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ScienceDirect
Diamond & Related Materials 17 (2008) 581 – 584
DIAMOND AND RELATED MATERIALS
www.elsevier.com/locate/diamond

Room-temperature synthesis and characterization of cobalt-doped carbon nanofibers

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Available online 9 February 2008

Abstract

The graphite surfaces were irradiated by Ar^+ ions with and without a simultaneous Co supply at room temperature. The sputtered surface without Co supply was characterized by densely distributed conical protrusions with aligned carbon nanofibers (CNFs) on the tops, whereas Ar^+-bombarded surfaces with a simultaneous Co supply were covered with asparagus-like (micrometer order in base diameter) or nanofibrous (10–50 nm in diameter) structures depending on the supply rate of Co atoms. No CNF-tipped cones were observed to form. For the nanofibers containing carbon and cobalt, the hysteresis behavior observed in the magnetization property by applying magnetic fields in directions perpendicular and parallel (in-plain) to the substrate was almost identical, whereas a continuous 1 μm thick-Co film showed the strong in-plane anisotropy. Other materials could be readily incorporated into CNFs by choosing the suitable metal sources. Thus, the ion-irradiation method is expected to open up a new approach to fabricate ferromagnetic 1-D nanomaterials at room temperature.

Keywords: Amorphous carbon; Nanofibers; Ion bombardment; (others) magnetic properties

1. Introduction

Since the discovery by Iijima [1], carbon nanotubes (CNTs) and carbon nanofibers (CNFs) have attracted great attention in nanomaterials science and nanoelectronics technology. Taking advantage of their unique features, such as high aspect ratio, nanoscale diameter, high chemical stability and high mechanical strength, variety of applications have been proposed, including field electron emission sources, probes for scanning probe microscopes, chemical sensors, catalyst supports and so on [2]. CNT- or CNF-based nanocomposites with various metals will further extend their applications, for example, in high-density memory media. Thus, the synthesis of CNTs encapsulating ferromagnetic metals has been attempted [3–9]. However, high temperatures are generally required for their synthesis and the metals which could be encapsulated in CNTs are mainly limited to the catalyst generally used for the CNT growth.

In our previous papers, we have demonstrated that Ar^+-ion irradiation to bulk carbon and carbon-coated substrates induce the growth of CNFs on their surfaces without any catalyst even at room temperature [10–12]. Here we challenged the room-temperature synthesis of composite nanofibers consisting of ferromagnetic metal and carbon by the Ar^+-ion irradiation of carbon substrates with a simultaneous supply of ferromagnetic metal atoms, and their magnetic properties were measured. In addition, their structural characterization was also performed.

2. Experimental procedure

Samples employed were graphite plates, 10 mm × 10 mm in size (Toyo Tanso Co., Ltd. Japan). The sample surfaces were irradiated by Ar^+ ions at 45° from the normal to the surface using a Kaufman-type ion gun (Iontech. Inc. Ltd., model 3-1500-100FC) with and without a supply of Co simultaneously.

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0925-9635/$ - see front matter
doi:10.1016/j.diamond.2008.01.092

The sputtering rate was fixed at 170 nm/min and the Co supply rates (D) employed were 6.0, 7.8 and 15 nm/min. The diameter of the ion beam was 6 cm. Ion irradiations at 1 keV was done at room temperature for 60 min. The basal and working pressures of the growth chamber were 1.5×10^{-5} Pa and 2×10^{-2} Pa, respectively.

After sputtering, the topography of the sample surfaces and the crystalline structure of pristine and metal-incorporated CNFs thus grown were carefully observed by scanning [SEM (JEOL; JEM-5600)] and transmission electron microscopes [TEM (JEOL; JEM-3010)]. The magnetic properties of the samples were investigated by a vibrating sample magnetometer with a maximum field of 10 kOe.

3. Results and discussion

Fig. 1 shows a SEM image of a graphite surface Ar^+-sputtered without simultaneous Co supply, exhibiting that the whole surface was covered with conical protrusions with aligned CNFs on the tops, both pointing in the ion-beam direction. It should be noted that no CNF grew without cone bases and that only one CNF grew on the respective cone tip (more than one CNFs were never observed on a single cone tip). Their morphological features were almost identical with those observed previously for the Ar^+-sputtered bulk graphite and carbon-coated various kinds of substrates [10–12]. The average diameter, length and numerical density of CNFs were ~30 nm, ~1.2 μm and $\sim1.0\times10^6$ mm^{-2}, respectively.

Fig. 2 shows SEM images of graphite surfaces sputtered with a simultaneous Co supply at D=15, 7.8 and 6.0 nm/min. The highly Co-supplied surface (D=15 nm/min) was featured by relatively large "asparagus" like protrusions (several micrometers in the base diameter) consisting of tiny cones [Fig. 2(a)]. No CNF was observed on the tops. Thus, the growth of CNFs seemed to be suppressed by the excessive supply of Co. On the surface sputtered with a lower Co-supply rate [D=7.8 nm/min; Fig. 2(b)], large asparagus-like protrusions were observed with reduced numerical density and fibrous protrusions grew between the large asparagus structures. The large asparagus structures measured still 2–3 μm in the base diameter. A further reduction in Co-supply rate yielded the sputtered surface characterized by a mixture of fibrous and slender asparagus-like protrusions [D=6.0 nm/min; Fig. 2(c)]. Very interestingly, CNF-tipped structure was not observed for Co-supplied surfaces and fibers grew directly on the "ground."

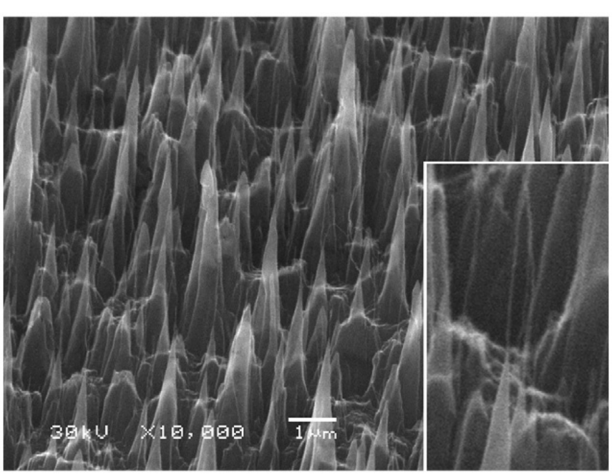

Fig. 1. SEM images of a graphite plate surface sputtered by Ar^+ ions without a simultaneous Co supply. Insets: Magnified SEM image.

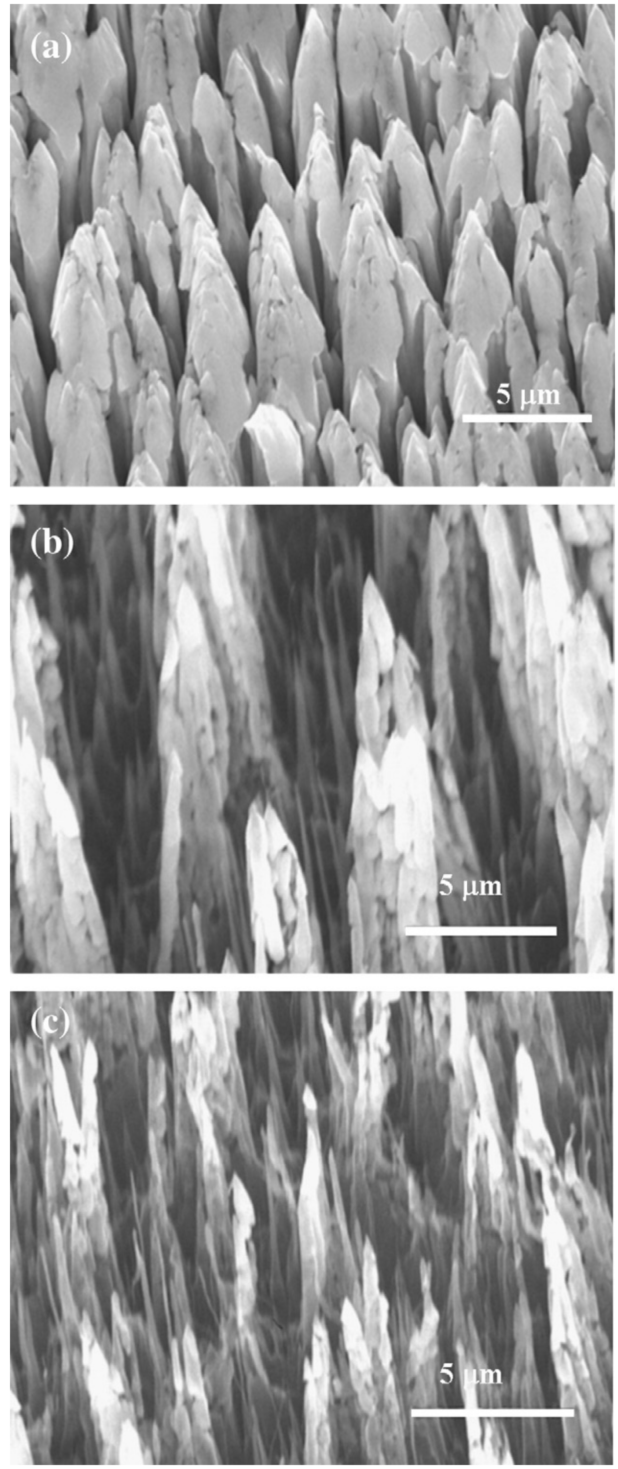

Fig. 2. SEM images of graphite plate surfaces sputtered by Ar^+ ions with a simultaneous Co supply at (a) 15, (b) 7.8, and (c) 6.0 nm/min.