Catalyst-Assisted Growth of Single-Crystalline Hafnium Carbide Nanotubes by Chemical Vapor Deposition

Song Tian, Hejun Li,† Yulei Zhang, Jincui Ren, Xinfa Qiang, and Jie Wang
State Key Laboratory of Solidification Processing, Northwestern Polytechnical University, Xi’an 710072, China

Single-crystalline hafnium carbide (HfC) nanotubes were synthesized by a one-step catalyst-assisted chemical vapor deposition (CVD) method. The typical nanotubes had uniform diameters of ~60 nm and wall thicknesses of ~15 nm and preferentially grew along [011]. From HRTEM/EELS analysis, the growth mechanism based on carbon nanotubes (CNT) tip growth and CNT-templated reaction was proposed for explaining the formation of HfC nanotubes. According to the mechanism, CNTs were first formed by diffusion of C atoms on the surface of solid Ni catalyst particles. Then, gaseous Hf species reacted with C atoms from CNTs to form HfC nanotubes. During the entire growth process, Hf atoms did not participate in the catalytic reaction. Thus, this process was distinguished from the conventional vapor–liquid–solid process.

I. Introduction

One-dimensional (1D) nanostructures, such as nanowires and nanotubes, of metal carbides have important applications as structural reinforcements in nanocomposites due to their high melting point, high hardness, high modulus of elasticity, and excellent chemical stability. These metal carbide nanowires have also attracted increasing attention under vacuum micro-electronics for functional applications. For example, nanowires of HfC, TiC, Al4C3, and WC have been reported to be potentially high-performance cold cathodes of (FE)-based devices due to their low work function, high aspect ratio, and good mechanical stability. In particular, HfC, as a key cathode material for FE, has very low work function about 3.4 eV, which makes it easier to release electrons compared to other metal carbides. To date, a wide range of metal carbides, including Al4C3, Fe3C, TiC, NbC, ZrC, HfC, TaC, as well as VC, have been made into nanowire and nanotube structures by a common route based on carbon nanotube-template (CNTT) reaction, which is a one-step reaction process. Two steps are outlined as follows: first, carbon nanotubes (CNTs) are synthesized; next, the as-synthesized CNTs are used as templates to react with the metallic precursors (e.g., pure metal, metal halide, and metallic oxide) to synthesize the metal carbide nanowires and nanotubes. From above process, metal carbide nanotubes can be obtained by controlling the reaction temperature. Although CNTT reaction has been confirmed to be an effective approach to fabrication of metal carbide nanowires, it is difficult to synthesize high-quality single-crystalline metal carbide nanotubes. Accordingly, the synthesis of metal carbide nanotubes, especially with perfect single-crystalline structures, was seldom reported. Herein, we synthesized single-crystalline HfC nanotubes by a one-step catalyst-assisted chemical vapor deposition (CVD) that is expected to be a general route for the synthesis of other metal carbide nanotubes. In addition, it is found that the HfC nanotubes have a unique growth process, which is different from conventional vapor–liquid–solid (VLS) mechanism usually used to explain the growth of 1D nanostructures of binary compounds by the catalyst-assisted CVD.

II. Experimental Section

HfC nanotubes were synthesized in a variable-temperature vertical tube furnace mounting a thin alumina tube with a diameter of ~8 cm and a length of ~150 cm. In detail, the HfC nanotubes were grown on graphite substrate covered with well-dispersed Ni(NO3)2 particles. The synthesis temperature was set to 1050°C. Mixed methane (CH4) and hydrogen (H2) gases were introduced into the furnace at a total flow of 1000 sccm (volume ratio 1:10). The pressure inside the furnace tube was adjusted to 0.02 MPa. Ni(NO3)2 particles served as the catalyst; CH4 (99.9%) gas and hafnium tetrachloride (HfCl4) (99.9% purity; Alfa Aesar, MA) powders acted as carbon sources and hafnium sources, respectively. High-purity H2 (99.999%) was used as both reducing agent and carrier gas. The graphite substrate was positioned at the center of heating zone; a quartz crucible loaded with sufficient HfCl4 powders was positioned at ~20 cm upstream from the center of heating zone. Before the heating process, the furnace system was purged with high-purity argon (Ar) (99.999%) for three times to remove oxygen and water vapor, and then the alumina tube was evacuated to below 0.02 MPa. Next, heating started at a rate of 7°C/min till the temperature of the reaction zone reached 1050°C, during which a constant flow of H2 gas was introduced into the system to reduce Ni(NO3)2 particles into Ni particles. When heated to 1050°C, the evaporated HfCl4 powders were carried by mixed CH4 and H2 gases with a total flow of 1000 sccm into the reaction zone and reacted with CH4 gas by the catalysis to form HfC nanostructures on the graphite substrate. The morphology and structure of the product was characterized using a FEI Quanta 600 FEG field-emission scanning electron microscope (SEM; FEI company, Hillsboro, OR) operated at 20 keV electron energy and a Tecnai F30 G2 field-emission transmission electron microscope (TEM) with energy-dispersive X-ray (EDX) and electron energy loss spectrometer (EELS) mapping capabilities (operated at 300 kV accelerating voltage). The nanostructures were well dispersed in ethanol by ultrasonication. A few drops of suspension were then transferred to a holey copper grid coated with a carbon film for TEM analysis.

III. Results and Discussion

Figure 1 shows SEM images of the products, from which we can observe that large-scale 1D nanostructures have been synthesized. The inset shows the nanostructures have a diam-
eter of about 50 nm and length of tens of microns. Figure 2(a) shows a typical low-magnification bright-field TEM image of a single HfC nanotube with uniform diameter around 60 nm and wall thickness of ~15 nm. Based on TEM observation, hollow HfC nanotubes were obtained. It can be observed that the nanotube have a ~50 nm catalyst alloy particle at the tip which is sheathed by a ~5 nm thin layer. The chemical composition of the HfC nanotube was studied by EDX analysis. Figure 2(b) is an EDX spectrum recorded on the column of the nanotube in Fig. 2(a), from which C and Hf were identified (Cu signal is from the TEM holey copper grid). It implies that high-purity nanotubes containing Hf and C without any other impurity elements (e.g., oxygen) were obtained.

To identify the crystal structure of the synthesized nanotubes, we analyzed the high-resolution TEM images (HRTEM) taken along the [T12] zone axis direction from the column of the HfC nanotube. Figure 2(c) is a high-resolution electron micrograph taken from the square area “1” shown in Fig. 2(a), which is ~250 nm away from the tip of the nanotube. Almost no structural defect or surface disorder was observed. The inset in Fig. 2(c) is the corresponding fast Fourier transform (FFT) pattern, consistent with the face-centered cubic (fcc) [T12] zone axis direction diffraction pattern. The lattice spacing was measured to be 0.265 nm, which is close to the value for the {111} planes of fcc HfC (JCPDS 65-0964, d_{(111)} = 0.2685 nm). Based on the HRTEM and FFT results, it can be concluded that the HfC nanotube grows along the [201] direction. The atomic structures of the square area “2” (~200 nm away from the tip) and “3” (~150 nm away from the tip), closer to the tip, are displayed in Figs. 2(d) and (e), respectively. The lattice fringes are identical with area “1.” It is clearly to see the area “2” and “3” have a ~2 and ~3 nm polycrystalline layer on the surface of the tube, respectively. This implies that the thickness of the polycrystalline layer decreases with increase in the distance along the axis from the tip of the nanotube.

To determine the chemical composition at the closed tip, energy filtered TEM was used to show elemental mappings from the same nanotube in Fig. 2(a). C, Ni, and Hf maps of the nanotube in Figs. 3(a)–(c) were formed with the energy loss windows centered at the C K-ionization edge of 284 eV, Ni K-ionization edge of 855 eV, and Hf K-ionization edge of 1662 eV, respectively. Figures 3(a) and (b) clearly show C elemental distribution of the nanotube tip is mainly concentrated on the thin layer, whereas Ni is present in the entire
catalyst particle. However, Hf is absent at the tip as shown in Fig. 3(c). It implies that Hf atoms from decomposition of volatile HfCl₄ are not involved in the reaction at the tip during the nanotube growth. Further structural characterization of the nanotube tip using HRTEM is depicted in Figs. 3(c) and (d). HRTEM images were taken from the square area “4” and “5” of the tip shown in Fig. 2(a). In detail, it is clearly to see that the nanotube column and the encapsulated catalyst particle are separated but linked by a ~5 nm thin layer which enclosed the catalyst particle, and the linkage region between the column and particle has slight shrinkage in diameter. The lattice spacing of the layer is 0.335 nm, well corresponding to the \{002\} planes of graphite (JCPDS 02-0456, d(002) = 0.3360 nm). For the catalyst particle, the spacing between two adjacent lattice fringes is 0.206 nm, which is consistent with the \{111\} planes of fcc Ni (JCPDS 01-1258, d_{(111)} = 0.2040 nm) and fcc NiC (JCPDS 14-0020, d_{(111)} = 0.2039 nm). However, it is difficult to determine the chemical state of the catalyst duo to very close lattice constants of Ni and NiC. From above analysis, it is assumed that the Ni or NiC particle at the tip is enclosed by a multilayer graphite nanostructure.

Thus, it is deduced that the growth of the HfC nanotubes possibly follows a mechanism involving the tip-growth process of CNTs and a template-mediated reaction as illustrated schematically in Fig. 4. According to the Ni-C binary phase diagram, Ni or NiC is solid at 1050°C. Previous studies have confirmed that bulk diffusion of C atoms in solid catalyst particles is not favored due to high-energy barrier during the growth of multiwall CNTs. In addition, it is known that Hf atom has a much larger diameter than C atom. Thus, Hf atoms and C atoms, from decomposition of hafnium halide and hydrocarbon gases, respectively, are difficult to dissolve into and diffuse through the solid catalyst particle. The catalyst particle cannot initiate the catalytic reaction of Hf and C inside itself and directly precipitate HfC. However, according to the growth mechanism of CNTs, C atoms can diffuse on the surface of solid Ni or NiC catalyst particle and are assembled to form CNTs. This is consistent with the morphology feature of the tip in Fig 2(a). Accordingly, two possible main steps are rationally speculated for the growth of the HfC nanotubes. Given that the Ni or NiC particle is encapsulated with the multilayer graphite nanostructure, the tip-growth process of CNTs occurs while Hf atoms are not involved in this process in the initial stage of the growth. As CNTs continuously grow, gaseous Hf species are transported to the column of CNTs at a position which has a certain distance from the catalyst particle. Then, Hf atoms react with C atoms from the as-grown CNTs to form HfC. Moreover, the hollow structure of CNTs is replicated. In this stage, the polycrystalline HfC wall is...
first formed, which is similar to template reaction growth of metal carbide nanowires. As the growth continues, the crystalline structure of the wall appears to become single-crystalline along the growth direction via Ostwald ripening. Finally, the encapsulated catalyst particle is lifted up by the hollow column. In this mechanism, some processes are not understood and need further research. For example, CNTs that are initially hollow cannot be transformed into solid HfC nanotubes, unlike the growth of reported metal carbide nanowires through the reaction of as-prepared CNTs with metal or metal halide.6–10 In our work, the HfC nanotubes are obtained from the HiCl4–CH4–H2 system by the one-step catalyst-assisted CVD. This probably has close relationship with the preparation process. According to conventional VLS mechanism,11 the growth of binary compound nanowires is derived from absorption and precipitation of atoms of two different elements on the catalyst. However, during the whole growth process of the HfC nanotubes, only Hf atoms are involved in absorption and precipitation processes on the catalyst whereas Fe atoms are not involved in both processes. This distinguishes from the VLS process of the HfC nanowires11 as well as binary semiconductor nanowires.

IV. Conclusions

In summary, single-crystalline HfC nanotubes have been synthesized from the HiCl4–CH4–H2 system by a one-step catalyst-assisted CVD method. The synthesized HfC nanotubes have uniform diameters of ~60 nm and wall thicknesses of ~15 nm. The growth involves the tip-growth process of CNT followed by a CNTT-mediated reaction. The synthesis of the HfC nanotubes would offer opportunities for fabrication of large-scale HfC or other metal carbide (e.g., TiC, ZrC) nanotubes by controlling proper synthesis conditions. The synthesis of HfC nanotubes open the possibility to applications of the HfC nanotubes as nanofibrous fillers in refractory metal and ultrahigh-temperature ceramic matrix nanocomposites and unique building blocks for new nanoscale functional devices.

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References


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