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Simultaneous growth of graphene and vertically aligned single-walled carbon nanotubes at low temperature by chemical vapor deposition

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We present the simultaneous growth of single-walled carbon nanotubes and graphene with the optimal conditions of the synthesizing parameters. The dense and vertically aligned SWNTs having the length of over 100 μm was grown by 2 nm-thick Fe catalytic layer. From 650 °C, the vertically well-grown SWNTs were obtained by increasing the temperature. The several-layered graphene was synthesized with the gas mixing ratio of 15 : 1(H_2 : C_2H_2) at 650 °C and higher temperatures. With these optimal conditions, the vertically well-grown SWNTs and the several-layered graphene were synthesized simultaneously. The presence of SWNTs and the layer of graphene were verified by field emission scanning electron microscopy and high resolution transmission electron microscopy. From the result of this simultaneous synthesizing approach, the possibility of one step growth process of CNTs and grapheme could be verified.

Key words: Graphene, Single-walled carbon nanotube, Simultaneous growth, Chemical vapor deposition.

Introduction

Nowadays carbon nanotubes (CNTs) and graphene have become one of the most intensely studied nanostructures due to their unique electronic and extraordinary mechanical properties. [1-5] Fundamental structure of carbon nanotube and graphene is known as one-dimension and two-dimension respectively. CNTs are allotropes of carbon with hollow cylindrical one dimension carbon structures while graphene is a single layer of carbon packed in a hexagonal lattice. In particular, the graphene-carbon nanotubes combined structures have been receiving much attention for a wide variety of applications such as transistors, sensors and solar cell devices. [6-12] To implement these carbon materials to the devices, the micro fabrication processes including the catalytic layer deposition and the synthesis are needed. To fabricate the hybrid structured micro, nano systems with CNTs and graphene grown directly, especially, the whole processes for the catalytic layer fabrication of CNTs and graphene are needed twice. In this case, it might cause the problems of the process compatibility and give some damages to the synthesized CNTs or graphene in the previous process.

This work presents the simultaneous growth of SWNTs and graphene with the optimal conditions of the synthesizing parameters. This approach could bring the benefits of simplification and process compatibility for the micro-fabrication having CNTs and graphene hybrid system.

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Experiments

Sample preparation

Among the synthesis techniques for carbon materials, CVD method is widely used because of its many advantages such as a good uniformity and a large scaled synthesis. In this work, the hybrid vacuum system combined plasma enhanced chemical vapor deposition (PECVD) and thermal CVD was operated to synthesize CNTs and graphene as shown in Fig. 1. To grow SWNTs, the iron layer was deposited on an Al_2O_3/SiO_2/Si substrate sized with 10×10 mm^2. P-type silicon wafer with ~10 ohm-cm was used. 300 nm-thick SiO_2 layer was grown by the oxidation and Al_2O_3 layer with 10 nm thickness was deposited by an atomic layer deposition (ALD). To investigate the effect of metal catalyst thickness, iron layer was deposited with 1 nm, 1.5 nm, and 2 nm by an e-beam evaporator respectively. For the graphene, a 300 nm-thick nickel thin film as the metal catalyst was deposited on a piece of SiO_2/Si wafer using an e-beam evaporator.

Parameters for carbon materials synthesis

It is generally accepted that CNTs and graphene can be synthesized by three steps: the dissociation of

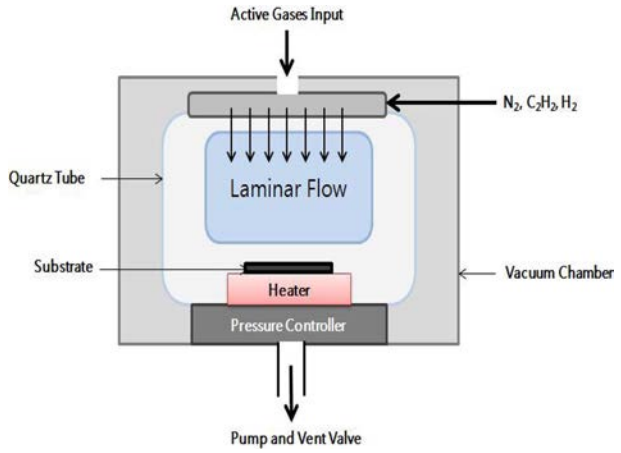

Fig. 1. A schematic diagram of the hybrid vacuum system for synthesizing carbon nanotubes and graphene.

hydrocarbon gas, the diffusion into a metal catalyst, and the accumulation and precipitation of carbon atoms on the surface. For applying to micro-fabrication devices, carbon materials should be grown at as low temperature as possible. Acetylene can be dissociated at lower temperature in comparison with other carbon source gases such as methane and ethylene. [13-15] In this work, acetylene was used as a carbon source gas. In general, nickel and copper are used as a thin film catalyst for graphene synthesis. Because nickel has a higher solubility than copper, the precipitation process is needed in the graphene growth with nickel.

For the SWNTs and graphene growth, Fe samples were inserted in a reactor tube and flushed the gases mixture of acetylene and hydrogen ($1 : 15 = C_2H_2 : H_2$) which was studied in the previous work. [16] For the simultaneous growth of SWNTs and graphene, samples are loaded in the chamber with the obtained optimal conditions. To investigate the presence of SWNTs and graphene, a Raman spectroscopy (Horiba Co.) operating at a wavelength of 532 nm and a field emission scanning electron microscopy (FE-SEM, Hitachi S-4800) was used. High resolution transmission electron microscopy (HR-TEM) was used to investigate the presence of few-layered graphene.

Results and Discussion

The SWNTs growth

For finding the optimal thickness of catalyst metal to grow the SWNTs, 1 nm, 1.5 nm, and 2 nm thick-Fe thin film samples were experimented. Fig. 2 shows the SEM images of the growing results. As shown in Fig. 2 (a), 1 nm thick-Fe catalytic thin film was too thin to form the catalytic islands for CNTs growth after annealing. Because the SWNTs can grow vertically by van der waals interaction among CNTs, CNTs could not be grown vertically from the sparse catalytic islands. Even the SWNTs were grown with 1.5 nm-thick Fe catalytic layer in Fig. 2 (b), they were sparse

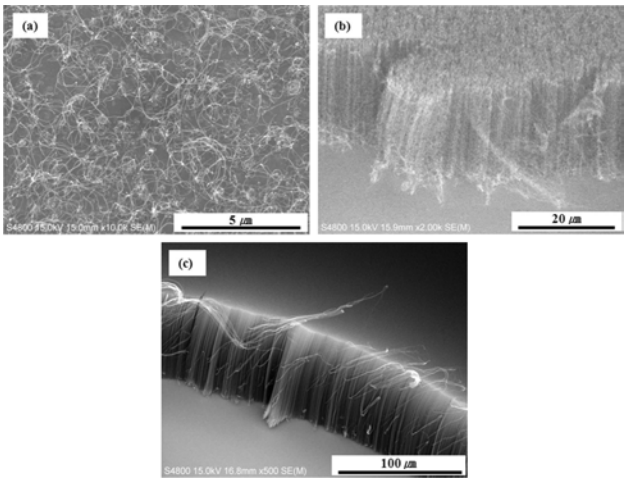

Fig. 2. SEM images of SWNTs grown on (a) 1 nm-thick, (b) 1.5 nm-thick and (c) 2 nm-thick Fe catalytic thin films.

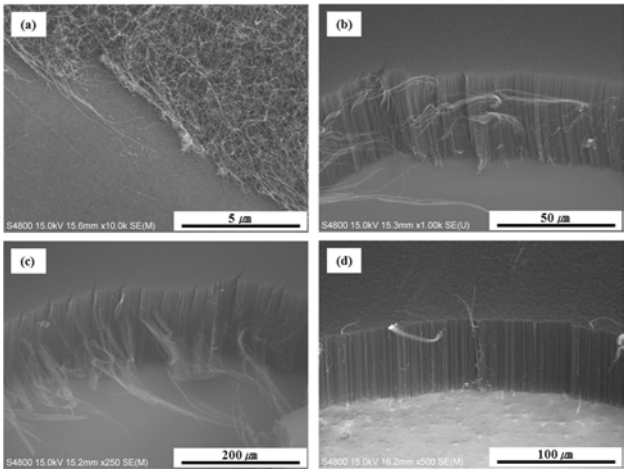

Fig. 3. SEM images of SWNTs grown at the growing temperature of (a) 550 °C, (b) 650 °C, (c) 750 °C and (d) 850 °C.

and had a short length of around 20 μm. Very dense and vertically aligned SWNTs having the length of over 100 μm with 2 nm-thick Fe catalytic layer was obtained in this work (Fig. 2(c)). For applying to micro-electro-mechanical system (MEMS) devices, carbon materials such as CNTs and graphene should be grown at low temperature. Fig. 3 shows the results according to various CNTs growing temperature. At growing temperature of 550 °C, CNTs was synthesized but was not grown vertically. From 650 °C, the well vertically grown SWNTs were obtained as shown in Fig. 3(b)-(d).

Graphene synthesis

Fig. 4 (a) shows the Raman spectra of graphitic layers according to the various synthesizing temperature. In the Raman spectrum of graphene, there are three prominent modes, the G peak (~1580 cm^1), 2D peak (~2700 cm^1) and D peak (~1340 cm^{-1}). As shown in Fig. 4(a), the graphene was obtained at the synthesizing temperature of 650 °C. Because, acetylene used in this

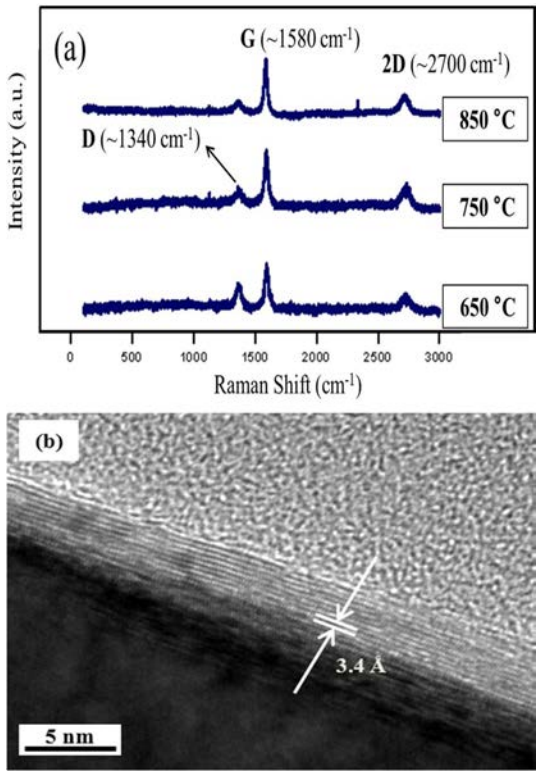

Fig. 4. (a) Raman spectra for the graphene films synthesized at various synthesizing temperatures with the gas mixing ratio of 15 : 1 ($H_2 : C_2H_2$) and (b) HR-TEM image of few-layered graphene synthesized at 750 °C.

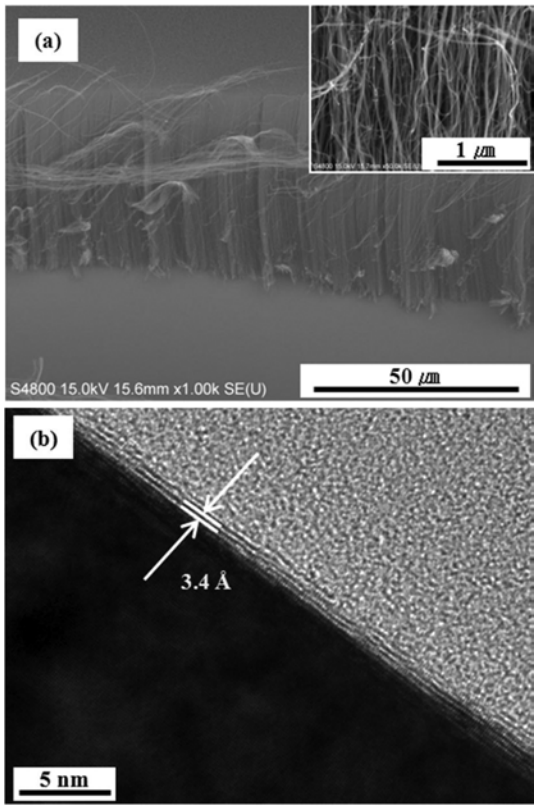

Fig. 5. (a) FE-SEM image of the SWNTs and (b) HRTEM image of several-layered graphenes. They were synthesized simultaneously at the same conditions of growing parameters.

work is dissociated at lower synthesizing temperature than methane or ethylene, graphene can be synthesized at low temperature relatively. Under the active temperature of 650 °C, however, graphene was not synthesized because the temperature is too low to dissociate the hydrocarbon source gas, acetylene. Fig. 4 (b) shows the HR-TEM image of few-layered graphene synthesized at 750 °C.

Simultaneous growth of SWNTs and graphene

With the conditions of growing parameters for the SWNTs and graphene, the SWNT and graphene were synthesized simultaneously at the same conditions. Fig. 5 shows the results of SWNTs and graphene grown at the same time. They were grown at 650 °C simultaneously and the gas mixing ratio was 15 : 1 of $H_2 : C_2H_2$. The thickness of Fe for the SWNTs was 2 nm and Ni for graphene was 300 nm. Fig. 5(a) shows the SEM image of SWNTs, and the HR-TEM image of several-layered graphene is shown in Fig. 5(b). The simultaneous growth of CNTs and graphene has the benefit of simplification for the micro-fabrication processes and the process compatibility.

Conclusions

The simultaneous synthesis of single-walled carbon nanotubes and graphene was investigated. The dense and vertically aligned SWNTs having the length of over 100 μm was grown by 2 nm-thick Fe catalytic layer. The SWNTs were grown with the various growing temperatures. For applying to the MEMS devices, the process temperature is needed as low as possible. From 650 °C, the vertically well-grown SWNTs were obtained by increasing the temperature. The several-layered graphene was synthesized with the gas mixing ratio of 15 : 1($H_2 : C_2H_2$) at 650 °C and over. With these optimal conditions, the vertically well-grown SWNTs and the several-layered graphene were successfully synthesized simultaneously. The FE-SEM and HR-TEM results verify the vertical structure of SWNTs and the presence of several-layered graphene. This result confirms the possibility of one step growth process of CNTs and graphene. The simultaneous growth of CNTs and graphene can give the benefits of process simplification and process compatibility in micro- and/or nano-fabrication system.

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