Microwave Plasma-Enhanced Chemical Vapor Deposition of Carbon Nanostructures Using Biological Molecules

To cite this article: Masamichi Yoshimura et al 2005 Jpn. J. Appl. Phys. 44 1562

View the article online for updates and enhancements.

Related content
- Non-Catalytic Low-Temperature Synthesis of Carbon Nanofibers by Plasma-Enhanced Chemical Vapor Deposition in a CO2/Ar/O2 DC Discharge System
  Shinsuke Mori and Masaaki Suzuki
- Long-Ranged and Short-Ranged Electrostatic Interaction Between Modified Silicon Surfaces and Recombinant Ferritin Molecules
  Tomohiro Hayashi and Masahiko Hara
- Simulation of Gas-Phase Nanoparticle Dynamics in the Plasma-Enhanced Chemical Vapor Deposition of Carbon Nanostructures
  P P Rutkevych, K Ostrakov, I B Denysenko et al.

Recent citations
- Preparation of thin carbon nanotubes by catalytic pyrolysis on a support
  Eduard G Rakov
Microwave Plasma-Enhanced Chemical Vapor Deposition of Carbon Nanostructures Using Biological Molecules

Masamichi YOSHIMURA, Kei TANAKA and Kazuyuki UEDA

Nano High-Tech Research Center, Toyota Technological Institute, Hisakata, Tempaku-ku, Nagoya 468-8511, Japan

(Received October 12, 2004; accepted November 29, 2004; published April 8, 2005)

Biological molecules are used as catalysts for the growth of carbon nanostructures by microwave plasma-enhanced chemical vapor deposition. Large and small carbon nanotubes are formed perpendicular to the silicon substrate. The dependence of the initial coverage of ferritin molecules on the surface as well as the bias voltage dependence on the structures grown are investigated. The ferritin molecules tend to diffuse and coalesce at high temperatures and high bias voltages, which gives rise to the large carbon nanotubes with a few tens of nanometers in diameter. The density of the small nanotubes increases with decreasing bias voltage. [DOI: 10.1143/JJAP.44.1562]

KEYWORDS: ferritin, CVD, CNT, AFM, biology

1. Introduction

Since the physical properties of carbon nanotubes (CNT) are determined by their diameter, chirality and number of layers, intensive studies have been devoted to control them by various synthesis techniques such as chemical vapor deposition (CVD) and an arc discharge method. Among these, CVD is expected to be the most appropriate for the control of the growth direction, which is crucial for applications such as field emitters. The key to realizing homogeneous growth in size and density is the control of catalysis on the substrate. A biological molecule, ferritin, is an interesting catalyst, since it has a spherical shape and contains an Fe cluster 6 nm in diameter as its inner shell. Several groups have reported the growth of carbon nanostructures using ferritin molecules as catalysts. Recently, Li et al. have applied plasma-enhanced (PE) CVD to fabricate a semiconducting single-wall nanotube preferentially over a metallic nanotube. Thus, to the best of our knowledge, there are no reports on the growth of CNT perpendicular to ferritin-adsorbed substrates by PECVD. In this study, we used ferritin molecules as catalyst for the growth of carbon nanostructures on silicon substrates by microwave PECVD (MPECVD).

2. Experimental

PECVD was conducted using a mixed gas of CH₄ and H₂. The total pressure was 1.7 Torr. The flow rates of CH₄ and H₂ were 20 and 80 sccm, respectively. The growth time was 10–15 min and the growth temperature was 600–700°C. The bias voltage 100–300 V was applied between electrodes. The substrate used was a silicon wafer, 5 × 5 × 0.38 mm. The substrate surface was hydrophilically prepared by SC1 treatment. Then the ferritin molecule (concentrate solution, 34 mg/ml) diluted in deionized water was fixed to the substrate surface by a dip-coating method. The surface structure was characterized by tapping-mode atomic force microscopy (AFM) in air. The AFM instrument used was NanoScope III, Digital Instruments. Prior to CVD growth, the ferritin-adsorbed substrate was annealed at 400°C for 1 h in air to peel the outer shell off the ferritin molecules. The growth structures were characterized by field-emission scanning electron microscopy (FE-SEM).

3. Results and Discussion

Figure 1 shows the dependence of the density of ferritin on the surface on the formation of the carbon nanostructures. Figures 1(a)–1(c) show AFM images after dip-coating in 30 µl ferritin/10 ml water (referred to as 30/10 hereafter), 150/10 and 300/10, respectively. Figure 1(a) shows a flat morphology consisting of ferritin molecules, while Figs. 1(b) and 1(c) show large clusters due to the coalescence of the ferritin molecules. After sintering at 400°C in air, MPECVD growth was performed (bias voltage, 200 V), and the surface structures shown in Figs. 1(a)–1(c) changed to the carbon nanostructures shown in Figs. 1(d)–1(f), respectively. Carbon nanotubes a few tens of nanometers in diameter, labeled “A”, were observed not over the entire surface area but in a limited region. The structures were formed perpendicular to the substrate surface. The density of the carbon nanotubes increased almost in proportion to the initial coverage. In the inset of Fig. 1(d), straight, small carbon nanotubes, labeled “B”, were observed; these carbon structures were probably fewer than the large nanotubes (A). In the figure, cone structures made of silicon atoms, labeled “C”, were also observed, indicating that the etching of the silicon layers proceeds during the CVD process, as was reported by Fujimori et al. The scattered formation of carbon nanostructures indicates the coalescence of ferritin molecules during the growth at higher temperatures between 600 and 700°C.

Figure 2 shows the bias voltage dependence of CVD growth of carbon nanostructures. The dip-coating was carried out using the 300 µl ferritin/10 ml water solution. Figures 2(a)–2(c) show the SEM images obtained at the bias voltages of 200, 150 and 100 V, respectively. It was found that the density of total carbon nanostructures grown increases with the bias voltage, and the number of small nanotubes is larger at lower bias voltages. This implies that under higher voltage conditions the ferritin molecules tend to coalesce due to high-energy ions or radicals during the CVD process.
We successfully fabricated carbon nanostructures using biological ferritin molecules on silicon substrates by MPECVD. The large and small carbon nanotubes were formed perpendicular to the substrate surface, depending on the type of substrate. The ferritin coverage as well as bias voltage dependence on the formation of carbon nanostructures were investigated by AFM and SEM. Ferritin molecules tended to coalesce at high bias voltages during high-temperature CVD growth. The number of carbon nanotubes was controlled by the initial coverage of ferritin molecules.

Acknowledgement

This work was partly supported by the Grant-in-Aid for Scientific Research (B), Japan Society for the Promotion of Science. We would like to thank Ms. Michiko Ishikawa for her help in the experiment.


Fig. 1. AFM images of ferritin molecules on silicon surfaces before growth (a)–(c) and SEM images of grown carbon nanostructures (d)–(f). Large and small carbon nanotubes are labeled A and B, respectively. Cone structures, labeled C, are formed due to the etching of surface silicon layers.

Fig. 2. SEM images of grown carbon nanostructures at bias voltages of (a) 200 V, (b) 150 V and (c) 100 V.