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Full Length Article

High-aspect-ratio HfC nanobelts accompanied by HfC nanowires: Synthesis, characterization and field emission properties

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ABSTRACT

As a key refractory carbide, hafnium carbide (HfC) is commonly used as structural materials while the field emission (FE) application of HfC in the field of vacuum microelectronics is almost the only one for functional material purposes. Based on its outstanding physical and chemical characteristics, HfC is identified as a potential candidate with satisfactory mechanical properties and long-term and/or high-temperature FE stability for future applications in high-performance field emitters. However, the development of HfC in various FE applications is hindered because it is not facile to fabricate large-scale low-dimensional HfC field nanoemitters. Herein, High-aspect-ratio HfC nanobelts accompanied by HfC nanowires were synthesized on a large scale by a traditional and simple catalytic chemical vapor deposition (CVD) method. Classical vapor–liquid–solid (VLS) theory was employed to explain the growth of the HfC nanowires and nanobelts along axial direction. The thin HfO_2 shell and thin C layer surrounding the nanostructures might give rise to the diameter fluctuation of HfC nanowires and the width increase of HfC nanobelts in lateral direction. Field emission results show that the high-aspect-ratio HfC nanobelts accompanied by the nanowires are promising field nanoemitters, which exhibit excellent field emission properties with a fairly low turn-on field of ~1.5 V μm^{-1} and a low current fluctuation less than ~10%. This suggests that HfC ceramics with high-aspect-ratio nanostructures are ideal cathode material for various field emission applications.

1. Introduction

Refractory transition metal carbides have a great industrial importance, not only in traditional structural applications such as ultrahigh-temperature shielding and various wear-resistant machine parts because of their strength and refractory nature, but also in new and promising fields of electronics and optoelectronics. These metal carbides possess both the physical properties of ceramics and the electronic properties of metals, as a result of the close-packed interstitial structures with a combination of metallic, covalent, and ionic metals [1]. As a key member of the transition metal carbide family, hafnium carbide (HfC) has a series of particular properties, including ultrahigh melting point, high hardness, high strength, high thermal and electrical conductivities, and excellent thermal and chemical stability [1–5]. Due to the outstanding physical and chemical properties, HfC is commonly used as high-temperature and/or wear-resistant structural material, including thermal protective coating or additive of ultrahigh-temperature composites [5–11], cutting tools, and abrasives [12,13]. However, up to now, little work has been centered on its applications as functional material. Although HfC is mainly used for structural material purposes, it is suggested that HfC is an attractive cathode material for field emission (FE) applications in the field of vacuum microelectronics due to high conductivities, high thermal and chemical stability. Furthermore, low work function (~3.3 eV) [14]; defined as $\Phi = \varphi - E_f$ [15], where φ is the vacuum level and E_f is the Fermi level) of HfC make it easier to release electrons, which indicates that HfC has huge potential to exhibit positive functionality on FE devices. Considering its outstanding physical and chemical characteristics originating from the unique structure, it is well-established that HfC is an appealing high-performance FE material with satisfactory mechanical properties and long-term and/or high-temperature emission stability for future applications [16].

Despite the huge potential as the cathode material, the development of HfC in various FE applications is hindered because it is still a big challenge to obtain large-scale single-crystal HfC nanos-

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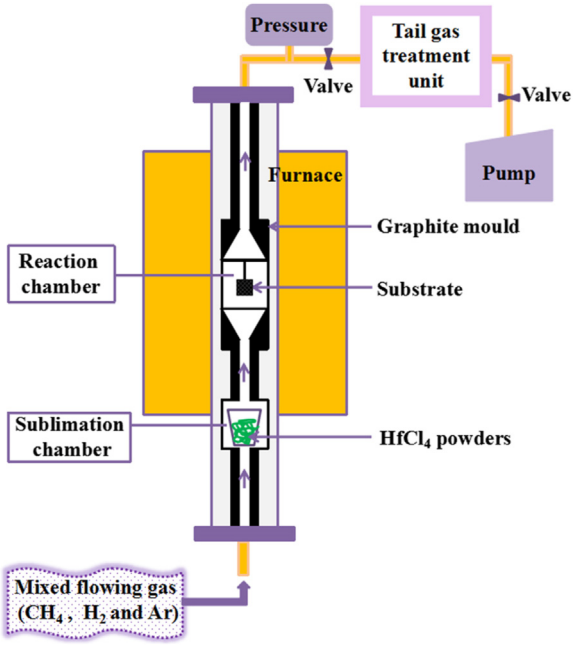

Fig. 1. Diagrammatic drawing of the experiment setup for the low-dimensional HfC nanostructures production.

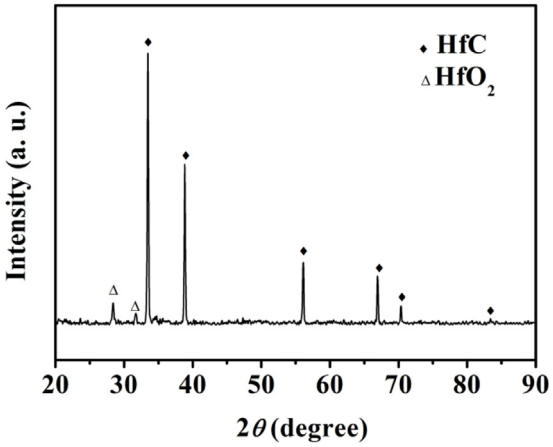

Fig. 2. XRD pattern of the sample synthesized by the catalytic CVD.

tructures with high quality, especially for one-dimensional (1D) nanostructures and quasi-1D nanostructures with high aspect ratio. Before our previous reported work [17–20], single-crystal HfC field emitters were mainly prepared by a relatively complex method, in which micrometer-sized single-crystal HfC rod was first fabricated by arc floating zone refinement from sintered stock and then electrochemically etched to obtain the HfC field emitter with a submicron tip [14,21]. In this paper, we synthesized large-scale high-aspect-ratio HfC nanobelts accompanied by the nanowires by a facile one-step catalytic chemical vapor deposition (CVD) method. The field emission properties of a mixture of the nanobelts and nanawires were investigated. From the FE measurements, the synthesized nanostructures exhibited excellent performance with a low turn-on field of ~1.5 V μm^{-1} and a low current fluctuation less than ~10%. Additionally, based on the mechanical performance and high temperature performance of the bulk HfC, the low-dimensional HfC nanostructures are expected to be promising candidates for future applications as ideal fibrous filler materials, which are used to fabricate ultrahigh temperature ceramic matrix nanocomposites [22–25].

2. Experimental

The synthesis of the low-dimensional HfC nanostructures was performed by a catalytic vacuum CVD method in a variable-temperature vertical tube furnace. The furnace was equipped with an alumina tube with an inter diameter of ~75 mm and a length of ~1500 mm. A graphite mould with both cylindrical low-temperature and high-temperature chamber was placed along the alumina tube. The low-temperature chamber with an inter diameter of 55 mm and a height of 70 mm was used to sublimate $HfCl_4$ (Alfa Aesar, 99.9%) powders. The high-temperature chamber with an inter diameter of 52 mm and a height of 70 mm was used to grow the nanostructures. $HfCl_4$ powders were loaded into a quartz crucible that was placed in the sublimation chamber. $Ni(NO_3)_2$ particles were uniformly distributed on the surface of a graphite sheet (5 mm × 5 mm × 6 mm, 2.2–2.3 g cm^{-3}) by impregnation. The graphite sheet with $Ni(NO_3)_2$ particles was vertically hung in the high-temperature reaction chamber and served as the substrate for the nanostructure growth. Diagrammatic drawing of the furnace system was given in Fig. 1. $Ni(NO_3)_2$ served as the catalyst; $HfCl_4$ and CH_4 (99.9%) served as precursors; high purity H_2 (99.999%) served as reducing agent and carrier gases. Before the heating, the furnace system was purged with high purity Ar (99.999%) for 3 times to remove oxygen and water vapor. Then, the alumina tube was evacuated and maintained at ~60 Torr. Next, the reaction chamber was heating to 1080 °C at a rate of 7 °C/min under a constant flow of H_2 and maintained at 1080 °C for 8 h. When heated to the synthesis temperature, CH_4 and H_2 gases were simultaneously introduced into the furnace system at a total flow of 800 sccm (volume ratio 1:15) and mixed. The mixed gases flowed through the sublimation chamber and carried the evaporated $HfCl_4$ vapor into the reaction chamber to catalytically synthesize the nanostructures. When the synthesis ended, the furnace was cooled to room temperature in a protective Ar atmosphere. Finally, the graphite substrate was taken out, with the wool-like sample appearing dark brown.

Detailed morphological and structural characterizations were performed using a Rigaku D/max-3C X-ray diffractometer (XRD) with a Cu Kα radiation source, a FEI Quanta 600 FEG field-emission scanning electron microscope (FESEM), and a Tecnai F30 G^2 field-emission transmission electron microscope (TEM) with energy-dispersive X-ray (EDX) mapping capabilities, respectively.

3. Results and discussion

The crystal structure of the synthesized sample was analyzed based on XRD pattern, which was obtained at a scanning rate of 0.27 deg/s. As shown in Fig. 2, HfC and HfO_2 were detected from the sample. The diffraction peaks of HfC were readily indexed to the face-centred cubic (fcc) structure of bulk HfC with lattice constants of $a = b = c = 0.465$ nm (JCPDS file 65-0964). The amount of HfO_2 was so small that only two characteristic peaks with low intensity were present in this pattern. In experiments carried out in a CVD system, it is difficult to avoid forming oxides. Formation of HfO_2 is attributed to reaction between Hf and impurity O, the latter which probably arose from inlet gases and air due to impossibly absolute seal in the entire reaction systems.

To characterize the morphologies of the as-synthesized product, a series of SEM images were taken using FESEM at an electron energy of 20 keV. Fig. 3a shows a typical low-magnification SEM image of large-area low-dimensional HfC nanostructures with high aspect ratio grown on the substrate. As shown in Fig. 3a, 1D wire-like structures (nanowires) and quasi 1D belt-like structures (nanobelts) have a length of 100–200 μm. Most of the nanobelts have two unparallel side edges and an increasing width rang-