Formation and transformation of carbon nanoparticles under electron irradiation

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This article reviews the phenomena occurring during irradiation of graphitic nanoparticles with high-energy electrons. A brief introduction to the physics of the interaction between energetic electrons and solids is given with particular emphasis on graphitic materials. Irradiation effects are discussed, starting from microscopic mechanisms that lead to structural alterations of the graphite lattice. It is shown how random displacements of the atoms and their subsequent rearrangements eventually lead to topological changes of the nanoparticles. Examples are the formation of carbon onions, morphological changes of carbon nanotubes, or the coalescence of fullerenes or nanotubes under electron irradiation. Irradiation-induced phase transformations in nanoparticles are discussed, e.g. the transformation of graphite to diamond, novel metal–carbon phases in nanocomposite materials or modified phase equilibria in metal crystals encapsulated in graphitic shells.

Keywords: carbon; nanostructures; electron microscopy; irradiation

1. Introduction

Until the discovery of the fullerenes in 1985 (Kroto et al. 1985), it was the general belief that graphitic materials always consist of more or less flat graphite layers. Although early electron microscopy studies of graphitic soot (Heidenreich et al. 1968) have already shown that graphitic filaments can be strongly curved, the ability of graphite to form a world of geometries (spheres, cylinders, cones or more complex shapes) was not recognized until fullerenes (Krätschmer et al. 1990) or nanotubes (Iijima 1991) were available in quantities for detailed structural determination.

Taking a flat sheet of a basal layer of graphite as a building block, it appears to be quite simple to build up these geometrical bodies with sizes of a few nanometres (Dresselhaus et al. 1996; Saito et al. 1999; Harris 1999). Tubes can be made just by rolling a layer cylindrically (against small steric stress) and closing dangling bonds at the seam. Spherical curvature needs the introduction of defects into the web of hexagons; 12 uniformly distributed pentagons ensure complete spherical closure. Heptagonal rings lead to negative (saddle-like) curvature. Due to the high energy of the covalent carbon–carbon bond, there is a strong tendency to close open bonds at the edge of an isolated sheet; accordingly, all closed graphitic structures are very

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stable. Once a cylindrically or spherically closed layer, e.g. a single-wall nanotube or a fullerene molecule, exists, further basal layers can be added from outside so that nested multi-shell graphitic particles are generated.

Since the beginning of the era of fullerenes and nanotubes, transmission electron microscopy has proved to be one of the most useful and versatile techniques for their characterization. However, during imaging or spectroscopy in the transmission electron microscope (TEM), the objects are inevitably exposed to irradiation with high-energy electrons. Above a certain threshold of the electron energy, the atoms of the object can be displaced from their positions so that structural transformations are unavoidable. Radiation damage of materials is a well-known subject in electron microscopy and has been studied for decades (Cosslett 1978; Urban 1979; Jung 1991). However, this phenomenon, which is normally unwelcome since it alters the structures of interest, revealed a variety of unexpected and highly interesting structural transformations in carbon nanoparticles (Banhart 1999). Nowadays, irradiation of graphitic structures is carried out deliberately, and many other predicted or unexpected transformations have been observed.

Electron irradiation is, thus, capable of cutting graphite layers and curving or bending the sheets by introducing topological defects. Therefore, existing particles are morphologically transformed, new particles are generated from graphitic precursors, or initially separate particles are welded together under the beam. Examples are the formation of carbon onions (Ugarte 1992), irradiation-induced encapsulation of foreign materials by graphitic shells (Banhart et al. 1998) or the welding of fullerene molecules (Smith & Luzzi 2001) or carbon nanotubes (Terrones et al. 2000, 2002). The advantage of such in situ transmission electron micrography studies is that structural modifications can be monitored in real time with atomic resolution. Heating or cooling stages allow us to vary the temperature of the objects during imaging and irradiation.

A more detailed review of radiation effects in carbon nanostructures has already been published (Banhart 1999). Here, an updated overview of the hitherto observed formation and transformation of graphitic nanoparticles as well as the coalescence of particles under electron irradiation is given with a certain emphasis on the author’s own work. Furthermore, irradiation-induced phase transformations in carbon or metal–carbon systems are treated. Although carbon nanoparticles have also been irradiated with ions, protons, neutrons or photons, this review concentrates on electron irradiation since this technique enables us to observe all structural changes in situ in the electron microscope.

2. The physics of irradiation effects

When a solid is irradiated with high-energy massive particles such as electrons, some mechanisms of energy transfer create persistent structural damage in the object while others leave the object unaltered (Cosslett 1978; Urban 1979; Jung 1991; Banhart 1999). Energy or momentum can be transferred either to the electron system or to the nuclei. Whereas electronic excitations such as ionization or bond breaking cause damage of insulators, metals or graphite are generally not affected due to the quenching of electronic damage by the presence of conduction electrons. Phonon excitation is not harmful unless the solid melts, but heating of typical carbon nanoparticles by electron beams in TEMs is normally negligible.
However, when the electron energy exceeds the threshold for atom displacements, atoms in the target can be knocked from their positions. Due to the rules of momentum conservation and the huge difference in masses, an electron can only transfer a small amount of its energy to a nucleus. The energy $T$ which is transferred is a function of the scattering angle:

$$T(\theta) = T_{\text{max}} \cos^2 \theta.$$  \hspace{1cm} (2.1)

Here $\theta$ is the angle between the initial direction of flight of the electron and the direction into which the nucleus is scattered. $T_{\text{max}}$ is the maximum energy which is transferred at $\theta = 0$ (head-on collision). Momentum conservation gives the following relationship between the energies of electron $E$ and nucleus $T$ for a central collision

$$T_{\text{max}} = \frac{2E(E + 2m_e c^2)}{Mc^2},$$  \hspace{1cm} (2.2)

where $m_e$ and $M$ are the masses of electron and nucleus, respectively, and $c$ is the speed of light. To create a stable interstitial–vacancy pair (that does not spontaneously recombine), the threshold electron energy $E_d$ is needed which leads to the transfer of the much lower displacement threshold energy $T_d$ to the nucleus. In graphite, for example, electrons of an energy of $E_d \approx 100$ keV are necessary to transfer the threshold energy of $T_d \approx 15$ eV to the nuclei (as will be discussed in §3, the threshold in graphite is anisotropic and depends on the direction of incidence relative to the lattice).

Of particular importance is the knowledge of the displacement cross-section which reflects the probability of a scattering event. The displacement rate is given by the product of the displacement cross-section and the beam current density. Generally the cross-section increases with increasing scattering angle because a central collision is less likely than a large-angle scattering event. The cross-section decreases with increasing transferred energy $T$; however, collision cascades, where a displaced atom has enough energy to displace further atoms, can lead to a net increase of the displacement rate with increasing energy $E$. Displacements close to the surface of a solid can lead to sputtering of atoms (Cherns et al. 1976; Jung 1991); here the threshold energy is slightly lower than for bulk displacements because atoms are more easily knocked out into an open space than onto an interstitial position.

A Frenkel pair (interstitial–vacancy), once created, can either recombine immediately or persist. The threshold energy needed to create a persistent Frenkel pair can be determined experimentally just by observing the onset of structural damage by electron microscopy. In densely packed lattices, it is more difficult to produce stable Frenkel pairs than it is in open structures. For example, the displacement threshold energies in diamond ($E_d \approx 200$ keV, $T_d \approx 30$ eV) are much higher than in graphite ($E_d \approx 100$ keV, $T_d \approx 15$ eV).

Single point defects (vacancies or interstitials) can either recombine with defects of opposite sign or form agglomerates with defects of the same sign. The evolution of the defect structure (Urban 1979) is governed by the defect mobilities, which generally show an Arrhenius-like function of the temperature. In most crystals, interstitials have much higher mobilities than vacancies, so that the interstitial migration determines the kinetics of defect annihilation or aggregation. The clustering of defects, in particular of interstitials, is of importance since this is directly accessible to observation in the electron microscope. At sufficiently high specimen temperatures, the
mobility of interstitials may be high enough to lead to fast recombination with vacancies before agglomeration takes place.

In the past two decades, irradiation effects have been discussed in the context of self-organization. Under intense electron irradiation, the systems are far from thermal equilibrium and highly dissipative since only a tiny amount of the energy which flows through the system is stored in lattice defects. In view of the high flux of free energy, we may assume that the export of entropy exceeds the internal entropy production; then the conditions for ordering (i.e. a decrease in entropy of the system) can be fulfilled. Symmetry breaking and the amplification of fluctuations may then lead to the formation of highly ordered metastable phases (Martin et al. 1993) or the formation of ordered defect arrangements (Seeger & Frank 1988; Seeger 1989). Self-organization in the sense of non-equilibrium thermodynamics plays an important role in the irradiation of graphitic nanoparticles.

3. Irradiation effects in the graphite lattice

Detailed experimental studies of graphite are difficult since no large single crystals are available. Studies of irradiation effects have been carried out extensively by using different polycrystalline materials or highly oriented pyrolytic graphite (HOPG). As a consequence, the data in the literature differ considerably; a compilation of earlier results was given by Kelly (1981) and Thrower & Mayer (1978). With the appearance of carbon nanoparticles, the renewed interest in graphitic structures has initiated further studies on radiation effects (Koike & Pedraza 1994; Zhou et al. 1994, Niwase 1995; Burden & Hutchison 1996; Chopra et al. 1996; Muto & Tanabe 1997; Banhart 1999; Smith & Luzzi 2001; Ewels et al. 2002, 2003; Telling et al. 2003; Lehtinen et al. 2003).

The displacement threshold energy in graphite is highly anisotropic (Crespi et al. 1996; Smith & Luzzi 2001); knocking carbon atoms onto interstitial positions is easier normal to the plane than it is in any direction parallel to the plane. However, this anisotropy is hardly observed when graphitic nanoparticles are irradiated. Firstly, the particles are curved so that in most possible geometries all possible directions of incidence prevail. Furthermore, when the beam energy clearly exceeds the displacement threshold, large-angle scattering events dominate due to their higher displacement cross-sections. The onset of damage is therefore observed when the first atoms are displaced, and these are the easiest displacements normal to the basal planes. Single-shell particles such as fullerenes or single-wall nanotubes are more easily damaged than multi-layer structures. Experimental studies of fullerenes revealed a displacement threshold electron energy \( E_d \) below 80 keV (Füller & Banhart 1996). For single-wall nanotubes, a value of 86 keV has been reported (Smith & Luzzi 2001). For multi-layer graphitic structures, the value is slightly higher, \( E_d \approx 100 \) keV, due to the limited space for interstitials between the layers.

Interstitials and vacancies play quite different roles in graphitic nanoparticles. Due to their high mobility, interstitials govern the dynamic processes, namely defect agglomeration and annealing kinetics. Vacancies, on the other hand, are almost immobile up to temperatures above 1000 °C but lead to structural modifications in the basal planes and hence to curvature and topological changes of the structure. The configuration of interstitials in graphite has been discussed controversially for decades. Meanwhile, first-principles calculations have given a refined picture that

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Figure 1. A divacancy in a graphite sheet (the two encircled atoms are removed) leads to a rearrangement of bonds so that the pentagons change their positions and the number of hexagons is reduced by one.

fits the experimental observations quite well (Heggie 1991; Telling et al. 2003; Ewels et al. 2002, 2003; Lehtinen et al. 2003; Krasheninnikov et al. 2004). Although the interstitials are located in the gallery between the layers, they form covalent bonds to one layer or both adjacent layers. This reduces their mobility parallel to the layers but opens the possibility of migration normal to the layers via site exchange.

The migration energies of interstitials and vacancies depend sensitively on their configurations. The experimentally determined migration energy of vacancies of 3 eV (Thrower & Mayer 1978) prevents their migration at moderate temperatures. The migration energy for interstitials is much smaller, but the bonding configuration of the interstitial between the layers (which again depends on the presence of vacancies or other defects such as non-six-membered rings) determines the mobility. If the temperature of graphitic specimens in the electron microscope is raised above 300–400 °C, no more radiation damage, visible as agglomeration of interstitials, is obtained. From this observation (Burden & Hutchison 1996; Banhart et al. 1997), an average migration energy of the interstitials slightly below 1 eV can be derived. Locally, the migration energy might be higher or lower (Lehtinen et al. 2003; Telling et al. 2003; Krasheninnikov et al. 2004), depending on the defect configuration.

An important topic is the attraction between two adjacent layers in graphite by the presence of interstitials or vacancies. The covalent bonding between two layers via an interstitial locally reduces the inter-layer distance. Even two vacancies in adjacent layers can lead to the formation of a bridge between the layers because a twofold coordinated atom next to the vacancy can protrude out of the plane and form a covalent bond to a protruding atom in the next layer (Telling et al. 2003).

The topology of graphitic particles is determined by the defect structure, in particular by the presence of vacancies. The arrangement of pentagons or heptagons can be changed locally by rearrangement of bonds or vacancy migration. Such rearrangement have been suggested by Stone & Wales (1986), for example, the transformation of four hexagons into two pentagons and two heptagons. An interstitial–vacancy pair can cause a Stone–Wales transformation. Another important transformation occurs when a divacancy is formed as shown in figure 1. Rearrangement leads to the migration of the pentagons, hence to a local change in curvature, and to the loss of one hexagon. This is believed to be an important process in electron irradiation of graphitic structures since it reduces the surface area of graphitic nanoparticles and locally changes their topology. In order to create new graphitic particles or to transform the topology of existing particles by electron irradiation, it is essential that

the rupture of basal planes and the agglomeration of interstitials is suppressed. This can be achieved by keeping the objects at temperatures above 300–400 °C (Banhart et al. 1997). Then, interstitial–vacancy recombination is fast enough so that local lattice destruction does not occur. However, rearrangements of the Stone–Wales type and curvature of graphite layers take place and new structures such as carbon onions or interconnected nanotubes can be obtained.

4. Topological transformations of carbon nanoparticles under irradiation

(a) Shape transformations

As we have seen in the preceding sections, irradiation of graphitic structures leads to the formation of vacancies which, in turn, create topological transformations. Therefore, isolated basal layers curve and bend under electron irradiation. Since radiation defects are created on random positions in the lattice, shape transformations of the layers are not uniform. However, as soon as dangling bonds from opposite edges of the curved sheets approach each other, closure of the bonds leads to a stabilized cylindrical or spherical object.

This process can be monitored under irradiation in the TEM. Isolated graphite layers bend or curl in such a way that eventually closed spherical fullerene-like cages are formed (Burden & Hutchison 1996; Füller & Banhart 1996). The local change of curvature becomes also apparent during the irradiation of single-wall nanotubes (Ajayan et al. 1993, 1998; Smith & Luzzi 2001). Straight cylinders develop a wavy surface, shrink in diameter and finally bend to such an extent that the tubes break. The defect evolution in single-wall nanotubes under irradiation has also been treated theoretically by simulations (Krasheninnikov & Nordlund 2001).

The situation is more complicated in three-dimensional graphitic crystals where several graphite layers are attached to each other by van der Waals interaction. Curvature of individual basal layers is hindered by adjacent layers. Frenkel pairs can effectively recombine and sputtering-induced loss of atoms is much smaller than in isolated layers. Indeed, TEM observations show that multi-shell particles such as polyhedral onion-like graphite grains or multi-wall nanotubes appear more stable under irradiation than their single-shell analogues. However, after extended periods of intense irradiation, multi-layer graphitic sheets bend and close upon themselves so that multi-shell onion-like spherical cages form as reported by Ugarte (1992). This observation initiated many further irradiation studies of carbon nanoparticles (Ugarte 1993b; Lulli et al. 1995; Zwanger et al. 1996; Ru et al. 1996; Ozawa et al. 2002; Troiani et al. 2003). The total electron dose needed for the complete transformation of graphitic material to onions is quite high. Depending on the morphology of the precursor material, electron-beam current densities of the order of magnitude 100 A cm$^{-2}$ have to be applied for $10^3–10^4$ s. The structure of spherical carbon onions was modelled in several theoretical studies (Terrones & Terrones 1996, 1997); one possible model is shown in figure 2.

When carbon onions are generated under irradiation at temperatures above 400 °C (i.e. in the regime where no extended radiation defects occur), several unique phenomena can be observed. The spherical shells are highly perfect and the layer spacing in the c-direction decreases towards the centre of the onions to values as small as
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Figure 2. Model of a spherical carbon onion consisting of pentagons, hexagons and heptagons. (Reproduced with permission from M. Terrones.)

Figure 3. A carbon onion is attached by a single graphite sheet to an encapsulate of a cobalt crystal within graphitic shells. Local compression effects can be deduced from the graphite inter-layer spacings (indicated) and lattice distortions in graphite and cobalt.

0.22 nm (Banhart et al. 1997). This self-compression of carbon onions under irradiation can be explained by the continuous sputtering of atoms from the outer shells, closure of divacancies, the reduction of the number of hexagons and the concomitant reduction of surface area. The diminishing surface generates ‘surface tension’, which

can be enormous due to the extreme strength of each graphite shell. Zaiser (1999) has shown that the migration of interstitials radially along the pressure gradient towards the surface leads to the increase of pressure towards the centre. Figure 3 shows an example of a compressed carbon onion which is attached by a single graphite sheet to an encapsulated cobalt particle. Even the forces emerging from the graphite sheet manifest themselves in locally reduced inter-layer distances and bending effects. We can assume that the self-compression is further promoted by the inter-layer attraction due to the presence of interstitials between the layers or vacancies in both layers (Telling et al. 2003). The pressure in the centre of carbon onions can reach values high enough for the nucleation of diamond crystals (Banhart & Ajayan 1996).

Carbon onions have been considered as possible constituents of interstellar dust (Henning & Salama 1998). TEM studies of pre-solar carbon meteorites showed the presence of carbon onions (Smith & Buseck 1981). Recently, experimental evidence for carbon onions as the origin of the 217.5 nm interstellar absorption feature have been presented (Chhowalla et al. 2003). One may speculate about the role of irradiation with particles which occurs in the environment of stars (or much more violently around supernovae) during the formation of carbon onions in space. The question whether the formation of interstellar diamond grains (Ott 1993) can be explained by a nucleation mechanism inside carbon onions deserves further studies.

(b) Coalescence of nanoparticles

Densely packed fullerene molecules within a fullerite crystal or single-wall nanotubes within a bundle are stable although merging of these objects into larger cages or cylinders with less curvature would lower the energy of the systems. However, the coalescence of two adjacent fullerene cages or single-wall nanotubes can occur once the structures are defective to such an extent that a certain number of vacancies and dangling bonds exist close to the point of contact. This kind of damage can be created by electron irradiation. The driving force for the coalescence is the smaller curvature, thus the decrease in tension as the particles grow larger.

Indications for the coalescence of C\textsubscript{60} molecules within a crystal have already been observed in early TEM studies of fullerites (Wang & Buseck 1991). More detailed work showed how two or more C\textsubscript{60} molecules merge into a larger irregular cage (Füller & Banhart 1996). Meanwhile, single-wall nanotubes can be filled with C\textsubscript{60} molecules so that objects resembling ‘pea pods’ are generated (Smith et al. 1998). In these arrangements, the C\textsubscript{60} molecules are confined in the inner hollow of the nanotube. Heating or irradiation can be carried out and the behaviour of the fullerenes can be observed by TEM. The result of such an irradiation study is shown in figure 4 (Hernández et al. 2003). It is apparent that the spherical molecules tend to merge and form elliptical cages. After longer irradiation (not shown here), all cages within the tube coalesce so that a double-wall nanotube is left.

Single-wall nanotubes have a strong tendency to occur in bundles of parallel tubes during catalyst-assisted high-temperature synthesis. Irradiation of such a bundle with electrons can lead to the coalescence of two parallel tubes so that a tube with double diameter is generated (Terrones et al. 2000). This is shown in figure 5; here the bundle appears in cross-section where its axis is normal to the image plane. Since single-wall tubes are rapidly damaged by the electron beam at room temperature, these experiments were carried out at temperatures of 600–800 °C. The necessity

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Figure 4. Coalescence of fullerene molecules within a nanotube ('pea pod') under electron irradiation. (Reproduced with permission from M. Terrones.)

Figure 5. Coalescence of two parallel single-wall nanotubes (arrowed) within a bundle under electron irradiation: (a) before and (b) after electron irradiation at $T = 800$ °C.

of vacancies and dangling bonds for the merging process has been confirmed by molecular dynamics simulations (Terrones et al. 2000). An important precondition for the coalescence of two tubes is that both tubes have the same chirality.

Another way of joining nanotubes is to establish a junction between crossing tubes. This is of interest in view of possible applications of nanotubes as devices or conducting nanowires in electronics. Two crossing nanotubes normally would not join, even at high temperature, because the structure of a junction, containing heptagons in the regions of negative curvature, is less stable than two perfect individual tubes. Again, the presence of vacancies and dangling bonds at the point of contact can induce the formation of a junction. This has been achieved in an in situ experiment in the TEM (figure 6) and confirmed by molecular dynamics simulations (Terrones et al. 2002). Irradiation of two crossing single-wall nanotubes with a certain electron dose leads to the formation of bonds as links between the tubes and, successively, to

the merging of the tubes. Irradiation with ions was also predicted to be able to form junctions between single-wall nanotubes (Krasheninnikov et al. 2002).

5. Irradiation effects in nanocomposite particles

Graphitic nanoparticles can be combined with other crystalline materials such as metallic or inorganic nanocrystals in ‘core–shell’ arrangements (Banhart et al. 2001). For example, a metallic core of a few nanometres in diameter can be encapsulated by graphitic shells. Cylindrical arrangements, i.e. nanotubes containing metallic nanowires, as well as spherical objects, where a carbon onion encapsulates a metal crystal, have been synthesized. Electron irradiation of such metal–carbon nanocomposite structures has shown to result in several unexpected phenomena.

Isolated metal crystals with sizes in the nanometre range are normally not much affected by electron irradiation. The proximity of surfaces and the instability of dislocations leads to a rapid annealing of defects. By contrast, graphitic structures curve and form onion-like particles under irradiation. If a mixture of metal crystals and graphitic material (e.g. a by-product of metal-catalysed nanotube synthesis) is irradiated with electrons, the graphitic layers curve and bend around the metal crystals and eventually form spherically closed encapsulates of metal cores in graphitic shells. This irradiation-induced encapsulation is an alternative to the formation of encapsulates during co-evaporation of metal and carbon. Several metals (Al, Fe, Co, Ni, Au, Pd, Sn, Pb, or Bi) have been encapsulated in carbon onions under irradiation (Ugarte 1993a; Banhart et al. 1998, 2000, 2003; Oku et al. 1998; Xu & Tanaka 1998). Examples are shown in figures 7 and 10.

The property of carbon onions to self-compress under irradiation becomes also apparent when metal crystals are encapsulated in their cores. As shown in figure 7, such an encapsulate changes in size and composition if exposed to sustained electron irradiation. Although the metal crystals are confined within the graphite shells,
they shrink in size until they vanish completely (Banhart et al. 1998). Concomitantly, the carbon onions collapse. Since metal atoms can hardly diffuse through hexagonal rings in the graphite lattice, the only possibility of metal atoms reaching the surface of the onions is diffusion along the pressure gradient via vacancies and temporary site occupancy in the graphite lattice. Further studies of the diffusion of metal atoms through graphitic networks showed that new metal–carbon phases appear when metal atoms are ‘forced’ into the graphite lattice. The migration of nickel atoms through compressed carbon onions induced the formation of at least two hitherto unknown carbon–nickel phases (Banhart et al. 2000). As shown in figure 8, ordered arrangements of carbon and nickel atoms appear either within the curved shells or as isolated crystallites. However, these phases are presumably metastable configurations that are formed under the non-equilibrium conditions of irradiation.

Irradiation effects on foreign materials inside nanotubes have also been reported. For example, SnO crystals in multi-shell nanotubes are seen to migrate and rearrange under electron irradiation (Sloan et al. 1997). Other studies of metal-filled nanotubes show rearrangements and other structural changes under electron irradiation (Kiang 2000; Ding & Wang 2002).

6. Phase transformations in nanoparticles under irradiation

It has been known for a long time that electron irradiation of solids can cause phase transformations. The relaxation of a metastable into a stable phase under the electron beam can be used, for example, to synthesize carbon nanotubes from less stable
carbon phases. Irradiation of a polyyne-containing precursor can lead to the growth of carbon nanotubes, a process which has been monitored in situ in a TEM (Yasuda et al. 2002). The opposite process, i.e. the formation of metastable from stable phases by electron irradiation, is of interest because the principles of self-organization in dissipative systems can be applied (Martin et al. 1993). The nucleation and growth of diamond crystals in carbon onions under electron irradiation as shown in figure 9 (Banhart & Ajayan 1996; Banhart 1997) is an example of the irradiation-induced formation of a highly ordered but metastable phase.

The nucleation of diamond cores in carbon onions is observed when the onions are exposed to sustained electron irradiation above 400 \degree C (an upper temperature limit has not been explored yet). Several aspects are believed to be responsible for the nucleation. Firstly, the pressure in the centre of the onion is quite high; rough estimates yield pressures clearly above 10 GPa. A second contribution is due to an increase of the diamond-like sp\(^3\) type of bonding when sp\(^2\)-bonded graphite layers are increasingly curved. Furthermore, cross-links between the layers exist with local covalent sp\(^3\) character when the graphitic layers are defective.

Once nucleated, the diamond crystals in carbon onions are observed to grow, although the pressure is gradually decreasing (Banhart 1997). Further studies showed that the irradiation-induced phase transformation of graphite to diamond can be carried out on a general scale, even when no pressure is applied (Lyutovich & Banhart 1999). The application of non-equilibrium thermodynamics (Zaiser & Banhart 1997) and more refined experimental work (Zaiser et al. 2000) explained the growth of diamond at the expense of graphite as a reversal of phase stability under the conditions of irradiation in the temperature range 300–1000 \degree C (under normal irradiation intensities in the TEM). The reverse transformation, i.e. from diamond to graphite, can be carried out by irradiation either at temperatures below 300 \degree C or above 1000 \degree C. For example, nanodiamonds were converted to carbon onions by electron irradiation at room temperature (Qin & Iijima 1996; Roddatis et al. 2002).

Carbon onions can also be used as ‘nanolaboratories’ to induce phase transformations in other materials that are encapsulated in their shell structure or in their cores. The generation of a new carbon-nickel phase as mentioned in §5 can serve as an example. If pressure is exerted on an encapsulated material, phase equilibria can be drastically altered. This has been shown in a melting experiment of Sn and Pb crystals encapsulated in graphitic shells as illustrated in figure 10 (Banhart...
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Figure 10. Melting and solidification of tin particles within graphitic shells. (a) Solid Sn crystal at $T = 500 \, ^\circ\text{C}$ (superheated). (b) Liquid (‘liq’) Sn at $T = 100 \, ^\circ\text{C}$ (undercooled). A bare (uncovered) crystalline Sn crystal is indicated (‘sol’) for comparison.

et al. 2003). These metals showed an unexpectedly large melting hysteresis, i.e. a much higher melting temperature and a lower solidification temperature than the bulk value. For example, Sn crystals, which normally melt at $232 \, ^\circ\text{C}$, did not show melting up to ca. $500 \, ^\circ\text{C}$ and solidified upon cooling at $100 \, ^\circ\text{C}$ when encapsulated in graphitic shells. Besides the pressure on the crystal, the surface coverage with graphite layers plays an important role since phase transformations like melting, that normally start from the surface, are suppressed by the rigid graphite shells.

7. Further irradiation effects in carbon nanostructures

A phenomenon that is observed quite frequently in scanning and transmission electron microscopy is the deposition of hydrocarbon contamination on the irradiated areas of the specimen. Hydrocarbon molecules originating from contamination of the specimen prior to microscopy or from the vacuum chamber of the electron microscope are highly mobile on the specimen surface. Once they diffuse into the specimen area under the electron beam, cracking occurs so that immobile amorphous carbon is left. Further irradiation of the deposit can lead to graphitization. In such a way, carbon can be deposited on the specimen surface in a controlled way (Hart et al. 1970). This technique has been used to manipulate carbon nanotubes on the nanoscale, for example, for contacting nanotubes (Yu et al. 1999) or to establish a connection (‘soldering’) between two nanotubes (Banhart 2001). Under certain conditions of deposition, the aggregates tend to ramify and form tree-like carbon objects on the nanoscale (Banhart 1994; Reyes-Gasga et al. 1997; Wang et al. 2002).

8. Non-carbon graphitic structures under irradiation

Several inorganic compounds occur in a graphite-like layered structure. Examples are hexagonal boron nitride (h-BN) or the dichalcogenides of tungsten or molybdenum. Irradiation of these compounds with electrons has also shown structural transformations. However, such a variety of irradiation phenomena as in graphitic carbon was not observed to date. The reason for this might be the defect annealing kinetics in diatomic compounds which is more complicated than in elemental carbon. Displaced atoms of one species can only recombine with vacancies of the same type. In situ annealing of irradiation defects at higher specimen temperatures

was not observed in TEM studies of h-BN or W/Mo-dichalcogenides. Another difference of h-BN to graphite is the difficulty of forming pentagonal or heptagonal (generally, odd-membered) rings because two atoms of the same species would form unfavourable bonds. Therefore, fullerene-like BN structures with pentagons might not exist.

Nevertheless, a few effects of morphological transformations have been reported. Hexagonal BN has been irradiated in the TEM, and onion-like particles appeared (Banhart et al. 1994; Stéphan et al. 1998; Golberg et al. 1998). More perfect particles were observed under irradiation of BCN precursors (Golberg et al. 1999a, b). The bending and closure of open dangling bonds (‘nanoarches’) in h-BN crystals is observed quite frequently (Collazo-Davila et al. 1998). This is just a cylindrical curvature without the necessity of non-six-membered rings. Onion-like structures were also seen in particles of WS$_2$ (Hershfinkel et al. 1994) and MoS$_2$ (José-Yacamán et al. 1996) under electron irradiation.

The transformation of hexagonal to cubic boron nitride under electron irradiation has remained a challenge. Although indications have been observed (Banhart et al. 1994), a reproducible experiment has not been reported to date. Another interesting phenomenon of phase transformations inside BN cages has been described by Golberg et al. (2002). EELS studies indicate the formation of solid nitrogen under high pressure in the cores. However, the pressure might here originate from the chemical synthesis of the BN cages rather than from electron irradiation.

9. Conclusions

Since the last review on this subject was written (Banhart 1999), many new applications of the irradiation-induced modification of graphitic particles have been found, and new as well as unexpected phenomena have been discovered. The inevitable electron irradiation in the electron microscope often resulted in the accidental observation of alterations in nanostructures. As known by every electron microscopist, dynamic processes are always standing out from static images, and this often changed the original objectives of the studies. Meanwhile, there is general agreement on the fact that irradiation with high-energy electrons does not only damage the objects but also leads to the formation of new structures that can otherwise, e.g. by chemical reactions, not be generated. We may therefore expect that irradiation studies will continue to play an important role in the research on carbon and related nanoparticles. Several achievements in this field will be seriously considered as a basis for technological applications in future production of complex arrangements of carbon nanostructures, for example, carbon nanotubes as components for electronic devices.


References

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