SiC-assisted growth of tubular graphenic cones with carbon nanotube tips

Hao Zhuanga, 1, Bing Yanga, 1, Lei Zhanga, Steffen Heusera, Xin Jianga, b, *

a Institute of Materials Engineering, University of Siegen, Paul-Bonatz-Str. 9-11, 57076, Siegen, Germany
b Shenyang National Laboratory for Materials Science, Institute of Metal Research (IMR), Chinese Academy of Sciences (CAS), No. 72 Wenhua Road, Shenyang, 110016, China

1. Introduction

Carbon nanotubes (CNTs) have received intensive research attention in the past decades, owing to their wide applications in scanning probe microscopy, field electron-emitters, energy storage, sensors, drug delivery and bio-imaging, etc. [1] Recently, the fabrication of tubular graphenic cones (TGCs), a conical form of CNT, has been demonstrated with interesting morphology and noticeable monochirality [2]. Later the successful synthesis of TGCs with single crystal CNT tip also came into reality [3–5]. Such an endeavor makes a significant advance, as the structure combines the high mechanical stability of TGCs (having micrometer-sized root) with the inherent properties of CNTs. It is thus advantageous in handling CNTs for scanning probe microscopy, field electron emitter and drug delivery applications, etc.

Similar to CNTs a metal catalyst (i.e., Fe) is normally involved to catalyze the growth of TGCs [2–7]. In spite of the improving yields over time [3], the remaining metal-catalyst in the final structure poses a main drawback. It affects the intrinsic properties (chemical, redox and magnetic properties, etc.) of TGCs as well as the CNT tip, which in turn strongly threatens their potential applications [8,9]. For example, the metal nanoparticles can be toxic in bio-samples, limiting its application in biological environments [10]. In addition, the fabrication of TGCs with high yields is now only possible on Fe substrate [3], which limits its further manipulation. Keeping the above issues in mind, in this contribution, we aim at developing an approach to direct fabricate TGCs with CNT tip without involving any metal catalysts. To be more ambitious, we expect the approach to be applicable on various substrates to enable the universal integration of TGCs.

To achieve this goal, the essential part is to find a suitable starting point to initialize the growth of graphene, because TGC as well as CNT is actually only a curved form of graphene-based carbon. Among the various semiconductor and oxide particles [8,11–18] that have been employed for the growth of CNT, we finally choose SiC in the present study. This is because SiC is the most widely used and the first non-metal catalyst to initiate the
growth of graphene-based carbon according to the literature [19]. Its history can be traced back to 1997, when the formation of CNT was observed during SiC sublimation [12]. Even though the pioneer work in the metal-catalyst-free synthesis of CNT was demonstrated using SiO2 [8], it was later revealed that SiO2 may also be converted into SiC before it initiates the growth of CNT [20]. Very recently, the growth of high quality epitaxial graphene on flat SiC substrate through CVD technique has been reported [21], making a significant advance in the carbon community. In addition to the above, it is also important to notice that, SiC is a material which can be deposited on various substrates by thermal [22] and plasma CVD [23] with a wide parameter window. Moreover, its deposition conditions even overlap with those of TGCs. The typical growth temperature of SiC film is 700–1300 °C [22–25], which includes the temperature range for the growth of TGCs (700–1100 °C) [2–5].

The precursors for the SiC growth contain both silicon and carbon, where carbon is also required for the growth of TGCs. Being inspired by this, we report in this paper, the first direct growth of TGCs with the assistance of in situ formation of SiC crystallites. A systematic study on the growth mechanism was carried out. It reveals that SiC crystallites constrain the growth of graphene, which leads to the formation of curved graphene layers. These curved graphene layers finally initiate the growth of TGCs on SiC. Both TMS and TMB in the gas phase are 230 ppm and 173 ppm, respectively. Even though these concentrations are kept constant throughout the whole process, it is clearly observable that a large amount of TGCs exists (Fig. 1a). They are homogeneously distributed on the whole substrate (1 × 2 cm²) with a density of (3.1 ± 0.3) × 10⁵ cm⁻². This density is 1 order of magnitude higher than the one achieved by us previously using bulk steel or iron coating as catalyst [3,5], indicating a high yield of TGCs in the present study. Fig. 1c depicts the SEM image of TGCs from the cross-sectional view. All the TGCs “stand” in arrays on the substrate with certain tilting angles. They feature a length ranging from 2.5 to 4 μm and a root diameter of ~0.5 μm. Straight CNT with a length of 1–3 μm exists at the tips of the TGCs, indicating the successful fabrication of TGCs with CNT tip. A close-up observation of the CNT tip is shown in Fig. 1d. Besides the TGCs, a thin graphene-based carbon film also exists beneath the TGCs as a side product, which is clearly observable in Fig. 1c. A cross-sectional view of this layer (Fig. S1 in Supplementary data) demonstrates that its upper-half consists of a layer-by-layer stacking of nanosheets. Due to their low bonding strength, the nanosheets could be readily separated from the surface forming graphene. The dashed arrow in Figure S1a indicates one graphene nanosheet peeling off from the surface while breaking the substrate to prepare for cross-sectional observation.

Raman analysis was carried out, too. No obvious differences are observed in the Raman spectra along the TGCs (see Fig. S2 in Supplementary data). This might be due to the low spatial resolution of the Raman spectroscopy, which makes it unavoidable to gather the signal from the surrounding. As a result, the spectrum obtained in the present study gathers the overall information from the TGCs, CNTs and the underlying graphene-based carbon film. One typical Raman spectrum is shown in Fig. 1e. It depicts clearly the typical features of graphene-based carbon including the sharp G band and 2D band as well as the higher intensity of G band than that of 2D band [26]. Other peaks like D band, D' band, D + D' band, D + D' band and 2D band are also present, indicating the existence of defects in the structures [26], which is commonly observed in TGCs [7] as well as other graphene-based nanostructures [26].

To gain a deeper understanding of the structure of TGCs, they were transferred from the substrate to a copper TEM grid using mechanical scratching followed by ultrasonic dispersion for transmission electron microscopy (TEM) analysis. The results are

3. Results and discussion

Fig. 1a and b depict the scanning electron microscopic (SEM) surface images of nanostructures on the (001) Si substrate. It is clearly observable that a large amount of TGCs exists (Fig. 1a). They are homogeneously distributed on the whole substrate (1 × 2 cm²) with a density of (3.1 ± 0.3) × 10⁵ cm⁻². This density is 1 order of magnitude higher than the one achieved by us previously using bulk steel or iron coating as catalyst [3,5], indicating a high yield of TGCs in the present study. Fig. 1c depicts the SEM image of TGCs from the cross-sectional view. All the TGCs “stand” in arrays on the substrate with certain tilting angles. They feature a length ranging from 2.5 to 4 μm and a root diameter of ~0.5 μm. Straight CNT with a length of 1–3 μm exists at the tips of the TGCs, indicating the successful fabrication of TGCs with CNT tip. A close-up observation of the CNT tip is shown in Fig. 1d. Besides the TGCs, a thin graphene-based carbon film also exists beneath the TGCs as a side product, which is clearly observable in Fig. 1c. A cross-sectional view of this layer (Fig. S1 in Supplementary data) demonstrates that its upper-half consists of a layer-by-layer stacking of nanosheets. Due to their low bonding strength, the nanosheets could be readily separated from the surface forming graphene. The dashed arrow in Figure S1a indicates one graphene nanosheet peeling off from the surface while breaking the substrate to prepare for cross-sectional observation.
The diameter of the nanotube tip is measured to be ~70 nm (Fig. 2a). A hollow interior with a diameter of ~10 nm exists throughout the TGC and the CNT tip, as depicted in Fig. 2b. High-resolution TEM (HRTEM) image demonstrates that the TGC as well as the CNT tip is composed of graphene layers with interplanar spacing of 0.34 nm (Fig. 2c), which is in good accordance with the Raman results in Fig. 1e. Moreover, more than 10 layers are observed at the sidewall of the CNT tip, indicating it belongs to...
The apex angles of the TGCs are measured to be in the range of $22^\circ - 45^\circ$ with an average value of $(36 \pm 5)^\circ$ based on 40 individual TGCs. Fig. S3 in Supplementary data shows the detailed structure at the apex of one TGC. It can be clearly observable that conical shape of TGC is formed by the accumulation of the coaxial graphene edges, which is in accordance with our previously obtained TGCs using Fe as the catalyst [2]. In this context, the apex angle is formed by the different growth rates between the inner layers and the outer layers, which is similar to the nanocones obtained at high temperature using pyrolytic carbon [27–29]. Nevertheless, it is very different from the carbon cones that are formed by a disclination mechanism [18]. In the disclination mechanism, the nanocones are only allowed to form with certain defined apex angles. In the present study, however, the apex angles of the nanocones vary continuously from 22 to 45°. The relatively wide distribution of the apex angles in the present study implies that the shape of cone tip is sensitive to the deposition conditions, as suggested by Monthioux et al. in their work [28]. Therefore, fluctuation in the local deposition conditions, i.e., gas composition and temperature, may result in a certain distribution in their shape, leading to the different final apex angle. A precise control in the deposition conditions is thus required in the future in order to achieve a uniform apex angle of the cones.

All the observations shown above clearly indicate the successful fabrication of TGCs with CNT tip in the present study with improved yield. Different from the previous metal-catalyst-free growth of carbon nanostructures, no pre-existing semiconductor catalyst particles are required on the substrate prior to the deposition process. In this context, the gas phase composition as well as the plasma process holds as the keys to the successful growth of TGCs. To be more specific, the introduction of TMS for the initial 30 min plays a remarkable role. Without TMS, only island-like diamond crystallites form (see Fig. S4 in Supplementary data). As we have already mentioned, the existence of TMS in the gas phase contributes to the formation of SiC, which is expected to initiate the growth of graphene. To confirm this and further understand the growth process of the TGCs, cross-sectional TEM analysis is carried out.

Fig. 3a shows the high-angle annular dark-field (HAADF) image of the layer grown on the substrate. Owing to its high sensitivity to the atomic number of the imaged material, a high contrast exists with the bright phase identified as 3C–SiC and the dark one as carbon (see discussions below). No other phases are observed. Fig. S5 in the Supplementary data shows the energy-dispersive X-ray spectroscopy (EDX) analysis along the cross-section from the Si wafer to the tip of the TGC (analyzed on Fig. 4a shown later). It confirms the whole structure is composed solely by carbon and silicon. No other contaminations are detectable. In Fig. 3a, two parts are clearly observable. The first part, being adjacent to the Si substrate, consists of a mixture of nanometer-sized 3C–SiC crystallites and graphene. Above it, pure graphene layers form as the second part. In the following, special attention will be given to study the structural information on the SiC/graphene mixture layer, as it represents the starting point for the formation of graphene-based carbon in the present study. In the mixture layer, a dense and well-oriented 3C–SiC crystal plates with a thickness of ~100 nm firstly cover the whole substrate. The 3C–SiC crystallites in this layer lie at an angle of 55° to the substrate surface ([001] Si substrate). This is a characteristic angle between the [111] and [001] facets in the crystals with face-centered-cubic (FCC) structure (i.e., 3C–SiC and Si), hinting the highly oriented growth of the 3C–SiC crystallites with [111]_3C=SiC//[111]_Si. To further understand their orientation, the high resolution TEM (HRTEM) image of one such crystallite is shown in Fig. 3b. The corresponding selective area electron diffraction (SAED) pattern is depicted in the inset. A careful examination of the diffraction spots of 3C–SiC and Si leads to the conclusion that a good epitaxial matching between 3C–SiC and Si is achieved. To confirm this, the HRTEM image of the interface between the Si substrate and the 3C–SiC crystallite is shown in Fig. 3c. The yellow lines indicate the (111) planes of both 3C–SiC and Si. It can be seen that every five SiC (111) planes match with four Si (111) planes, which is in good accordance with the lattice constant data of 3C–SiC and Si (4.3596 Å for 3C–SiC and 5.4307 Å for Si). This finding proves the hetero-epitaxial growth of 3C–SiC crystallites on the Si substrate. Therefore, we call this layer as the “initial epitaxial layer” in the following. Moreover, no carbon structures are
observable at the interface between the Si wafer and the SiC crystallites. Such a fact along with the epitaxial matching between the 3C\textsuperscript{e} SiC crystallites and the Si indicates that the 3C\textsuperscript{e} SiC crystallites grow directly on the Si wafer and prior to the carbon structure. On the \{111\} facets of the 3C\textsuperscript{e} SiC crystallite, the formation of multi-layered graphene is observable (see Fig. 3b). The HRTEM image (Fig. 3d) taken at the graphene/SiC interface clearly depicts that the basal plane of graphene is parallel to the \{111\} planes of 3C\textsuperscript{e} SiC, indicating the epitaxial growth of graphene on the 3C\textsuperscript{e} SiC crystallite, which is in good accordance with the literature\cite{30,31}.

The above phenomenon clearly conveys the information that the 3C\textsuperscript{e} SiC crystallites are the starting points for the formation of graphene in the present study. Unlike the previously reported CVD deposition of graphene on 3C\textsuperscript{e} SiC\cite{21,30}, the absence of high substrate temperature (i.e., >1200 °C) and substrate pretreatments (i.e., surface reconstruction, smoothening and etching) implies a higher degree of simplicity in the present process. This can be attributed to nucleation of graphene during the growth of 3C\textsuperscript{e} SiC crystallites. It is already known that graphene prefers growing epitaxially on the \{111\} planes of 3C\textsuperscript{e} SiC\cite{21}. As closely packed planes, the growth rate of the \{111\} planes is the lowest in comparison to the other planes in 3C\textsuperscript{e} SiC, due to their low surface energy\cite{32}. During the epitaxial growth of the 3C\textsuperscript{e} SiC crystallites, the \{111\} facets are always exposed to plasma and expand in a layer-by-layer manner. The surface conditions of the \{111\} planes, such as atomic configuration, termination, smoothness, and reactivity, etc., thus continuously change under plasma. Once they become suitable for the formation of graphene, the nucleation and growth of graphene start.

Apparently, further expansion of graphene in size and thickness finally leads to the formation of TGCs in the present study. It is noteworthy to mention that, above the initial epitaxial layer, some “large” SiC crystallites with a height larger than 200 nm are observed in Fig. 3a. These “large” SiC crystallites are always seen under the TGCs. One of them is indicated by arrow in Fig. 4a, where the low magnification TEM image of the root of one TGC is depicted. Such an observation hints their importance in triggering the growth of TGCs. This is further confirmed by a separate study that employed a lower TMS concentration (115 ppm) in the first 30 min deposition. Because of the reduced growth rate, a low density of “large” 3C\textsuperscript{e} SiC crystallites exists on the initial epitaxial layer (see the dark field cross-sectional TEM image in Figure S6a in Supplementary data). As a result, a low density of TGCs is observed on the surface (7.4 × 10\textsuperscript{5} cm\textsuperscript{-2}, counted from the SEM image shown in Figure S6b in Supplementary data). This observation strongly indicates that the “large” 3C\textsuperscript{e} SiC crystallites are responsible for the formation of TGCs. To further understand their roles, detailed HRTEM observations around the root of the TGC are shown in

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**Fig. 4.** (a) TEM image of the root of TGC, the arrow indicates one of the large 3C–SiC crystallites beneath the TGC; (b) HRTEM image of the curved graphene layers in the initial epitaxial layer; (c) Curved graphene layer above the initial epitaxial layer away from TGC; (d) Straight graphene layer at the top region away from the TGC; (e) HRTEM image of one large 3C–SiC crystallite above the initial epitaxial layer, the arrow indicates the growth direction of the crystallite, the dashed line indicates one \{111\} plane, and the curved line indicates the curved graphene layer; (f) HRTEM image of the interface between the large 3C–SiC crystallite and the graphene layers, the dots indicates the position of the 3C–SiC lattice and the formation of atomic-steps is clearly observable, the curved lines indicate the curved growth of the graphene layers; (g)–(i) HRTEM image of the curved onion like graphene-based carbon (g) and bowl-shaped graphene-based carbon (h and i) between the large SiC crystallites. (A colour version of this figure can be viewed online.)
and continues growing. Of course, the graphene layer not only
another graphene layer or a (111) 3C
because of its good
this happens, the graphene layer starts to bend during growth
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TGC and 2) slightly away from the TGC. Fig. 4b shows
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TGC and 2) slightly away from the TGC. Fig. 4b shows firstly the
graphene layers in the initial epitaxial layer. The yellow line in the
figure clearly indicates the occurrence of curvature/bending of
graphene in the layer. This can be understood as the constrained
growth of graphene by the SiC crystals. The [111] facets of 3C–SiC
lie at an angle of 70° to each other. Since the graphene layers are
epitaxially grown on the [111] facets, they also lie at 70° to each
other as well as to some of the [111] facets of 3C–SiC. During the
expansion of the graphene layer, it is not avoidable to encounter
another graphene layer or a (111) 3C–SiC facet lying 70° to it. Once
this happens, the graphene layer starts to bend during growth
because of its good flexibility. Curved graphene layer thus forms
and continues growing. Of course, the graphene layer not only
expands in its size but also grows in its thickness. When it gets
thicker, it can be viewed as graphene based carbon rather than
graphene. In case the graphene fully cover a SiC crystallite, it stops
the further growth of the crystallite. Therefore, regions with only
small SiC crystallites exist (See Fig. 3a). On these regions, further
growth of the graphene is not constrained any more by the SiC
crystallites. They thus compete with each other and grow by
geometrical selection [33]. As shown in Fig. 4c and d, their ordering
continuously improves during growth. In the end, “straight” graph-
ene layers are observed at the top of the film (Fig. 4d), but no TGC
forms.

For 3C–SiC crystallites whose growth front is not fully blocked
by graphene, however, they continue growing under the supply of
TMS and “large” 3C–SiC crystallites form. Fig. 4e shows the HRTEM
image of one such “large” 3C–SiC crystallite. Unlike the crystallites
in the initial epitaxial layer, its growth direction (indicated by the
yellow arrow) is no longer associated with the <111> crystal di-
rrections of 3C–SiC (dashed lines shows one of the [111] planes). The
growth of graphene layer follows the shape of the SiC crystallite, as
indicated by the yellow line. Fig. 4f shows the HRTEM image of the
interface between the 3C–SiC crystallites and the graphene layer. It
is clearly observable that atomic-steps exist on the surface of the
crystallite. The bending of the graphene layers occurs when they
encounter these atomic-steps during growth. Two of such curved
graphene layers are clearly indicated by the yellow lines in Fig. 4f. It
should be noticed that, in this region, curved onion-like structures
(Fig. 4g) and bowl-shaped structures (Fig. 4h and i) form and
dominate this region.

The formation mechanism of the atomic-steps on the “large”
3C–SiC crystallite can be understood as the disturbed growth of
the [111] facets of SiC in the presence of graphene. Once gra-
phene covers certain areas of the [111] SiC facets, it blocks their
further layer-by-layer growth. In the neighboring area where no
graphene exists, however, the layer-by-layer expansion along the
<111> directions continues. As a result, an atomic-step forms at
the boundary of these two regions. As the growth of graphene
goes on, it meets these steps and starts to bend. The growth of
the curved graphene again blocks the expansion of the [111] SiC
facets, causing the formation of another step on the surface,
which in turn leads to a change in the growth direction of SiC.
Continuing such a process creates a high degree of curvature in
the graphene layers. Therefore, it looks as if the graphene layers
follow the shape of the SiC crystallite (see the yellow line in
Fig. 4e). As a result, the constrained growth of graphene becomes
much stronger in this region in comparison with that in the
initial epitaxial layer, leading to the formation and domination of
curved onion-like structures and bowl-shaped structures in this
region.

Since TGCs are observed to form on top of this region, it is
reasonable to believe that the curved graphene based carbon
structures, i.e. onion-like and bowl-shaped structures, are the
starting points to initiate the growth of the TGCs in the present
study. A more detailed TEM observation hints that CNT actually
grows prior to the TGCs. Fig. 5a shows the TEM image of the broken
root of one TGC, which clearly depicts the existence of a nanotube
at its geometrical center. In addition, Fig. 5b shows one TGC after
only 1 h growth. The CNT tip is already clearly observable. These
results strongly imply the prior formation of CNT before TGCs. This
is not surprising. A similar phenomenon has also been reported by
Monthioux et al. while they were using pyrolytic carbon as the
precursor for the growth of carbon nanostructures [27–29]. It is
already known that CNT can grow from the curved graphene based
carbon structures, especially the onion-like and bowl-shaped
structures, since their edge is chemically active and acts as incor-
poration sites for carbon adatom [34,35]. Here, the plasma process
Fig. 6. Schematic illustration of the growth process of TGCs in the present study. (a) Graphene layer is firstly formed on the {111} facets of 3C–SiC; (b) the growth of graphene leads to the formation of atomic steps on the {111} SiC planes, these atomic steps in turn lead to the curved growth of the graphene layer; (c) the SiC crystallites lying 70° to each other also constrain the growth of graphene, forming a high density of curved graphene layers, i.e. onion-like structure or bowl-shaped structure, in between; (d) the curved graphene layers start to initiate the growth of CNT; (e) once the nanotube reaches out of the surface, it attracts the reactive species to its tip; the energy at the open end of the tip is higher in comparison to that of the sidewall of the CNT, resulting in a high growth rate of CNT along its longitudinal direction; some reactive species also reaches the sidewall of the CNT, contributing to its radial expansion with lower rate through a layer-by-layer growth process; (f) the growth of the TGC starts and continues to the end of the deposition; (g) TGC with a CNT tip form. The black arrow indicates the reactive species contributing to the longitudinal growth of the TGC, and the orange arrow indicates the reactive species contributing to the radial growth of the TGC. (A colour version of this figure can be viewed online.)

Fig. 7. (a)–(d) SEM images of the TGCs grown on different substrates: (a) diamond, (b) GaN, (c) SiO2 and (d) 2H–SiC; (e) Raman spectra of the overall structures on different substrates. (A colour version of this figure can be viewed online.)
is responsible in guaranteeing the occurrence of the above process and controlling the conical shape of the TGCs. At first, it creates highly reactive carbon species, which facilitates their bonding to the active edges of the curved graphene structures. When CNTs form from the curved graphene layers, the plasma discharge allows the reactive species to be attracted to the tip of the CNTs [36], leading to the localized high concentration of the reactive species. This ensures a sufficient supply of reactive carbon species for the growth at the tip of the CNTs. It is known that the energy of the open end at the tip is higher in comparison to that of the sidewall of the CNTs, leading to a high growth rate of CNTs along their longitudinal direction [37]. Nevertheless, the bonding of carbon atoms to the sidewall of the CNTs cannot be avoided, which results in the radial expansion of the CNTs. Its expansion rate is, however, much lower in comparison to that of the longitudinal direction, not only because of the lower concentration of the reactive species at the sidewall, but also because of the lower reactivity of the sidewall [37]. As a result, TGCs with CNT tip form in the end. With increasing deposition time, the TGCs as well as the CNT tip grow in size because of the layer-by-layer expansion of the graphene layer. The above process is schematically summarized in Fig. 6 for a better illustration.

Here, it should be mentioned that boron plays an important role in accelerating/guaranteeing the continuous growth of TGCs. If the supply of boron is shut after the initial 30 min, only small TGCs are observable (the total deposition duration is 3 h), as indicated by arrows in Fig. 5c. The back-scattered electron (BSE) image (Fig. S7 in Supplementary data) shows that the 3C–SiC crystallites are even not fully covered by the graphene layers, indicating the very low growth rate of the graphene layers. In the microwave plasma, TMB is decomposed through electron impact dissociation. The chemical reactions occurring in the plasma are very complicated. Nevertheless, atomic boron can be produced with high reactivity according to Taylor's experimental investigation [38]. Other boron containing species such as BHx (x = 1–3) also exist in the plasma according to the theoretical study [39]. At cooler region of reactor, i.e., substrate surface, they react with carbon containing species [39], getting incorporated in TGCs. The study on such an intricate aspect forms one of the scopes in our future work. The accelerated growth of TGCs by boron inclusion might be due to the increased amount of impurity centers created by boron. These impurities centers can act as the nucleation center and facilitate the bonding of carbon atoms on to the TGCs. The similar phenomenon has also been observed during the growth of CNTs [20] and diamond [40].

From the results shown above, keys to the fabrication of TGCs in the present study are 1) the initiating and constraining the growth of the graphene layers from 3C–SiC crystallites; 2) accelerating/guaranteeing the continuous layer-by-layer growth of the graphene-based structures by boron; and 3) plasma process for creating reactive species and controlling the shape. The Si substrate in the present study acts only as the starting point for the epitaxial growth of CNTs with CNT tip is thus achieved on various substrates in the present study, showing the high compatibility of the current approach.

4. Conclusions

The growth of TGCs with CNT tip has been achieved via in situ formation of SiC crystals in the microwave plasma chemical vapor deposition process. No pre-existing metal or semiconductor catalyst particles are required on the substrate prior to the deposition process. Instead, the in situ grown SiC crystallites serve as the catalyst for the growth of TGCs. It is revealed that 3C–SiC crystals grow epitaxially on the Si substrate and the graphene layer grows epitaxially on the {111} facets of the 3C–SiC crystals. The 3C–SiC crystals further constrain the expansion of graphene, leading to the formation of the curved graphene layers, which in turn initiates the growth of TGCs. The process is compatible to a wide range of substrates, including SiO2, SiC, GaN, Si and diamond, etc., making the integration of TGCs on various substrates possible.

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Appendix A. Supplementary data

Supplementary data related to this article can be found at http://dx.doi.org/10.1016/j.carbon.2015.09.015.

References

[17] J. Dong, W. Shun, F. Kang, B. Tataruch, Whiskers with apex angle 135°...


