



## Characterization of SiC nanowires prepared on C/C composite without catalyst by CVD

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**Abstract:** SiC nanowires were prepared on C/C composite surface without catalyst by chemical vapor deposition (CVD) using  $\text{CH}_3\text{SiCl}_3$  as precursor. SEM images of the CVD-product reveal that some long nanowires have grown to tens of micrometers with some gathered as a ball. Some short nanowires agglomerate like chestnut shell with many thorns accompanied by some deposited nano-particles. XRD, Raman-spectrum and FTIR patterns indicate that the product is a typical  $\beta$ -SiC. TEM images show that the nanowires have a wide diameter range from 10 to 100 nm, and some thin nanowires are bonded to the thick one by amorphous CVD-SiC. A SiC branch generates from an amorphous section of a thick one with an angle of  $70^\circ$  between them, which is consistent with the [111] axis stacking angle of the crystal. SAED and fast Fourier transform (FFT) patterns reveal that the nanowires can grow along with different axes, and the bamboo-nodes section is full of stacking faults and twin crystal. The twisted SiC lattice planes reveal that the screw dislocation growth is the main mechanism for the CVD-SiC nanowires.

**Key words:** SiC nanowires; C/C composite; chemical vapor deposition; growth mechanism; characterization

### 1 Introduction

Carbon fiber reinforced carbon matrix composite (C/C composite) has been widely used as thermal structural material, for example, brake material, seal ring, rocket nozzle and throat insert, which is benefited from low density, low coefficient of thermal (COF), high special strength and thermal conductivity [1]. But one obvious defect, easily being oxidized in air above  $450^\circ\text{C}$ , has limited the application of C/C composite. Therefore, oxidation-resistance is a key technology for C/C composite to ensure the properties in harsh surrounding [2].

After decades of research, SiC has become a kind of good material to prepare oxidation- and ablation-resistant coating for C/C composite [3,4]. But thermal residual stress, caused by different COFs between C/C composite and SiC, would induce micro-crack and be a fatal defect for the coating to deteriorate the property when facing severe temperature changes [5].

SiC nanowires, with high elastic modulus and decent chemical stability, have been widely used to reinforce ceramic-matrix composite [6,7]. LI et al [8] prepared the nanowires to reinforce SiC coating for C/C

composite using Ni or Co as catalyst and proved good effect. Therefore, it is worth preparing SiC nanowires at first, which could improve the bonding between C/C composite and the coating [9].

SiC nanowires can be gotten by chemical vapor deposition (CVD), hydrothermal reaction, in-situ reaction, precursor pyrolysis and so on. For example, QING et al [10] prepared SiC nanowires at low temperature using silica sol, glucose, urea, PAM and nitric acid as raw materials, but the oxygenated chemicals would react with carbon material and influence the property of C/C composite. EICK and YOUNGBLOOD [11] produced the SiC nanowires from the spinning of poly (carbomethylsilane) with pyrolysis to ceramic, LI et al [12] also got it by using the off-gas from polycarbosilane-derived SiC. It is an interesting and good challenge for the coating-preparation on C/C composite. LIU et al [13] prepared the nanowires by deposited silicon on carbon nanotube and then annealed it at  $1200^\circ\text{C}$ . KIM et al [14] synthesized the nanowires by a solid-vapor reaction between carbon nanowires and SiO vapor using Ni-Fe, Fe-Al and Ni-Fe-Al as catalysts. XU et al [15] and LIU et al [16] also got the nanowires by using  $\text{CH}_3\text{SiCl}_3$  as raw materials and Ni as catalyst. Those technologies have produced the

nanowires with good properties, but the catalyst is difficult to be removed thoroughly and the coating might be impure. Thus, it is necessary to prepare the nanowires on C/C composite surface without such residual metal-impurity.

Therefore, in this work, we prepared SiC nanowires on C/C composite surface without catalyst, and analyzed their nano-structure and CVD mechanism.

## 2 Experimental

C/C composite with the density of  $1.83 \text{ g/cm}^3$  was provided by Hunan Boyun New Material Company Limited, China. It was machined to dimensions of  $30 \text{ mm} \times 30 \text{ mm} \times 5 \text{ mm}$  firstly, followed by being polished with 3000# SiC abrasive paper, cleaned in alcohol using ultrasonic cleaner and then dried prior to the test.

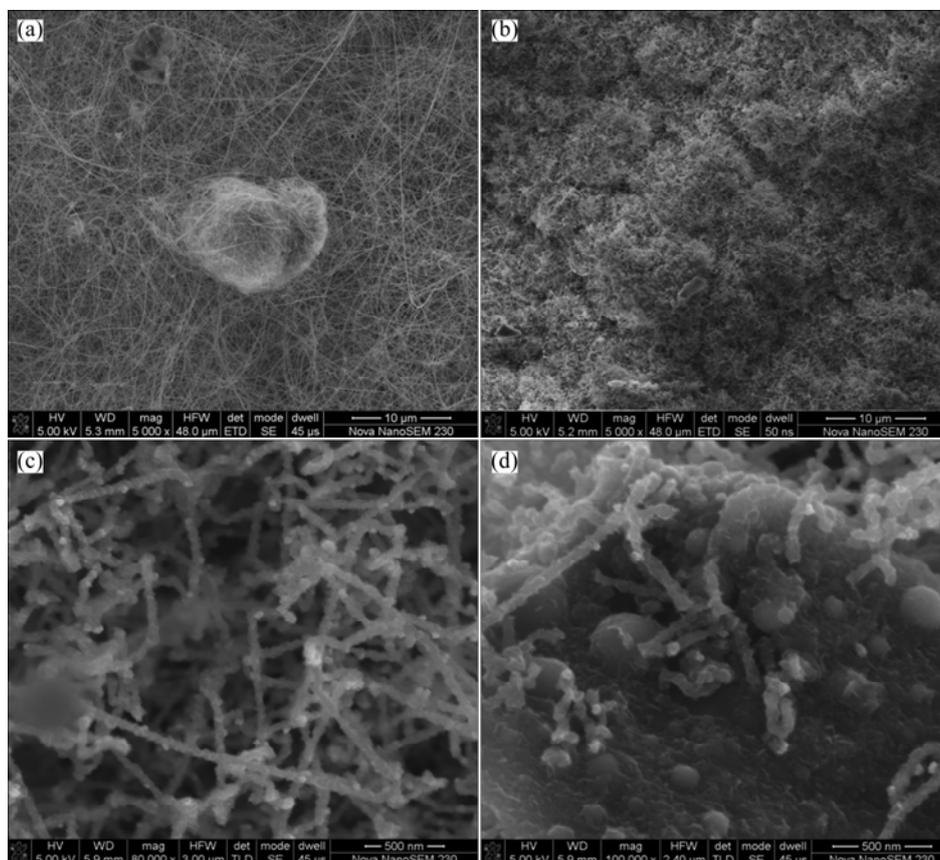
The preparation of SiC nanowires was conducted in a home-made isotherm and isopiestic CVD furnace.  $\text{CH}_3\text{SiCl}_3$  was used as a precursor with  $\text{H}_2$  as carrier- and dilution-gas. CVD temperature was selected in the range of  $1000\text{--}1100 \text{ }^\circ\text{C}$  under pressures of  $0.5\text{--}1.0 \text{ kPa}$  in the deposited area. The deposited time was chosen as  $1\text{--}3 \text{ h}$ .

The morphology and structure of the CVD-product were detected using an FEI-Nova Nano 230 SEM, a

JEM2100F TEM and a D/max2550 XRD, respectively. Infrared spectrum of the product was detected using an AVATAR-360-FTIR Fourier transform infrared spectrometer with a resolution of  $2 \text{ cm}^{-1}$  and a scanning range of  $500\text{--}4000 \text{ nm}^{-1}$ . Raman spectrum was detected using an ALMEGA confocal micro-Raman spectrometer with wave length of  $32.81 \text{ nm}$ .

## 3 Results and discussion

Figure 1 presents FESEM images of the product on C/C composite surface. As shown in Fig. 1(a), some SiC nanowires gather into a ball, some straight or curved nanowires are distributed on the surface randomly. Similar to this study, many researches using catalyst also produced such randomly-deposited SiC nanowires [12–15]. This indicates that similar nanowires can be obtained with or without catalyst. As shown in Fig. 1(b), the short aggregated nanowires, prepared using a modified CVD technique, look like some tightly accumulated Chinese chestnut shell with many thorns. As shown in Fig. 1(c), the short nanowires form an irregular multi-dimensional network. Furthermore, many nano-particles are found on the surface of nanowires, which indicates that the nanowires are favorable deposited sites for the following CVD matter. At the



**Fig. 1** FESEM images of SiC nanowires on C/C composite surface: (a) Long SiC nanowires; (b) Short SiC nanowires; (c) Irregular multi-dimensional SiC nanowire network; (d) Randomly-deposited SiC nanowires and hemispheric particles

same time, we found many tiny pieces bonded with several crossed nanowires. This demonstrated that the flowing CVD-matter was blocked in the crossed nanowires region, which had to be deposited directly on the nanowires surface and grew, and then connected to form a large one [15]. However, it should be pointed out that the grown piece might block the following CVD-gas from infiltrating into the beneath layer, which would result in some closed-holes in the coating. As shown in Fig. 1(d), the randomly-deposited nanowires were bonded with C/C composite surface tightly. It might be a good 3D reinforcement phase for the following CVD coating [8]. In the meantime, many nano-hemispheric particles with different sizes are found to be deposited on C/C composite surface. It also revealed that some SiC particles nucleated and deposited directly on C/C composite surface, which could be the cores for the following nanowires or coating [13,15]. Thereafter, it is good supplement for the nanowires to reinforce the bonding between the coating and C/C composite.

Figure 2 shows XRD pattern of the product. It reveals that the nanowire is a typical  $\beta$ -SiC with the diffraction peaks ( $2\theta$ ) located at  $35.6^\circ$ ,  $59.9^\circ$  and  $71.5^\circ$ , which correspond to the (111), (220) and (311) crystal faces, respectively [6,7].

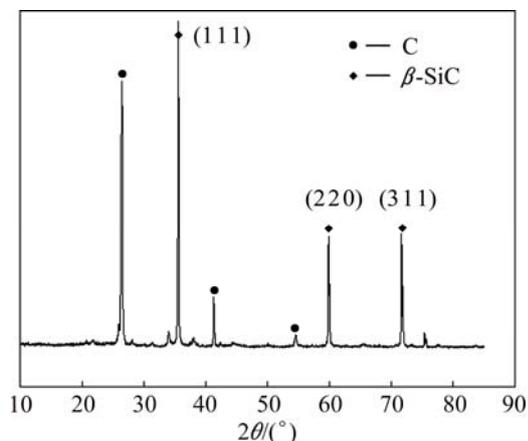


Fig. 2 XRD pattern of SiC nanowires

$\beta$ -SiC has two peaks in Raman spectrum. One is a transverse optical (TO) mode at  $796\text{ cm}^{-1}$ , the other is longitudinal optical (LO) one at  $972\text{ cm}^{-1}$  [6]. As shown in Fig. 3, two peaks present at  $795\text{ cm}^{-1}$  and  $972\text{ cm}^{-1}$ , which are corresponding accurately to the TO and LO of  $\beta$ -SiC, respectively.

Figure 4 shows a FTIR spectrum of SiC nanowires. It agrees with the results in Refs. [7,8]. A strong absorption peak at  $804\text{ cm}^{-1}$  and a wide acromion close to  $874\text{ cm}^{-1}$ , correspond to the TO and LO of Si—C, respectively. BOROWIAK-PALEN et al [7] found that the peak at  $804\text{ cm}^{-1}$  is shifted to low wave of  $6\text{ cm}^{-1}$ , which can be attributed to the small size effect of nano-

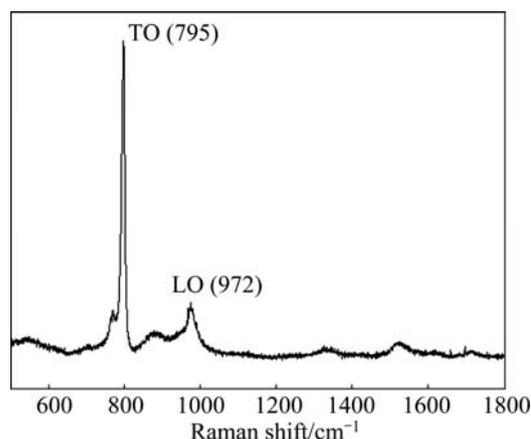


Fig. 3 Raman spectrum of SiC nanowires

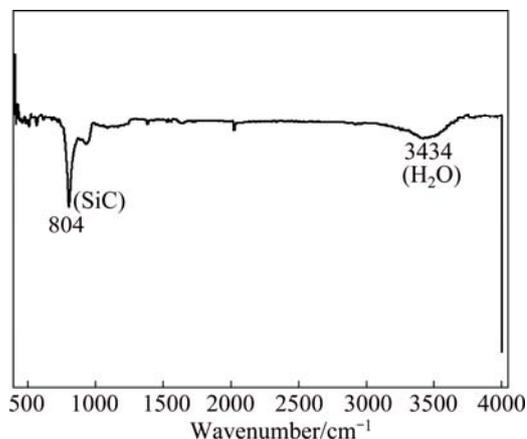
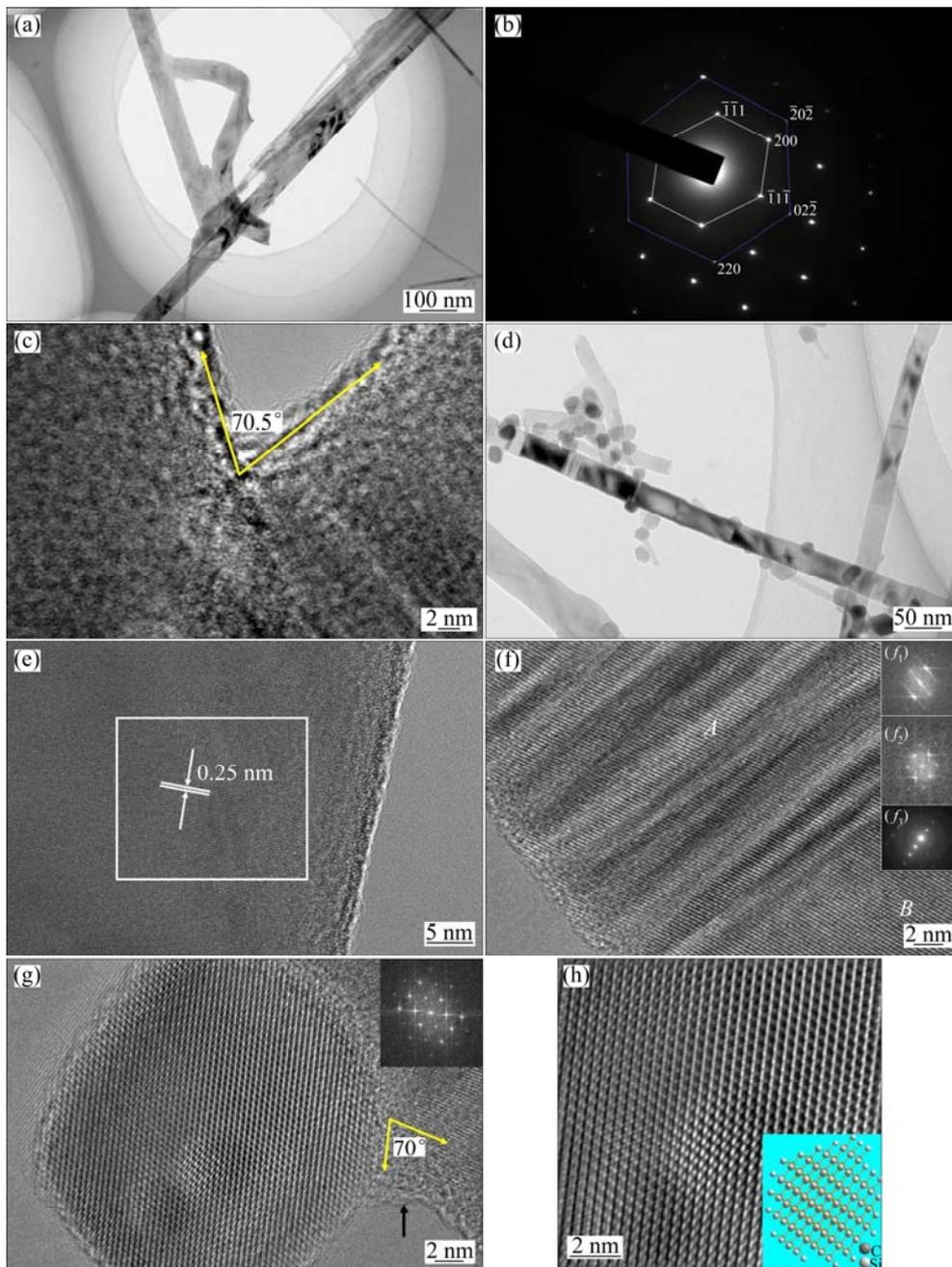


Fig. 4 FTIR spectrum of SiC nanowires

material. Several weak peaks correspond to that of  $\text{H}_2\text{O}$  and  $\text{CO}_2$  which are introduced during the testing.

Figure 5 shows TEM and SAED images of the nanowires taken from C/C composite surface. As shown in Fig. 5(a), one straight large nanowire with the diameter of 100 nm can be found. A twisted one with similar diameter, which seems to generate from the straight one and connects with the straight one again can also be found. In addition, some small nanowires with the diameter of 10 nm, are bonded with a large one by extra-CVD-SiC. SAED pattern in Fig. 5(b), reveals that the wires are a face-centered cubic SiC. One pattern system shows that the nanowires have typical structure corresponding to [011] axis. The other pattern, corresponding to [111] axis, indicates that the nanowires can grow along with different directions. HRTEM image of the amorphous area near the branch, shown in Fig. 5(c), indicates that the normal deposition- process is disturbed due to the fluctuation or supersaturation of local CVD gas [17]. But the angle of  $70^\circ$ , between the trunk and the branch, is consistent with  $70.53^\circ$  of any two adjacent (111) faces in cubic SiC crystal [18,19]. As shown in Fig. 5(d), two nanowires with bamboo-shape



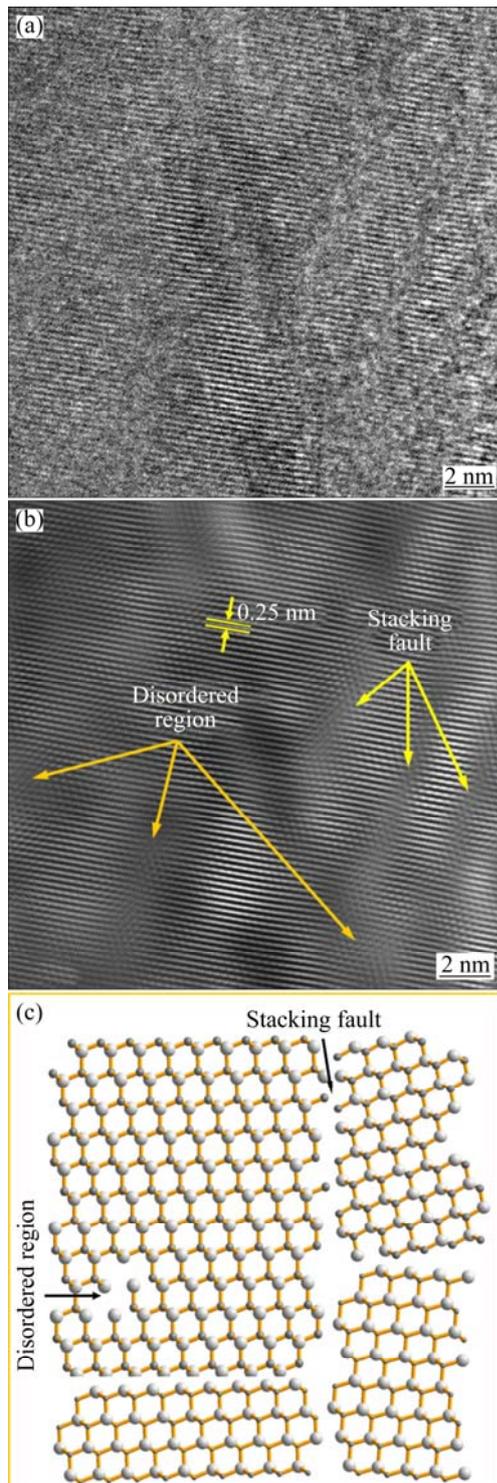
**Fig. 5** TEM images and SAED pattern of SiC nanowires and nanoball: (a) Some large SiC nanowires; (b) SAED image of Fig. 5(a); (c) Image of one branch; (d) Bamboo shape of nanowire; (e) Interlamellar space of SiC nanowire; (f) HRTEM and SAED images of SiC nanowire; (g) SiC nanoball; (h) IFFT image of Fig. 5(g)

trunk are attached by some nano-particles. The interlamellar spacing of 0.25 nm in Fig. 5(e) reveals a typical (111) crystal plane of 3C-SiC in the trunk. As shown in Fig. 5(f), one FFT image (small inserted figure  $f_1$ ) gotten from Area *A* in the bamboo node, indicates a typical stacking faults or twin crystal due to the prolonged scattered spots [18]. The small figure  $f_2$  from Area *B*, indicates a perfect 3C-SiC structure. But the SAED pattern for all areas, shown in small figure  $f_3$ , reveals that the nanowires grow along  $[\bar{1}23]$  axis. The rough edge is partly caused by the mixed arrangement of

amorphous and regular SiC layer. It might be induced by the dangling bond, from silicon or carbon atoms, which resulted in an unbalance stress state for the surface atoms [19] and then forced some atoms or cells to deviate from the perfect lattice position. As shown in Fig. 5(g), a nano-particle with perfect 3C-SiC structure, is bonded with the trunk tightly by extra-amorphous CVD-SiC in the junction (marked with black arrow). The angle of  $70^\circ$ , measured from the lattice plane between the bonding SiC and the trunk, is also accorded with the growth rule of the (111) face. The amplified image, as

shown in Fig. 5(h), reveals that the ball has grown along  $[\bar{1}12]$  face.

Figure 6 presents a magnified, IFFT and simulated images taken from the white block in Fig. 5(e). As shown in Figs. 6(a) and (b), a lot of stacking faults, dislocations and disordered area scatter randomly. This suggests that the residual stress induced by highly curved surface, irregularly arranged atom or atomic clusters near

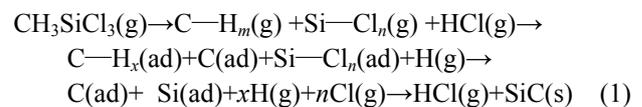


**Fig. 6** Magnified (a), IFFT (b) and sketched (c) images of SiC nanowire taken from Fig. 5(e)

the surface and high free surface energy, would be released by such defects in the nanowires [20–22]. Therefore, it introduces tiny amorphous phase into the nanowires during the CVD process.

JIN et al [19] and KOH et al [23] found that screw dislocation growth was the main mechanism for SiC nanowires produced in vapor deposited process. HE et al [24] considered that anisotropic growth was the main reason and suggested that the nanowires were anisotropic materials and grew preferentially in a certain direction.

During the CVD process, MTS is decomposed into carbon, silicon, hydrogen atom or other different compounds as the following chemical equation [15]:



where  $m, n, x=0, 1, 2, 3$ ; ad represents adsorbed atoms; g represents gas; s represents solid.

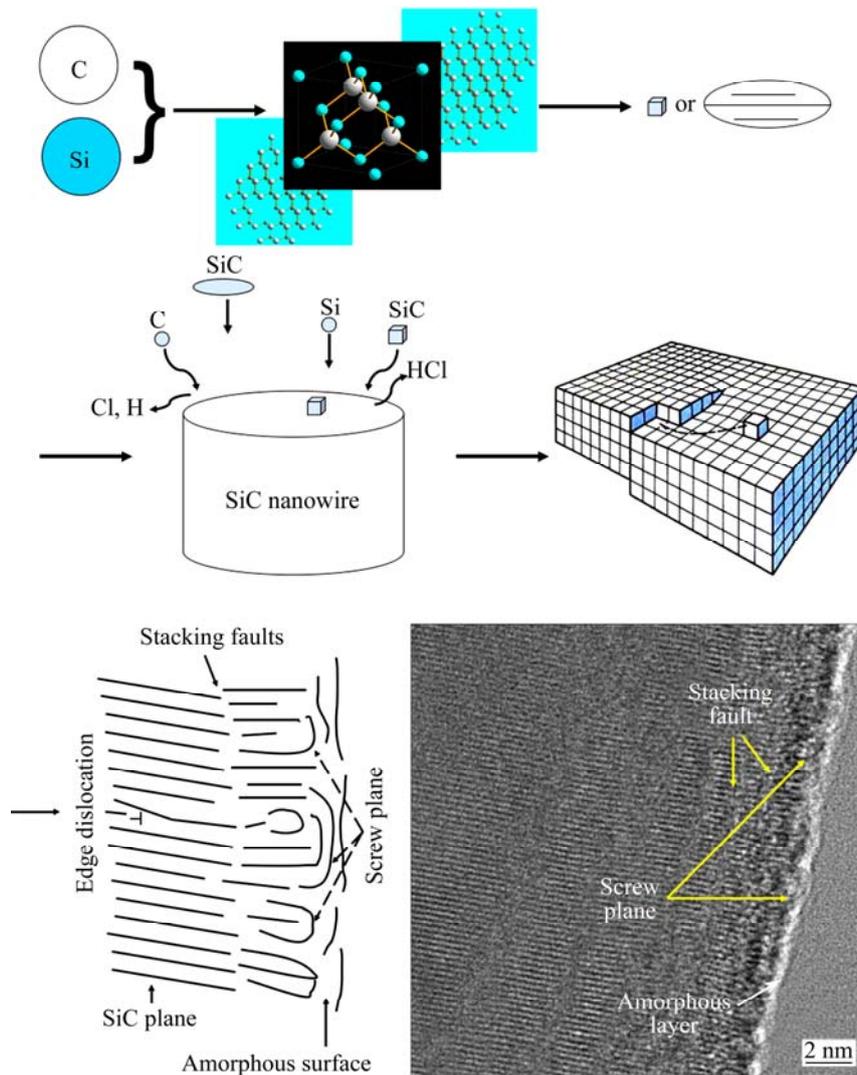
According to the heterogeneous nucleation mechanism, it is easier for the new-generated atoms, cells or clusters to deposit, arrange and grow regularly on solid surface than to nucleate and grow only by themselves. Therefore, as shown in Fig. 1 and Fig. 5(e), most of the nanowires and hemispheric particles can be found to be deposited on the surface of C/C composite or the advanced-formed nanowires.

For the SiC nanowires, the tightest arrangement of atoms is along (111) and screw dislocation growth is the main mechanism [15]. Therefore, it is easy for the deposits, for example, carbon and silicon atoms, SiC-cell and cluster to deposit and grow along this plane due to the lowest energy. At the same time, the deposits would diffuse and topo-gather at the top of growing nanowires due to the concentration difference in the boundary layer [18], which restrains the nanowires to grow thick or only omit a little CVD-matter to deposit on the side surface. Some curved SiC crystal planes near the edge grow with screw dislocation which is similar to that of graphene [25]. The growth process of nanowires is presented in Fig. 7.

## 4 Conclusions

1) SEM images show that many straight or curved nanowires with length of tens of micrometers are distributed on the surface randomly with some gathered as a ball. Some short nanowires, gotten by a modified CVD technique, are agglomerated like chestnut shell with some deposited nano-particles. XRD, Raman and FTIR results reveal that the CVD-product is a typical  $\beta$ -SiC.

2) TEM images show that the nanowires have a wide diameter from 10 to 100 nm. Some thin nanowires



**Fig. 7** Schematic diagrams of screw dislocation growth of SiC nanowires and their TEM image

are bonded to thick one by amorphous SiC. SAED image indicates that the nanowires grow along different axes. In the bamboo node section, FFT image reveals that it is full of stacking faults or twin crystal, which can be proved by the prolonged scattered spots.

3) The intersection angle of  $70^\circ$ , measured from the amorphous section of branched SiC nanowires or from the bonded particle and nanowire trunk, is consistent with the (111) face growth mechanism of 3C-SiC crystal.

4) The screwed SiC lattice planes near the rough surface indicate the main mechanism of screw dislocation growth for the CVD nanowires.

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## C/C 复合材料表面无催化剂 CVD 制备 SiC 纳米线的结构表征

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**摘要:** 在无催化剂条件下, 以 CH<sub>3</sub>SiCl<sub>3</sub> 为前驱体, 采用化学气相沉积技术(CVD)在 C/C 复合材料表面制备 SiC 纳米线。SEM 形貌表明: CVD 产物有大量数十微米长的纳米线, 部分纳米线团聚呈球状, 同时也发现类似带刺板栗外壳的短纳米线聚集, 且纳米颗粒在其表面沉积等现象。XRD、拉曼光谱和红外光谱分析结果表明, 此产物为典型的 β-SiC。TEM 形貌表明, 此类纳米线的直径分布范围为 10~100 nm, 一些较细的纳米线可通过无定形 SiC 与较粗的纳米线结合在一起。在一根较粗 SiC 纳米线的无定形区域长出一根与其直径相近的分支, 二者之间的夹角为 70°, 其与 β-SiC 晶体中[111]轴堆垛夹角一致。SAED 和 FFT 结果表明, 纳米线的生长轴线较多, 在纳米线的竹节状区域存在大量堆垛层错和孪晶。边缘弯曲的 SiC 纳米线晶格面表明, 螺旋位错生长为其主要的生长机制。

**关键词:** SiC 纳米线; C/C 复合材料; 化学气相沉积; 生长机制; 表征

(Edited by Wei-ping CHEN)