Liquid Gallium Columns Sheathed with Carbon: Bulk Synthesis and Manipulation

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It is impossible to fabricate isolated gallium nanomaterials due to the low melting point of Ga (29.8 °C) and its high reactivity. We report the bulk synthesis of uniform liquid Ga columns encapsulated into carbon nanotubes through high-temperature chemical reaction between Ga and CH_4. The diameter of filled Ga liquid columns is ∼25 nm, and their length is up to several micrometers. The thickness of the carbon sheaths is ∼6 nm. Simultaneous condensation of a Ga vapor and carbon clusters results in the generation of Ga-filled carbon nanotubes. A convergent 300 kV electron beam generated in a field emission high-resolution electron microscope is demonstrated to be a powerful tool for delicate manipulation of the liquid Ga nanocolumns: they can be gently joined, cut, and sealed within carbon nanotubes. The self-organization of a carbon sheath during the electron-beam irradiation is discussed. The electron-beam irradiation may also become a decent tool for Ga-filled carbon nanotube thermometer calibration.

I. Introduction

One-dimensional (1D) nanomaterials have attracted considerable attention due to their potential applications as building blocks in nanoscale circuits and optoelectronic devices.[1] Nanotube filling with foreign elements, compounds, and/or substances is a relatively new and exciting field of nanomaterial research.[2−9] 1D nanomagnets, nanocables, and other functional nanomaterials may be synthesized by taking advantage of the tiny nanotube channel dimensions and related confinement effects, and functional properties of guest species encapsulated within, e.g., ferromagnetism, piezoelectricity, electro- and thermoconductivity, etc. Metallic gallium melts at nearly room temperature and has one of the widest liquid ranges among all metals. Gallium possesses unusual crystallization behavior.[10] Similarly to water, metallic Ga expands as it freezes. Ga displays a rather complex phase diagram exhibiting many stable and metastable phases. At ambient pressure, the α-Ga(I) phase is orthorhombic with eight atoms in the unit cell of a *Cmca* space group lattice. In this structure a Ga atom is bonded to the nearest neighboring Ga atom in the manner of a diatomic molecule. With respect to the second closest neighbors located at distances 10−13% longer than that of the first coordination sphere, the atom retains metallic properties. It is suggested that covalent and metallic bonds coexist in the Ga metal. In addition, a number of metastable phases including β, γ, and δ have been identified.[11] At low temperature Ga metal becomes a strong-coupling superconductor with a well-defined superconducting transition temperature, as confirmed by tunneling experiments.[12]

Due to the low melting point (29.8 °C) and high reactivity, the preparation of isolated metallic Ga nanomaterials is a difficult task. Recently, it has been shown that Ga encapsulated in carbon nanotubes has a potential application as a nanothermometer due to its temperature-dependent expansion and contraction within a range of −20 to +500 °C.[13,14] Although Ga was used to mediate the growth of multiwalled carbon nanotubes, the continuous Ga filling failed due to the open tube ends.[15] Herein we demonstrate an effective approach for the bulk synthesis of liquid Ga nanocolumns sheathed with carbon in an induction furnace. Ga originates from the sublimation and decomposition of GaN, whereas carbon comes from the decomposition of methane (CH_4) at a high temperature. A nanosized electron beam generated within a 300 kV field emission transmission electron microscope is demonstrated to be a powerful tool for the delicate manipulation of the nanostructures due to local atom collisions with high-energy electrons.[16−21] We particularly demonstrate that liquid Ga nanocolumns can be effectively joined, cut, and sealed using a convergent electron beam.

II. Experimental Section

Liquid Ga columns sheathed with carbon were synthesized in a vertical induction furnace. The furnace consisted of a fused-quartz tube and an induction-heated cylinder made of high-purity graphite coated with a carbon fiber thermoinsulating layer, as illustrated in Figure 1 in the Supporting Information. The system had the inlet and outlet pipes made of graphite on its top and base, respectively. A graphite crucible, containing 0.5−2 g of gallium nitride powder was placed at the center cylinder zone. After evacuation of the quartz tube to $\sim 10^{-3}$ Pa, pure N_2 and CH_4 flows were set within the carbon cylinder at a constant rate of 500−3000 and 5−20 sccm, respectively. The top inlet N_2 flow was fixed at a constant rate of 2000 sccm. The furnace was heated to and kept at 1300 °C for 30 min. After the reaction was terminated and the furnace cooled to room temperature, a gray product was collected from the outlet carbon pipe in the induction-heated cylinder.

The morphology of the product was examined using a JSM-6700F scanning electron microscope operated at 10 kV. The product was ultrasonically dispersed in ethanol and transferred

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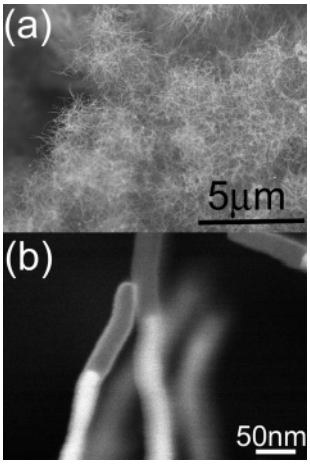

Figure 1. (a) SEM image of the as-obtained liquid gallium columns sheathed with carbon. (b) High-magnification SEM image displaying the tips of the nanostructures.

to a carbon-coated copper grid for transmission electron microscopy (TEM) observations. A field emission JEM-3000F high-resolution electron microscope operated at 300 kV and equipped with an energy-dispersive X-ray spectrometer was used to perform the microanalysis. Electron irradiation experiments were carried out with electron beams 5−100 nm in diameter. A 300 kV voltage was used throughout the experiments.

III. Results and Discussion

A representative scanning electron microscopy (SEM) image of a sample is shown in Figure 1a, which indicated the product is composed of wirelike nanostructures with a length of up to several micrometers. High-magnification SEM analysis reveals that the wirelike nanostructures have core−sheath structures. Figure 1b shows the end of a core−sheath structure. The synthetic temperature seems to play an important role in the generation of the Ga−C core−sheath structure. When the synthetic temperature was reduced to 1150 °C, some curly nanostructures were produced (see Figure 2 in the Supporting Information). Detailed structural and chemical analysis of individual nanostructures was carried out using TEM, high-resolution (HR) TEM, electron diffraction (ED), and energy-dispersive X-ray spectroscopy (EDS). Figure 2a shows a TEM image of a product. The image displays uniform core−sheath structures. The diameter of a metallic Ga core is approximately 25 nm, whereas its sheath is ∼6 nm thick. The nanostructure length can reach several micrometers. EDS analyses conducted on the nanocables using a nanoprobe display that the core and a sheath are composed of Ga and C, respectively. A representative EDS spectrum is depicted in Figure 2b. A selected-area electron diffraction pattern (Figure 2c), taken on a Ga−C core−sheath nanostructure, exhibits a pair of weak (002) diffraction arcs and additional diffraction rings, which suggests that the carbon sheaths are poorly ordered, as compared to standard carbon nanotubes made up of cylindrically wrapped graphene layers. The Ga cores are in a liquid state. Both ends of the Ga−C core−sheath composite nanostructures are enclosed with carbon, as revealed by Figure 2d,e. A cavity in the vicinity of one nanotube end is formed due to Ga contraction confined with a carbon nanotube when the whole structure cools from high to room temperature.

During the synthetic process, GaN sublimes and decomposes at high temperature (approximately 1300 °C) to produce a Ga vapor. This vapor condenses at a low temperature (approximately 800 °C) to form Ga droplets. When a CH_4 gas flows

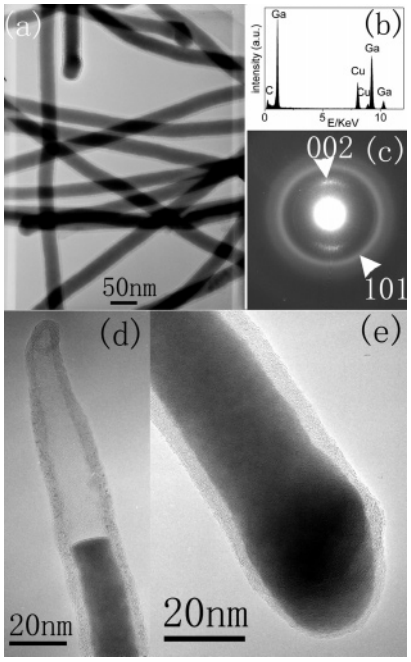

Figure 2. (a) TEM image of Ga nanocolumns sheathed with C. (b) EDS spectrum recorded from a composite nanostructure. (c) Selected-area electron diffraction (SAED) pattern taken from an individual nanostructure. (d, f) TEM images displaying the opposite ends of a given nanostructure.

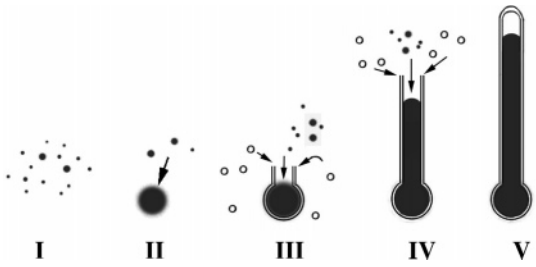

Figure 3. Growth scenario for the formation of liquid gallium columns sheathed with carbon: (I) vaporization of gallium, (II) condensation of gallium vapor to form gallium droplets, (III) nucleation of carbon nanotubes, (IV) growth of carbon nanotubes and in situ filling with gallium, (V) sealing of carbon nanotubes.

through the induction furnace at high temperature, it decomposes to produce carbon clusters. Ga droplets induce the anisotropic growth of carbon nanotubes; simultaneously the nanotube cavities are filled with liquid Ga. The simultaneous generation of a Ga vapor and carbon clusters promotes the uniform filling of carbon nanotubes. The growth process is shown in Figure 3.

After the reaction was terminated, the furnace cooled from 1300 °C to room temperature over 30 min. It is suggested that rapid cooling may cause the discontinuity of encapsulated Ga columns. Figure 4a shows a TEM image of a Ga column having a gap of approximately 70 nm between its two segments. The incident electron energy (E_p) of a beam can be determined from the equation $E_p = mc^2(1/(1 - \beta^2)^{1/2} - 1)$, where m is the rest mass of an electron, c is the speed of light, v is the velocity of an electron, and $\beta = v/c$.[22] When a high-energy electron passes through a specimen, its energy may partially be transferred to the target and enhance the movement of atoms. Consequently, this energy may cause the local temperature rise or the transformation of crystal structures.[23,24] When an electron beam is focused within a spot of ∼100 nm in diameter and is moved up and down along the bottom fraction of a Ga column (Figure 4a), the column segment continuously expands due to beam-induced heating. Finally, the bottom segment joins the top one.

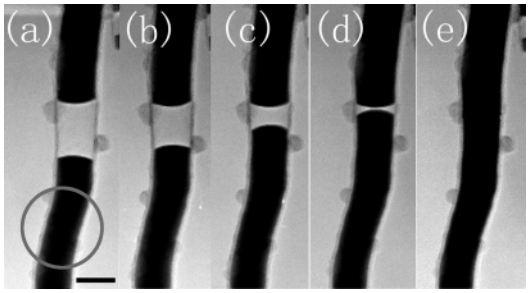

Figure 4. Consecutive TEM images showing joining of two discrete liquid Ga segments under electron-beam irradiation: (a) 0 min, (b) 2 min, (c) 5 min, (d) 8 min, (e) 10 min. The circle marks the electron beam. The scale bar is equal to 50 nm.

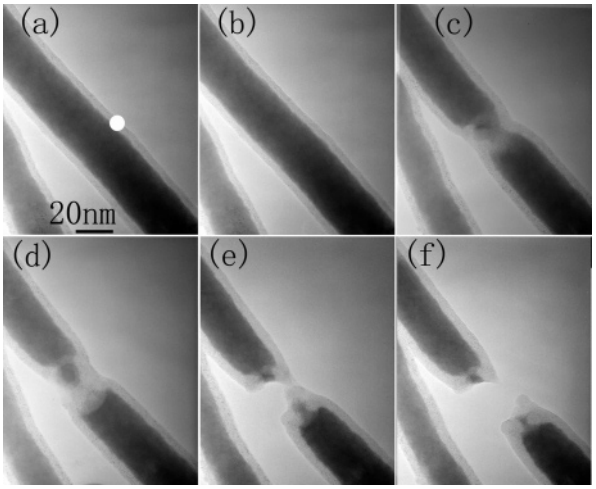

Figure 5. TEM images depicting the morphological changes of a Ga−C composite structure when it is irradiated with a scanning electron beam: (a) the white dot shows the electron beam position, (b) 0 min, (c) 2 min, (d) 4 min, (e) 7 min, (f) 9 min.

Figure 4 displays the consecutive stages of the Ga expansion. Owing to the considerable expansion coefficient (1.015×10^{-4}/T) and good thermal conductivity of liquid Ga,[25] notable expansion of the Ga column can be observed under electron-beam irradiation. A wetting angle between the liquid Ga and carbon sheath slightly changes during irradiation. This change may also be caused by a thermal effect of the irradiation. Our estimates show that a specimen can typically be heated to approximately 100 °C during the irradiation using the present irradiation dose,[24] which is far above the melting point of metallic Ga (29.8 °C). The top Ga segment remains unchanged throughout Figure 4. This implies that the thermal conductivity of the carbon sheath is negligible in contrast to that of metallic Ga. Thus, the thermal effect of an electron beam only comes into effect within the irradiated region. On the other hand, the expansion of the lower Ga segment is an indicator of the sufficient electron-beam-induced heating.

When an electron beam strikes a specimen, the inelastic and energy-loss electrons are generated with abundant signals. These include X-rays and secondary electrons useful for the material analysis.[26] If the beam intensity is above the threshold, it may cause the damage of a target. The beam damage of a graphitic carbon and metals is generally dominated by direct displacement of atoms from a specimen, namely, knock-on displacement. This creates point defects. Apart from beam-induced heating, we also demonstrate the possibility to cut carbon-sheathed Ga nanocolumns by high-energy electrons. Figure 5 displays this process in detail. The beam is ∼5 nm in diameter, as marked with the white dot on the initial TEM image in Figure 5a. The convergent

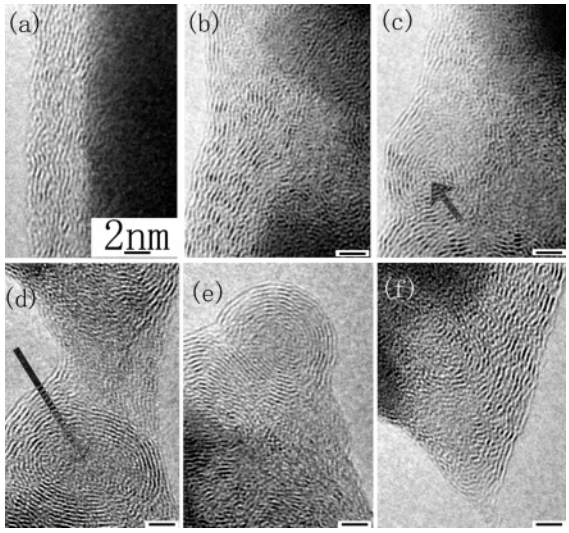

Figure 6. HRTEM images displaying the structural changes of a Ga−C composite nanostructure under electron-beam irradiation, in accord with Figure 5b−f. End of the lower Ga−C segment after (a) 0 min, (b) 2 min, (c) 4 min, (d) 7 min, and (e) 9 min. (f) End of the upper segment after 9 min.

electron beam is then moved across the tube back and forth. After intense irradiation over 2 min (Figure 5c), the irradiated region becomes thinner. The image contrast in this irradiation region becomes lighter, suggesting that metallic Ga is partially removed. A further 2 min of irradiation can completely remove Ga from the irradiated region (Figure 5d). The nanostructure is finally separated into two discrete parts (Figure 5e,f). Detailed structural transitions caused by the electron irradiation were studied using HRTEM. Parts a−f of Figure 6show the HRTEM images taken from the irradiated regions during consecutive irradiation stages, corresponding to Figure 5b−f. As suggested, on the basis of the electron diffraction patterns (Figure 2c), a carbon sheath does not possess a well-structured graphitic network. In fact, the HRTEM image of a sheath does not display a well-defined layered structure peculiar to carbon nanotubes produced via arc discharge or chemical vapor deposition with transition-metal nanoparticles as catalysts.[27,28] After 2 min of irradiation, the layer crystallinity is improved, while the carbon sheath shrinks (Figure 6b). This result implies that the growth defects, e.g., undulating, dangling carbon sheets, dislocation edges, and local irregularities, are annealed in situ after a few minutes of electron irradiation with 300 kV electrons. In some respects, an intense irradiation resembles a high-temperature treatment, allowing interstitials and vacancies to aggregate into clusters and reduce their free energy.[17,29,30] Further electron irradiation causes the complete shrinkage of the carbon sheath, and a nested carbon nanostructure forms, as indicated by the arrow in Figure 6c. A longer irradiation creates a notable cleft within the composite nanostructure. Moreover, an elliptical carbon "onion" of ∼15 nm diameter is generated. Figure 6d depicts an elliptical C onion connected to the structure top segment through an 8 nm wide graphitic neck. This carbon neck is further completely peeled off by electron-beam irradiation, thus resulting in the creation of two separated composite nanostructures. A spherical nested carbon structure of ∼10 nm diameter is left on the top right corner of the bottom segment (Figure 6e). The top segment terminates with a sharp tip, as shown in Figure 6f. Figure 6 clearly demonstrates that the encapsulated liquid metal does not hinder the reconstruction of the carbon sheath under intense electron-beam irradiation. Once the C sheath shrinks, the liquid Ga column is ready to recede

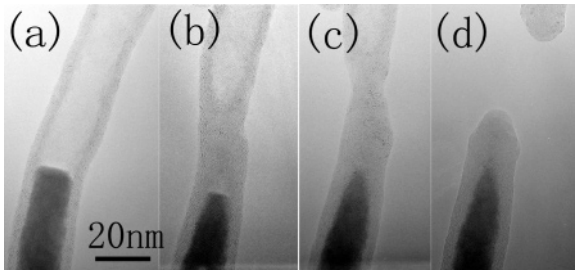

Figure 7. TEM images illustrating the morphological changes of the C sheath of a Ga−C composite nanostructure under electron-beam irradiation: (a) 0 min, (b) 2 min, (c) 4 min, (d) 8 min.

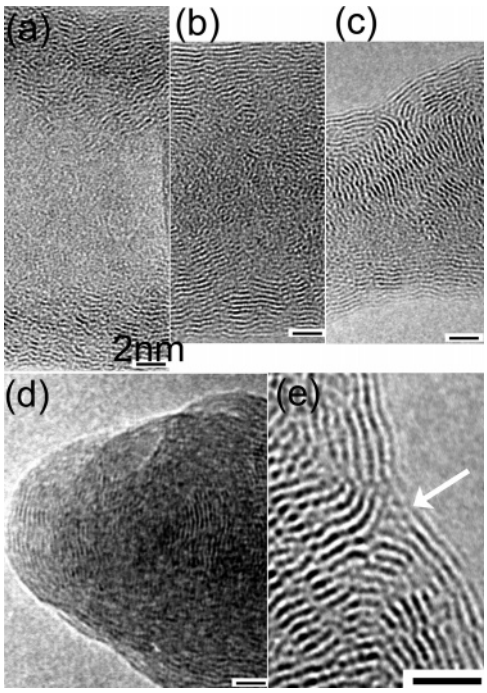

Figure 8. HRTEM images showing the structural changes of the C sheath of a Ga−C composite nanostructure under electron-beam irradiation. The images correspond to TEM images in parts a−d of Figure 7: (a) 0 min, (b) 2 min, (c) 4 min, (d) 8 min. (e) An enlarged view of Figure 6c indicating a separation site between the two fractions.

and separate into two domains due to its liquid state. The electron-beam irradiation anneals the carbon sheath and simultaneously causes the knock-on damage. Moreover, self-organization phenomena also take place to form spherical carbon onions on the tip of a separated Ga−C composite nanostructure due to a sufficient structural fluidity under irradiation.

Generally, a cavity is present at one end of a given 1D Ga−C composite nanostructure at room temperature (Figure 7a). Electron-beam irradiation can eliminate this cavity and makes a Ga column completely sealed with a carbon sheath. First, an electron beam of 5 nm diameter irradiates the carbon sheath above the Ga column over ∼2 min. This results in the collapse of the sheath. A short solid carbon rod forms (Figure 7b). Continuous irradiation at one side of the sheath may cause its bending (see the Supporting Information). Knock-on damage makes the rod thinner as the irradiation proceeds. Finally the unfilled tube part is removed, as shown in Figure 7c,d. The HRTEM images (Figure 8) shed additional light on the structural changes within a sheath during irradiation. Structural characteristics peculiar to annealing (Figure 8b), knock-on damage (Figure 8c), separation, and self-organization into carbon onion-like nanostructures (Figure 8d) are visible. Figure 8e is an enlarged view of the selected area in Figure 8c. The position indicated by the white arrow demonstrates a separation site. After separation of the filled and unfilled tubular parts, an onion-like tip end is formed on a 1D Ga−C composite nanostructure. This carbon onion may prevent further liquid Ga spilling from the tube.

IV. Conclusion

In conculsion, uniform liquid-Ga-filled carbon nanotubes have been generated during a high-temperature chemical synthesis utilizing CH_4 and GaN reagents in an induction furnace. The diameter of filled Ga liquid columns is ∼25 nm, and their length is up to several micrometers. The thickness of the carbon sheaths is ∼6 nm. Electron-beam irradiation inside an electron microscope has been documented to be a powerful tool for delicate manipulation of the prepared one-dimensional nanostructures. We thoroughly demonstrate that the 1D Ga−C composite nanostructures can be joined, cut, and sealed using electron-beam irradiation. Since the electron-beam irradiation can cause local structural transformations within the carbon sheath, it may be possible to calibrate Ga-filled carbon nanotubes as thermometers by producing marks on their periphery. The bulk synthesis and manipulation of 1D Ga nanostructures are envisaged to open further prospects for studies on their unusual physical properties, i.e., electrical and thermal, and potential applications.

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Supporting Information Available: Schematic diagram of a vertical induction furnace used for the synthesis, SEM image of products obtained at 1150 °C, TEM image displaying the bending of a C sheath under a constant 2 min electron-beam irradiation at one nanostructure side, consecutive TEM images showing two discrete liquid Ga segments under heating, and TEM image showing a thermometer-like structure. This material is available free of charge via the Internet at http://pubs.acs.org.

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