Transactions of the Materials Research Society of Japan 29 [2] 501-504 (2004)

Synthesis of Twisted Carbon Nanofiber by Catalytic CVD Method

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Helical carbon nanofibers (HCNF) were synthesized by the catalytic CVD method. The catalyst was a compound comprised of nickel (Ni) and copper (Cu), or their oxides, in the form of a multi-layer or mixture-layer film. They were prepared on a quartz substrate by physical vapor deposition (PVD) and sol-gel drop-coat methods. First, the dependence on source gas and dependence on presence/absence of a hot-filament assist were tested using Ni/Cu PVD film as a catalyst. The dilute gas used was helium (He). When acetylene (C_2H_2) gas was used, carbon nanocoils (CNCs) and carbon nanoropes (CNRs) were deposited without hot-filament assist and with assist, respectively. When ethylene (C_2H_4) gas was used with hot-filament assist, carbon nanotwists (CNTws) were deposited. Secondarily, the catalyst mixture of Ni oxide (NiO)/Cu oxide (CuO), prepared by the sol-gel drop-coat method, was tested for use with C_2H_2 gas. The influence of the mixing ratio of catalysts, process temperature, and the source/dilute gas ratio was examined. Optimum conditions for efficient HCNF synthesis were found to be as follows: NiO/CuO ratio, 2/8; process temperature, 500-600°C; C_2H_2/He flow rate ratio, 3/10 – 4/10. The obtained product in the latter experiment was mainly CNTw.

Keywords: helical carbon nanofiber, carbon nanotwist, catalytic CVD, Ni/Cu multi catalysts, optimization

1. INTRODUCTION

Since 1953, when carbon fiber with a helical structure was first reported [1,2], various types of chemical vapor deposition (CVD) methods have been developed, a variety of catalysts have been examined under various process conditions, and many carbon fiber growth models have been proposed. In 1990, Motojima *et al.* fabricated regular-coiled carbon fibers with high reproducibility [3]. They are referred to in review articles [4, 5]. Recently, helical, spiral, or twisted carbon fibers on an under-submicron scale, have been prepared by the CVD method with an ion (Fe) on indium-tin-oxide (ITO) film [6], and nickel (Ni) or zinc (Zn) on a copper (Cu) substrate [7-10]. Such helical carbon nanofibers (HCNFs) have field emission properties [9, 11], and are considered to be useful for various applications such as nano-springs, electric nano-inductors, electromagnetic shields, gas storage, fillers in polymers and various types of rubbers.

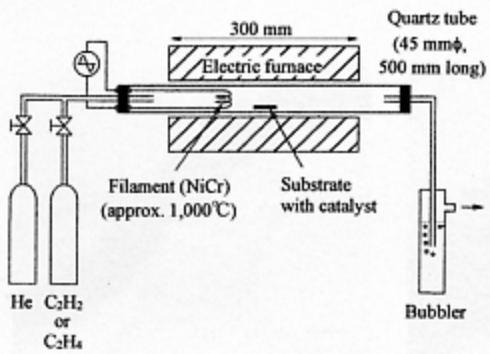

Fig. 1. Experimental setup of the catalytic CVD apparatus with hot-filament.

In the present paper, HCNFs were fabricated using a compound catalyst of nickel (Ni) and copper (Cu), or their oxides (NiO, CuO). First, various shapes of HCNFs were synthesized by a Ni/Cu multi-layer catalyst of thin solid film prepared by physical vapor deposition (PVD) using the vacuum arc plasma. Second, the influence of mixing ratios of catalysts, process temperatures, and the source/dilute gas ratio was examined using an NiO/CuO compound film prepared by the sol-gel drop-coat method.

2. EXPERIMENTAL DETAILS

Figure 1 shows the experimental setup of the catalytic CVD apparatus with a nickel-chromium alloy (NiCr) hot-filament. The electric furnace and the quartz tube process chamber were horizontally arranged. Source gases were acetylene (C_2H_2) and ethylene (C_2H_4). The dilute gas was helium (He). When the hot filament was turned on, the temperature was set at 1,000°C approximately 30 mm upstream from the substrate. The substrate was quartz measuring approximately 10×10 mm^2 and 1 mm in thickness. The experimental procedure was as follows. After the catalyst-coated substrate was placed at the center of the quartz tube, the temperature of the electric furnace was increased from room temperature to the set temperature during approximately 1 hour with He gas flow of 420 ml/min. Then the source gas was introduced for 10 or 20 min with/without the hot filament assist. After the deposition process, the furnace was cooled down to the room temperature over approximately 1 hour with He gas flow