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Transformation of silicon nanoparticles on a carbon nanotube heater into hollow graphitic nanocapsules via silicon carbide

Koji Asaka *, Tomohiro Terada, Yahachi Saito

Department of Quantum Engineering, Graduate School of Engineering, Nagoya University, Furo-cho, Chikusa-ku, Nagoya 464-8603, Japan

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ABSTRACT

The changes in the structure and composition of silicon (Si) nanoparticles supported on a multiwall carbon nanotube (MWCNT) during Joule heating of the MWCNT were studied by *in situ* high-resolution transmission electron microscopy. The Si nanoparticles reacted with the outer layers of the MWCNT to form silicon carbide (SiC) nanoparticles with increasing temperature. At temperatures of up to approximately 1900 K, silicon atoms were entirely sublimated from the SiC nanoparticles, and the remaining carbon atoms formed hollow carbon nanocapsules consisting of multilayered graphene shells on the MWCNT.

1. Introduction

A multiwall carbon nanotube (MWCNT) has a current-carrying capacity of over 10^9 A/cm^2 [1] and exhibits a thermal conductivity of more than 3000 W/m K at room temperature [2]. These properties are particularly suitable for their use as electrical wires and interconnects in molecular-scale electronic devices, transparent conductive sheets, and transparent film heaters [3–6]. The temperatures of individual MWCNTs can be raised to more than 2273 K by passing current through them [7,8]. Hence, the MWCNT has been used as a nanoscale heater to heat nanometer-sized materials on the MWCNT surface, and nanoscale phenomena induced at high temperatures have been investigated using the MWCNT heater, such as the graphite–diamond phase transformation in carbon onions [9], graphitization of amorphous carbon [10,11], phase changes in chalcogenide [12], the formation of carbon nanocages using gold nanoparticles [13], and the melting of tungsten nanoparticles [14]. It was also reported that silicon, titanium, and niobium react with carbon on MWCNT surfaces to form carbide materials at their interfaces via a direct solid–solid reaction at high temperatures [15]. Among these, the carbide of silicon has attracted great interest from the viewpoint of device applications [16–18] and it is thus necessary to understand the reaction process in detail. In this study, in order to elucidate the detailed dynamics of the solid–solid reaction between an MWCNT and silicon at high temperatures, we used the MWCNT as a heater and studied structural changes in silicon nanoparticles on the MWCNT surface at elevated temperatures by *in situ* high-resolution transmission electron microscopy (TEM).

2. Experimental

MWCNTs produced using an arc discharge method were attached to the edge of a 50-μm-thick gold (Au) plate by dielectrophoresis in an isopropyl alcohol solution [19]. Silicon (Si) was vacuum-deposited by electron beam evaporation onto the MWCNTs at 873 K. The average thickness of the deposited Si was about 10–20 nm, and the deposited Si formed crystalline nanoparticles. The Au plate with the MWCNTs was mounted on a movable stage on the specimen holder of a TEM. A tungsten needle coated with a 10-nm-thick Au film by electron beam evaporation was mounted on an opposite stationary stage of the specimen holder. An MWCNT protruding from the edge of the Au plate was manipulated toward the tip of the Au-coated tungsten needle and brought into contact with the Au surface at the needle tip in the TEM. Structural changes occurring in the Si nanoparticles on the MWCNT during Joule heating of the MWCNT were observed by *in situ* high-resolution TEM, operated at 120 kV, using a television system. The images were recorded at a time resolution of 20 ms. The voltage and current applied to the MWCNT were measured using the two-terminal method and the optical emission from the MWCNT was simultaneously recorded by a spectroscopy system with a charge-coupled device camera. An illustration of the *in situ* observation system is shown in Fig. 1.

* Corresponding author. Tel.: +81 52 789 4464; fax: +81 52 789 3703.
E-mail address: asaka@nuqe.nagoya-u.ac.jp (K. Asaka).

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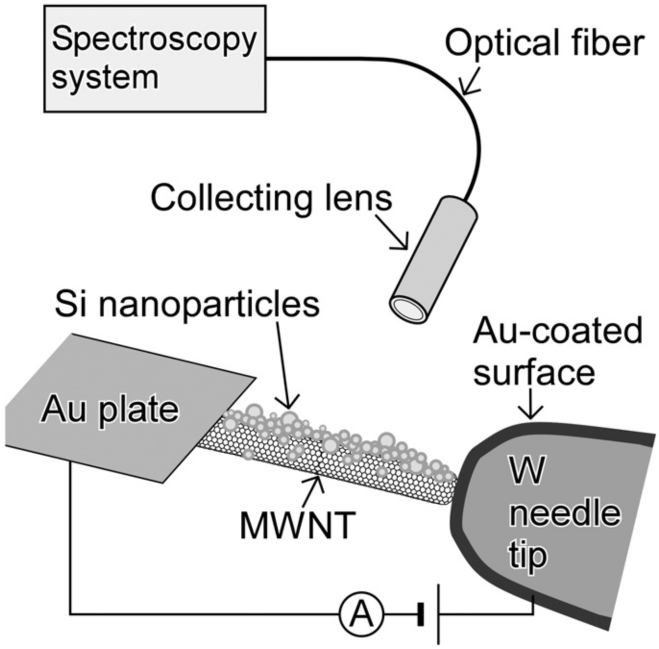

Fig. 1. Illustration of the experimental arrangement in the transmission electron microscope. The TEM images, voltage and current, and optical emission spectra were simultaneously recorded using a computer, and analyzed at synchronized intervals.

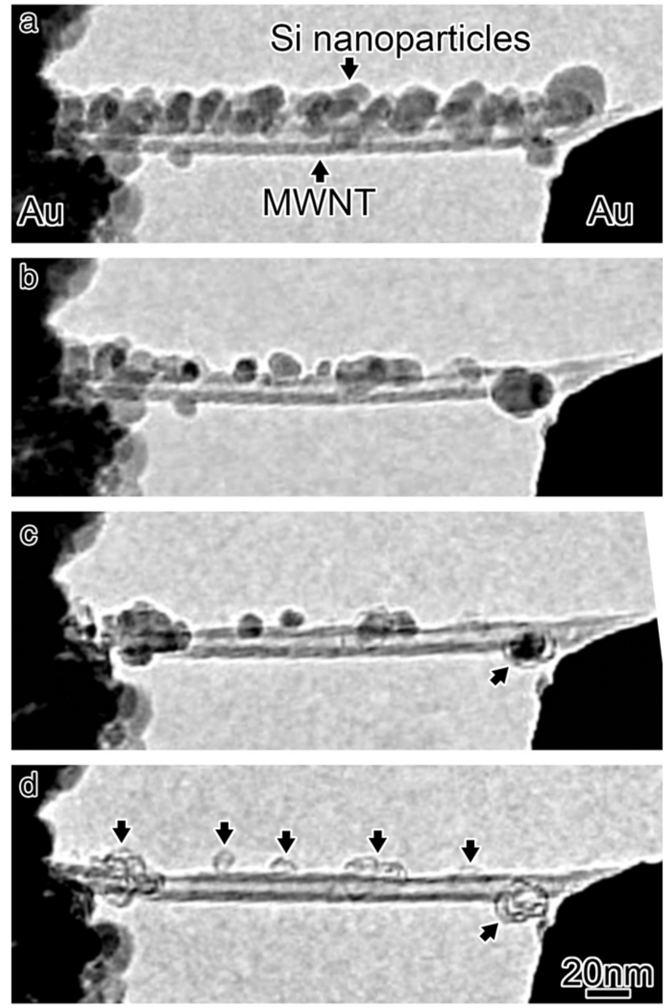

Fig. 2. A sequential time series of low-magnification images of structural changes in Si nanoparticles supported on an MWCNT during Joule heating of the MWCNT. The currents passed through the MWCNT were (a) 0, (b) 43.4, (c) 49.3, and (d) 90.7 μA.

3. Results and discussion

Fig. 2 shows a sequential time series of low-magnification images of the structural changes in Si nanoparticles deposited on an MWCNT during the heating process. The dark regions on the left-hand and right-hand sides in Fig. 2 are Au electrodes, and the bright region is vacuum. The MWCNT bridges the two surfaces of the Au electrodes. The outer and inner diameters of the MWCNT are approximately 14 and 4 nm, respectively. The bridge length of the MWCNT is about 245 nm. The mean thickness of the Si deposited on the MWCNT is 20 nm. When the voltage was increased up to 1.46 V, the corresponding current increased abruptly to 43.4 μA, and some of the Si nanoparticles on the MWCNT evaporated, as shown in Fig. 2(b). Subsequent application of voltage up to 1.60 V led to a rise in the current to 49.3 μA, and the diameter of the Si nanoparticles decreased. Besides these Si nanoparticles, some nanoparticles started to be covered by a thin layer, as indicated by the arrow in Fig. 2(c). After the voltage was once decreased to 0 V, the voltage was applied again. When the current reached 90.7 μA, the nanoparticles completely disappeared, and hollow nanocapsules covered with thin layers remained on the MWCNT, as shown by the arrows in Fig. 2(d).

In order to examine in detail the structural changes in the Si nanoparticles on the MWCNT during the heating process, the structures of the individual Si nanoparticles under the applied current were studied by *in situ* high-resolution TEM. Fig. 3 shows a sequential time series of high-resolution images of the structural changes in a Si nanoparticle with a diameter of about 12 nm supported on an MWCNT. Fig. 4(a) is a high-magnification image of the Si nanoparticle shown in Fig. 3 before applying the voltage. The Si nanoparticle is not covered with natural oxide layers. The 0.31-nm-spaced fringes observed in the nanoparticle are the (111) lattice fringes of Si. The MWCNT supporting the Si nanoparticle consists of 15 carbon atomic layers with an outer diameter of approximately 16 nm. When the current applied to the MWCNT was increased to 73.0 μA at a voltage of 1.91 V, the diameter of the Si nanoparticle decreased as shown in Fig. 3(a) and (b), and the outermost carbon layer of the MWCNT with which the Si nanoparticle was in contact disappeared as indicated by the arrows in Fig. 3(c). Upon a subsequent increase in current, the second outer carbon layer in the contact region disappeared at 74.4 μA (see Fig. 3(d)). A further increase in the current to 75.4 μA resulted in the disappearance of the third outer carbon layer from the vicinity of the edge of the disappeared layers, as shown by the arrows in Fig. 3(e). Finally, three carbon layers disappeared entirely in the contact region between the nanoparticle and the MWCNT, and the nanoparticle shifted to the right-hand side as seen in Fig. 3(f). The width of the disappeared layers is about 11 nm, which is approximately the same as the diameter of the nanoparticle. The observation time from Fig. 3(a) to (f) is about 126 s. Fig. 4(b) shows a high-magnification image of the nanoparticle seen in Fig. 3(f) after heating. The lattice fringes with a spacing of 0.25 nm observed in the nanoparticle correspond to the (111) planes of the 3C structure of the bulk SiC.

The present observations demonstrate that the Si nanoparticles react with the outer carbon layers of the MWCNT surface by Joule heating to form SiC nanoparticles. No structural changes of the MWCNT into a SiC wire were observed. According to previous reports, formations of SiC due to the reaction between Si and carbon nanotubes at 1343 K [15] and between Si and graphite at 1673 K [20] were observed. In these reactions, the formation of SiC results from impregnation of Si atoms into nanotubes and graphite. On the other hand, in the present study, it is noted that the diffusion of carbon atoms from the MWCNT into the Si nanoparticles leads to the formation of