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養成技術者の研究・研修成果等

１．養成技術者氏名：　安田　歩

２．養成カリキュラム名：　分子素子構築へ向けたナノテクノロジーの習得

３．養成カリキュラムの達成状況

「産業技術フェローシップ事業」にふさわしい研究成果、論文(12件)・口頭(23 件)発表をしており、当初の計画を達成したと考える。

世界に類のない電子線によるカーボンナノチューブの作製方法を開発しており、さらに研究を継続することにより電子素子・部品への応用可能性が広がるなど産業界への貢献が期待できる。また、カーボンナノチューブの成長過程を世界で最初に電顕撮影することに成功し、アカデミックな意味でのナノテクノロジーの進歩に貢献してきた。

プリカーサーからの成長条件は概ね把握できたと考えられるので、プリカーサーによるカーボンナノチューブの直径・カイラリティの制御の研究に移行している。これに関しては、まだ途中である。高いニーズがあるにもかかわらず、まだ誰も成功していない内容で難易度が高く、途中であるのもやむを得ない。この部分での研究の更なる進展が期待される。

４．成果

Title：Electron Beam Conversion of a Carbon Precursor to a Carbon Nanotube

Abstract

A new way to form 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, the obtained resuts are summarized.

INTRODUCTION

After finding CNTs, this material have attracted much attention for its unique structure and prospective applications. CNTs have been synthesized by an arc discharge, an arc discharge with a metal catalyst, chemical vapor deposition. As a new process, an electrochemical preparation has been reported as well.

The authors have been studying a new process, where a carbon precursor is heated and irradiated by an electron beam. The growth can be carried out in a TEM, and is observed in an in-situ way.

The in-situ way observation is versatile for understanding the growth mechanism, while this technique has a possibility to be applied to a device fabrication as well.

With an electron-beam process, CNTs are obtained 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 has a potential to be applied to a large-scale manufacturing. In addition,

this process is associated with a future electron-beam nanolithography based on the electron's Compton wave length(2.42pm)。

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.

EXPERIMENTAL SECTION

A 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.

For the preparation of the polyyne-containing carbon, poly(tetrafluoroethylene) (PTFE, DuPont) films are reduced electrochemically by a two-electrode method (anode: magnesium, cathode: stainless steel) under argon at 0°C. The PTFE films (10mm x 10mm x 60μm) are charged in a flask with a solvent containing supporting salts (tetrahydrofuran (THF): 30ml, LiCl: 0.8g, $FeCl_2$: 0.48g). A DC voltage (40V) is applied between the anode and the cathode for 10 h. After the reduction, the films are washed with THF and dried in a 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; ARM1250, JEOL, 1.25 MV). The specimen is heated to 600-900°C to grow CNTs.

RESULTS AND DISCUSSION

The analysis of the prepared polyyne-containing carbons, *i.e*. the precursor for the CNT formation, is summarized first. The details have been published on other papers.

The TEM photograph of the reduced PTFE film shows that only the surface of the film is reduced to the carbonized material. The reduced layer is *ca*. 1 μm thick and low in density, which is consistent with the reaction scheme, *i.e*. elimination of fluorines. The reduced layer contains sp and sp^2 carbons, as concluded from the Raman, IR, XPS analyses, while sp^3 carbon is negligible. The ratio of sp and sp^2 carbons is not well analyzed in this work. The eliminated fluorines remain in the carbonized layer in the form of anion.

The electron irradiation of the film after heating up to 600°C led to formation of CNTs. The yield can not be measured because of the too small size of the specimen. So far, the low-accelerating-voltage TEM (accelerating voltage: 100 kV, current intensity: *ca*. 1A/cm^2) has been used by us, and is replaced by an HRTEM (accelerating voltage: 1.5 MV, current intensity: *ca*. 50 A/cm2) for this study. Though the accelerating voltage and the current intensity are greatly higher than before, the CNTs are formed almost in the same way. The difference is in the displacement of the CNTs during the formation. During the formation, the CNTs move side-ways like spring rods by the highly-accelerated electron beam (1.25 MV), in contrast to that the displacement is not observed at 100 kV. Therefore, the high-resolution observation of the whole CNTs is not carried out and a series of photographs are taken at the bottom, where the movement is negligible. In addition, the observation faces difficulty of focusing. Quick focusing to follow the CNT formation is difficult and the photographs are sometimes not well focused.

The temperature rise of the specimen during the observation is assumed negligible, though its direct measurement is experimentally difficult. The excitation of phonons, leading to a heating of the specimen, is mainly due to an inelastic scattering of the projectile by electrons. The mean free path of the projectile in the sample depends on its mass and energy, and is more than 100 nm for a highly-accelerated electron, typical in a TEM. Therefore, in small objects such as carbon nanostructures, which are of some 10-100 nm in size, electron irradiation is expected not to heat the specimen by more than a few degrees.

A series of photographs during the graphitization are taken at an interval of a few minutes. As already presented, the CNT formation is comprised of two steps: the fast formation of a rod, and the slow formation of a hollow inside the rod, accompanied by the graphitization. The first step is too quick (a few second at 800°C and *ca*. 1 min. at 600°C) and failed to be taken into photographs. As of

now, the photographs of the second slow step are successfully taken.

The rearrangement of graphemes of the wall is observed. The connection between the first layer from the top and the second is broken. The connection is formed again between the second layer and the third. The connection is broken again, whereas the big strain is exerted to form the sharp edge. The connection is formed again between the second and the third, and moves further between the third and the fourth. The rearrangement includes sometimes many layers, which move dynamically.

The round-shaped graphene (possibly a pristine form of fullerene) appears and fuses into a few layers. Through the rearrangement of a few layers, the highly-ordered graphene layers are completed. The round-shaped graphene is covered by a graphene layer and does not come out to form a complete fullerene.

The findings are summarized schematically. At the beginning of the graphitization process, the tubular shape is already formed by the partially aligned small graphenes. The hollow is not formed and filled with the micro-graphenes. The rearrangement and the fusion of the small graphenes take place to form the aligned, larger-size graphenes. Parallel to that, the hollow inside the rod is formed by the diffusion of the micro-graphenes through the premature CNT wall. In the course of this stage, the round-shaped graphene, which is possibly a primitive form of fullerene, appears occasionally. The rearrangement and fusion of the graphenes proceed, parallel to the completion of the hollow formation. Finally, the graphitization of the CNT is completed.

A primitive form of a CNT has been reported to be turned into onion-like-carbon by an electron-beam irradiation. This transformation is not observed in this experiment, and a selective formation of CNTs and carbon nanoparticles (CNPs) is observed instead. The precursor employed here is unstable and at a damaged place, where the precursor is oxidized and has higher surface tension, the CNPs are formed preferentially to reduce the surface energy.

CONCLUSION

The graphitization process during the CNT formation was observed in an in-situ way by an HRTEM. The observation shows that the micro-graphenes exist from the early stage of the formation process and develop to form highly-ordered graphene layers, accompanied by evaporation of micro-graphenes. The graphitization is assumed to proceed through fusion and rearrangement of micro-graphenes and graphene layers.

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（3）特許等
なし。