Proceedings of the 15th International Heat Transfer Conference, IHTC-15
August 10-15, 2014, Kyoto, Japan

IHTC15-9063

GROWTH AND APPLICATIONS OF HORIZONTALLY ALIGNED SINGLE-WALLED CARBON NANOTUBES

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ABSTRACT

Single-walled carbon nanotube (SWNT) is a rolled-up graphene. SWNT is one of the most important materials in nano-technology and many SWNT applications have been proposed. Especially, the field-effect-transistors (FETs) with SWNT-channels attract much attention. For the fabrication of such SWNT electric devices, alignment and position control of SWNTs is important. Additionally, pure semiconducting SWNT arrays is needed for SWNT-FETs with high performance. Here, we present the growth of horizontally aligned SWNTs (HA-SWNTs) and fabricate pure-semiconducting SWNT-FETs using a selective removal technique. We used iron nanoparticles as the catalyst, ethanol vapor as the carbon source for SWNT growth. HA-SWNTs are synthesized on single-crystal (R-cut) quartz substrates. In advance, the R-cut quartz substrates were annealed at 900 °C in air for 12 h and iron was deposited in a strip pattern. The sample was heated up in Ar/H_2 (3%) mixture gas. At 800 °C, ethanol vapor was introduced together with Ar/H_2 (3%) gas and CVD growth was performed. The SWNTs were aligned along the direction of the x-axis of R-cut quartz. The density of HA-SWNTs depended on CVD conditions and the partial pressure of ethanol vapor was key point. HA-SWNTs were analyzed by scanning electron microscopy (SEM) and scanning Raman scattering spectroscopy. For selective removal of metallic SWNTs, we used thermal-lithography technique and an organic film-assisted electrical breakdown method. For thermal-lithography technique, HA-SWNTs were covered with molecular glass thin film and applied electric voltage to HA-SWNTs. Only metallic SWNTs were Joule-heated and they became exposed owing to thermocapillary flow of molecular glass. By etching exposed metallic SWNTs, the SWNT-FETs with higher on/off ratio could be obtained. In the case of the electrical breakdown method, metallic SWNTs covered with films were Joule-heated. The heated parts of metallic SWNTs was oxidized and removed. The cover films significantly extended the removed length of metallic SWNTs.

KEY WORDS: carbon nanotube, horizontal alignment, CVD, field effect transistor

1. INTRODUCTION

Single-walled carbon nanotube (SWNT) [5] is a rolled-up graphene. While the diameter is a few nano-meter, its length achieve millimeter order. SWNT is one of the important materials in nano-technology, because of high mechanical strength, high thermal conductivity, high chemical stability and so on. Owing to these excellent properties, many SWNT applications have been proposed. The electric conductivity of SWNTs (metallic or semiconducting) depend on their atomic structure (so-called chirality) and metallic SWNTs are expected to have higher maximum current density than copper and gold wires. On the other hand, semiconducting SWNTs can be used as channels of field-effect-transistors (SWNT-FETs) [4] and high-density array of pure semiconducting SWNTs is required for the fabrication of high-performance SWNT-FETs. Horizontally aligned

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DOI: http://dx.doi.org/10.1615/IHTC15.XXX.XXX

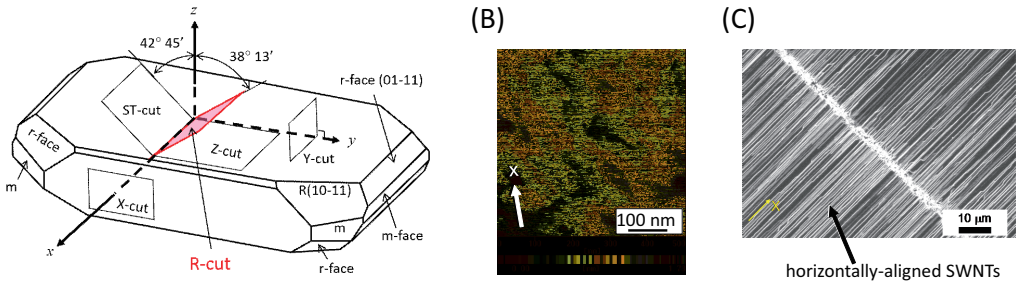

Fig. 1 (A) Schematic image of quartz block and quartz substrates with various cutting angles. (B) AFM iamge of unetched R-cut quarts surface. (C) SEM image of horizontally aligned SWNTs on R-cut quartz surface.

SWNTs are synthesized on single-crystal substrates, such as sapphire [7] and crystal quartz [9]. Although aligned SWNTs are grown on these crystal substrates, the alignment mechanism is not fully understood in atomic scale and the density control growth technique is not established. Additionally the as-grown SWNTs are a mixture of semiconducting and metallic SWNTs and it is difficult to grow semiconducting SWNTs selectively. Therefore, post-growth separation [1] or metallic SWNT removal techniques [3, 8] are important. In this study, we performed horizontally-aligned growth of SWNTs on R-cut crystal quartz substrates and investigated the growth control techniques. Moreover, SWNT-FETs were fabricated using the selective removal techniques of metallic SWNTs. The FETs with highly-aligned and dense pure-semiconducting SWNTs showed high on/off ratio.

2. EXPERIMENTAL

SWNTs were grown on R-cut crystal quartz substrates (Kyocera Corp. Japan) [2] based on alcohol catalytic CVD method [10]. R-cut quartz substrates is cut from synthetic quartz blacks parallel to R-plane (10-11), as shown in Fig. 1(A). On the R-cut quartz substrates, SWNTs are horizontally aligned along to the x-axis [2]. R-cut quartz substrate were annealed at $900\ ^\circ\mathrm{C}$ in air for 13 h. The annealing treatment improves the alignment of SWNTs. And then, iron was deposited on the R-cut substrates in a stripe pattern as the catalyst using photolithography, thermal evaporation, and lift-off. The nominal thickness of iron was $\sim 0.2\,\mathrm{nm}$. The iron strip width and interval were $3\,\mu\mathrm{m}$ and $50\,\mu\mathrm{m}$, respectively. Ethanol vapor was used as the carbon source of SWNTs. The quartz substrate with iron catalysts were heated in $\mathrm{Ar}/\mathrm{H_2}(3\%)$ gas. After the temperature reached $800\ ^\circ\mathrm{C}$, ethanol gas was introduced together with $\mathrm{Ar}/\mathrm{H_2}(3\%)$ and CVD growth was performed.

For selective removal of metallic SWNTs, we performed a thermocapillary-induced removal technique of metallic SWNTs [8]. The horizontally aligned SWNTs were grown on crystal quartz substrates and the SWNTs were transfered onto p-doped silicon substrates with $\mathrm{SiO_2}$ layer (100 nm in thickness). After the fabrication of SWNT-FETs on the silicon substrates, a molecular glass film was coated and the SWNTs in the film were heated by Joule-heating. Metallic SWNTs was heated up more than semiconducting SWNTs and trench structure on the film surface appeared along metallic SWNTs owing to thermocapillary phenomena. Metallic SWNTs, which were exposed in the trench bottoms, were removed by argon plasma etching. We also developed an organic film-assisted electrical breakdown technique [11] for selective removal metallic SWNTs based on Joule-heating breakdown [3] and polymer coating methods [8]. By performance of electric breakdown in organic films, longer parts of metallic SWNTs. In order to characterize SWNTs, scanning electron microscopy (SEM) and atomic force microscopy (AFM) were performed.

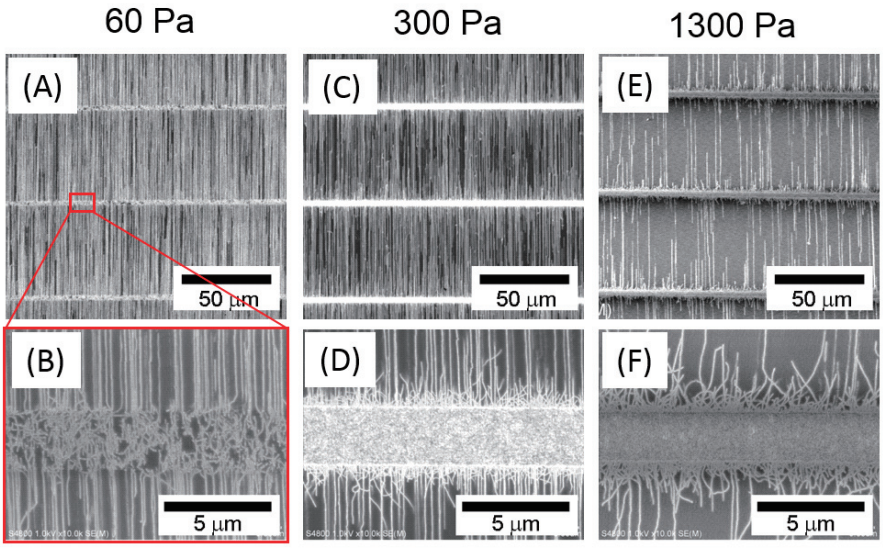

Fig. 2 Ethanol vapor pressure dependence of aligned SWNT growth. (A, B) 60 Pa, (C, D) 300 Pa and (E, F) 1300 Pa.

3. RESULTS AND DISCUSSION

3.1 Horizontally Alignment Growth of SWNTs

AFM image of the surface structure of R-cut quartz substrates was shown in Fig. 1(B) [2]. Clear step and terrace structure was observed and the step height was the almost equal to the lattice spacing of the (10-11) plane. On the R-cut substrates, SWNTs were apparently aligned along the x-axis of quartz crystal structure. SEM image of horizontally aligned SWNTs is shown in Fig. 1(C). Many SWNTs were grown from the catalyst are and most of them were aligned, which indicated that SWNT alignment came from atomic structure of (10-11) plane of crystal quartz.

In order to investigate the CVD condition effects on the alignment growth, SWNTs were synthesized with different partial pressure of ethanol vapor. The partial pressure ranged from 60 to 1300 Pa. In Fig. 2, SEM images showed that while the amount of aligned SWNTs in the catalyst area decreased with increasing the partial pressure, the number of aligned SWNTs increased [6]. The growth rate generally become faster with higher ethanol pressure, because the supply rate of carbon atoms to the metal catalyst is high. At the same time, the incubation time, which is the period before the onset of SWNT growth, became shorter. It suggested that neighboring SWNTs started growing simultaneously in higher pressure condition and the possibility of entangle and bundle structure formation became high. The bundle structure disturbed the interaction between SWNTs and quartz surface and decreased the alignment growth.

3.2 Selective Removal of Metallic SWNTs and SWNT-FET Fabrication

For the fabrication of high-performance SWNT-FETs, pure semiconducting SWNT array is required. Since the selective growth technique of semiconducting SWNTs have not been established, post-growth removal of metallic SWNTs is important. We performed thermocapillary-induced removal technique using a molecular glass film [8]. SEM image (a) in Fig. 3(A) showed as-grown SWNT-channels of SWNT-FETs. They were a mixture with metallic and semiconducting SWNTs. The molecular glass film was formed on the SWNT-FET and SWNTs were heated by Joule-heating. Two trenches clearly appeared after Joule-heating, as shown in AFM image (b) ((Fig. 3(A)) and they indicated the existence of metallic SWNTs. While semiconducting SWNTs were inside the film, metallic SWNTs were exposed. Therefore only metalic SWNTs were removed by

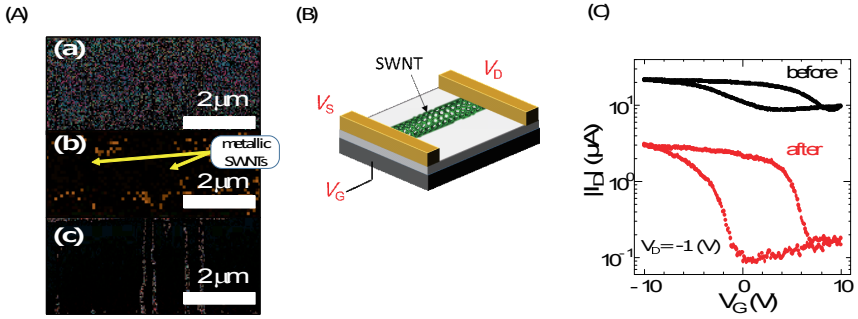

Fig. 3 (A) Metallic SWNTs removal process. (a) SEM image of as-grown SWNT array, (b) AFM image of the molecular glass file with trench structure and (c) SEM image after the selective removal treatment. (B) Schematic image of SWNT-FET structure. (C) $I_D - V_G$ characteristics of SWNT-FET before and after the removal treatment.

argon plasma etching treatment and SEM image (c) in Fig. 3(A) represented the selective removal of metallic SWNTs. In order to confirm the metallic SWNT removal, the transfer characteristics of the SWNTs were investigated. Figure 3(B) shows the schematic image of SWNT-FETs. They have back-gated FET structures, as shown in Fig. 3(B) and the characteristic of the SWNT-FET before and after the argon plasma etching treatment were shown in Fig. 3(C). The improvement of the on/off ratio indicated that some of metallic SWNTs were removed. If all of the metallic SWNTs is removed, the on/off ratio should increase more than 10^4.

The electrical breakdown technique [3] is generally used for the removal of metallic SWNTs, although the length of removed parts of SWNTs is only around 100 nm. We developed an organic film-assisted electrical breakdown [11] in order to extend the removal length of SWNTs. Figure 4 shows the SEM images of (A) before and (B) after the organic film-assisted electrical breakdown. After SWNTs were covered with a polymethylmethacrylate (PMMA) film, SWNTs were Joule-heated and electrical breakdown was performed with high current density. SEM image (Fig. 4(B)) indicated the longer part of SWNT was removed ($> 1\ \mu\mathrm{m}$) and the polymer film clearly extended the length of removed SWNTs. Although the mechanism of organic film-assisted electrical breakdown is not so clear, the oxidation spread of SWNTs is one of the key points. An SWNTs is heated by Joule-heating and the highest-temperature point along the SWNT is oxidized. After the Joule-heating stop, the length of SWNT oxidization depend on the balance between heat generation from chemical reaction and heat dissipation to environment.

Because the organic film-assisted electrical breakdown is simpler than the thermocapillary-induced removal technique, it exhibits that the spatial resolution is better than ca. 55 nm. The high spatial resolution is one of the important advantages for the fabrication of high-density SWNT-FETs.

4. CONCLUSIONS

We synthesized horizontally aligned SWNTs on crystal quartz substrates and investigated the alignment mechanism. The thermal-lithography and the organic film-assisted electric breakdown were performed as the removal techniques of metallic SWNTs. The high density and pure-semiconducting SWNT array produced high performance SWNT-FETs, which showed high On/Off ratio.

ACKNOWLEDGMENTS

A part of this work was financially supported by Grant-in-Aid for Scientific Research (22226006, 23760179, 25630063). A part of this work was conducted in Center for Nano Lithography & Analysis, The University of

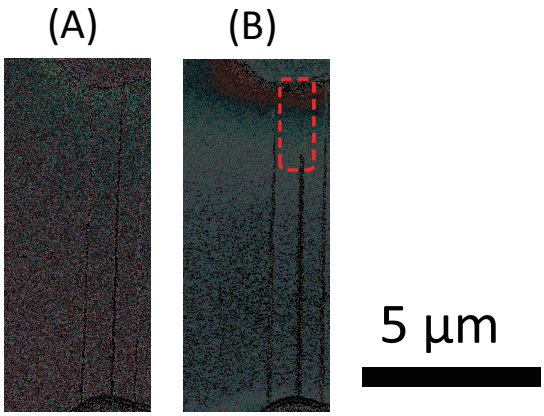

Fig. 4 Electrical breakdown for removal of metallic SWNTs in PMMA polymer films ((A) before and (B) after).

Tokyo, supported by the Ministry of Education, Culture, Sports, Science and Technology (MEXT), Japan, and in VLSI Design and Education Center (VDEC), the University of Tokyo.

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