# Scanning electron microscopy study of carbon nanotubes heated at high temperatures in air

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Multiwalled carbon nanotubes (MWNTs) were dispersed in 2-butanol and dropped onto a *V*-ridge, lithographically patterned Si substrate that was coated with a thin layer of gold. These MWNTs were shown by scanning electron microscopy (SEM) to conform to the *V*-ridge surface topology at room temperature, which is thus useful for introducing kinks (at the apex of the *V*-ridge and the bottom of the trenches between *V* ridges). The substrate-supported MWNTs were then heated in air at temperatures from 673 to 1173 K for varying exposure times and were monitored with SEM. A $122\,\mathrm{kJ\,mol^{-1}}$ activation energy for complete oxidation was obtained, and preferential oxidation at kink sites was observed on some MWNTs at high temperatures. The dominant mode of oxidation was either thinning of the walls of the MWNTs or sequential oxidation of the component tubes in bundles. Some MWNTs, which at room temperature conformed to the *V*-ridge surface topology, detached (''sprang'' away) from the substrate surface, demonstrating that the MWNTs are under tensile stress, but are held to the surface by van der Waals attractive forces, which can be overcome by exposure to higher temperatures. © *1999 American Institute of Physics.*
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## I. INTRODUCTION

Because of their remarkable physical and electronic properties, carbon nanotubes are promising materials for many applications.[1] The behavior of carbon nanotubes at high temperature in air is relevant for some of these applications, such as a reinforcing fiber in composites intended for use in atmospheric reentry. Heating carbon nanotube samples in air or in an oxygen atmosphere is also an effective way of purifying the samples from other forms of carbon.[2] Some studies have reported the gasification of carbon nanotubes in air,[3,4] in an oxygen stream,[5] or under a flow of carbon dioxide gas.[6] Thinning of nanotubes, opening of the caps, and pit formation on the surface were observed in these studies. All of these studies were conducted over a limited temperature range and in limited time periods. Only one study observed the same nanotubes before and after heat treatment,[5] while all other studies mentioned above observed heat-treated nanotubes and compared them with raw material. In this work, we report a systematic study of carbon nanotubes heated in air over a large temperature range and for long times. The same carbon nanotubes were observed by scanning electron microscopy (SEM) throughout a sequence of heat treatments. We further report the preferential oxidation behavior at carbon nanotube kink sites.

## II. EXPERIMENT

Multiwalled carbon nanotubes (MWNTs), donated by Smalley's group at Rice University, were used for the present study. The MWNT material was made in an arc apparatus.[7] As formed, this material was a black disk, consisting of MWNTs with diameters ranging from 2 to 50 nm with lengths up to 10 $\mu$m, nested polyhedral particles, and some amorphous carbon. The MWNTs we obtained underwent the following treatment in Smalley's group before reaching us: the material was baked in dry air at 1023 K until approximately 98% of the original mass was removed. This treatment preferentially oxidized away the amorphous carbon, nested polyhedral particles, and nanotube ends. We then dispersed these MWNTs in 2-butanol by extensive ultrasonic agitation. A drop of this suspension was dispensed onto a specially prepared *V*-ridge substrate (NT-MDT TGG01), where the peaks of the ridges are 3.0 $\mu$m apart and 1.7 $\mu$m tall with a peak angle of 70°. This substrate had been prepared by sputter coating a ~10-nm-thick gold film and heating at 1173 K for 5 min in air. The high temperature broke up the gold film, producing small gold particles. These particles not only improved the conductivity of the substrate, but also provided focusing objects in the scanning electron microscope (Hitachi S-4500 SEM; 15 kV accelerating voltage). The dispensed drop was then air dried.

This *V*-ridge substrate introduces kink sites in the MWNTs,[8,9] which we then observe after exposure to oxidative conditions. The kinked sites on these nanotubes exhibit heightened chemical reactivity, as explored by recent theoretical work by Srivastava *et al.*, which has led to the idea of using kinks in nanotubes for site specific chemistry.[9] By providing a route to selective reactions along an otherwise undifferentiated nanostructure, such ''kinky chemistry'' may find applications in the fabrication of nanodevices. The samples were heated in a Lindberg quartz tube furnace to controlled temperatures for specified times. Both ends of the furnace tube were open to air during each heat treatment, and no effort was made to either cause or prevent air flow. During the oxidation, the sample was placed in a quartz cylinder,

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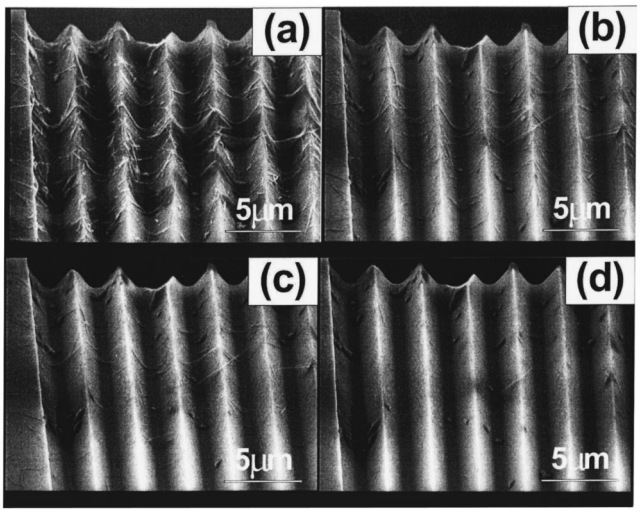


FIG. 1. (a)SEM micrographs of MWNTs dispersed on a *V*-ridge silicon substrate, and heated in air at 1073 K for (b) 1 min, (c) 2 min, and (d) 4 min.

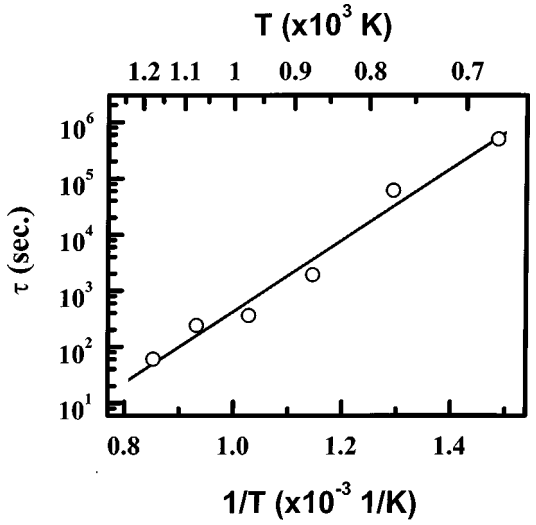


FIG. 2. Persistence of MWNTs as a function of temperature of heating in air.

or ''boat,'' that was 6.6 cm long, and had a 2.5 cm outer diameter and a 0.16 cm wall thickness. The furnace tube and quartz boat were first brought to the desired temperature and allowed to equilibrate for more than half an hour, since the whole system had a very large thermal inertia. The boat was pulled to one end of the furnace tube, and the sample was quickly inserted before rapid replacement of the boat in the furnace tube. The entire process took less than 5 s. Once the boat was replaced, the clock was started to count heating time. The boat was removed from the furnace tube at the desired time, and the sample was immediately moved from the boat to a large aluminum sheet to ensure rapid heat dissipation. The removal process also took less than 5 s. The small thermal inertia of the sample substrate, a 1.5 mm$\times$2 mm silicon wafer, should make the heating and cooling time of the sample negligible, particularly for the data points with long heating times. The samples were inspected with SEM after each heat treatment at a given fixed temperature until the carbon nanotubes on the substrate were all burned off. The process was repeated with further sets of temperature/time profiles.

## III. RESULTS AND DISCUSSION

Figure 1 shows SEM micrographs taken at consecutive time intervals during the 1073 K heat treatment of the MWNTs. Figure 1(a) shows the MWNTs as dispersed. The nanotubes follow the morphology of the substrate closely because of the van der Waals attraction between the nanotubes and the surface. Figure 1(b) was taken after 1 minute heating; Fig. 1(c) was taken after another 1 minute heating, the cumulative heating time was thus 2 min; Fig. 1(d) was taken after 4 min cumulative heating time; these figures show the nanotubes being burned off gradually. After 4 min of heating, very little residual carbon from the nanotubes was left on the substrate, as shown in Fig. 1(d). We define the minimum cumulative time to remove essentially all the nanotubes as the persistence $\tau$, our criterion for assigning $\tau$ is by visual inspection of the SEM images. Figure 1(d) shows that the time to remove the nanotubes at 1073 K in air is $\sim$4 min. By measuring $\tau$ in this way at different temperatures, a relationship between $\tau$ and temperature was established as shown in Fig. 2.

Fitting a line to the Arrhenius plot in Fig. 2 gives an activation energy of 122 kJ mol$^{-1}$. Since carbon nanotubes can be approximated as graphite sheets rolled into cylinders, we have compared this activation energy to those observed for graphite. Our value falls in the lower range of reported activation energies for graphite oxidation, which varied between 100 and over 300 kJ mol$^{-1}$.[10] (Remarks about the wide range of reported values for the activation energy of oxidation of graphite are also given in Ref. 10.) The curvature of the graphitic sheets in the nanotubes implies that the carbon atoms are more reactive than in graphite.[11,12] Therefore, compared to graphite oxidation, we expect a lower activation energy for carbon nanotubes. For comparison, Ajayan *et al.*[3] obtained an activation energy of 225 kJ mol$^{-1}$ by measuring mass losses of nanotubes burned for a given time at different temperatures; this value also falls in the range of reported activation energies of graphite oxidation, but is considerably higher than the most recently measured value of 175$\pm$3 kJ mol$^{-1}$.[10]

Figure 3 shows an individual nanotube over the course of repeated heat treatments; it thinned very uniformly along the observed (interior) 2000-nm-long section. In general, although we observe that the nanotubes do shorten at the ends, the dominant burn-off mechanism appears to be the uniform thinning of the walls. An alternative possibility is that the

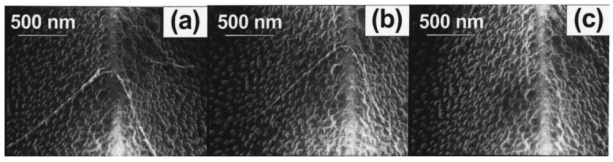


FIG. 3. SEM micrographs of a MWNT on ridge heated in air at 773 K for (a) 25 min, (b) 5 h and 10 min, and (c) 17 h and 13 min.

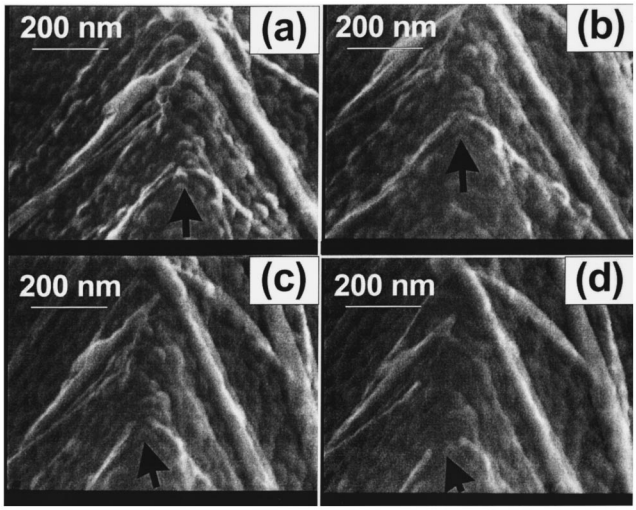


FIG. 4. SEM micrographs of MWNTs on a ridge heated in air at 973 K for (a) 1 min, (b) 3 min, (c) 4 min (c), and (d) 6 min. The arrows point to the kink site where the nanotube broke.

observed tubes are actually bundles, and the observed thinning is actually the sequential oxidation of the component tubes. Experiments are currently under way that should distinguish between these possibilities. While most tubes oxidized as shown in Fig. 3, we did observe preferential oxidation at kink sites on some nanotubes. Figure 4 shows preferential oxidation at such a site at 973 K. The kink site of the nanotube in the lower part of the figures started to be oxidized after 3 min heating, as shown in Fig. 4(b). The nanotube was broken at the kink site after 4 min heating as shown in Fig. 4(c), and the gap between the newly formed ends increased when the heating time increased to 6 min, as shown in Fig. 4(d). More nanotubes showed this ''kink effect'' when the heating temperature was increased to 1073 K, but most of the nanotubes still underwent uniform oxidation. Figure 5 shows the behavior of kink sites of two nanotubes heated at 1073 K, one nanotube exhibited preferential oxidation at the kink site, while the other nanotube showed uniform thinning. Nanotube ''breaks'' were observed only near the top of the ridges or at the bottom of the trenches (where the nanotubes are also kinked due to the high curvature). This strongly suggests that any breaking of nanotubes was indeed induced by preferential oxidation at kinked sites. A possible contributing factor, in addition to the deformation of the nanotubes at each *V*-ridge apex or the bottom of each trench, is that these MWNTs are also under tensile stress (see discussion of Fig. 7 below).

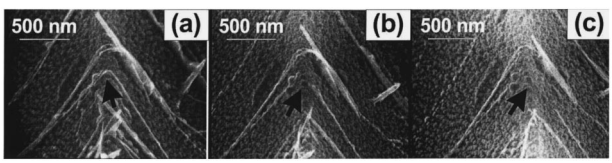


FIG. 5. (a)SEM micrographs of MWNTs on a ridge as-dispersed, heated in air at 1073 K for (b) 1 min and (c) 2 min. The arrows point to the kink site where the nanotube broke. Note that another nanotube in the figure did not break at its kink.

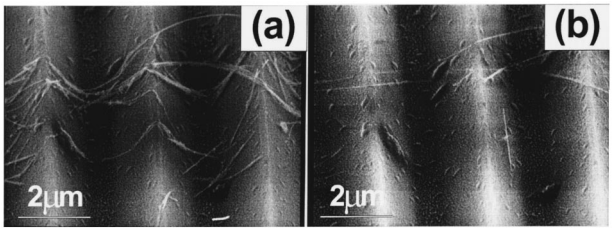


FIG. 6. SEM micrographs show MWNTs detached from the surface in a *V*-ridge trench region. The sample was heated in air at 1173 K for (a) 10 s and (b)40 s.

When the heating temperature was further increased to 1173 K, we observed no such preferential oxidation of kinks; this was largely because the nanotubes detached from the surface as shown in Fig. 6, removing many of the kink sites. Figure 6(a) was taken after heating for 10 s, and shows both nanotube thinning and surface detachment. Figure 6(b) was taken after heating for 40 s and shows that either the nanotubes were oxidized away, or were no longer conforming to the *V*-ridge surface.

We note that although nanotubes also detached from the surface at temperatures as low as 773 K, this occurred only after long heating times, as shown in Fig. 7. After 5 min at 773 K, Fig. 7(a), the MWNT in the center still follows the *V*-ridge topology and is clearly attached to the surface over three adjacent ridges. But after one hour, Fig. 7(b), it has detached over one part (between the two adjacent ridges on the left). Upon further heating, this detachment continued, and after 5 h and 10 min, Fig. 7(c), the MWNT is completely detached from the surface in the trench region between the two adjacent ridges on the left. Figure 7(d), after 17 h and 13 min, shows further detachment of the nanotube and significant shortening by oxidation.

We suggest the following as a possible explanation for some of the nanotubes detaching following heat treatment. When the nanotubes are dropped onto the *V*-ridge substrate,

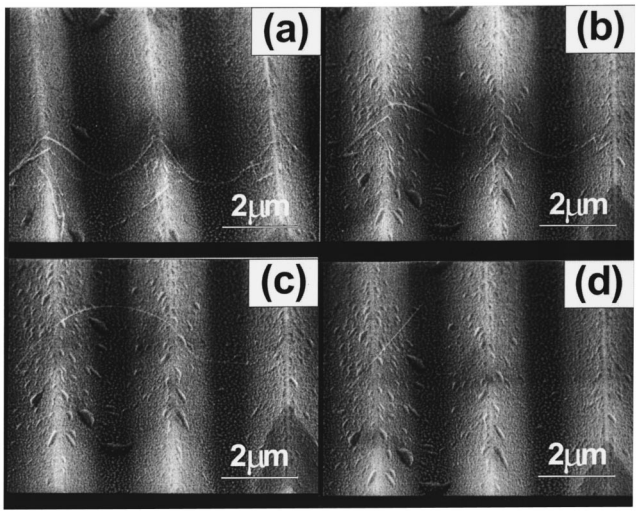


FIG. 7. SEM micrographs show MWNTs detaching from the surface in *V*-ridge trench region after long time heating at 773 K in air. The sample was heated for (a) 5 min, (b) 1 h, (c) 5 h and 10 min, and (d) 17 h and 13 min.

capillary forces play a role in bringing the nanotubes into intimate contact with the surface as the 2-butanol evaporates. The fact that we observe nanotubes, when heated, detaching from the surface in the trench regions shows that the nanotubes are in a metastable configuration prior to heating: van der Waals attractive forces hold them in contact with the surface so that they follow the *V*-ridge topology. When energy is supplied by heating, this attraction is overcome, allowing the MWNTs to detach from the surface, and ''spring'' away from it.

Oxidation of nanotubes occurs through a multistep process, involving initiation of the oxidation at vulnerable sites (endcaps, defects, and sites of local conformational strain),[3,9] and then propagation down the tube from those sites. The activation energy measured in this study is for total oxidation of the nanotubes, and therefore will be that of the rate-limiting step. The nanotubes in this study exhibiting the ''kink effect'' clearly show an initiation rate greater than the propagation rate, since all of the several walls in the MWNTs recede from the original site of the kink in unison. This is to be expected because the local energy is raised significantly at the kink sites, lowering the barrier to reaction significantly.[9] However, the majority of the tubes in the samples studied here oxidized through either a wall-thinning mechanism or through the sequential oxidation of tubes in a bundle. This suggests that for the majority of tubes, initiation at the kinks was not accelerated sufficiently to allow uniform simultaneous shortening of the walls, perhaps due to the irreproducibility of the magnitude of local strain induced by kinking the tubes over the ridges. Thus, it is likely for the majority of the tubes that initiation and propagation compete in rate. Similar oxidation rates are therefore expected on flat substrates, where oxidation would be seeded only at defects and endcaps. Given a relatively constant frequency of defects along the tubes, we expect oxidation rates should be independent of length. Smaller tube diameters should increase the oxidation rates, since the local strain energy will be raised along the entire length of the tube due to decreased radius of curvature.

## IV. CONCLUSIONS

In summary, we have prepared dispersions of multiwalled carbon nanotubes (MWNTs) in 2-butanol and dropped these onto *V*-ridge lithographically patterned Si substrates coated with a thin layer of gold, and observed by SEM that the MWNTs follow closely the surface topology of the substrates. Exposure of these nanotube coated substrates to air at elevated temperature for varying times demonstrates that: (a) the nanotubes are under tensile stress on the substrate surface, and some of them detach from the surface upon heating; (b) some kink sites present on those nanotubes that continue to follow the surface topology oxidize preferentially; (c) essentially complete oxidation of the nanotubes, as assessed by SEM imaging at successive time intervals, follows an Arrhenius-type temperature dependence, which yields an activation energy for oxidation of 122 kJ mol$^{-1}$; and (d) the observed dominant oxidative removal mode of carbon is either wall thinning, or sequential oxidation of the component tubes in bundles.

The method of inducing kink deformation used here is straightforward, but suffers from the tensile stress of the nanotubes, which are subject to detaching from the surface upon heating. Further studies on other surface topologies, such as flat surfaces, are indicated.

## ACKNOWLEDGMENTS

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