In situ transmission electron microscopy of individual carbon nanotetrahedron/nanoribbon structures in Joule heating

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Collapse of a carbon nanotube results in the formation of a nanoribbon, and a switching of the collapse direction yields a nanotetrahedron in the middle of a nanoribbon. Here, we report in-situ transmission electron microscopy observations of the behavior of carbon nanotetrahedron/nanoribbon structures during Joule heating to reveal their thermal stability. In addition, we propose that the observed process is related to the formation process of the structure. © 2014 AIP Publishing LLC.
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Stability of nanomaterials such as nanotubes and nanowires under Joule heating is crucial when they are utilized for electronic devices and wiring; therefore, the behavior of nanomaterials under Joule heating has been investigated by means of transmission electron microscopy (TEM) by many research groups.[1–4] For example, we reported in-situ TEM observations of Joule heating of nanowires such as Si nanochains [5,6] and SiC nanowires.[7,8] These studies show that both Si nanochains and SiC nanowires are converted into carbon-nanotubes by Joule heating. In the conversion of Si nanochains to carbon nanotubes, the carbon source is the surface carbon contamination, and the empty core of the nanotube is formed by vaporization of the Si oxide of the chains. In the conversion of SiC nanowires to carbon nanotubes, the graphitization of SiC nanowires is induced by Si vaporization. One of the important points of the transformation by Joule heating lies in the possibility to convert a highly resistive nanostructure (Si nanochain) to an excellent conductor (carbon nanotube). The relative ease of Joule heating—a simple application of high current by microprobes—makes the nanostructures transformations a very important candidate for nanowiring applications. It is therefore clear that structural changes of nanomaterials by Joule heating are an important topic with yet undiscovered possibilities. In the final analysis, both the good durability and the structural change can be utilized if the behavior is understood well.

We previously reported the formation of carbon nanoribbons by flattening of carbon nanotubes, and the formation of nanotetrahedra by switching of the flattening direction (see Fig. 1).[9] The structure consisting of nanotetrahedra inside a nanoribbon host is interesting since it may modulate the charge transport properties and could be useful for nanodevices. In addition, a junction of a nanotetrahedron and a nanoribbon could be utilized to change the direction of nanowiring. All these possible applications require knowledge of the durability of the nanostructures against Joule heating. In this study, we investigate the structural changes and durability of the nanotetrahedron/nanoribbon structure by means of in-situ TEM observation. We show that carbon nanotetrahedra have an excellent thermal durability and do not change their shape up to the temperature at which carbon nanoribbons are broken off near the electrode. In addition, we observed a process in which a carbon nanotetrahedron was absorbed in the tip of a W probe keeping its shape of tetrahedron. We propose that this could be the reverse process of its formation, or provides a clue to the understanding of the formation mechanism of the carbon nanotetrahedra.

We fabricated the carbon nanotetrahedron/ribbon structures by the chemical vapor deposition (CVD) method. A Si (100) substrate was roughened with SiC powder, then a 20 nm thick film of iron was deposited on the substrate at a pressure of 1.0×10^{-3} Pa. The sample was sealed in an evacuated silica tube (inner diameter 6 mm, length about 20 cm) with 0.8 mg of hexadecanoic acid [$C_{15}H_{31}C(=O)OH$] as the carbon source. The tube was heated to 1000 °C for 30 min, followed by cooling down to room temperature. Grown
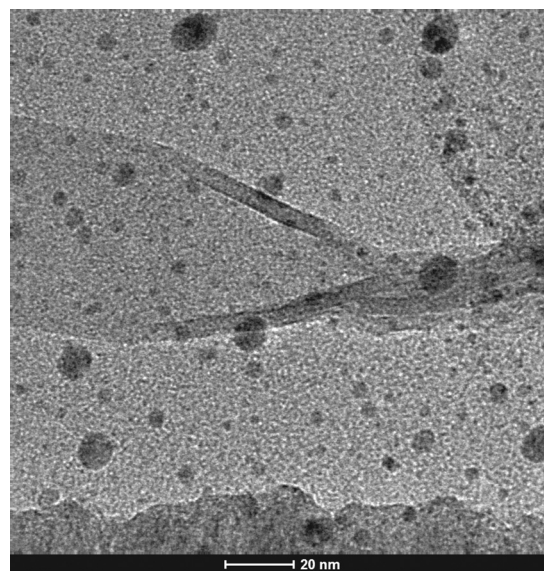

FIG. 1. TEM image of a carbon nanotetrahedron formed in the middle of a flattened multiwalled carbon nanotube.

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nanotetrahedron/ribbon structures were mounted on a Au wire. We used a commercial piezo-driven micromanipulator system, Nanofactory TEM-STM holder, to apply voltage and measure electric current, and the Au wire was set in the holder. The tip of a mobile W electrical probe was located near a nanotetrahedron structure using the micromanipulator, so the nanotetrahedron structure was situated between the tip of the W probe and the Au wire. Then a voltage was applied between the W probe and the Au wire, which increased as a linear function of time. Individual nanotetrahedron/ribbon structures were observed during Joule heating on a TEM. The CCD camera images were recorded at a rate of 2.6 frames per second with a resolution of 512×512 pixels.

Figs. 2 and 3 show an in-situ TEM observation of a carbon nanotetrahedron/nanoribbon structure during Joule heating. The nanoribbon was about 50 nm in width and a nanotetrahedron was located about 200 nm apart from the W probe. From Figs. 2(a) to 2(c) as the applied voltage was increased, we did not observe any marked change in the structure of the nanotetrahedron/nanoribbon and the W probe. At the moment of Fig. 2(d), the tip of the W probe changes its shape presumably due to partial melting; however, the nanotetrahedron/nanoribbon structure remained intact. The nanotetrahedron/nanoribbon just moved slightly toward the W probe, possibly owing to enhanced contact with the molten tip of the W probe. Finally, as a result of Joule heating, a part of nanoribbon was broken near the
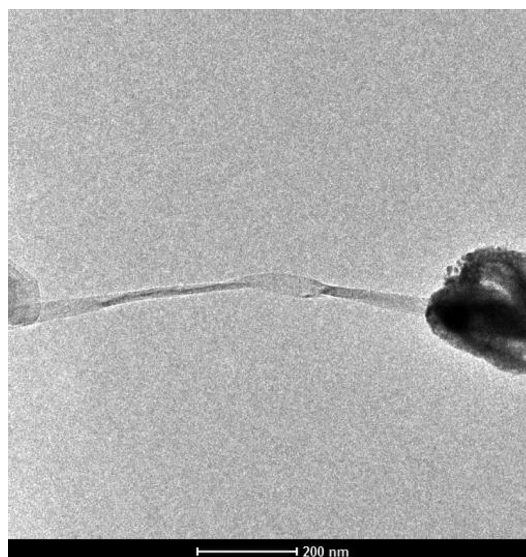
FIG. 3. Movie of Fig. 2 (Multimedia view). [URL: http://dx.doi.org/10.1063/1.4894003.1]

contact to the W probe Fig. 2(e). Nevertheless, the nanotetrahedron did not change its shape.

Just before the moment when the nanoribbon structure broke off, the tip of the W probe melted and noticeably changed its shape. Therefore, the temperature at which the nanoribbon structure was broken off was estimated to be around the melting temperature of tungsten, which is 3695 K for bulk crystal. However the curvature radius of the tip of the W probe is of the order of 10^{-8} m; therefore, we have to take account of the size effect which lowers the melting temperature below that of bulk W crystal of 3695 K. The following formula[10] can be used to estimate of the melting temperature of a nanoparticle:

$$T = T_0 \left(1 - \frac{4}{\rho_s L d} \left(\sigma_s - \sigma_l \left(\frac{\rho_s}{\rho_l} \right)^{2/3} \right) \right),$$

in which T is the melting point of a nanoparticle, T_0 is the melting point of the bulk, L is the latent heat, d is the diameter of a nanoparticle, ρ_s is the density of solid phase of a nanoparticle, ρ_l is the density of liquid phase of a nanoparticle, σ_s is the surface tension of solid phase, and σ_l is the surface tension of liquid phase. The estimated melting temperature for a nanoparticle that has the same radius as that of the tip of the W probe was 1676 K, using the flowing values for the parameters: $T_0 = 3695$ K, $L = 35$ kJ/mol, $d = 10$ nm, $\rho_s = 19$ g/cm^3, $\rho_l = 18$ g/cm^3, $\sigma_s = 3.5$ N/m, and $\sigma_l = 2.5$ N/m. This temperature is the lowest estimation for the tip of the W probe, since the tip of the W probe is not an isolated nanoparticle. Therefore, the actual melting point of the tip of the W probe is considered to be between 1676 K and 3695 K. The local temperature of the tip of the W probe when the breakdown occurred is considered to be higher than this melting point because the process was very fast and might not be in equilibrium with other part of the W probe. The breakdown of the nanoribbon at the contact suggests that the Joule heat was produced mainly at the contact due to the contact resistance, and the temperature of this part of the
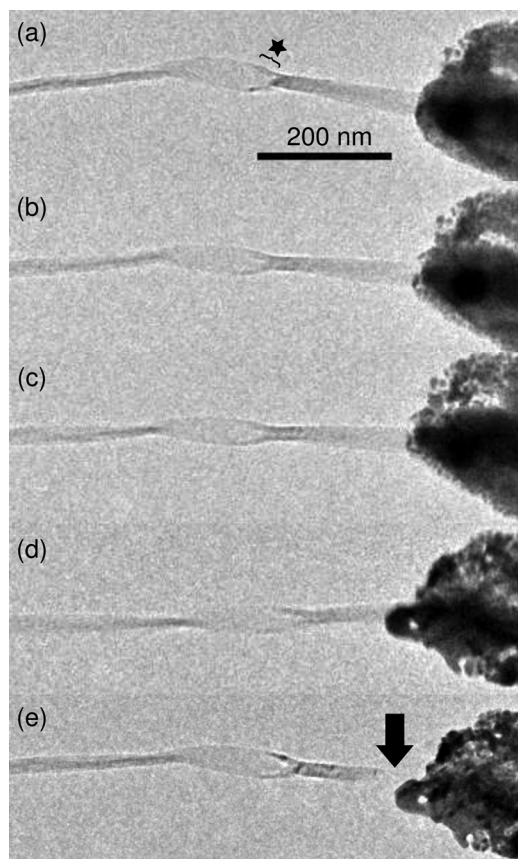

FIG. 2. A series of TEM images of a nanotetrahedron/ribbon structure during the first Joule heating. The position of the nanotetrahedron is indicated by the star. The tip of the W probe was attached to the right of the nanoribbon. The nanoribbon was broken off at the moment between (d) and (e) at the position indicated by the arrow.
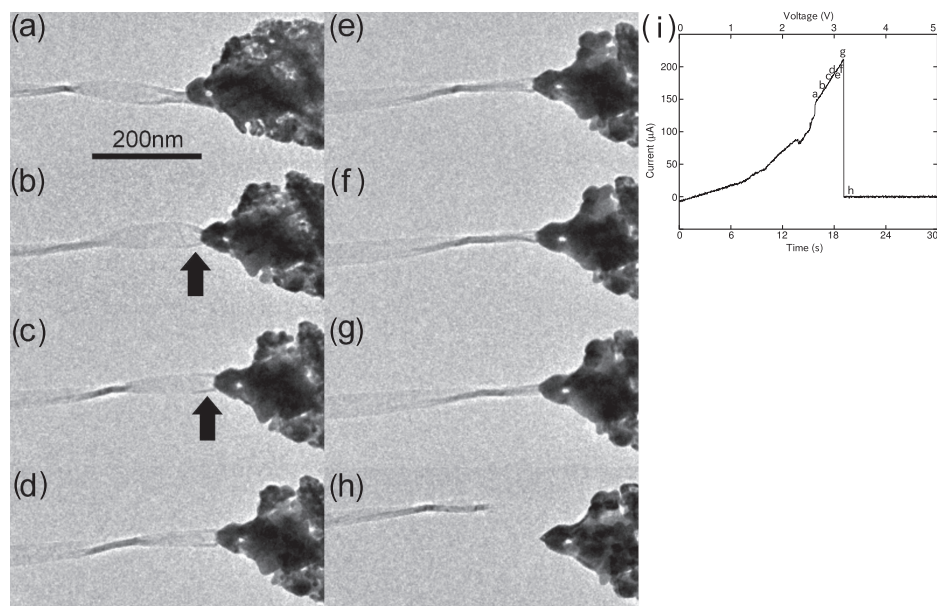
FIG. 4. A series of TEM images of a nanotetrahedron/ribbon structure during the second Joule heating. (b)–(d) The nanotetrahedron (indicated by the arrows) was absorbed to the W probe, then the nanoribbon was broken off between (g) and (h). (i) Current plotted as a function of time. The values of applied voltage and measured current: (a) [2.54 V, 108 μA], (b) [2.70 V, 151 μA], (c) [2.92 V, 180 μA], (d) [2.97 V, 185 μA], (e) [3.03 V, 193 μA], (f) [3.08 V, 199 μA], (g) [3.14 V, 207 μA], and (h) [3.19 V, $\sim$0 μA].

nanoribbon is higher than at least the melting point of carbon, 3773 K. The nanotetrahedron was apart from the contact by about 200 nm; therefore, the temperature around the nanotetrahedron should have been slightly lower than this temperature. The nanoribbon was about 800 nm in length between the two electrodes. Given that the contact resistance of the left contact was very low and the Joule heating was negligible at the left contact, the simple linear temperature distribution gives the estimation of the temperature at the nanotetrahedron to be approximately 2900 K, which is the lowest estimation.

After the first Joule heating, the tip of the W probe was moved to make a contact to the nanoribbon again near the nanotetrahedron structure for the second Joule heating as shown in Fig. 4(a). The second in-situ TEM observation revealed that the nanotetrahedron structure was absorbed with keeping its shape to the W probe during Joule heating as shown in Figs. 4(b)–4(d). Then, a part of nanoribbon was also absorbed in the W probe [Figs. 4(d)–4(f)]. Finally, the nanoribbon structure was broken off again [Fig. 4(h)], where the bias voltage was about 3.2 V and the current was about 210 μA [Fig. 4(i)]. The movie of the in-situ observation is in Fig. 5.

We speculate that the phenomenon in which the nanotetrahedron was absorbed in the probe tip might give a clue to the understanding of the formation process of nanotetrahedron/nanoribbon structures. In our previous paper,[9] we proposed a formation mechanism of our nanoribbons and nanotetrahedra, which we call the origami mechanism; when a carbon nanotube is expelled from a Fe catalyst nanoparticle, its geometry forces the nanotube's wall to converge, resulting in the immediate flattening in a superior direction,
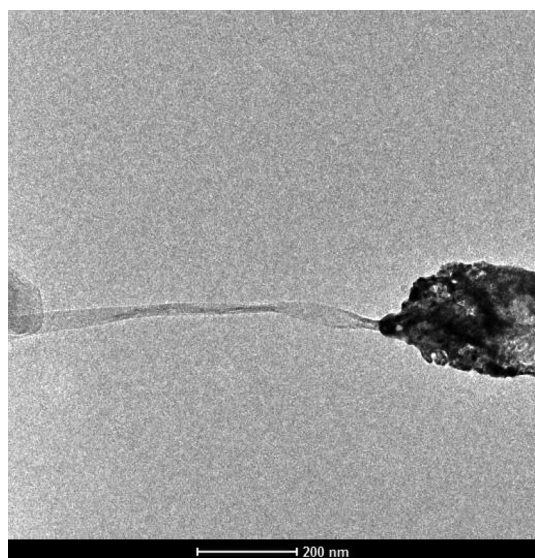

FIG. 5. Movie of Fig. 4 (Multimedia view). [URL: http://dx.doi.org/10.1063/1.4894003.2]
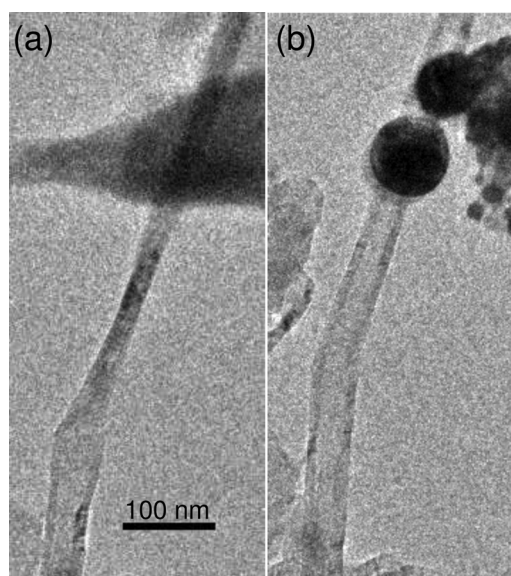

FIG. 6. (a) Before Joule heating of a nanoribbon/nanotube structure and (b) after Joule heating. The part of ribbon (upper part) in (a) changed to the tubular form in (b). The values of applied voltage and measured current: (a) [8.97 V, 248.5 nA] and (b) [9.61 V, $\sim$0 μA (due to the breakdown of the contact)].

and a nanotetrahedron is formed if the flattening direction changes during the growth. It is also possible that the whole part of a nanotube is formed first, then it flattens. We think it is possible to build a hypothesis that the process shown in Figs. 4 and 5 is approximately the *reverse process* of the formation process, in which the tip of the W probe worked as a catalyst. If a nanotetrahedron/nanoribbon structure can be absorbed in a metal catalyst keeping its form, it would also be possible that it is expelled from a metal catalyst forming its shape immediately. Accordingly, the TEM observation in Figs. 4 and 5 supports our origami mechanism for the formation of our nanoribbons and nanotetrahedra.

We also examined a nanoribbon/nanotube structure as shown in Figs. 6 and 7. Its wall number was estimated to be around 27 using its wall thickness. Before the Joule heating, the upper part of the structure was flattened, while the lower part had a tubular form: the inner wall was visible in the lower part showing that it was a tube (Fig. 6(a)). During the Joule heating, the flattened part expanded to take a tubular form then the whole part in the TEM view became a nanotube Fig. 6(b). The change was so fast and within the frame rate that its details of the transition could not be observed. The W probe located at the upper part became molten by the Joule heating; therefore, the temperature must have been as high as the melting point of the tip of the W probe. The local melting point of the W tip shown in Fig. 6 is approximately estimated to be 3500 K using $d = 100$ nm. The experimental fact that the nanoribbon/nanotube did not break suggests that the temperature of the nanoribbon/nanotube was below the melting point of carbon, 3773 K during the structural change. This result suggests that a nanotetrahedron/nanoribbon structure would be thermally more stable than a nanotube/nanoribbon structure. We speculate that structural defects such as five-membered, seven-membered, and eight-membered rings are necessary to form a nanotetrahedron and they are produced simultaneously with its growth, while such structural defects are not necessary to form a flattened nanotube. Some defects would be generated at a nanotube/nanoribbon junction; however, it requires less density of defects than a nanotetrahedron. Therefore, a nanotetrahedron is very stable once it is formed owing to the structural defects, while only the adhesion of the inmost wall to itself by van der Waals force needs to be broken to make a flattened nanotube take a tubular form, making a simple flattened nanotube not as stable as a nanotetrahedron. We note that the current measured in the experiment of Fig. 6 was much lower than that of Fig. 4. We speculate that this was due to poor contact between the nanoribbon and the W tip in Fig. 6.

Senga *et al.*[11] also reported in-situ TEM observations of Joule heating of simple flattened multi-walled carbon nanotubes, not nanotetrahedra. When their flattened MWCNT was Joule-heated, a part of the ribbon expanded and took a tubular form. Furthermore, the interface of the tubular and the flattened parts moved in accordance with the intensity of the electric current, namely temperature. The transition between the tubular and the flattened states was reversible and as slow as it could be recorded using a CCD camera equipped with their TEM. This slow and reversible transition between the two states indicates that the
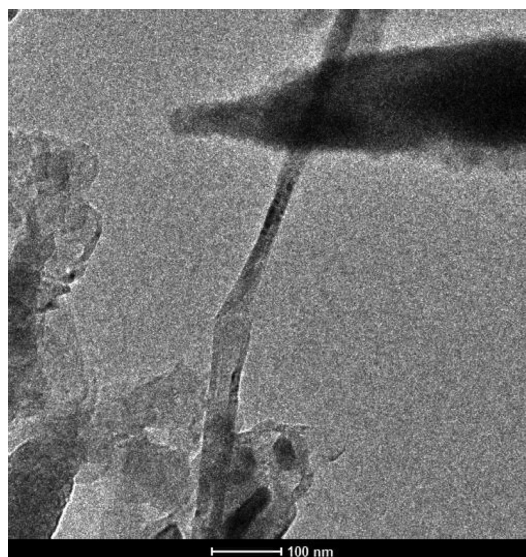

FIG. 7. Movie of Fig. 6 (Multimedia view). [URL: http://dx.doi.org/10.1063/1.4894003.3]

energy barrier between the two states was relatively low and its height was not sensitive to the transitional structure since the wall number of their MWCNT was only several layers, and also that the difference in energy of the tubular and the flattened states was small with a lower energy for the flattened state. In contrast, the very fast structural change observed in the nanotube/nanoribbon structure in Figs. 6 and 7 suggests that the energy barrier between the tubular state and the flattened state was relatively high and the height had strong dependence on its transitional structure, and also that the tubular state had a much lower energy than the flattened state since our structure had a thicker wall. It is very likely that once a weak pinning at the nanotube/nanoribbon interface is broken, it lowers the energy barrier and the structure falls down immediately to the deep ground state, namely the tubular form. It is also considered that the energy barrier was so high for our nanoribbon/nanotetrahedron structures owing to the dense structural defects that the Joule heating could not make them jump over the barrier.

In summary, we investigated the behavior of carbon nanotetrahedron/nanoribbon structures during Joule heating by in-situ TEM. Our nanotetrahedron/nanoribbon structures were thermally stable and did not transform into a tubular form up to a temperature at which they were broken off. This excellent durability implies a certain mechanism of stabilization of the structure, and promising for application in nanodevices and nanowiring. We also proposed a hypothesis that the process in which a nanotetrahedron/nanoribbon was absorbed in the W probe was the reverse process of its formation.

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