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Amorphous Carbon Fibrilliform Nanomaterials Prepared by Chemical Vapor Deposition

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Carbon nanomaterials were prepared by chemical vapor deposition (CVD) and hot-filament CVD (HF-CVD) methods. The substrates were silicon ⟨100⟩ and copper plates on which catalytic metal or metal-oxide thin films were coated by means of the cathodic arc deposition technique. Ethylene gas was used as a precursor. HF-CVD with a filament temperature of 1,000°C yielded a larger amount of carbon deposit at a lower furnace temperature of 600°C. High-resolution microscopic observation revealed a variety of amorphous carbon nanomaterials, such as frost columns, coral beads, microcoils, nanocoils, and amorphous nanotubes.

KEYWORDS: carbon nanomaterials, nanocoil, chemical vapor deposition, hot-filament assist

1. Introduction

Carbon nanotubes have attracted considerable interest as potential materials for use in field-emission devices, nano-size probe tips and hydrogen containers, among other devices. One of the preparation methods of carbon nanotubes is chemical vapor deposition (CVD) with a precursor of hydrocarbon gas, such as methane (CH_4),[1)] acetylene (C_2H_2),[2,3)] ethylene (C_2H_4),[4)] or benzene (C_6H_6),[5)] or of hydrocarbon vapor of powders such as ferrocene[6)] or triazine.[7)] In CVD preparation, catalysts such as iron (Fe),[1,4,6)] cobalt (Co),[2,7)] and nickel (Ni)[2,8,9)] are usually employed. The nanotubes prepared by CVD are multiwalled and capped, and the nanotube diameters range from 5 to 100 nm. The significant advantage of the CVD method is the possibility of the direct growth of a well-aligned nanotube array.[4,6)]

In the present study, we also intended to fabricate carbon nanotubes by means of CVD and hot-filament CVD (HF-CVD) using C_2H_4 gas as a precursor. As a result, we observed a variety of amorphous carbon fibrilliform nanomaterials, instead of conventional carbon nanotubes.

2. Experimental

Catalytic thin films were coated on silicon (Si) ⟨100⟩ and copper (Cu) substrates by means of the shielded cathodic arc deposition technique,[10,11)] which is an ion plating method. The prepared films were of Fe, Ni, Cr, Ti, and Zn, and also of their oxides. Film thickness ranged from 2 to 10 nm.

The experimental setup of the CVD system is depicted in Fig. 1. The sample substrate was located in the quartz tube (45 mm inner diameter, 500 mm long) and heated using a temperature-controlled tubular electric furnace (300 mm long). The quartz tube was first purged with argon (Ar) gas at a flow rate of 400 sccm and then the furnace temperature was gradually increased to the desired value within 30 to 45 min under Ar gas flow. After the desired temperature was reached, the Ar gas flow was stopped and C_2H_4 gas was introduced. The furnace temperature was maintained for a certain length of time and then the sample was cooled with Ar gas at a flow rate of 400 sccm for 60 to 70 min. For HF-CVD, the temperature of the nickel-chromium (NiCr) filament was approximately 1,000°C.

The deposit on the substrate was observed using a high-resolution scanning electron microscope (HR-SEM, Topcon; ABT-150F) and a high-resolution transmission electron microscope (HR-TEM, JEOL; HR-2010).

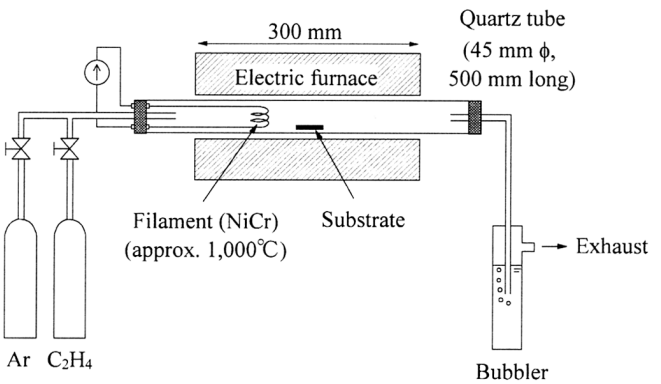

Fig. 1. Experimental setup of hot-filament chemical vapor deposition apparatus.

3. Results

In the case of the CVD experiment, a Si substrate was used. A black deposit was sometimes observed on Fe, Fe oxide, Ni, Ni oxide, Zn, and Zn oxide-coated substrates under the following preparation conditions: furnace temperature, 700°C; heat-treatment time, 80–120 min; C_2H_4 flow rate, 40–100 sccm. An example of HR-SEM observation of the black deposit is shown in Fig. 2; this sample was prepared on a Ni-coated substrate. The carbon fibers were formed under a condensed surface, and resembled "frost columns".

The use of a hot filament enhanced the deposition efficiency and enabled lower temperature (550–600°C) deposition on Ni, Zn and their oxide-coated substrates. Consequently, a deposited material of different morphology was observed. Figure 3 shows the HR-SEM micrograph of the deposit prepared on a Zn-coated Si substrate, which resembled "coral beads". Figure 4 shows the microcoil, which is very similar to the structure reported by Motojima and Chen[12)] and Chen and Motojima.[13)]

Figure 5 shows the twisted nanocoil which was sometimes observed in the deposit prepared on a Ni-coated Cu substrate. Similar fibers were also found on a Zn-coated Cu substrate. The HR-TEM micrograph of the twisted nanocoil is shown