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3 Epitaxial Graphene and Carbon Nanotubes on Silicon Carbide

Goknur Cambaz Büke

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3.1 EPITAXIAL GRAPHENE AND CNTS ON SiC

Graphene (i.e., a single layer of graphite) and carbon nanotubes (CNTs; i.e., graphene rolled into a cylinder) are excellent candidate materials for advanced applications because of their unique electrical, optical, and mechanical properties combined with a high surface area. The successful development of graphene-/CNT-based technology depends on large-scale availability of the high-quality, reproducible, and uniformly ordered material. One of the most versatile methods to produce vertically, self-aligned CNTs and epitaxial graphene is the vacuum annealing of silicon carbide single crystals [1,2]. This is a very versatile method because carbon is supplied from the carbide lattice as known from the synthesis of carbide-derived carbons (CDCs, see Figure 3.1) and, as no catalysts or secondary phases are utilized; the produced graphene and CNTs exhibit extremely high purity. However, to increase the grain/domain size and quality of these carbon nanostructures, further control of the process is needed.

Understanding the effects of experimental parameters of the processes is the basis for tailoring the resulting material so as to enable applications. Therefore, this chapter describes the factors (as summarized in Figure 3.2) influencing the vacuum-annealing process of SiC and the reaction mechanisms.

3.1.1 HISTORY ON THERMAL DECOMPOSITION OF SiC

Initially, studying thermal decomposition of solids was for the purpose of examining thermal stability of materials. With the discovery of epitaxial growth of graphene and self-aligned CNTs on the crystal surfaces of silicon carbide, thermal decomposition has developed into a facile method of producing catalyst-free, high-purity, and highly homogeneous carbon.
FIGURE 3.1  Schematic drawing of the formation of SiC-derived carbon resulting in layers of CNT and graphene.

FIGURE 3.2  Cross-sectional HRTEM images showing surfaces of the C face heated at (a) 1250°C, (b) 1300°C, (c) the Si face heated at 1350°C for half an hour, (d) C face, and (e) Si face heated at 1700°C for half an hour. Inset in (d) shows the CNT film observed along a CNT axis plane–view direction. (Adapted and modified from Kusunoki, M. et al., Philosophical Magazine Letters, 1999. 79(4): 153–161; Kusunoki, M. et al., Applied Physics Letters, 2000. 77(4): 531–533.)
The first documented observation of carbon formation by vacuum annealing of SiC was published in 1962 (employing temperatures up to 2150°C) [3]. A decade later, Bommel et al. [4] found monolayers of graphite on SiC after annealing at 800°C and enhanced graphitization around 1500°C. Later, in the 1980s and 1990s, the work of Bommel was confirmed by Muehlhoff et al. [5], Forbeaux et al. [6], and Charrier et al. [7] who reported similar results. However, graphitic structures were not the only structures reported. A new interest in the thermal decomposition of SiC arose in 1997 when Kusunoki et al. [8] discovered the growth of self-organized carbon nanotube films by heating SiC wafer at 1700°C for half an hour in a vacuum furnace \( (P = 1 \times 10^{-4} \text{ Torr}) \) [9]. Later, a model was proposed for the formation mechanism of the CNT film on SiC that consisted of three stages. At temperatures above 1000°C (stage I), several graphene sheets were formed parallel to the (0001) SiC plane. At around \( \approx 1300°C \) (stage II), carbon nanocaps grow. At stage III, the graphite sheets align upward and CNTs grow toward the interior of the SiC crystal.

Further investigations were carried out on both the Si- and C-terminated basal plane of hexagonal silicon carbide faces by using cross-sectional high-resolution transmission electron microscopy (HRTEM) at lower temperatures [10]. A remarkable difference between the carbon structures formed on (0001)Si and (0001) C-faces of a 6H-SiC single crystals was shown. Although CNT growth was observed under various experimental conditions on the C-face, only flat graphite sheets parallel to the surface were found to be stable on the Si-face (Figure 3.2).

To study the initial growth process of CNTs at lower temperatures (\( \approx 1300°C \)), Watanabe et al. [11] observed the \textit{in situ} formation of CNTs on \( \beta \)-SiC (111) single crystal inside a TEM and proposed that the caps of the CNTs were formed by a lift of a part of the graphene through the generation of pentagons and heptagons. It was confirmed that around 1360°C amorphous carbon with many holes and defects forms because of the desorption of Si atoms. Afterward, these carbon layers crystallize into graphitic layers. Successive heating at the appropriate temperature results in two types of CNTs: \textit{single-walled} carbon nanotubes (SWCNTs) with a diameter of 0.8 and 1.5 nm and \textit{double-walled} carbon nanotubes (DWCNTs; Figure 3.3). It was confirmed by scanning tunneling microscopy (STM) measurements that the ends of the CNTs were closed (capped).

However, these studies did not explain why different carbon structures occur on Si and C faces and why the results provided by different research groups differed so greatly. In 2004, the parallel publication of the electrical response of graphene by Novoselov et al. [12] and Berger et al. [13] provided new motivation to optimize the growth conditions of graphene on SiC that required a deep understanding of the processes involved at the atomic level during decomposition.

### 3.1.2 Factors Affecting the Carbon Growth on SiC

The reactions that take place when SiC is heated can be summarized as follows:

1. SiC surface reconstruction and surface-oxide removal
2. SiC decomposition: breaking of Si–C bonds (SiC \( \rightarrow \) C(s) + Si(g))
3. Si desorption
4. C diffusion on the surface (self-organization of carbon atoms into carbon nanostructures) that results in carbon islands/graphene nucleation
5. Growth of the nucleus

The nucleation and growth of graphene/CNT are highly dependent on SiC surface morphology and the general growth conditions [14] (as summarized in Figure 3.4), which are outlined in more detail in the following sections.

#### 3.1.2.1 SiC Polytypism

The morphology of epitaxial graphene/CNT is highly influenced by the underlying SiC structure. The basic building block of a silicon carbide is a tetrahedron with four carbon atoms and a single...
silicon atom in the center (Figure 3.5a). SiC crystals are constructed with these units that structurally share one joint corner. Silicon carbide exists in a variety of more than 250 different crystal structures called polytypes that are cubic, hexagonal, or rhombohedral. Different polytypes of SiC are composed of different stacking sequences of Si–C bilayers where each single Si–C bilayer can be viewed as a planar sheet of silicon atoms coupled with a planar sheet of carbon atoms (Figure 3.5b).

**FIGURE 3.3** Examples of *in situ* HRTEM images of CNTs at 1360°C. (a) SWNT with a diameter of 0.8 nm, near the size of a fullerene C$_{60}$, 0.7 nm, (b) SWNT with a diameter of 1.5 nm, (c) DWNT, and (d) DWNT shaped like a water drop. An inner ring in concentric circles has a weak intensity compared to the outer ring. It is suggested that the inner ring forms after the formation of the outer ring. (From Watanabe, H. et al., *Journal of Microscopy*, 2001. 203(1): 40–46.)

**FIGURE 3.4** Summary of the factors that are covered in the chapter.
The plane formed by a bilayer sheet of silicon and carbon atoms is known as the basal plane, and the stacking direction [0001] (direction for hexagonal structure), and [111] (direction for cubic structure) are defined as normal to Si–C bilayer plane. In this direction, all bilayers are stacked on top of each other with possible positions as A, B, and C by arranging the sheets in a specific repetitive order.

The different polytypes are constructed by permutations of various stacking of these three positions. The only cubic polytype in SiC is called 3C-SiC, following the Ramsdell notation, which has the stacking sequence ABC. The simplest hexagonal structure is 2H-SiC, which has a stacking sequence AB and the two commercially and application-related important polytypes, 6H-SiC and 4H-SiC, have stacking sequences ABCACB and ABCB, respectively. The number in the Ramsdell notation first determines the number of layers before the sequence repeats itself along the stacking direction and the latter determines the resulting structure of the crystal: C for cubic, H for hexagonal, and R for rhombohedral. Cubic SiC is also referred to as β-SiC that has a zinc blende structure. The noncubic polytypes of SiC are also usually summarized and referred to as α-SiC, which shows a characteristic Wurtzite-type structure [15]. Studies on the epitaxial growth of graphene on SiC have, so far, focused on hexagonal polytypes. The unit cells of the two commonly used SiC hexagonal polytypes 6H-SiC and 4H-SiC are given along with the data for 3C-SiC in Figure 3.6.

When considering the carbon density in SiC, to produce a single graphene layer, the decomposition of approximately three bilayers of SiC is needed. Interestingly, it was shown that the growth of graphene appears to be independent of the polytype (whether 4H- or 6H-SiC) [17].

### 3.1.2.2 SiC Material Type

#### 3.1.2.2.1 SiC Whiskers

Figure 3.7 shows the ordered graphitic CDC structures obtained by annealing of SiC whiskers for 30 min in vacuum at 1700°C. The small whisker diameter enables direct observation in the transmission electron microscope (TEM). The vacuum-annealed whiskers kept their original shape as shown in scanning electron microscopy (SEM) micrographs. On increasing the vacuum-treatment temperature to 2000°C, the entire whisker transforms into well-ordered graphitic carbon. The same cross-sectional shape as found in the SiC whisker was confirmed by SEM and TEM after complete transformation. Raman spectra (Figure 3.7) obtained from vacuum-treated whiskers at 1700°C and 2000°C verified the ordered graphite structure of the CDC by demonstrating a high-intensity graphitic G band. Increasing the vacuum-treatment temperature from 1700°C to 2000°C resulted in a further increase in graphite ordering.

Some large multiwalled CNT-like structures were also observed on the basal plane of the whiskers with a broken tip that has sufficiently large flat area (Figure 3.8). Owing to the irregular shape of the whisker and its relatively small diameter, the shape of the nanotubes was highly distorted and the average wall thickness of the formed structures noticeably exceeded that of CNTs obtained by Kusunoki et al. [19].

#### 3.1.2.2.2 SiC Wafers

Most of the vacuum-decomposition experiments were performed on SiC hexagonal single-crystal-line wafers; however, there has been a controversy in structures formed on the Si- and C-terminated
FIGURE 3.6 SiC crystal structure showing (a) the stacking sequence of bilayers along c-axis (0001) and (b) the plane of the three most common SiC polytypes. (Cambaz, G.Z., Formation of Carbide Derived Carbon Coatings on SiC, in Materials Science and Engineering. 2007: Philadelphia, PA: Drexel University.)

<table>
<thead>
<tr>
<th>SEM</th>
<th>TEM</th>
<th>Raman</th>
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<tbody>
<tr>
<td>As-received SiC whisker</td>
<td>![TEM image](100 nm)</td>
<td>![Raman spectrum](1400, 1600 cm(^{-1}))</td>
</tr>
<tr>
<td>Vacuum annealing, (P_a = 10^{-6}) Torr, (T = 30) min</td>
<td>![TEM image](100 nm)</td>
<td>![Raman spectrum](1592, 1369, 1357 cm(^{-1}))</td>
</tr>
<tr>
<td>(T = 1700^\circ)C</td>
<td>![TEM image](5 nm, 10 nm)</td>
<td>![Raman spectrum](1583, 1557 cm(^{-1}))</td>
</tr>
<tr>
<td>(T = 2000^\circ)C</td>
<td>![TEM image](100 nm)</td>
<td>![Raman spectrum](1400, 1600 cm(^{-1}))</td>
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FIGURE 3.7 SEM, TEM, and Raman studies on as-received and vacuum-annealed SiC whiskers.
face (i.e., the (0001) plane and (000\overline{1}) plane, respectively). This crystallographic aspect is discussed in more detail below. Indeed, some results from certain studies could not be reproduced by other groups although the presumably same synthesis conditions had been applied. Cambaz et al. [14] pointed out that, in fact, both graphene and CNT formation are possible on either Si- or C-face depending on the surface morphology and experimental parameters.

### 3.1.2.3 SiC Substrate Surface Morphology

#### 3.1.2.3.1 Surface Orientation

As mentioned previously, a big difference was observed in the behavior of (0001) and (000\overline{1}) planes and usually, CNTs are observed on the (000\overline{1}) plane, whereas graphene is observed on the (0001) plane. Moreover, Kusunoki [20] also studied the decomposition of the (000\overline{1}) (\textit{t}00) and (1\overline{1}0\overline{0}) planes. It was shown that although CNTs formed on the (1\overline{1}0\overline{0}) plane, they were disordered; on the (\textit{t}00) and (000\overline{1}) planes, well-aligned CNTs were formed.

SiC is a polar semiconductor along the \textit{c}-axis, in that one surface normal to the \textit{c}-axis is terminated with silicon atoms, whereas the opposite normal \textit{c}-axis surface is terminated with carbon atoms; these surfaces are referred to as the Si-face (0001) and C-face (000\overline{1}), respectively (Figure 3.1) [21]. Although both faces exhibit the same processes (carbon formation) during heating, both the growth of graphene and its structure are intrinsically different for the C-face compared to the Si-face [17,22]. Although for the Si face, the graphene growth proceeds in a nearly layer-by-layer manner; on the C-face, it proceeds in a more three-dimensional (3D) manner [5,23,24].

There are also differences in the carbon structure formed on the two faces. On the Si-face, graphene grows layer by layer epitaxially with an orientational phase rotated 30° relative to SiC, whereas C-face films can have multiple orientational phases [4,25]. Moreover, on the Si-face, small graphene domains (30–100 nm in diameter) are formed, whereas on the C-face, larger domains (∼200 nm) of multilayered graphene are observed [26]. The different decomposition of SiC on the Si- and C-face is related to differences in their surface reconstruction and surface energies, but possibly also to the presence of surface oxides and nanofacetting.

#### 3.1.2.3.1.1 Surface Reconstruction

Before transformation into carbon, the SiC surfaces undergo a number of surface reconstructions that are dependent on the temperature and the crystal polarity (i.e., different processes occur on the Si- or C-terminated face). In the case of the Si-face, heating more than 1050°C results in a well-defined $\sqrt{3} \times \sqrt{3}$ (\textit{R} phase; further heating more than 1100°C causes a mixture of $6\sqrt{3} \times 6\sqrt{3}$ \textit{R} and $\sqrt{3} \times \sqrt{3}$ phases to develop. Continued heating more than 1200°C results in a $6\sqrt{3} \times 6\sqrt{3}$ (\textit{R} pattern with the epitaxial graphene layers forming a well-ordered $6\sqrt{3} \times 6\sqrt{3}$ superstructure [6].
On the C-face, heating SiC results in several different reconstructions: heating at 1050°C for 15 min removes the native oxide layer and gives a (3 × 3) reconstruction [27,28]. Continued heating at 1075°C produces a (2 × 2) C phase in coexistence with the (3 × 3) phase [29]. Graphene grown on the C-face is much more randomly oriented that is indicative of a much weaker substrate influence [26].

3.1.2.3.1.2 Surface Oxides

The oxide layers on C- and Si-terminated faces of SiC differ in composition and structure [27,30]. The oxide layer is directly connected to the topmost SiC bilayer by a Si–C bond on (0001) whereas a linear Si–O–Si bridge makes the contact on (0001). The latter structure leads to a stronger bonding and a slower decomposition rate of the Si-face. Zinovev et al. [31] observed a thicker oxide layer on the Si-face compared to the C-face. X-ray photoelectron spectroscopy (XPS) analysis of SiC wafers detected SiO$_x$C$_y$ on the C-face and Si-face; however, the oxygen content was higher on the C-face. Therefore, the thermal stability of the surface oxides at elevated temperatures (>1300°C) was reported to be higher on the Si-face compared to the C-face.

3.1.2.3.2 Surface Defects

3.1.2.3.2.1 Roughness

Although very high-quality SiC wafers are already state of the art in industrial-scale production, some surface scratches from polishing remain in the highest-grade SiC wafers even after mechanochemical polishing. Cambaz et al. [14] introduced scratches on the polished Si-face of SiC, wafer and it was shown that scratching and related structural deterioration leads to accelerated transformation of SiC on the Si-face to carbon [14] (Figure 3.9).

An effective method to remove surface oxides and residual polishing damage/scratches on SiC substrate is H$_2$-etching at high temperatures [32–34] at 1500°C for 10–30 min. However, such treatments also change the surface morphology and cause typically significant step bunching [35–37]. This type of microstep formation was explained in terms of etching kinetics and surface energies by Nakamura et al. [35]. It is important to clarify the most stable surface termination on the vicinal surface because the surface energy affects the kinetics (adsorption, desorption, and diffusion) [38].

3.1.2.3.2.2 Surface Steps

SiC wafers are generally grown, cut, and polished such that the c-axis direction is perpendicular to the surface of the substrate. However, in some cases, for example, to control the defect density, off-axis cuts can be preferable. Miscut tolerances can be as high as ±0.5° off-axis, leaving terraces on the surface that can measure multiple unit cells height. The atomic structure of the step depends on the crystal structure, vicinal angle, and the direction.

The formation of step bunches and/or facets on hydrogen-etched Si- and C-faces of 6H-SiC has been studied by Nie et al. [38], using both nominally on-axis and intentionally miscut (i.e., vicinal) substrates. For nominally on-axis substrates, H$_2$-etching produced uniformly distributed step-terrace arrays on both Si- and C-faces, as shown in Figure 3.10. The step arrays form because of the miscut of the surface (the average miscut values for the substrates of Figure 3.10a and b are

FIGURE 3.9 Accelerated transformation of Si face to carbon at 1700°C induced by a scratch on Si face. (From Cambaz, Z.G. et al., Carbon, 2008. 46(6): 841–849.)
0.28° and 0.18°, respectively [38]). Step edges perpendicular to the [1100] directions were observed for both faces. Other studies show that these step directions have the lowest surface energy on the (0001) basal plane; in other words, the H₂-etching is slowest in these directions [35,39,40]. The observed step height from Figure 3.10 is 1.5 nm (i.e., six bilayers; a full unit-cell height) for the 6H-SiC Si-face whereas it is 0.75 nm (three bilayers; a half unit-cell height) for the 6H-SiC C-face.

TEM studies by Norimatsu et al. [41] and Robinson et al. [42] showed the importance of nano-facets because they are the initial points for graphene formation; this is related to the low number and weaker bonding with silicon atoms [41,42]. Therefore, understanding the dynamic behavior of steps is important for the control of graphene formation on SiC. On the vicinal surfaces, the width of the terraces and the morphology of steps depend on miscut direction and angle. It was shown that depending on whether the miscut angle is toward the [1100] or [1120] direction, the nanofacet makes an angle of ≈25 or 13–14° from the basal plane [38]. Much less facetting is observed on mis-cut (0001) surfaces (Figure 3.11).

Many researchers have interpreted these steps as the in-preferred defects. However, by defect engineering, Sprinkle et al. [43] used the facets as templates for bottom-up growth of graphene ribbons for top-gated transistors (Figure 3.12).

FIGURE 3.10 Atomic force microscopy (AFM) images of nominally on-axis 6H-SiC surfaces: (a) Si-face and (b) C-face. Step edges are normal to (1100) directions. Dashed lines indicate the paths of the line scans displayed in (c) and (d), respectively. The images are displayed with gray-scale ranges (height difference between white and black gray levels) of (a) 1.4 nm and (b) 0.9 nm. A linear background subtraction has been applied to the data of (c) and (d) compared to that of (a) and (b). (From Nie, S. et al., Surface Science, 2008. 602(17):2936–2942.)

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3.1.2.3.2.3 Pits and Dislocations Another localized region, where the step density is higher, is related to the pits that form during heating. Hannon et al. [44] imaged the evolution of surface morphology during annealing above 1200°C using low-energy electron microscopy (LEEM) on the
Although the starting surface consisted of a well-ordered array of straight steps, the state of the surface when graphene forms was found to be rough. The steps were no longer straight and deep pits were observed.

In another study, Hite et al. [45] also showed that at the initial stages graphene was formed in localized areas on C-face 6H-SiC substrates. Graphene areas were determined to lie below the level of the surrounding substrate and showed different morphologies based on size. Employing electron-channeling contrast imaging, the presence of threading screw dislocations was indicated near the centers of each of these areas. After graphene was removed, these dislocations were revealed to lie

**FIGURE 3.11** (a) Stepped vicinal surface consisting of equidistant steps of monolayer height. (b) An alternating array of singular facets (terraces) separated by vicinal facets. (c and d) Cross-sectional TEM images obtained from (c) Si and (d) C-face of 6H-SiC miscut at 12° toward (1100). In (c), facet orientations of (0001) and (100n) with \( n = 12 \) are seen on the surface, whereas in C-face, only an average orientation 12° from (000\(\bar{1}\)) is observed. Both images are acquired with the electron beam directed along (1120) (c and d are from Nie, S. et al., *Surface Science*, 2008. 602(17): 2936–2942.)

**FIGURE 3.12** Process for tailoring of the SiC crystal for selective graphene growth and device fabrication. (a) A nanometer-scale step is etched into SiC crystal by fluorine-based RIE. (b) The crystal is heated at 1200–1300°C (at low vacuum), inducing step flow and relaxation to the (100n) facet. (c) On further heating at 1450°C, self-organized graphene nanoribbon forms on the facet. (d) Complete device with source and drain contacts, graphene nanoribbon channel, Al\(2\)O\(3\) gate dielectric, and metal top gate. (From Sprinkle, M. et al., *Nature Nanotechnology*, 2010. 5(10): 727–731.)
within the SiC substrate. Such hollow-core screw dislocation (often called micropipes) is indeed a common structural defect in SiC wafers. In the light of observations, they suggested that screw dislocations act as preferred nucleation sites for graphene growth on C-face SiC (Figure 3.13).

3.1.2.4 Growth Conditions

3.1.2.4.1 Temperature, Time, and Pressure

The minimum temperature for the formation of graphitic bonds, as determined by K-resolved inverse photoelectron spectroscopy (KRIPES) spectra, is approximately the same for graphene grown in ultrahigh vacuum (UHV) on the Si-face or C-face and ranges between 1080°C and 1100°C measured by an infrared pyrometer using an assumed emissivity of 0.9 [25]. However, the data in Figure 3.14 show that graphene starts to form at a significantly lower temperature on the C-face (=1100°C) compared to the Si-face (=1250°C) [5,17,24]. XPS, atomic emission spectroscopy (AES), and electron energy loss spectroscopy (EELS) indicated that on the Si-face, the UHV-grown graphene film thickness increases slowly, whereas on the C-face the films grow much faster. Thus, for a given temperature, a thicker graphene film forms on the C-face than on the Si-face [17,24]. It can be seen from Figure 3.14 that about nine monolayers are formed on the C-face at about 1250°C, whereas only one monolayer is formed on the Si-face [24]. Moreover, Hass et al. [17] showed that the number of graphene layers grown on Si-face in UHV is more insensitive to the growth time and depends more strongly on the growth temperature.

![Figure 3.13](image-url)

**FIGURE 3.13** Secondary electron image (a) and electron-channeling contrast image (b) showing that screw dislocations were near the centers of graphene areas. (From Hite, J.K. et al., *Nanoletters*, 2011. 11(3): 1190–1194.)

![Figure 3.14](image-url)

**FIGURE 3.14** Graphene thickness as a function of annealing temperature for 6H-SiC {0001}-r faces, showing results for C-face (annealing time 20 min) and Si-face (annealing time 40 min). (From Luxmi et al., *Physical Review B*, 2010. 82(23): 235406.)
Kusunoki et al. [2] also studied the effect of temperature, time, and pressure. SiC wafers were heated at several temperatures (1300°C, 1500°C, and 1700°C) for 0.5 h in a vacuum of $1 \times 10^{-4}$ Torr, then were observed using TEM. At 1500°C, the length of the CNTs formed was 50 and 180 nm for 0.5 and 6 h, respectively. Moreover, when a wafer was heated at 1500°C for 0.5 h in a better vacuum ($1 \times 10^{-6}$ Torr), the length of the CNTs was only 25 nm; thus, decreasing the pressure results in CNTs with a shorter length.

Similarly, to investigate the graphene formation on SiC, Robinson et al. [42] studied the graphene formation on SiC at different temperatures (1225°C, 1325°C, and 1425°C; pressure $= 1 \times 10^{-6}$ Torr). Under these conditions, graphene exclusively formed at terrace-step edges and other topological defects. A variation in surface coverage as a function of growth temperature was also demonstrated with a lower coverage at high temperatures [42]. Moreover, as the temperature was decreased, the disorder in graphene increased (Figure 3.15).

3.1.2.4 Environment

3.1.2.4.2 Effect of Oxygen

Kusunoki et al. [2] mentioned that the segregation of oxygen was observed at the interface between the CNT film and SiC and this led to the suggestion that residual oxygen in the vacuum chamber might play an important role in the formation of CNTs. Perhaps, that was the reason why CNTs could not be reproduced by other research groups for a long time.

To investigate the effect of oxygen on carbon structures formed on SiC, Cambaz et al. [14] introduced a small amount of oxygen into a vacuum chamber during the thermal treatment of SiC. On the Si-face, a thicker graphite film was formed with wider wrinkles (up to 50 nm) (Figure 3.16a). On the C-face, the transformation was not as conformal as in high vacuum and surface features were not conserved. Moreover, SEM studies of fractured surfaces of the carbon coating
showed that the carbon was primarily nanotubular with graphite walls growing normal to the surface (Figure 3.16b). In that study, the crucible and the heating elements were all graphite; therefore, this raised the question of carbon transport via oxidation from the walls of a reaction vessel or crucible.

It is known that there are two modes of oxidation of the SiC surface: (1) passive oxidation, in which SiO₂ layer is formed on SiC surface passivating the surface and (2) active oxidation, in which the silicon-containing products are gaseous, such as Si or SiO [46–50]. Figure 3.17 shows a phase diagram for the interaction of O₂ with SiC surface [50].

Si removal from SiC may follow two possible paths [50,51]: SiC decomposition with carbon as a solid product (if there is no oxidizing species present) and active oxidation, as shown in the following reactions:

\[
\text{SiC}(s) \rightarrow \text{Si}(g) + \text{C}(s) \quad \text{(R.3.1)}
\]

\[
\text{SiC}(s) + \frac{1}{2} \text{O}_2(g) \rightarrow \text{SiO}(g) + \text{C}(s) \quad \text{(R.3.2)}
\]

(with g denoting a gaseous phase and s denoting a solid phase).

FIGURE 3.16 SEM images of (a) the graphite coating formed on Si face. (b) Dense CNT forest formed on the C-face by vacuum annealing for 4 h at 1900°C in a low vacuum. (From Cambaz, G.Z., Formation of Carbide Derived Carbon Coatings on SiC. 2007: Philadelphia, PA: Drexel University.)

The rate of SiC Reaction 3.1 is faster than that of Reaction 3.2 [50]. Additionally, taking into account that all lining and heating elements inside the vacuum furnace are made of carbon; carbon transport may occur in the presence of oxygen by Reaction 3.3 (Boudouard reaction).

\[ 2C(s) + O_2(g) \leftrightarrow 2CO(g) \]  \hspace{1cm} \text{(R.3.3)}

These results suggest that at higher oxygen pressures, the carbon-formation rate is increased due to the parallel processes of Reactions 3.1 through 3.3 including gas-phase carbon transport.

3.1.2.4.2.2 Effect of Crucible To investigate the hypothesis that carbon transport occurs from carbon lining, Cambaz [16] placed SiC wafers with the Si face and C face down onto graphite plates, assuming that a short distance (compared to the transport from the crucible or remote furnace heaters) would assist and accelerate the transport.

This experiment produced a much thicker CNT coating on C face (≈9 \(\mu\)m) and the surface features were lost. Moreover, this time, nanotube carpets were formed on the Si-face as well (Figure 3.18c); however, these nanotubes were shorter yet more ordered.

3.1.2.4.2.3 Effect of CO\(_2\) To further corroborate the observed effect of carbon transport through the gas phase, a small amount of CO\(_2\) into the vacuum chamber was introduced through a leak valve [14]. This led to a CNT coating on both C and Si faces (Figure 3.19), where single nanotubes were observed protruding from the surface (Figure 3.19b), suggesting growth from an external carbon source. Thus, carbon deposition by gas-phase transport at a low partial pressure of oxygen contributes to the growth of nanotubes upon decomposition of SiC. Similarly, the addition of CO also leads to a stabilized CNT growth.

![FIGURE 3.18 SEM micrographs of CNTs formed after 4 h at low vacuum (10\(^{-4}\) Torr) at 1900°C on the (a,b) C-face and (c) Si-face. Synchronous tilting of nanotubes after scratching the surface shows that their sides are not interconnected, and they are free to slide against each other.](image-url)
3.1.2.4.2.4 Impurities on the Surface  
To study the effect of impurities, a SiC wafer was patterned (Figure 3.20a) using organic materials and permanent markers that contain carbon. Surface painting led to an accelerated transformation of SiC on both the Si- and C-face to carbon (Figure 3.20b,c). Moreover, CNT growth was observed on both faces in the region covered by paint. These CNTs are embedded in the substrate with the tubes not rising above the wafer surface and, therefore, may offer significant advantages in device fabrication and printable electronics.

3.1.2.4.2.5 Presence of Inert Gas  
Surface-limited reactions are sensitive to the ease of removal of volatile products that may be hampered by the presence of an inert gas. Emtsev et al. [52] showed that the growth of epitaxial graphene on SiC-(0001) in an Ar atmosphere close to atmospheric pressure provides morphologically superior graphene layers in comparison with vacuum graphitization. The key factor in achieving an improved growth is the significantly higher annealing temperature of 1650°C that is attainable for graphene formation under argon at a pressure of 900 mbar as compared with 1280°C in UHV.

For a given temperature, the presence of a high pressure of Ar leads to a reduced Si evaporation rate because the silicon atoms desorbing from the surface have a finite probability of being reflected back to the surface by collision with Ar atoms. In an Ar atmosphere, no sublimation of Si from the surface is observed at temperatures up to 1500°C, whereas Si desorption commences at ≈1100°C in vacuum. The significantly higher growth temperature thus attained results in an enhancement of surface diffusion such that the restructuring of the surface is completed before graphene is formed. Ultimately, this leads to a significantly improved surface morphology.

FIGURE 3.19  SEM micrographs of CNTs formed (a) on the C-face with a thickness of 400 nm and (b) on the Si-face with a thickness of 310 nm by annealing for 4 h at 1700°C in CO₂. (From Cambaz, Z.G. et al., Carbon, 2008. 46(6): 841–849.)

![SEM micrographs of CNTs](image)

FIGURE 3.20  (a) Coating with a fluxing agent leads to localized formation of CNTs on the (b) C-face and (c) the Si-face of SiC. SEM micrograph showing that CNTs grow on the patterned areas, whereas graphite covers the remaining surface. Wafers were treated at 1700°C. (From Cambaz, Z.G. et al., Carbon, 2008. 46(6): 841–849.)

![SEM micrographs of CNTs with coating](image)
3.1.3 CNT and Graphene-Formation Mechanism on SiC

Explanation of all the details is not easily verified because in situ investigation of the aforementioned processes is hard and limited at high temperatures. However, imaging the produced features on the surface with atomic-scale resolution (using AFM, SPM, and HRTEM) provided considerable insight into the growth mechanism of carbon on SiC. Studies showed that the resultant carbon structure strongly depends on the nucleation rate of carbon at the initial stages. If the nucleation rate is high, nonuniform nucleation takes place as islands on the terraces on the (0001)-surface. This mostly results in disordered thick graphitic structures. However, if there is an extra carbon supply present, whether by CO, CO₂, or carbon transport from the crucible walls through oxidation, these islands become curved forming distinct caps that turn into CNTs as the reaction proceeds.

To form uniform graphene, the nucleation rate should be small and this can be achieved by pre-treatment. For the H₂-etched wafers, Kusunoki and coworkers [41] and Robinson et al. [42] proposed a very similar graphene growth mechanism (Figure 3.21) based on HRTEM results. According to the observations, the initial stages of the process can be summarized with the following subsequent steps:

1. Silicon atoms at the step are preferentially sublimed.
2. Multilayer graphene nucleates at the step edge.
3. The outermost graphene layer grows over the terrace region making the formation of single-layer graphene possible.
4. Graphene grows on other terraces.
5. Coalescence in the vicinity of the step.

The quality of graphene can be improved by annealing at higher temperature. However, in that case, to delay the reaction, the purge of inert gases such as Ar is needed.

FIGURE 3.21 Schematic illustration of the early stages of graphene formation. (a) Silicon atoms at the step are preferentially sublimed, (b) multilayer graphene nucleates at the edge step, (c) the outermost graphene layer grows over the terrace region making the formation of single-layer graphene possible, and (d) coalescence in the vicinity of step. (HRTEM images are adapted from Norimatsu, W. and M. Kusunoki, Physica E-Low-Dimensional Systems and Nanostructures, 2010. 42(4): 691–694; Robinson, J. et al., ACS Nano, 2010. 4(1): 153–158.)
3.2 SUMMARY

Annealing SiC single crystals in a vacuum furnace leads to the sublimation of silicon atoms from the surface and the subsequent formation of CNT or graphene layers by the remaining carbon atoms on the surface. For the controlled growth of the carbon structures (Figure 3.22) with high quality, factors affecting the process and the details of the formation process were covered. The nucleation and growth of monolayer graphene on SiC are highly dependent on the SiC surface morphology (surface orientation, defects) and growth conditions (temperature, time, pressure, and environmental gases). Moreover, pretreatments such as hydrogen etching or annealing at high temperature result in the transformation of the surface into a 3D surface with terraces exhibiting (0001) and (110) planes. Although the (0001) surface exhibits uniform bonding of all silicon surface atoms, many of the Si atoms along the (110) plane exhibit dangling bonds [35]. The formation of graphene is thought to begin at these step edges [28,42,52–55]. Having fewer steps along well-defined crystallographic directions reduces the nucleation density of multilayer graphene and, thus, single-layer graphene with a high quality may be obtained by few stepped, large-terraced SiC under Ar flow at very high temperature. Moreover, the graphene nanoribbons with controlled thickness can be produced by controlling the step width.

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