Diamond & Related Materials 19 (2010) 284–287

Contents lists available at ScienceDirect

Diamond & Related Materials

journal homepage: www.elsevier.com/locate/diamond

Diamond-graphite nanorods produced by microwave plasma chemical vapor deposition

Sobia Allah Rakha, Guojun Yu *, Jianqing Cao, Suixia He, Xingtai Zhou

Shanghai Institute of Applied Physics, Chinese Academy of Sciences, Shanghai 201800, PR China

ARTICLE INFO

Article history:
Received 26 June 2009
Received in revised form 16 October 2009
Accepted 5 November 2009
Available online 11 November 2009

Keywords:
Microwave plasma CVD
Nanocrystalline
Diamond nanorods
Electron microscopy

ABSTRACT

One dimensional C–C nanostructure, diamond–graphite nanorods, was synthesized by the argon rich microwave plasma chemical vapor deposition method. The nanostructures were characterized by scanning electron microscopy and transmission electron microscopy techniques. The diamond nanorods (DNRs) consist of single-crystalline diamond cores of 2–5 nm in diameter and several tens of nanometer in length. The DNRs are encapsulated in a graphitic shell of variable thickness. Raman and X-ray diffraction spectra also indicated the coexistence of diamond and graphite phases in the film. The addition of nitrogen is considered to be helpful for the highly efficient formation of graphite shell. The high content of methane in the gas mixture in the presence of argon rich environment is suggested to be responsible for the one dimensional growth.

1. Introduction

Nearly in the last 20 years, the production of sp^2-bonded one-dimensional nanocarbons, such as carbon nanotubes (CNTs) and graphene [1] has successfully realized by various techniques, while the synthesis of diamond nanorods (DNRs) – the one-dimensional sp^3-configured analogue of CNTs – is still difficult, particularly with few nanometers in the diameter. The first synthesis of DNRs was realized until 2001 by microwave plasma chemical vapor deposition (MPCVD) [2]. In this case, the nanorods have a polycrystalline structure and are about 300 nm in diameter. One dimensional diamond nanostructures have also been synthesized by plasma etching recently [3,4]. Theoretically, it is found that the structural stability of the diamond nanowires is dependent on their diameter and crystallographic direction, and has been predicted to be energetically favored at diameters ranging from 2.7 to 9 nm [5,6]. The band gap of diamond nanowires is found to be narrower than that of bulk diamond, and varies with the surface morphology, diameter and the orientation of the principle axis [5]. In this context, single crystalline DNRs attract much more interests. DNRs were synthesized by our group using hydrogen plasma treatment on the CNTs [7] and on nanodiamond films [8]. Recently, the DNRs were obtained [9] in Ar-rich MPCVD by the introduction of nitrogen in the feed gas and using methane (1%) as carbon source. In most of the cases, the DNRs were covered by amorphous carbon. Recently, we improved this MPCVD method to synthesize the DNRs. The methane percentage was increased (up to 10%) in the feeding gas. As a result, it was found that not only the DNRs could be produced efficiently; one-dimensional C–C nanostructures – diamond–graphite nanorods – were also observed. We believe this type of heteronanostructures, i.e., the DNRs shelled with other carbon allotropes such as graphite (graphene), CNT, fullerene, and even with noncarbon objects, can further extend the doors toward designing actuators, field electron emitters, novel composites (e.g., the superhard–superstrong C–C composites) and other applications.

2. Experimental details

The synthesis was performed on (100) n-type silicon (Si) wafers using $Ar/N_2/CH_4$ mixtures, in a 2.45 GHz microwave plasma system. The microwave power was kept at 1800 W, and the total gas flow maintained at 40 sccm with 20 sccm Ar, 16 sccm N_2 (40%) and 4 sccm (10%) CH_4. The substrate temperature and the plasma pressure were 850 °C and 80 Torr, respectively. Raman spectroscopic studies were performed on the DNRs sample using a Ranishaw Raman microscope with the 514.5 nm line from an argon ion laser. The samples were characterized with a scanning electron microscope (SEM, LEO 1530) for morphology studies. The Raman spectra were taken from different positions of the films to verify the reproducibility and consistency of the data. For the analysis from transmission electron microscope (TEM, JEOL 2010F) operated at 200 kV a small amount of the samples was scratched off from the silicon substrate and sonicated in acetone for 15 min before depositing onto the TEM grid. X-ray diffraction (XRD) measurement was performed by the use of synchrotron radiation beam at SSRF (Shanghai Synchrotron Radiation Facility) with effective X-ray energy of 10 keV. The incident monochromatic X-ray has a wavelength of 1.24 Å.

* Corresponding author. Tel./fax: +86 21 39194539.
E-mail address: yuguojun@sinap.ac.cn (G. Yu).

0925-9635/$ – see front matter © 2009 Elsevier B.V. All rights reserved.
doi:10.1016/j.diamond.2009.11.006

3. Results and discussion

Fig. 1a (lower magnification) and 1b (higher magnification) are the SEM images of the diamond film deposited for 2 h. These micrographs clearly demonstrate elongated morphology of the crystallites; ascribed as rod-like nanostructures with length of 1–2 μm. Low magnification cross-sectional SEM image (Fig. 1c) shows the thickness of film is about 6.5 μm after 2 h of deposition, indicating high growth rate deposition under high CH_4 content environment. Fig. 1d is the high magnification cross-sectional SEM image of the film, revealing many embedded nanorods.

TEM demonstrates structural details on the rod-like nanostructures. Fig. 2a shows the low magnification TEM micrograph demonstrating several nanorods in the matrix. Selected area electron diffraction (SAED) pattern (inset of Fig. 2a) taken over a 100 nm region, clearly shows the presence of two crystalline structures: diamond (D, characterized by the rings corresponding to the inter-planar distances $d_{111} = 0.21$ nm, $d_{220} = 0.12$ nm, and $d_{311} = 0.11$ nm) and graphite (G, characterized by the rings corresponding to the inter-planar distances $d_{002} = 0.34$ nm and $d_{110} = 0.12$ nm). Fig. 2b is the high resolution TEM (HRTEM) image focusing on a segment of one nanorod shown in Fig. 2a. This image clearly reveals a C–C heteronanostructure: single crystalline diamond core wrapped by graphite sheets, showing the one-dimensional diamond–graphite nanorods. The DNRs consist of single-crystalline diamond cores of 2–5 nm in diameter with orientation along [110] principle axis. The diameter of nanorods varies along the principal axis direction. Fig. 2c presents a schematic (left) corresponding to the complex lattice fringes (right) at the interface between DNR and graphite. In our observations, all of the DNRs have a principal axis direction parallel with the graphitic {002} facets, although the orientations of the $(111)_{diamond}$ planes are different from another. The lattice fringes of another nanorod can be seen in Fig. 2d, which also shows that the DNR grows along the [110] direction. The direction is quite matched with previous results reported by our group [5] and Gruen et al [9], respectively.

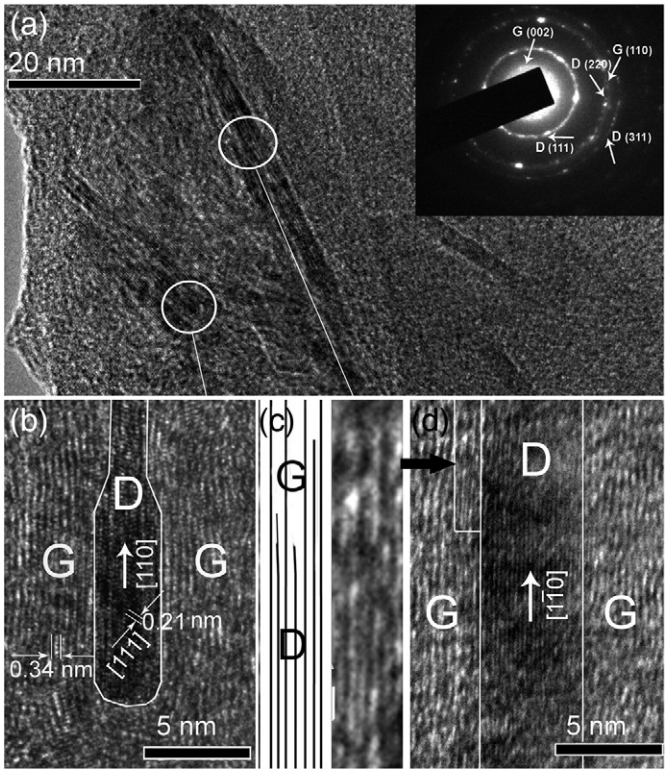

Fig. 2. (a) Low magnification TEM image indicating numerous nanorods. The inset shows the corresponding SAED pattern. The different diamond (D) and graphite (G) rings are indicated; (b, d) HRTEM images of diamond nanorods with an average d-spacing of 0.21 nm surrounded by ~5 nm thick graphite sheets with d-spacing of 0.34 nm. (c) Schematic indicating the lattice spacing of graphite and diamond structures.

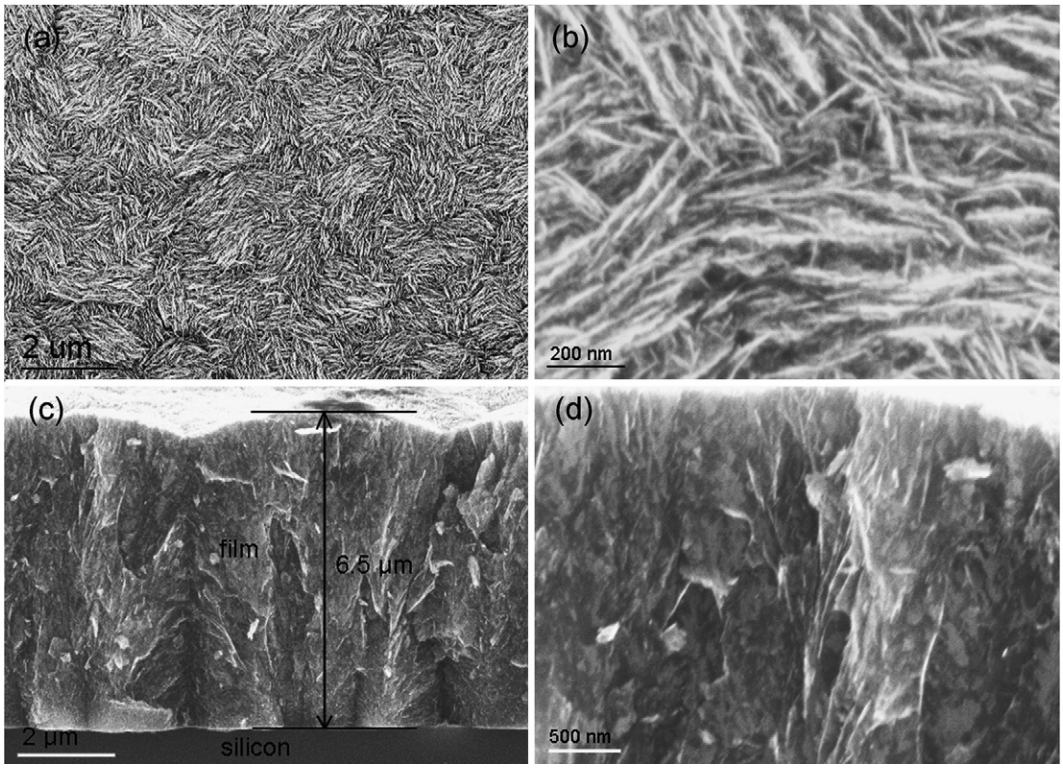

Fig. 1. Plane view SEM images of high density elongated nanocrystallites revealing the rod-like morphology (a) at low magnification and (b) at high magnification. SEM images of a cross section (c) indicate the thickness of ~6.5 μm after 2 h of deposition and (d) high magnification highlighting the many embedded nanorods in the film.