Mechanisms involved in the formation of onionlike carbon nanostructures synthesized by ion implantation at high temperature

Th. Cabioc'h, E. Thune, and M. Jaouen
Laboratoire de Métallurgie Physique, Université de Poitiers, UMR6630 CNRS, SP2MI, Téléport 2, Bd Pierre et Marie Curie, Boite Postale 30179, 86962 Futuroscope Cedex, France
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The origin of the formation of multishell fullerenes (carbon onions) produced by carbon ion-implantations performed at high-temperature into silver is discussed on the basis of high-resolution transmission electron microscopy observations. For low carbon fluences, one observes the formation inside the silver matrix of poorly organized carbon nanostructures the shape of which is roughly spherical. They progressively evolve towards perfect onionlike structures when the implanted carbon fluence increases. The catalytic effect of silver, which lowers the graphitization temperature of the carbon, the irradiation-induced displacements of the carbon atoms, and the effect of the temperature are proposed to be the key mechanisms that control the formation of the onionlike structures observed in such experiments.

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Onionlike carbon nanostructures, also called carbon onions, belong to the family of fullerene-related materials and are generally described as constituted of concentric spherical carbon layers. After the discovery of a reproducible technique to achieve their formation,[1] the literature devoted to this new kind of nanostructure mainly focused on their spherical structure. It was first proposed that every spherical layer was composed of carbon hexagons and pentagons.[2–4] More recently it was demonstrated that introducing heptagon-pentagon pairs better explained the spherical shape.[5–8] Furthermore, it has been theoretically proposed that such a structure could be considered as the most stable one as far as carbon nanostructures containing some hundreds, or thousands, of carbon atoms are considered.[9–11]

In parallel to these theoretical investigations, new efficient techniques were proposed for the synthesis of carbon onions.[12–14] Among all of them, the ion-implantation technique can be considered as one of the most powerful since it allows one to produce individual, well spherical carbon onions which size can be adjusted by varying the implantation parameters.[15,16] The usefulness of this method for producing carbon onions has already been discussed elsewhere, but their nucleation and growth mechanisms remain unclear. Indeed, it has been recently shown that carbon onions synthesized by ion implantation into silver (or copper) nucleate and grow inside the bulk of the metallic substrate.[17,18] As for the formation of rare-gas bubbles inside materials,[19] the formation of carbon nanostructures inside copper and silver can simply be attributed to the carbon precipitation into the metallic host with which carbon is poorly miscible. Therefore, the formation of carbon nanostructures embedded inside the metal can be viewed as a conventional dissolution-precipitation mechanism governed by the thermodynamic of the system. Nevertheless, the origin of the formation during the implantation process of such an original structure as the onion one has never been entirely addressed.

Up to now, the formation of carbon onions has generally been obtained under various, but often extremes, conditions. For instance, very high temperatures must be reached to transform diamond nanoparticles[13] or carbon black aggregates[14] into onionlike structures. In the same way, a long exposure to intense electron (or ion) beams is necessary to achieve the transformation of carbon nanostructures into carbon onions.[1] In this last case, it has been demonstrated that the numerous displacements induced by the elastic collisions between the incident energetic electrons and the carbon atoms are responsible for the progressive transformation of different carbon nanoparticles towards the most stable structure: that is, the carbon onions.[20,21]

To better understand the mechanisms that control the formation of carbon onions produced by the ion-implantation technique, low-fluence carbon ion implantations (10^{16}–10^{17} ions cm^{-2}) were performed into silver substrates at various temperatures (400–700 °C). Polycrystalline Ag samples, the purity of which is better than 99.99%, were fixed on a furnace mounted in an implantation chamber. A commercial apparatus from the EATON Co. was used to perform the implantation experiments. The ion energy was equal to 120 keV and the ion beam current density was kept constant ($\sim$15 mA cm^{-2}). The structure of the carbon nanostructures so obtained is analyzed using high-resolution transmission electron microscopy (HRTEM) observations performed at room temperature with a JEOL 3010 microscope working at 300 kV. To reach the electron transparency, the backside of the samples was thinned using an electrochemical polishing for plane-view observations whereas a conventional preparation of the samples was achieved for cross-sectional observations: the substrates were sticked together, cut, mechanically polished, and finally thinned with ion milling (Ar^+ ions of 2.5 keV).

Carbon and silver are very poorly miscible[22] and carbon atoms implanted far enough from the silver surface will precipitate in the bulk. One can thus expect the formation of a carbon precipitate the shape of which is spherical to minimize the interface energy. Figure 1 shows a typical HRTEM micrography of the nanostructures that are formed inside the bulk silver substrate after an implantation of 120 keV carbon ions performed at 500 °C with a low fluence (10^{16}ions cm^{-2}). One can easily observes that the so-

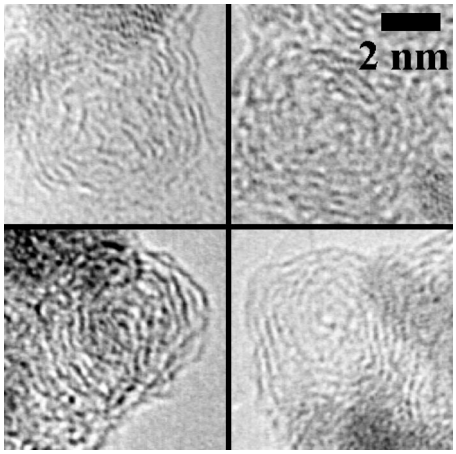

FIG. 1. HRTEM micrography of disordered carbon nanostructures obtained after a 120 keV carbon ion implantation performed at 600 °C (fluence: 10^{16} ions cm^{-2})

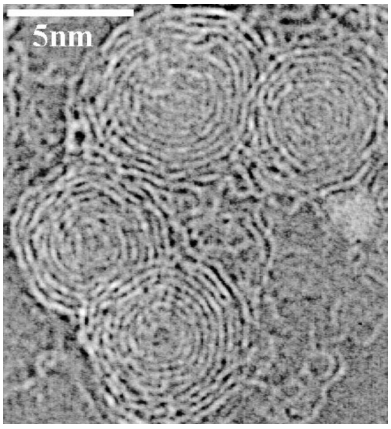

FIG. 2. HRTEM micrography of onionlike structures obtained after a 120 keV carbon ion implantation performed at 500 °C (fluence: 3×10^{16} ions cm^{-2}).

obtained structures are almost spherical in shape and poorly organized. Onionlike structures can be identified in some places, but most of them are very defective. At this stage, we want to outline that such nanostructures could correspond to defective onions formed during the implantation process but which have been progressively transformed into less-organized nanostructure when the implantation process stopped. Indeed, it has been demonstrated that defective carbon onions are unstable and that they progressively evolve towards poorly organized nanostructures[20,21] such as those shown in Fig. 1. Furthermore, when such nanostructures are annealed for 1 h at 850 °C in vacuum, almost perfect onionlike structures are obtained (not shown here). It is interesting to note that such an annealing temperature is much more lower than those usually used to transform carbon structure such as carbon black particles into carbon onions.[14] On the basis of these observations, we can thus conclude that the nanostructures obtained at the beginning of the implantation experiment (e.g., for a low fluence) are defective onions.

The fact that the carbon precipitates that formed inside the bulk of silver substrates adopt quite immediately an onionlike structure could appear at first surprising. We propose that such a particular organization of the first formed graphene sheets is promoted by a catalytic effect of silver that will lower the temperature needed for the carbon graphitization. Indeed, it is well documented that some metals, such as Ni,[23] Co,[24] or Ag,[25] promote the transformation of carbon into graphite at quite low temperatures (300–500°C). One of the most interesting phenomena that has been observed with these metals is the ability of carbon atoms to diffuse out of the metal and to precipitate at the surface where it forms graphene sheets parallel to the metallic surface, whatever the crystallographic orientation of the metal is. Such a result can be interpreted as follows: to minimize the interface energy, (0002) planes of graphite (or in our case graphene sheets), which have the lowest surface energy, are preferentially oriented parallel to the metallic surface. During the implantation process, when carbon atoms precipitate inside the silver matrix, one can expect the formation of carbon nanostructures which graphene sheets are parallel to the silver/carbon interface. These precipitates being spherical to minimize the interface energy, nanostructures having onionlike structures can thus spontaneously nucleate.

The influence of the temperature has also to be mentioned here since, as soon as temperatures lower than 500 °C are used to perform the carbon implantation into silver, the HRTEM observations (not shown hereby) do not revealed any onionlike structures, but only the presence of disorganized carbon nanostructures. This fact makes obvious that the mobility of carbon atoms must be high enough to allow the formation of well organized carbon layers. Such a temperature threshold was observed too for the synthesis of Ag-C thin films by a cosputtering technique[25]: graphene layers parallel to the surface of silver nanoparticles were always found only if the deposition process was performed at temperatures equal or higher than 500 °C.

When the implanted fluence increases, almost perfect onionlike structures can be identified. Furthermore, a growth of the carbon nanostructures can also be observed. Figure 2 shows a typical HRTEM micrograph obtained when the carbon implantation was performed with a fluence of 3×10^{16} ions cm^{-2} at 500 °C. Under these conditions, well circular dark contrasts, which correspond to the spherical graphene sheets, can easily be identified. To explain the evolution from a disorganized structure towards an onionlike one when the fluence increases, we propose that the displacements induced by the implanted carbon atoms play a major role. Indeed, during an ion implantation, the incoming energetic implanted carbon atoms can displace atoms from the target. To illustrate this effect, SRIM simulations[26] have been performed to estimate the number of displacement per atom (dpa) as a function of the fluence. Figure 3 shows the evolution of the number of dpa for a 120 keV carbon ion implantation with a fluence of 2×10^{16} ions cm^{-2} into a silver target containing 1% of carbon. This concentration corresponds to the one obtained close to the average projected range ($\sim$150 nm) after a carbon ion implantation of 10^{16} ions cm^{-2} into silver. Therefore, the number of dpa given in the Fig. 3 approximatively corresponds to that of the already implanted carbon atoms when the fluence increases from 10^{16} ions cm^{-2} to 3×10^{16} ions cm^{-2}. The carbon at-

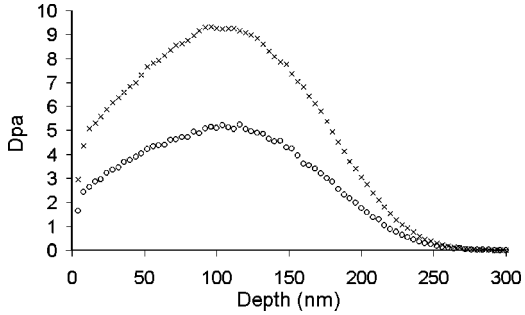

FIG. 3. SRIM simulation of the number of displacement per atom (carbon atoms, circles; silver atoms, crosses) as a function of the depth for a silver matrix containing 1 at.% of carbon atoms and submitted to a 120 keV carbon ion implantation (fluence: 2×10^{16} ions cm^{-2}).

oms inside the disorganized structures, as those shown in Fig. 1, are thus displaced but not more than 5 times when the fluence reaches a value of 3×10^{16} ions cm^{-2}. This value can be compared with the one calculated for the transformation of carbon nanostructures into carbon onions under electron beam irradiation in a TEM. For 200 keV electrons and a beam current density of $j=100$ A cm^{-2}, it gives 0.04 dpa s^{-1} at room temperature. The transformation of carbon nanostructures into carbon onions with such an electron beam needs at least 10 min. Thus, at least 20 dpa are needed to observe the progressive transformation of the carbon nanostructures into almost perfectly spherical carbon onions. Furthermore, much longer irradiation times are needed when the temperature is increased in the microscope ($\geqslant300°C$) because of the *in situ* annealing of interstitial-vacancy pairs due to the increased mobility of interstitials.[27] Therefore, several tens of dpa would be normally required to transform carbon nanostructures into carbon onions at the temperatures used in our implantation experiments ($>400\,°C$). Nevertheless, even if the number of dpa remains quite small during the ion-implantation experiments, it can explain the progressive transformation of a defective onionlike structure towards a well-organized one. To assess that point, it is interesting to consider that only the innermost shells are generally well organized, presenting few defects,

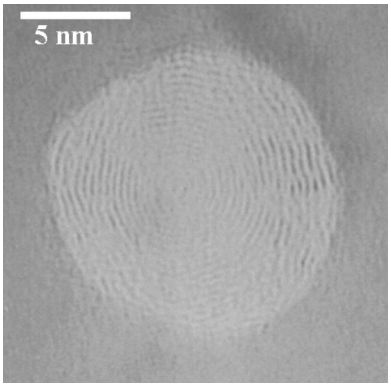

FIG. 4. Cross-sectional HRTEM micrography of an onionlike structure, embedded in the silver matrix, obtained after a 120 keV carbon ion implantation performed at 500 °C (fluence: 10^{17} ions cm^{-2}).

whereas the outermost shells present many defects such as disruptions of the graphene layer. This is confirmed by HRTEM observations (see Fig. 4) performed after implantations at more elevated fluences ranging from 5 to 30 $\times10^{16}$ ions cm^{-2}). Such an observation can easily be explained by considering that these outermost shells were the last to be formed by the precipitation of the new incoming implanted carbon atoms on the already formed carbon onions. In that case, only a few atomic displacements of the carbon atoms belonging to the outermost layers are required to induced atomic rearrangements leading to a better crystallization of the outer graphene layers. It is interesting to note that this last mechanism is in agreement with the formation of disordered graphene sheet that are parallel to the silver/carbon interface during the carbon precipitation. This point constitutes further evidence of the formation of defective onions at the beginning of the implantation process.

In summary, we have studied the origin of the formation of onionlike structures produced by carbon ion implantation at high temperature. From our analysis, we can conclude that the catalytic effect of silver that lowers the temperature for the carbon graphitization, the increased mobility of carbon atoms at high temperature, and the irradiation-induced displacements of the carbon atoms are responsible of the formation of such a particular structure.

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