Microscopy Study of the Growth Process and Structural Features of Silicon Oxide Nanoflowers

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High-quality SiO_x nanoflowers have been generated by heating mixed SiC/Co powder films in a CO atmosphere. The structural features associated with different stages of the growth were monitored by SEM, TEM, EDX, and XRD analysis. A plausible mechanism for the formation of exquisite flowerlike structures is proposed in which SiC reacts with CO, the Co particles acting as a catalytic template, to yield amorphous SiO_x branches. Numerous loops and branches were also observed which may arise either as a result of bifurcation or coalescence. Use of Co_2O_3 instead of Co as catalyst leads to abnormal flowers exhibiting secondary growth.

1. Introduction

Research into nanometer-scale materials has flourished in recent years because of their excellent mechanical properties combined with unique chemical, electronic, and magnetic behavior.[1] In particular, graphitic nanotubes possessing hollow cores have had a considerable impact on materials science because they exhibit tensile strengths close to the limit of the strongest chemical bond. Carbon nanotubes[2] and related structures containing heteroatoms, e.g., BC_3,[3] BC_2N,[4] BCN,[4,5] BN,[6] MoS_2,[7] and WS_2,[8] have been described, as have other classes of materials, including nanowires, e.g., C nanofibers,[9,10] Sn nanowires,[11] and nanorods, such as SiC,[12,13] GaN,[14] and Si_3N_4.[15] These novel nanostructures, composed of sheet materials at the molecular level, promise a revolution in nanotechnology and materials science. Preliminary studies of tubular structures indicate that they may be used as microscope probes,[16] field emission sources,[17] for gas storage,[18] and as semiconducting devices.[19] Si nanowires[20] and coaxial nanocables,[21] generated by a laser ablation technique, may provide new materials for the semiconductor industry. These discoveries have led to numerous proposals regarding growth mechanisms[22] and the development of alternative routes[23,24] to novel structures. However, due to complications associated with the production methods, e.g., arc discharge for carbon nanotubes,[2] laser ablation for Si nanowires,[20,21] etc., as well as the minute size of the structures themselves, the mechanism associated with growth has yet to be fully elucidated.

Recently, we generated remarkable SiO_x nanostructures by heating SiC in the presence of Co particles on a quartz plate.[25] After reaction, the plate was covered

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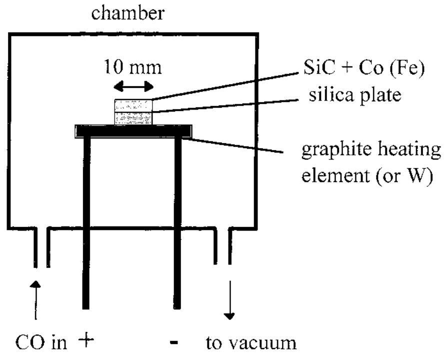

Figure 1. Furnace assembly.

by numerous elegant structures, consisting of branches attached to a central particle (the overall individual shape resembling a flower or octopus[26]). The number of arms may vary from tens to hundreds. In the original paper,[25] we briefly discussed the Co template effect on the growth, and since the production technique is quite straightforward, it should be possible, in principle, to study the process in situ. The mechanism for such a network may have an important bearing on the creation of other types of nanomaterials. We describe below an electron microscopy study of the growth process and detailed structural features of the SiO_x nanoflowers.

2. Experimental Section

A mixture of SiC (400 mesh) and Co (325 mesh) powders, prepared by ultrasonic dispersion in acetone and deposited on a quartz substrate (10 × 5 × 1 mm), was heated to ~1500 °C on a graphite heater element in a furnace (Figure 1) for various lengths of time (Figure 4), in the presence of CO (160 Torr) or Ar (400 Torr) as described previously.[25] Some of the resulting films, coated with Au, were examined by scanning electron microscopy (SEM). Uncoated samples were monitored by energy-dispersive X-rays (EDX), transmission electron microscopy (TEM), and X-ray diffraction (XRD).

3. Results and Discussion

3.1. Chemical Reactions. We have proposed a possible basic sequence which might generate the nanoflowers,[25] and which we here discuss further. The first step involves the reaction of the graphite heater element with the quartz substrate,

$$3C_{(s)} + SiO_{2(s)} \rightarrow SiC_{(s)} + 2CO_{(v)} \qquad (1)$$

resulting in the formation of CO and a yellow-green powder which, according to X-ray diffraction, is β-SiC. We conjectured that the CO, formed in situ, diffused through microfissures in the quartz substrate and reacted in the presence of Co (acting as a catalyst) with the SiC to form silicon oxide and carbon:

$$SiC_{(s)} + CO_{(v)} \rightarrow SiO_{(v)} + 2C_{(s)} \qquad (2)$$

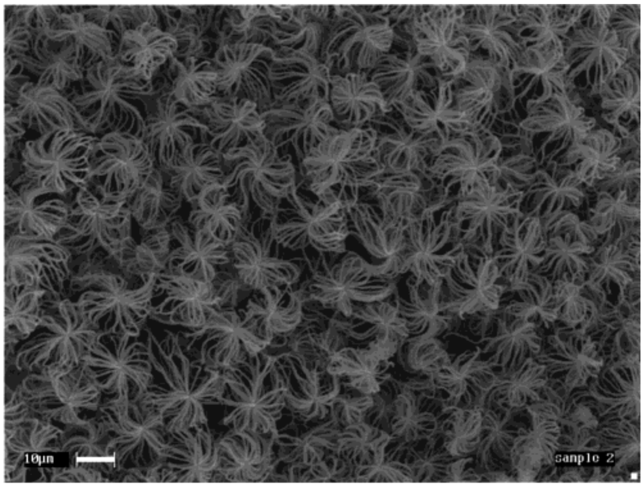

Figure 2. SEM image of a high quality 3D flower film. Experimental conditions: SiC/Co (1:1 wt %) powder; CO gas (600 Torr); graphite heater (~1500 °C for 40 min).

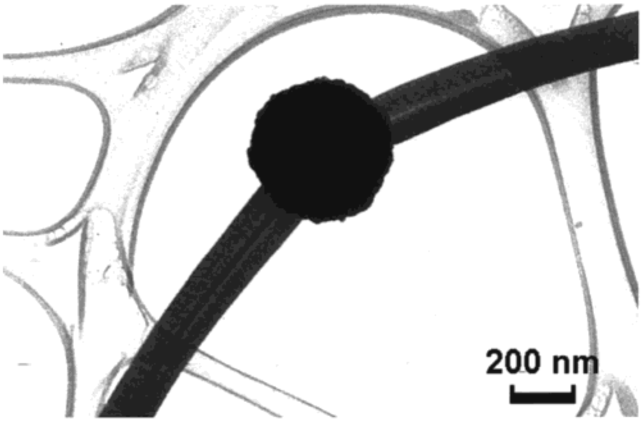

Figure 3. TEM image of a tubelike structure attached to a particle. The darker inner core, sheathed by amorphous SiO_x, is very narrow.

The presence of CO is therefore critical to the nanoflower (SiO_x) growth process, and to test this conjecture, we performed further experiments by passing CO (~160 Torr) directly into the system instead of Ar. As a result, better quality nanoflowers of strikingly uniform size were obtained (Figure 2), covering the whole surface.

It is also conceivable that gaseous SiO may react with carbon, or CO, to generate the more stable SiO_2:

$$C_{(s)} + 2\ SiO_{(v)} \rightarrow SiC_{(s)} + SiO_{2(s)} \qquad (3)$$

$$3\ SiO_{(v)} + CO_{(v)} \rightarrow SiO_{2(s)} + SiC_{(s)} \qquad (4)$$

Whether reaction 3 and/or 4 occurs depends on the supply of C and CO. If both SiO_2 and SiC are formed, a nanostructure similar to a coaxial nanocable[13,21] may result. Figure 3 shows one such nanowire with a SiC central core, sheathed by SiO_2. In a previous study, a similar structure[27] was generated in the absence of a metal catalyst, but at higher temperature (1700 °C). TEM studies indicated that most of the nanofibers consisted of only one phase (SiO_x, $x = 1-2$ according to XRD and EDX analyses) with no central core.

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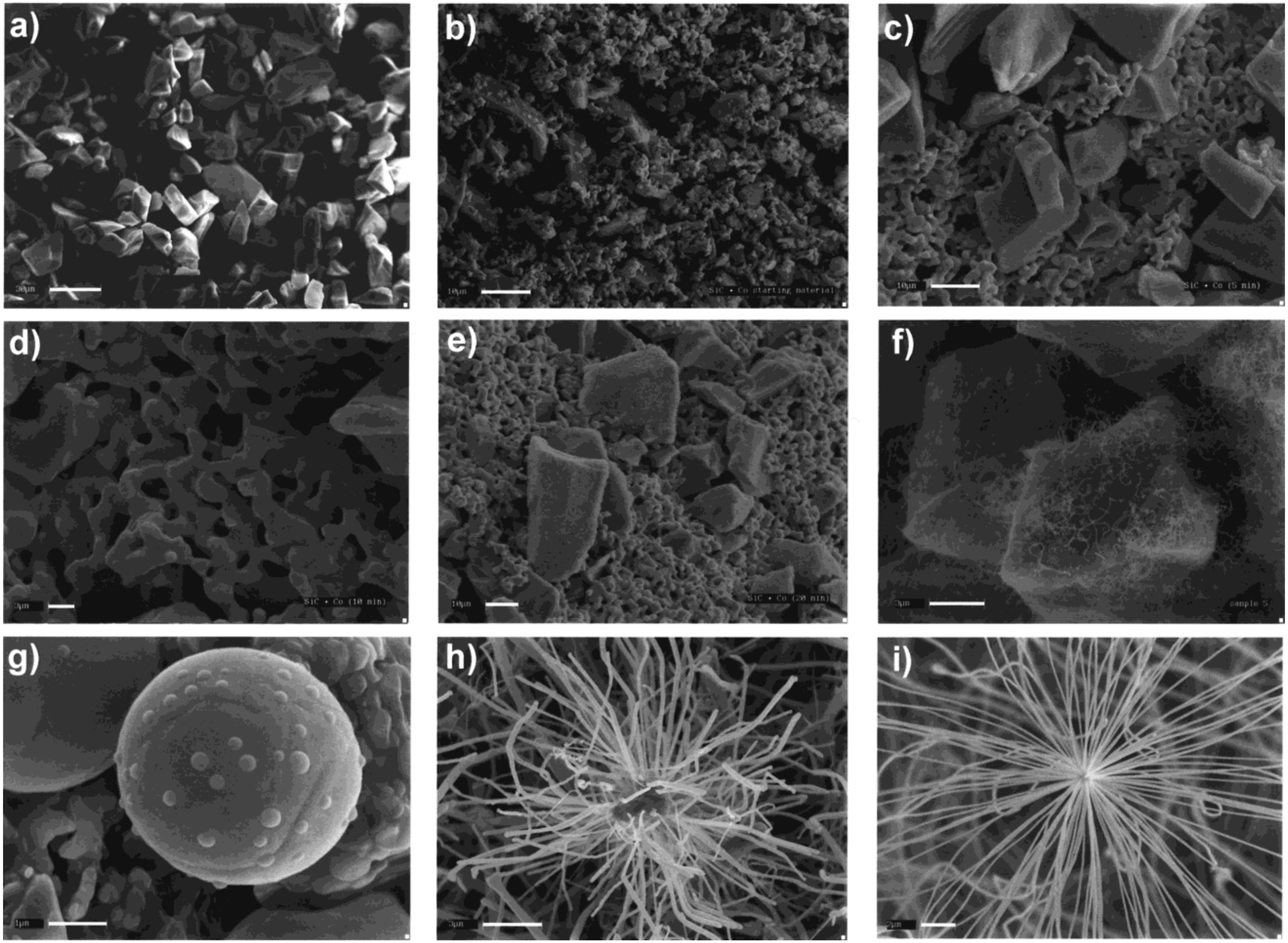

Figure 4. A series of SEM images obtained at different stages during the heating process. All the experiments were carried out under Ar (400 Torr): (a) the original SiC powder; (b) SiC/Co film before heating; (c) SiC/Co film after 5 min of heating; (d) SiC/Co film after 10 min of heating; (e) SiC/Co film after 20 min of heating; (f) SiC/Co film after 30 min of heating fibers starting to grow from the SiC particles; (g) Co spherical particle exhibiting random blisters; (h) intermediate growth stage of a flower (heated for 40 min); and (i) finally, a well-developed nanoflower exhibiting strong 3D features.

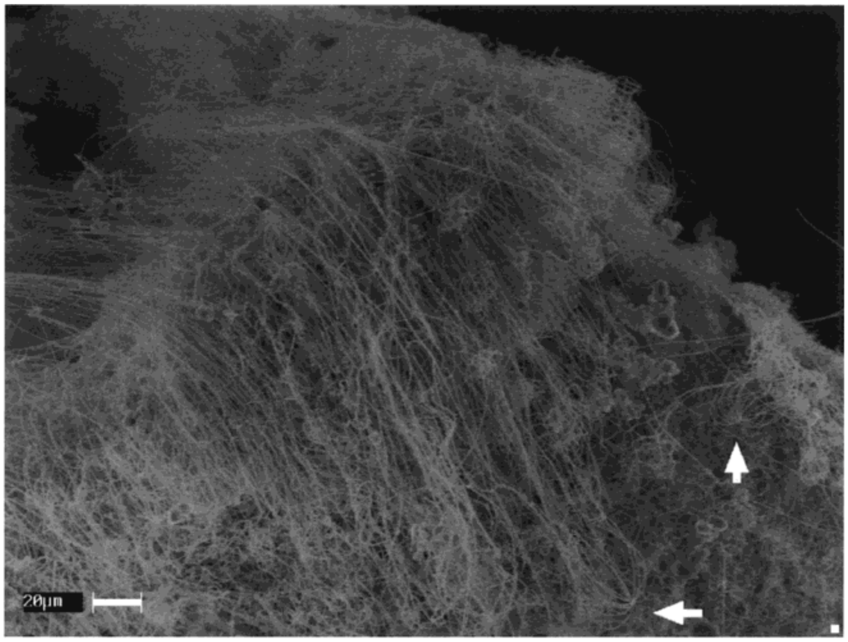

Figure 5. SEM image: film cross-section (after 1 h heating), revealing very long nanofibers. No SiC particles present. Two flowers arrowed.

As an alternative to reaction 1, the graphite heater may react with the quartz substrate (~1500 °C) according to reaction 5, thus leading to the same product (SiO):

$$2C_{(s)} + SiO_{2(s)} \rightarrow SiO_{(v)} + CO_{(v)} \qquad (5)$$

If this reaction occurs, SiC may conceivably play no role in the growth of SiO_x nanoflowers. To shed further light on the Co-catalyzed growth process, samples of SiC/Co powder were heated for various times and some of the products (depicted in Figure 4) were examined by SEM.

3.2. Observations Relating to Various Growth Stages. Figure 4a shows that the precursor SiC powder consists of irregularly shaped single crystals with smooth surfaces and sharp edges. The mixture of SiC and Co (Figure 4b) is fairly uniform, with the smaller Co particles attached to the larger SiC crystals. Figure 4c shows that after 5 min heating at 1500 °C, there has been no significant change in the SiC crystals; however, the Co particles have started to coalesce so reducing their surface energy. After 10 min (Figure 4d), the Co particles have continued to coalesce, and the surface of the SiC crystals has become rough (contrast Figure 4a) but with smoother, more rounded, edges. We believe the onset of reaction 2 occurs at this stage. After 20 min, spots can easily be observed (Figure 4e) on the SiC surface. Figure 4f shows hairy nanofiber growth from SiC particle surfaces, thus confirming SiC as a source material in our experiments. It is noteworthy that these nanofibers possess a small diameter. We suggest that minute Co clusters, acting as catalysts, may be located at the growing tips. At this stage, these nanofibers have no direct connection with the central Co particles (Figure 4g). We therefore believe that they may eventually grow into very long single nanofibers. During TEM examination, we noted that some of the isolated nanofibers may arise from such a growth (as those which have broken away from the nanoflowers usually have relatively larger diameter). At the same time spherical particles, presumed to be Co and thought to be the nuclei for nanoflower growth, form. Blisters on the particle surfaces (Figure 4g) may be the growth sites for the branches. Figure 4h shows an intermediate stage in flower growth, in which the branch lengths are still increasing. At the tip of some of them, a round particle with diameter slightly bigger than that of the branch itself is observed. This suggests growth involving vapor/liquid/solid (VLS) processes.[28] In fact, the above reactions 1 and 2 are typical of a complicated vapor phase step. Under our experimental conditions, the Co particles should melt below 1495 °C, leading to diffusion of the SiO_x into the liquid phase. Finally, a typical well-developed nanoflower is produced after 1 h (Figure 4i). These flowers exhibit exotic structures, often with more than 100 branches (each ~150 nm diameter) centered on a spherical particle of ~0.5 µm diameter.

Further compelling evidence for SiC being the source of the nanoflowers is provided by direct SEM observation of a cross-section of a sample (cut with a scalpel). This confirms that no SiC particles remain after ~1 h heating. Instead, partly aligned fibers up to 100 µm in length are observed (Figure 5). Several typical flowers are marked by arrows.

So far, it seems that through monitoring of the growth process at different stages, the nanoflowers originate mainly as a result of reaction 2 and that SiC is actually the source of Si for the nanofibers.

However, when we examined the boundary region of the quartz substrate by SEM, an interesting phenomenon was noticed. Buds, reminiscent of cotton, appeared to be attached to the quartz surface (Figure 6a). Focus-

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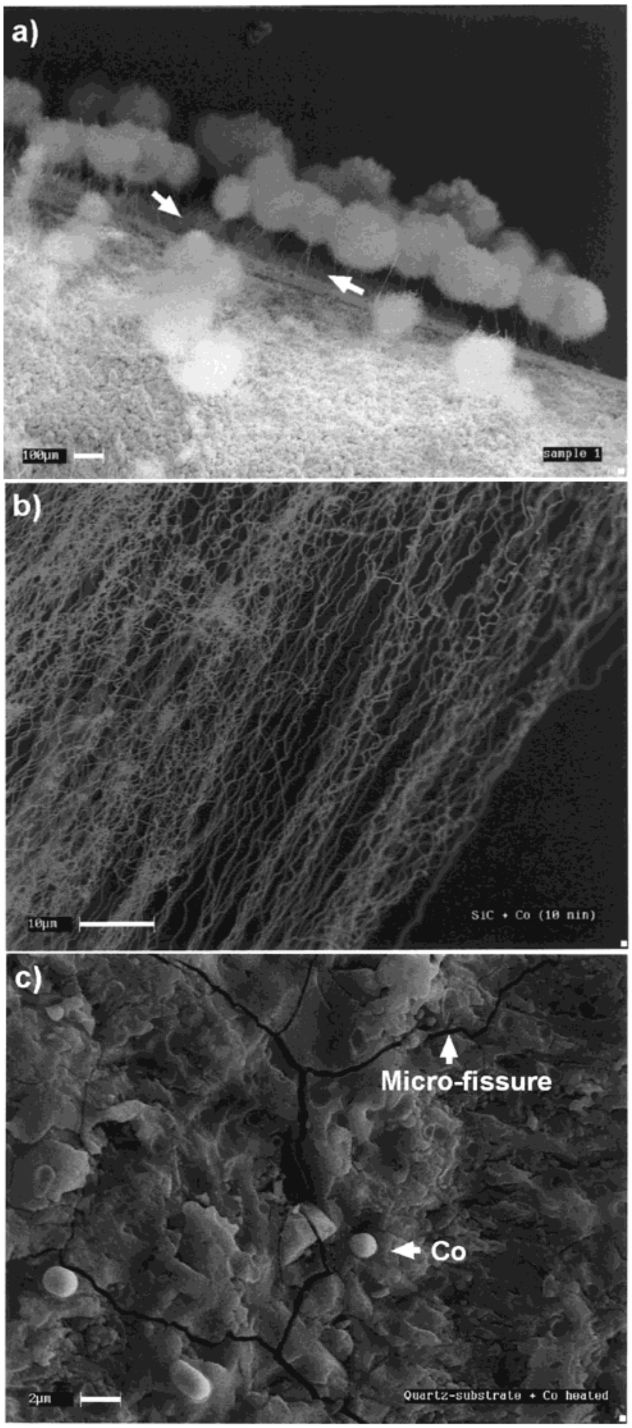

Figure 6. Substrate edge: (a) cotton-like structures (~100 μm diameter) connected to the substrate by large fibers; (b) the arrowed region in part a consisting of aligned fibers (~100−150 nm diameter; 100 μm length); and (c) heated SiO_2 substrate with Co. Nanofibers absent. Note microfissures.

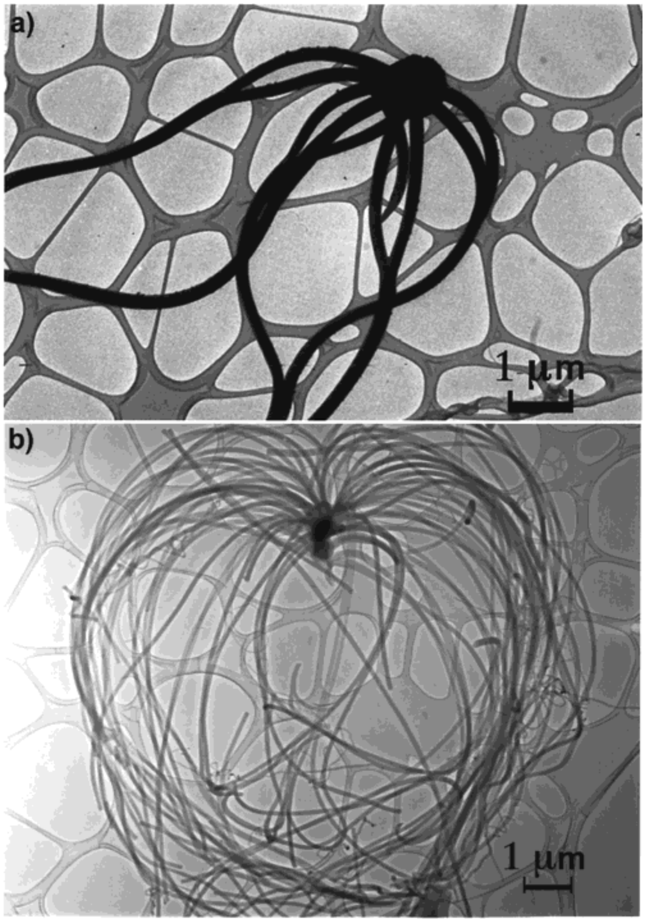

Figure 7. (a) Single nanoflower (TEM image at 100 kV). Some branches lost during sonication; (b) nanoflower with almost all branches remaining, fostering strong connections between nanofibers and Co particle (TEM image at 400 kV).

ing during SEM observations proved difficult because of the fine quality of these buds; however, they may consist of fine amorphous SiO_x filaments. For those areas marked by arrows in Figure 6a, very long moderately aligned fibers (Figure 6b), which are not particularly straight, are also attached to the quartz plate. These fibers were detected after 10 min of heating: nanoflower growth has yet to occur in the central area of the film sample. This result is not consistent with fiber growth via reaction 2. Reaction 5 remains a possibility, but it is not clear that it is involved in nanoflower growth. Experiments involving only Co and the quartz substrate, which did not produce such structures, support these conclusions. The Co melts to form a metal film, but nothing grows from it (Figure 6c).

The above analysis considers possible chemical reactions and different growth stages for the nanoflowers and provides support for a so-called VLS growth mechanism[28] involving catalytic particles.[25]

3.3. Characterization of the Nanoflowers. Figure 2 shows that the nanoflowers are of uniform size, each containing a similar number of branches or arms. Figures 2 and 4i (single flower) illustrate the characteristic flowerlike feature in which branches emanate radially in all directions from a central sphere. This phenomenon has also been observed by TEM (Figure 7a). We note that some of the branches are broken and/or separated from the central sphere (Figure 7a), an effect which may be due to breakage incurred during sample preparation (sonication in acetone). However, in some cases, connections between branches and central particles are preserved (Figure 7b).

Another interesting nanofiber structural feature occurs when two or three branches unite into single fibers

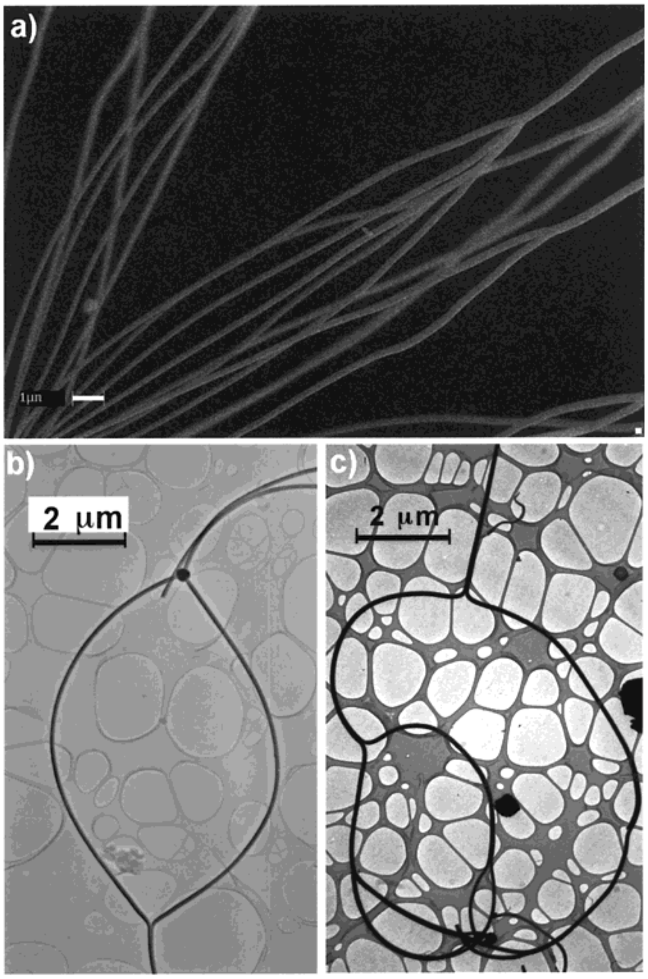

Figure 8. (a) Branched nanofibers (SEM image) presumably emanating from a central particle (located at bottom left); (b) closed loop including catalyst particle (TEM image at 400 kV); and (c) multiple nanofiber loops (TEM image at 100 kV).

as the distance from the central particle increases (Figures 7a and 8a). This phenomenon is believed to be related to the catalyst particles. In a previous experiment using so-called "bamboo-milk" (a natural form of SiO_2 containing ~5% Fe) to generate nanostructures in the presence of Co,[25] we found that the growing tip of the nanofiber often seemed to split into two, producing a bifurcated fiber (ref 25, Figure 8b). These fibers may subsequently grow toward each other, finally forming a loop. On the other hand, it is possible that the Co particles (located at the growing tips) may occasionally fuse or coalesce into a larger particle during radial growth (similar to the Co coalescence to form the initial spheres shown in Figure 4g), thus resulting in the loop structures (Figure 8b). At this stage, it is not absolutely clear whether a bifurcation or a coalescence step dominates in the loop structure growth. We favor slightly a bifurcation mechanism which is supported by close inspection of the interesting structural details observed at the base of the fibers (ref 25, Figure 8b)]. Figure 8c exhibits various closed loops, suggesting that bifurcation and/or coalescence must have occurred several times during growth. This effect differs from that observed for branched carbon filaments in which traces of other metals contained within the catalytic particles reduce carbon diffusion and solubility during growth.[10] In our experiments, we used pure Co and therefore particle coalescence at a specified temperature (~1500 °C) may be facile. Statistical factors probably militate against a coalescence mechanism.

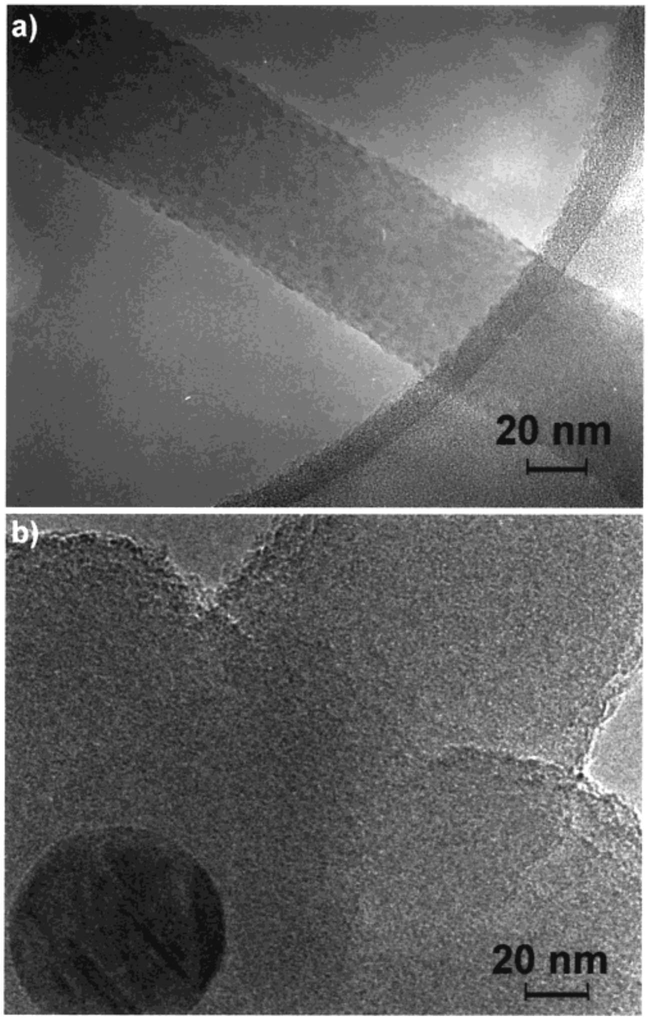

Figure 9. HRTEM images (400 kV): (a) amorphous SiO_x fiber (50 nm diameter) and (b) typical spherical Co particle (surrounded by amorphous SiO_x) responsible for radial nanofiber growth.

EDX analyses reveal that the branched nanofibers consist solely of the elements Si and O, with an O/Si atom ratio between 1 and 2. The compositions of branches and subbranches (containing Si and O) were similar and no obvious differences among them were detected. Co signals mainly arose from the central particles; X-ray powder diffraction studies show a broad reflection at $2\theta \approx 22°$, indicating that the nanoflower arms are mainly amorphous SiO_2.

HRTEM observations show that the arms are amorphous nanofibers (Figure 9a), and reveal the presence of rounded Co particles (~20 nm diameter) within the central spheres, covered by amorphous SiO_x (Figure 9b). We believe that these Co particles act as nucleation templates and are responsible for the agglomeration of SiO_x and subsequent multiarm radial growth.

Other typical regions exhibit smaller flowers with fewer branches (Figure 10a), the former growing close

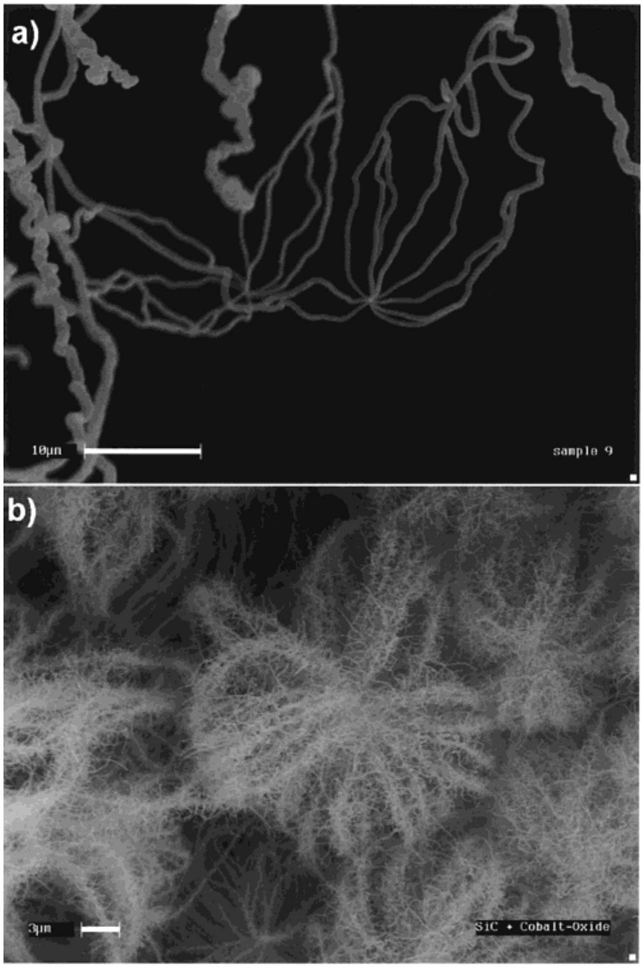

Figure 10. SEM images: (a) flower with fewer branched fibers, found close to the edge region and (b) abnormal flowers grown from Co_2O_3 catalyst; note secondary growth. Experimental conditions: SiC/Co_2O_3 (1:1 vol %), quartz substrate, Ar atmosphere (~400 Torr), graphite heater (~1500 °C for 40 min).

to the edge of the heated substrate. This result may be due to an inefficient reaction which may be favored at the periphery of the substrate (see reaction 5), in which the amount of gaseous SiO is insufficient for complete formation of nanoflowers.

When Co_2O_3 was used as a catalyst, under the same conditions as in the SiC/Co experiments, even more unusual flowers formed (Figure 10b). In this case numerous secondary short filaments are seen to grow perpendicularly from the surface of each primary fiber attached to the central particle. The structures are reminiscent of leaves growing from tree branches. This type of secondary growth has also been observed by others during carbon fiber production.[10]

4. Conclusions

The different stages in the growth of SiO_x nanoflowers, formed from SiC and CO, have been investigated by electron microscopy. The process is catalyzed by Co particles and appears to involve a VLS mechanism which generates nanofibers. Occasionally SiC nanowires, sheathed by amorphous SiO_2, are produced. Loop structures are sometimes observed and are thought to arise as a result of a bifurcation and/or a coalescence step during Co catalyzed growth. The resulting networks, and the novel growth process, may have important implications in semiconductor fabrication, possibly after further modification leading to other nanostructures based upon, e.g., pure Si or Si_3N_4 networks.

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