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Controlled Growth of Multi-walled Carbon Nanotubes Using Arrays of Ni Nanoparticles

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We have investigated the optimal growth conditions of carbon nanotubes (CNTs) using the chemical vapor deposition and the Ni nanoparticle arrays. The diameter of the CNT is shown to be controlled down to below 20 nm by changing the size of Ni particle. The position and size of Ni particles are controlled continuously by using wafer-scale compatible methods such as lithography, ion-milling, and chemical etching. Using optimal growth conditions of temperature, carbon feedstock, and carrier gases, we have demonstrated that an individual CNT can be grown from each Ni nanoparticle with almost 100% probability over wide area of SiO_2/Si wafer. The position, diameter, and wall thickness of the CNT are shown to be controlled by adjusting the growth conditions.

Keywords : Carbon nanotube, Controlled growth, Nanoparticle, Chemical vapor deposition.

Ⅰ. Introduction

The carbon nanotube (CNT) [1] is one of the most studied nanostructured materials for its excellent electrical and mechanical properties [2]. While multi-walled CNTs (MWNTs) show complicated electrical properties, single-walled CNTs (SWNTs) are either metallic or semiconducting depending on the atomic structure [3,4]. Utilizing such electrical properties, SWNTs have been applied to demonstrate single device performance including field-effect transistor [5], random access memory [6], room-temperature single-electron transistor [7], and logic gates [8-10].

Though the feasibility of individual devices has been demonstrated till now, the mass production of the practical CNT-based integrated devices requires to develop extreme control technologies. For example, CNTs of well-defined diameter, wall thickness, direction, length, and chirality should be placed at desired locations over wide area, with 100% probability, and at high speed compatible with the current Si industry.

There have been many efforts to achieve such a controllability. Placement of individual CNTs has been tried in several ways such as the attachment on functionalized patterns utilizing chemical interactions [11-13] or the electric-field-assisted trapping in the small gap between two electrodes [14,15]. The direction of CNTs on a substrate could be controlled by applying the electric field during the growth [16-18]. The

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diameter of CNTs was shown to be controlled by changing the size of catalytic nanoparticles [19-22]. In that perspective, metallic nanoparticles smaller than 10 nm were shown to be distributed within specific patterns over wide area with controlled density [23]. MWNTs thicker than 50 nm were directly grown from catalytic seed particles by plasma-enhanced chemical vapor deposition (CVD) [24,25], and SWNTs were also grown from ordered Co and Fe nanoparticles fabricated by electron beam lithography [26]. However, all these methods are yet far from the practical technology for mass production of CNT-based integrated devices.

In this work, we propose a simple and reliable method to grow multi-walled carbon nanotubes (MWNTs) in a controlled manner. The location and the size of MWNTs are controlled by using arrays of catalytic Ni particles which are positioned by lithography and reduced in size by ion-milling and chemical etching. Under the optimal growth conditions found in this work, an individual MWNT is grown from each Ni nanoparticle with almost 100% probability. The diameter and the wall thickness of the MWNTs can be controlled by adjusting growth conditions. The proposed procedure is compatible with the current silicon technology, and can be a useful step forward to the realization of integrated circuits of CNTs.

Ⅱ. Experiments

We choose thermal CVD in growing CNTs since it is simple and convenient for the mass production. We need at least three essential ingredients in the CVD growth of CNTs. (i) We use the ethylene (C_2H_4) gas as the carbon feedstock, for its low dissociation probability at high temperature makes it easier to control the growth of small-diameter CNTs, compared with C_2H_2. [22] (ii) We use nano-sized Ni particles as the catalytic seed. (iii) The 1:1 mixture of H_2 and Ar is used as the carrier gas to control the concentration of the C_2H_4 gas.

Firstly, we tried to establish the optimal growth condition of CNTs by varying four independent parameters - the size of catalytic particles, the growth temperature, the flow rate of C_2H_4, and the flow rate of H_2 and Ar. For that purpose, it is

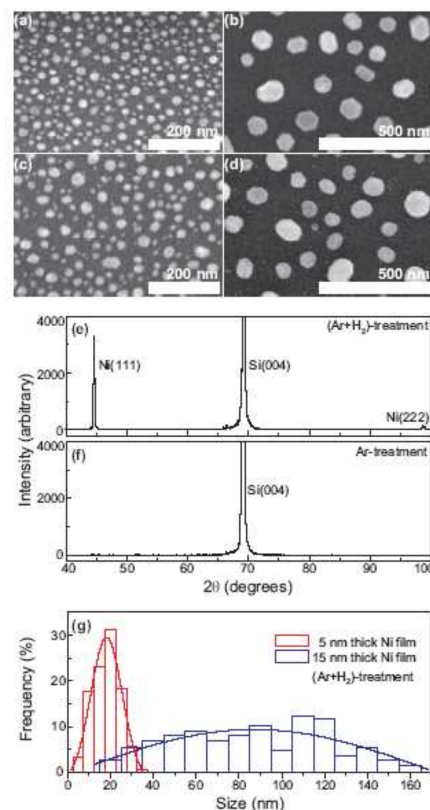

Fig. 1. The SEM images of Ni particles formed at 850 ℃ for 30 min under 200 SCCM of H_2 and Ar each from (a) 5 nm and (b) 15 nm thick Ni films on SiO_2/Si(001) wafer. (c) and (d) show Ni nanoparticles formed from 5 and 15 nm thick Ni films, respectively, under 200 SCCM of Ar only. The Ni nanoparticles in (b) show the flat hexagonal crystalline shapes. The X-ray diffraction spectra from the Ni nanoparticles treated in (e) (Ar+H_2) and (f) Ar only atmosphere. The thermal treatment of Ni film on SiO_2/Si(001) wafer in (Ar+H_2) forms crystalline Ni nanoparticles with the Ni(111) planes parallel to the substrate. In contrast, (f) the thermal treatment of Ni film under Ar only atmosphere makes the nanoparticles oxidized. (g) The size distribution of Ni particles formed from 5 and 15 nm thick Ni films by thermal treatment in (Ar+H_2) atmosphere.

efficient to use Ni nanoparticles of different sizes at once, for one can reduce the parameter space from four to three dimension. To prepare Ni nanoparticles with broad size distribution, Ni films with thicknesses of 5 and 15 nm are deposited on 500 nm thick SiO_2 film grown on Si(001) wafer.

Then the substrates are pretreated at 850 ℃ for 30 min with 200 SCCM of H_2 and Ar each to form nano-sized Ni particles. The total pressure in the CVD chamber is always maintained at 1 atmospheric pressure to reduce the possible evaporation of the Ni particles at high temperature. As shown in Fig. 1(b), most of the Ni particles made from 15 nm thick Ni film have the flat hexagonal shape characteristic of single crystalline phase. The strong Ni(111) peak in the X-ray diffraction spectrum verifies that the Ni nanoparticles are crystalline with the Ni(111) layers parallel to the substrate [Fig. 1(e)] [27]. The Ni particles formed from 5 nm thick Ni film are sized in the range of 5-30 nm, while those from 15 nm thick Ni film cover 20-150 nm.

In order to search for the optimal CNT growth condition in three-dimensional parameter space, we selected six growth temperatures of 520, 620, 720, 770, 820, and 920 ℃. At each temperature, the flow rate of C_2H_4 was varied among the values of 20, 50, 100, 200, and 400 SCCM, and the flow rate of H_2 and Ar among 50, 100, 200, 400, and 800 SCCM.

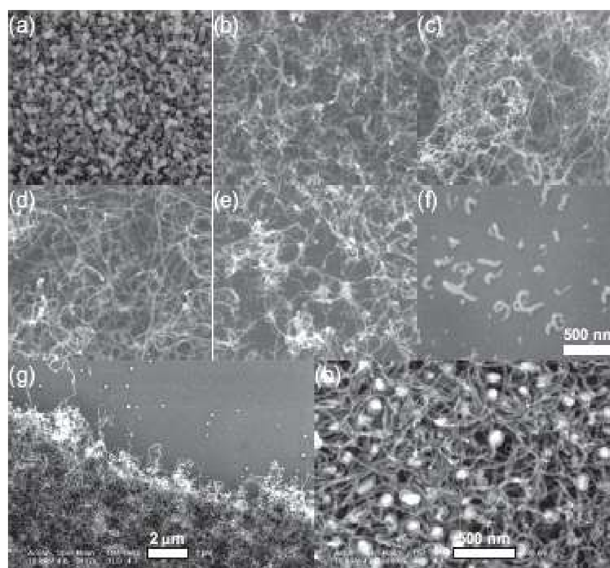

Fig. 2. The SEM images of CNTs grown for 30 s at (a) 520, (b) 620, (c) 720, (d) 770, (e) 820, and (f) 920 ℃. The Ni particles are prepared at 850 ℃ for 30 min from 5 nm thick Ni films deposited on SiO_2/Si(001) wafer under 200 SCCM of H_2 and Ar each. During the growth of CNTs, the flow rates of C_2H_4, H_2 and Ar are 100, 800, and 800 SCCM, respectively. (g) The SEM image showing the remnant Ni particles on the substrate after scratch and (h) the bottom view of the scratched CNTs. The CNTs in (g) and (h) are grown at 720 ℃ from Ni particles prepared from 15 nm thick Ni films with the supply of 100 SCCM C_2H_4 and 800 SCCM H_2 (Ar).

Ⅲ. Results

At 520 ℃ [Fig. 2(a)], under all the combinations of the flow rates of C_2H_4 and H_2 (Ar), the CNTs are grown at high density enough to cover the whole substrate, but are short with curly shape judged from the scanning electron microscope images. At 620, 720, and 770 ℃ [Figs. 2(b)-(d)], the CNTs are grown long and straighter with very high density. At 820 ℃ [Fig. 2(e)], the density of the CNTs is too low to cover the wafer. At 920 ℃ [Fig. 2(f)], the growth probability is very low. Since we are interested only in the ~100% growth probability of CNTs, we will henceforth focus only on the temperature range between 620 and 770 ℃.

The grown CNTs are too dense to directly count the numbers. To quantify the growth probability, we used alternative (indirect) approach. The sample surface was scratched with a sharp pin to turn over the entangled CNTs. The growth probability of CNTs is estimated to be (1 − the ratio of the remaining Ni particles on the substrate after scratch to the total number of Ni particles before the growth). It is noted that the real growth probability should be higher than the estimated values shown in Fig. 3, for the

remaining Ni particles after scratch are either the unreacted ones where no CNTs grew, or the reacted ones which have CNTs grown but were cut from them by the scratch due to the adhesion between the Ni particles and the substrate [Figs. 2(g) and 2(h)].

At 770 ℃, the region of high growth probability above 95% is narrow with the flow rate of C_2H_4 at 100 and 200 SCCM. Also larger CNTs are hardly grown from the larger Ni particles formed from the 15 nm thick Ni film at any flow rates of C_2H_4 and H_2 (Ar).

At 720 ℃, the growth probability is high over wider range of the flow rates of C_2H_4 and H_2 (Ar). From the smaller Ni particles prepared from 5 nm thick Ni film, CNTs grow with high density. In contrast, on the substrate with the larger Ni particles formed from 15 nm thick Ni film, the density of CNTs decreases when the flow rate of C_2H_4 is lower than 50 SCCM or that of H_2 (Ar) is below 200 SCCM. This shows that with the reduced supply of C_2H_4 or H_2 (Ar), CNTs are difficult to grow from the larger Ni particles. The growth probability of CNTs are above 99% from both of the substrates when the flow rates of C_2H_4 and H_2 (Ar) are 100 and 800 SCCM, respectively.

At 620 ℃, the region of high growth probability increases further over wide range of the flow rates of C_2H_4 and H_2 (Ar). Decreasing the flow rate of C_2H_4 below 100 SCCM or H_2 (Ar) below 400 SCCM, the growth probability of CNTs starts to decrease. This reduction in the growth probability appears faster in the larger Ni particles than in the smaller particles, which is reminiscent of the observed tendency at 720 ℃.

The distribution of diameter and wall thickness of CNTs grown under optimum conditions (indicated by hatched regions in Fig. 3) are plotted in Fig. 4. At higher temperature, the diameters are distributed around smaller values. Lowering the temperature, the diameter distribution is broadened towards larger values. As to the wall thickness, the CNTs grown at higher temperature are thinner than those grown at lower temperature as shown in Fig. 4(d). The larger and thicker CNTs are difficult to grow at higher

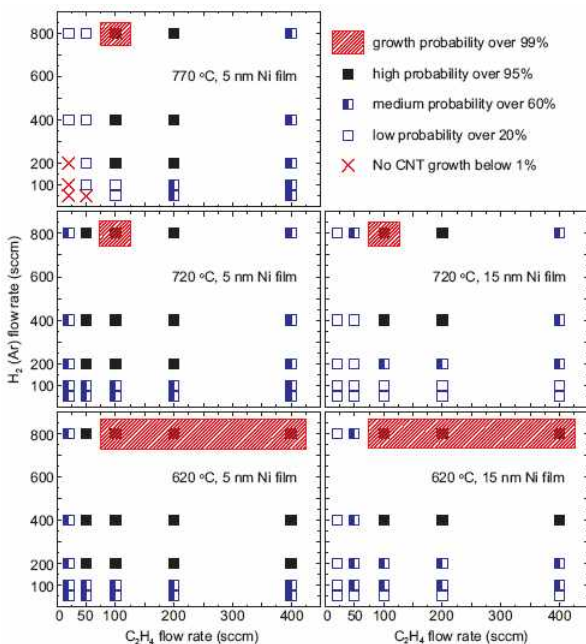

Fig. 3. The growth probabilities of CNTs for various combinations of the flow rates of C_2H_4 and H_2 (Ar) at 770, 720, and 620 ℃. At 770 ℃, only the small Ni particles prepared from 5 nm thick Ni film grow CNTs with high density. At 720 and 620 ℃, Ni particles formed from both 5 and 15 nm Ni films grow CNTs with high probability.

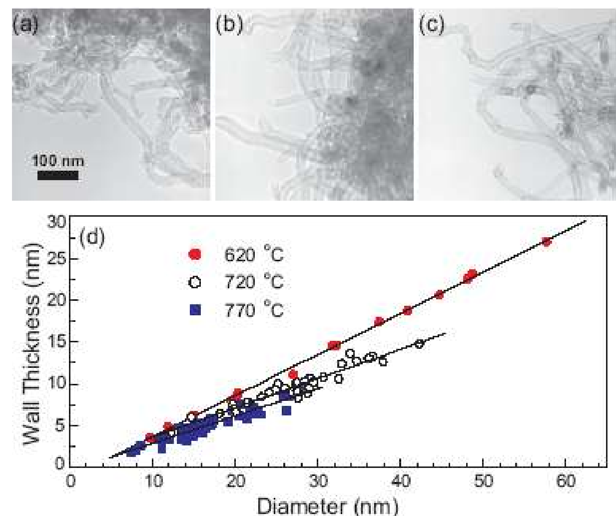

Fig. 4. The TEM images of the CNTs grown at (a) 620, (b) 720, and (c) 770 ℃. (d) The relations between diameters and wall thicknesses of CNTs grown at 620, 720, and 770 ℃.

temperatures, since the supply of C atoms to the catalytic seeds is inefficient due to the self-pyrolysis of C_2H_4 or increased turbulence. The same mechanism applies to the observed narrowness of conditions for guaranteeing high density CNT growth at elevated temperatures (e.g., 770 ℃).

After finding the optimal growth conditions, we tried to grow an individual MWNT from each Ni nanoparticle. For this purpose, a two-dimensional square array of Ni particles with the diameter of 250 nm is fabricated on the SiO_2/Si(001) wafer with periodicity of 1 ㎛ as shown in Fig. 5(a). The substrate is ion-milled to reduce the size of Ni particles, and etched by HCl to remove the Ni shreds created by ion-milling. With this procedure, the size of Ni particles can be reduced to below 20 nm in diameter as shown in Fig. 5(b). The CNTs are grown from the array of Ni nanoparticles for 20 s at 720 ℃

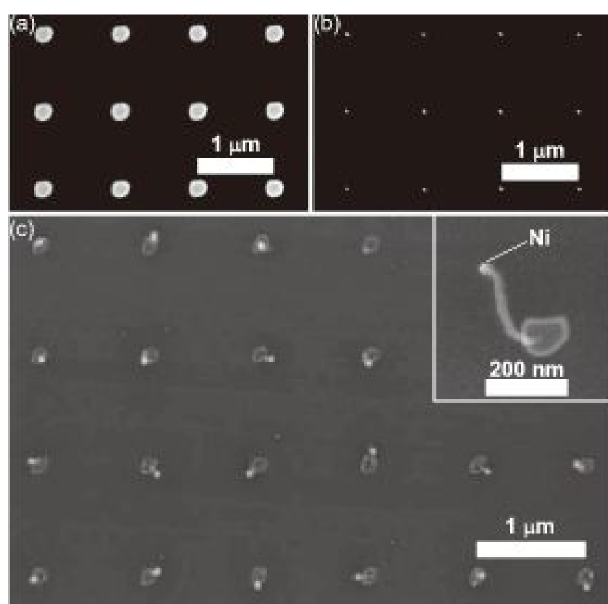

Fig. 5. (a) The 250 nm Ni particles deposited on SiO_2/Si wafer with periodicity of 1 ㎛ in x- and y-directions. (b) The substrate is ion-milled to reduce the size of Ni particles down to below 20 nm, and etched by HCl to remove the Ni shreds. (c) The individual CNT with the diameter smaller than 20 nm grown from each isolated Ni particle. Inset in (c) shows a magnified image of a CNT-Ni nanoparticle pair.

with the flow rates of 50 SCCM C_2H_4 and 800 SCCM H_2 (Ar). This growth condition is slightly off the optimum to slow down the growth speed of CNTs. Figure 5(c) demonstrates that an individual CNT is indeed grown from each Ni particle. The growth probability of the CNTs is found to be almost 100% by inspecting several hundreds of Ni particles. The CNT with the diameter smaller than 20 nm is grown out from the substrate.

All the processes including deposition of 250 nm Ni dots, ion-milling, etching by HCl, and thermal CVD, can be performed on a wafer scale. Thus the CNT growing method introduced in this work is applicable to plant individual MWNT smaller than 20 nm at arbitrary position over wide area of the substrate. In combination with the aligning method of CNTs by external electric field [16-18] or focused ion beam [28], we will be able to control the direction of MWNTs on a wafer scale. The grown MWNTs can be subsequently thinned controllably in diameter down to SWNTs by burning stepwise from the outer layers [29,30]. Such a controllability would enable the usage of CNTs as the tips of scanning probe microscopes or essential components in the integrated CNT-based devices in the future.

Ⅳ. Conclusions

We have found the optimal conditions of the thermal CVD growth of CNTs from nano-sized Ni particles from exhaustive search in the three-dimensional parameter space of the growth temperature and the flow rates of C_2H_4 and H_2/Ar. With the optimal growth conditions, adjusting the total pressure, and using the two-dimensionally ordered Ni particles, we have demonstrated that CNTs can be grown with controlled diameter, position, and length on a wafer scale. Since current optical lithography for Si technology can fabricate ~50 nm half-pitch and is targeting at

sub-20 nm in near future, we will be able to fabricate nanoparticles of transition metals smaller than ~5 nm by ion-milling and chemical etching. By combining such a technological advance and the control technology developed in this work, diameter and length controlled SWNTs would be grown at desired locations in a specified direction over wide area of Si wafer, which will be the essential element for the CNT-based integrated devices.

Acknowledgments

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Ni 나노입자의 배열을 이용한 다중벽 탄소나노튜브의 제어된 성장

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화학기상증착법과 Ni 나노입자 배열을 이용한 탄소나노튜브의 최적 성장 조건을 연구했다. Ni 입자의 크기를 변화시키는 방법으로 탄소나노튜브의 직경을 20 nm 이하까지 제어할 수 있었다. 개별 Ni 입자의 크기와 위치는 기존의 식각법 등을 이용하여 웨이퍼 수준의 대면적에서 연속적으로 제어가 가능하였다. 성장온도, 탄소원, 희석가스 등의 비율을 최적화 함으로써 SiO_2/Si 웨이퍼의 넓은 면적에서 각 Ni 입자로부터 단 한 개씩의 탄소나노튜브가 100% 확률로 성장 가능하다는 것을 보였다. 탄소나노튜브의 위치, 직경, 벽두께 등의 특성들은 성장조건을 조정하여 제어가능하다는 것을 보였다.

주제어: 탄소나노튜브, 제어된 성장, 나노입자, 화학기상증착

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