) of the substrate surface after the implantation. An important density of giant micrograins (fullerene onions) as well as the non-uniformity of their size is visible. The non-circular shape of some onions is an experimental artefact that comes from the shape of the AFM tip.

As some curved layers or closed cages are formed, some of the other carbon atoms that diffuse toward the surface will join them. Furthermore carbon clusters formed on the surface will modify the driving force of diffusion since carbon atoms that diffuse will be attracted by these aggregates. We can note that the surface diffusion is also enhanced by the irradiation effects and a rapid growth of the onions is made easier. These assumptions are supported by some quantitative approximations that can be made. If D_i is the diameter of the i^{th} spherical layer of an onion, this layer contains $I = 60(D_i/7.1)^2$ carbon atoms [5]. If an onion contains n spherical layers, the total number of carbon atoms present in this onion is given by

$$N = 1.19n[D_0^2] + 6.86D_0(n-1) + 7.84(n-1)(2n-1) \qquad (1)$$

where D_0 is the diameter of the first hollow closed carbon cage situated at the centre of the onion and with an interlayer distance of 0.343 nm. Table I gives some numerical results of the total number of carbon atoms present in an onion as a function of the number of spherical layers and of D_0. The column entitled "Dose" corresponds to the number of carbon atoms per square centimetre necessary to build the corresponding onion by assuming that all the carbon atoms of the onion come from the copper cylinder situated below the onion. As many onions have a size bigger than 100 nm and because the experimental dose is $5 \times 10^{17}\ \mathrm{cm}^{-2}$ we see that a diffusion towards the aggregates has occurred during the process and that the onion formation occurred at the beginning or during the implantation but not at the end of it. The growth mechanism of the giant onions will so appear when some carbon atoms will reach the closed cages. A spiral formation, as proposed by Kroto and McKay [12], or an epitaxy can occur for the growth of the onion. On this point, the presence of an amorphous layer on the surface of many onions provide other

TABLE I Evolution of the number of carbon atoms, N, present in an onion and of the radius R of this onion with the number n of spherical carbon layers and with D_0, the diameter of the first carbon cage

	$D_0 = 0.71$ nm			$D_0 = 1$ nm		
n	R (nm)	N	Dose (cm^{-2})	R (nm)	N	Dose (cm^{-2})
10	3.78	2.18×10^4	4.84×10^{16}	4.15	2.42×10^4	5.05×10^{16}
20	7.21	1.62×10^5	9.89×10^{16}	7.3	1.69×10^5	1.01×10^{17}
50	17.5	2.41×10^6	2.5×10^{17}	17.5	2.43×10^6	2.53×10^{17}
100	34.66	1.9×10^7	5.03×10^{17}	3.45	1.89×10^7	5.05×10^{17}
200	68.96	1.51×10^8	1.01×10^{18}	68.5	1.19×10^8	1.01×10^{18}
300	103.26	5.07×10^8	1.51×10^{18}	102.5	5×10^8	1.52×10^{18}
400	137.56	1.2×10^9	2.02×10^{18}	136.5	1.18×10^9	2.02×10^{18}

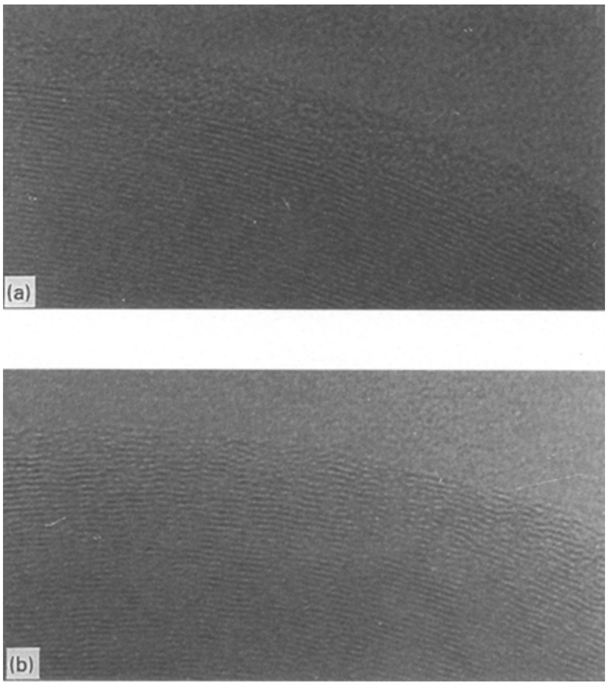

Figure 7 HRTEM image of the surface of a carbon onion. The distance between the curved layers is 0.343 nm. (a) An area with an amorphous layer where a less random organization can be seen on the internal face of the ribbon. (b) The same area after 2 min of irradiation by an intense electron beam. A crystallization of the amorphous layer occurs in epitaxy with the internal crystallized spherical layers.

informations. Fig. 7(a) shows a typical example of an onion surface where a less random organization of the carbon atoms is visible on the internal face of this amorphous ribbon, indicating that the formation of these circular planes occurs via an external atomic transport or rearrangement. In HRTEM, under normal working conditions, an amorphization of the onions appears after a few minutes. In contrast, when we focalize the electron beam in the microscope, as already proposed by Ugarte [5, 6], a crystallization of the amorphous layer occurs (Fig. 7(b)). The new carbon curved planes so formed allow the onion growth to continue on the area that has been irradiated. The presence of an amorphous layer on the onions, and between them, as already noted, can be a source of carbon atoms for the growth of the carbon onions.

Even if some assumptions have to be made to explain the formation of the onions, the implantation technique we use could be an interesting method for some further studies on onion formation and growth. With the experimental equipment we described above, a very well-controlled dose, ion flux, ion energy and substrate temperature can be chosen. Thus a more detailed study could be made on the formation of these onions. Such a study may produce some interesting new results since a comprehension of the basic mechanisms that occur during the onion formation will perhaps allow a better control of their size and then a better characterization of their physical properties. Moreover, fullerene compounds containing copper can now be thought of. For example, ion-beam assisted co-evaporation of copper and carbon will perhaps lead to some new mixed copper-fullerene compounds with new properties.

4. Conclusions

The results presented here show, for the first time to our knowledge, that carbon onions can be obtained by high temperature carbon-ion implantations into copper. TEM, HRTEM and AFM show that an important density of these onions appear on the copper at the end of all the implantations we performed. Some assumptions can be made on the way these onions are created. The presence of some pentagons and the elimination of the dangling bonds provide a driven force for the curvature and the closure of some carbon layers. As many carbon atoms can reach the closed cages by out-diffusion or surface diffusion, a growth of the onions by epitaxy appears. Some further high temperature carbon-ion implantations into copper with low controlled doses would bring new and interesting results.

Acknowledgments

The authors want to thank M. F. Denanot for performing TEM experiments and J. C. Girard for AFM images.

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Received 22 December 1994
and accepted 11 April 1995