Electron Beam Conversion of a Carbon Precursor to a Carbon Nanotube

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A new way to form a carbon nanotube (CNT) by an electron-beam irradiation has been found, where a carbon precursor is irradiated by an electron beam in a transmission electron microscope (TEM). This technique has two advantages: an in-situ observation of the growth and a direct formation on a substrate. The second is crucial to fabricate a CNT electronic device, and a variety of related works are underway. In this paper, two types of precursors, carbon-fragment and polyyne-containing carbon, are compared.
Keywords: carbon nanotube, polyyne, precursor, electron beam, TEM.

1. INTRODUCTION

After finding CNTs [1], this material has attracted much attention for its unique structure and prospective applications. CNTs have been synthesized by an arc discharge with [2, 3] or without [1] a metal catalyst, and a chemical vapor deposition [4]. In addition, an electrochemical preparation has been reported as well [5, 6].

The authors have been studying a new process, where a carbon precursor is heated and irradiated by an electron beam [7-11]. The growth is carried out in a TEM and is observed in an in-situ way. The in-situ observation is versatile for understanding the growth mechanism, which is crucial for material and process designs in regard to a device fabrication.

The electron-beam process provides CNTs without a metal catalyst that works as an impurity and should be avoided for an electronic device. This dry process is compatible with a present semiconductor process and is possibly applied to a large-scale manufacturing. In addition, this electron-beam process can be applied to a nanodevice fabrication (nanolithography) based on the Compton wave length of an electron (2.42 pm).

A variety of carbon precursors have been applied to this technique. In this paper, carbon-fragment and polyyne-containing-carbon precursors are compared in the view of CNT growth.

2. EXPERIMENTAL SECTION

The carbon-fragment thin film is deposited on a Cu mesh (carbon coater: MUE-ECO, ULVAC; carbon rod: #640, Nisshin EM). The depth is controlled about 100 nm.

The polyyne-containing carbon films are prepared by electrochemically reducing poly(tetrafluoroethylene) (PTFE, DuPont) films, using a two-electrode method (anode: magnesium, cathode: stainless steel) under argon at 0°C [12]. The PTFE films (10 mm x 10 mm x 60 μm) are charged in a flask with a solvent containing supporting salts (tetrahydrofuran (THF): 30 ml, LiCl: 0.8g, $FeCl_2$: 0.48 g). A DC voltage (40 V) is applied between the anode and the cathode for 10 hr. After the reduction, the films are washed with THF and are dried in vacuum.

The films are analyzed by an IR spectrograph (MagnaIR 760, Nicolet), Raman (HoloLab 5000, Kaiser), and XPS (ESCA 750, Shimazu). The specimen is embedded in an epoxy resin (Araldite CY211, Ciba) and is cut by a microtome (UltraCut, Leica).

The growth and the observation are carried out in a TEM (H7100, Hitachi, 100 kV). The specimen is heated to 600-900°C to grow CNTs.

3. RESULTS AND DISCUSSION

Though CNTs have been already found to be formed on polyyne-containing carbon by irradiating an electron beam, those are formed on a carbon-fragment thin film as well. First, a CNT formation on the carbon film is presented.

A thin carbon-fragment film is prepared by a conventional carbon coater, which is used to prepare a specimen for an SEM observation. A TEM observation shows that the film is not flat and is composed of carbon fragments, which are supposedly small graphenes and amorphous carbon. The film contains no tubular-shape carbon. The specimen is heated to 700°C and kept for 2 hr in a TEM without an electron-beam irradiation. An electron beam (100 kV, 1 A/cm^2) is irradiated for 30 min at 700°C. After stopping the irradiation and cooling down, the specimen is observed precisely at a room temperature.
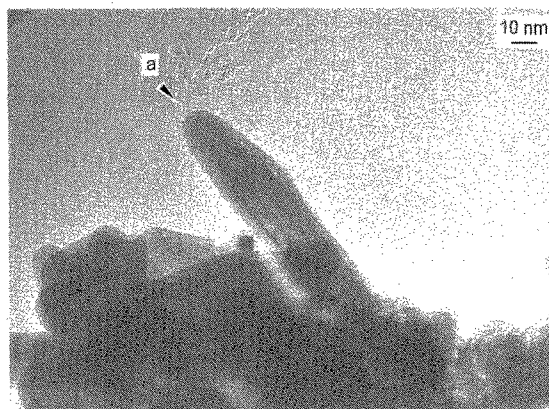

Fig. 1. Tubular-shape carbon grown on the carbon-fragment precursor (partially graphitized).
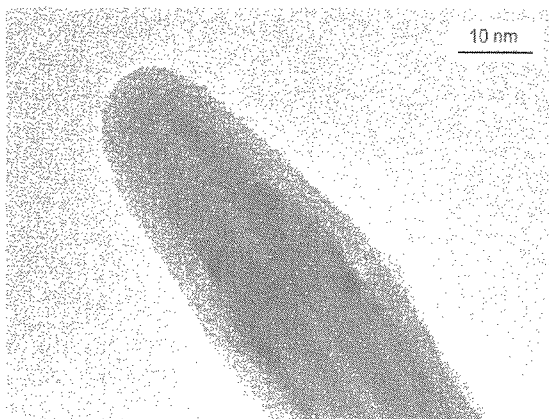
Fig. 2.   Magnified photograph of (a) in Fig. 1. Graphitized layers are observed at the core of the tube.
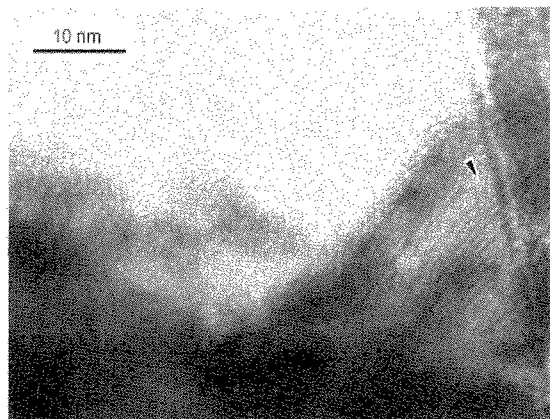

Fig. 5.   Magnified photograph of (b) in Fig. 3.   The arrow indicates graphitized layers of the wall.
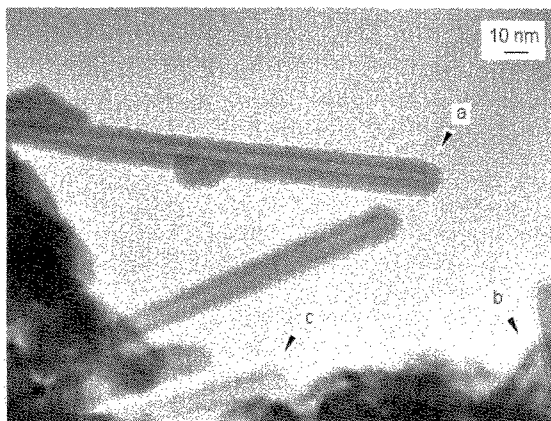

Fig. 3.   Tubular shape carbon grown on the carbon-fragment precursor.   The indicated parts (a), (b), and (c) are magnified in Fig. 4, 5, and 6, respectively.
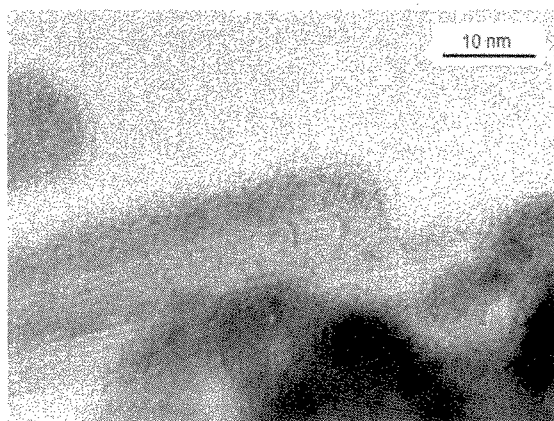

Fig. 6.   Magnified photograph of (c) in Fig. 3.   A graphitized layers are observed at the core of the tube.
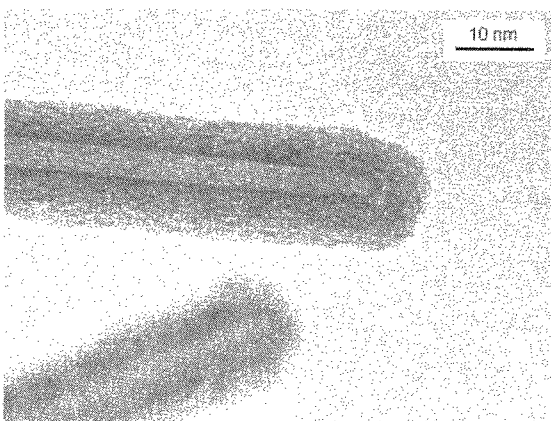

Fig. 4.   Magnified photograph of (a) in Fig. 3. Though a tubular shape and a hollow inside are formed, graphitization is not well completed.

Though the yield is almost negligible, a few CNTs grow on the film. Two types of tubular carbon are observed: partially graphitized (Fig. 1) and not graphitized ((a) in Fig. 3). The photographs of Fig. 1 and 3 are shot on the same specimen, and preparation conditions are the same. The partially-graphitized CNT is composed of a thick wall and shows graphene layers at its hollow (Fig. 2). Its wall is not well graphitized and looks being covered by carbon fragments. Another type of tubular carbon is not graphitized and is composed of carbon fragments. The magnified photograph shows that the carbon has hollow at the core (Fig.4).

Other tubular shapes are observed ((b) and (c) in Fig. 3). One is well-graphitized in its wall (Fig. 5) and another is well graphitized at the inner-shell of the wall (Fig. 6). Every tube has a hollow at its core regardless of being graphitized or not.

The carbon film is formed on a Cu mesh to avoid a catalytic effect of metals (Fe, Co, Ni). The graphitization proceeds only by the combination of heating and electron-beam irradiation. This combination provides a promising technique for a low-

temperature CNT formation.

The polyyne-containing carbon contrasts to the carbon fragments, where more CNTs grow than the fragments (Fig. 7). The CNT growth on the polyyne-containing carbon is presented in detail in other papers [7-12]. Both IR and Raman spectra of the polyyne-containing carbon show bands at 2100-2200 cm^{-1}, which are assigned to a triple bond of carbon [12]. A long chain of triple bonds is IR-inactive due to its symmetry. The triple bonds are, therefore, assumed short and not highly conjugated. An XPS analysis shows that the reduction of PTFE is complete. The carbon-to-fluorine bond is broken, whereas the carbon-to-carbon single bond is converted to a double or a triple bond. The eliminated fluorine remains as a fluorine cation, though some part of the fluorine flows away during the reduction and the washing. The effect of the fluorine is not well understood at present.
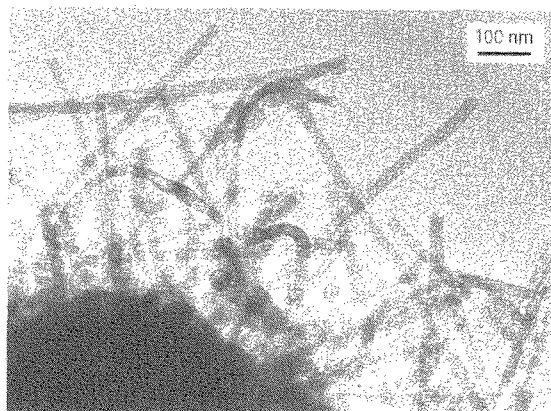

Fig. 7. CNTs formed on polyyne-containing carbon.

What is the difference between the precursors? The first is a density of the precursor. The polyyne containing carbon is low in density [12], which conforms to the reaction scheme of the reduction: elimination of fluorine. Fluorine is bulkier than hydrogen and its elimination results in voids in the precursor. In this technique, the CNT grows from the bottom where carbon is supplied from the precursor. Carbon migrates more easily in the low-density carbon than in the high-density.

The second is a viscosity of the precursor. The precursor is heated during the growth and the polyyne-containing carbon partially melts [11]. The melting promotes the flow of carbon and the growth of the tube. The melting is related to the preparation of the polyyne-containing carbon, where a linear chain of PTFE is reduced and the aligned linear structure is preserved, although cross-linking takes place, more or less. The carbon-fragment film does not flow easily and results in a thicker wall. In addition, the flow plays an important role for a graphitization as well. The graphitization proceeds through a transport and rearrangement of small graphenes [8], and does not proceed without a flow. The low-graphitization of the carbon-fragment precursor

is understood by the low mobility of the carbon.

The third is a reactivity of the polyyne, although the reaction of the polyyne under an electron-beam irradiation is not well understood. Generally speaking, an electron-beam process is classified to chemical and physical processes. At a lower accelerating voltage, the chemical process prevails, where a carbon anion or cation radical works as a reaction species. At a higher voltage, the physical process dominates and the reaction proceeds by a bombardment of an electron. At 100 kV (accelerating voltage employed here) and more, the physical process plays an important role and governs the present formation process. The reaction conditions employed here are enough for the polyyne to react, but not enough for the carbon fragments.

An in-situ observation of the CNT growth shows that the growth is comprised of two steps: a tubular shape formation and graphitization [8, 11]. The graphitization is understandable by applying the conventional graphite-formation mechanism, whereas the tube formation is more mysterious. A further study on the shape formation is expected.

4. CONCLUSION

By an electron-beam irradiation, CNTs grow on a carbon-fragment precursor without a metal catalyst, as well as polyyne-containing carbon. Now that the electron-beam is found powerful enough to form CNTs, a further study on controlling the diameter, the number of layers, and the chirality is expected.

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