Fabrication of Nano-sized Single-walled Carbon Nanotube Vias for Electronic Device Applications

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ABSTRACT

Vertically aligned single-walled carbon nanotubes (SWNTs) were synthesized at a low temperature of 600°C by radical chemical vapor deposition (CVD). For applying this technique to electronic devices, we synthesized SWNTs in nano-sized SiO_2 holes to fabricate SWNT-vias, which is expected to be used for multi-layer interconnects and vertically aligned field effect transistors (FET). SWNTs were grown in holes with various sizes and shapes patterned by electron beam lithography. We also show the concept of large area deposition of vertically aligned SWNTs by improved radical CVD system.

Keywords: single-walled carbon nanotubes, vertically aligned, nano-sized via, radical chemical vapor deposition

1 INTRODUCTION

Carbon nanotube (CNT) is one of promising materials for future electronic devices because of their excellent properties such as high current density and low electromigration. SWNT can be a channel of a transistor [1] because SWNT shows semiconducting behavior as well as metallic. Control of growth direction of SWNTs is necessary for electronic device applications. One of interesting growth of SWNTs is vertical alignment. Vertically aligned SWNTs have been synthesized by both thermal and plasma CVD [2-6]. By radical CVD, we have succeeded in growth of extremely dense and vertically aligned SWNTs [4,5]. MWNT-vias have been fabricated by some groups [7-9]. However, a reliable method for growth of densely-packed SWNTs in nano-sized holes has not been achieved. Dense SWNTs are very interesting for applications such as low resistive interconnect and high current transistors. In this study, we show fabrication of densely-packed SWNT-vias using the vertically aligned SWNT growth technique.

2 VERTICALLY ALIGNED SWNTS

Vertically aligned SWNTs were synthesized by a radical CVD apparatus [4,5] shown in Fig. 1, which has an antenna in the chamber and the sphere-shaped plasma is generated by microwave. Because the plasma is fixed at the tip of the antenna, a substrate holder can be far away from

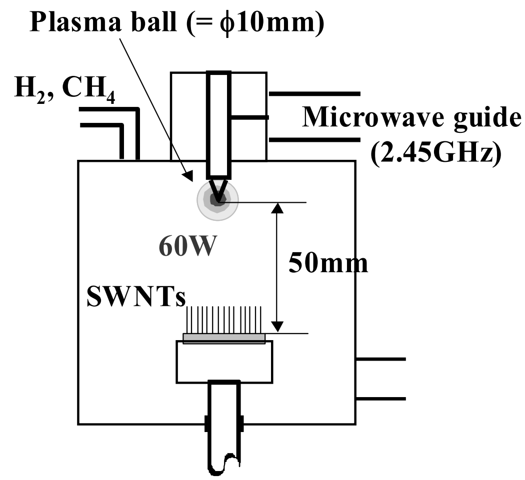

Figure 1: Radical CVD apparatus. The plasma is fixed at the tip of the antenna. No ions can arrive at the substrate. SWNTs are synthesized by only radicals.

the plasma. No ions can arrive at the substrate. When we apply a bias between the antenna and the substrate holder, no current is measured. Therefore, only radicals can be carbon precursors for SWNT growth. In addition, the growth temperature depends on only a substrate heater, which means that we can grow SWNTs at a low temperature.

Vertically aligned SWNTs were deposited on Si wafers with a sandwich-like structure of Al_2O_3 (0.5 nm)/Fe (0.5 nm)/Al_2O_3 (>5 nm) [4,5]. The Al_2O_3 layer beneath the Fe film (bottom Al_2O_3 layer) is a buffer layer to prevent reaction of Si and Fe catalysts during CVD process. The Al_2O_3 layer above Fe film (top Al_2O_3 layer) is also very important to grow vertically aligned SWNTs. This layer interrupts diffusion of Fe particles during the pre-heating period, so that a high density of Fe catalytic particles is obtained. As a result, densely-packed vertically aligned SWNTs can be synthesized. We speculate that SWNTs support one another with van der Waals attractions to be vertically aligned. So the high density of Fe particles is essential for growth of vertically aligned SWNTs.

For growth of SWNTs, the substrate was heated at 600-640°C for 5 min for pre-heating, and a microwave power of 60W was applied in a mixture of H_2 and CH_4 gases to grow

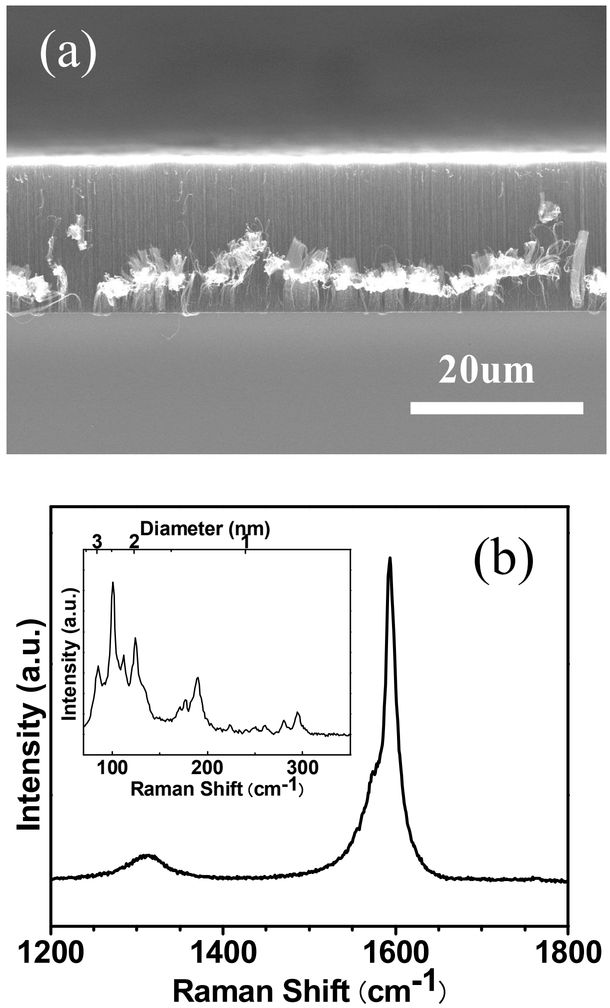

Figure 2: Vertically aligned SWNTs grown by microwave plasma CVD. (a) Cross sectional SEM image of vertically aligned SWNTs. (b) Raman spectroscopy of vertically aligned SWNTs, measured using a 633 nm laser. An inset shows Raman data for RBM.

SWNTs. The flow rates of H_2 and CH_4 were 45 sccm and 5 sccm, respectively and the total gas pressure was 20 Torr. Then, the plasma and heater were switched off, and the sample was cooled.

Figure 2(a) shows an SEM image of as-grown vertically aligned CNTs. All CNTs are vertically aligned and the sample has a very high density. We characterized the sample by micro-Raman spectroscopy. For measurements of Raman spectroscopy, we used an excitation laser with wavelengths of 633 nm. Radial breathing mode (RBM) peaks of SWNTs can be seen clearly in an inset of Fig. 2(b). The diameter was estimated using the correlation, $d = 232/(\nu-6.5)$, where d is the diameter of SWNT in nm and ν is the Raman shift in cm^{-1} [10]. The graph also shows a high ratio of G to D peak, indicating a good quality of our SWNTs. In addition, any MWNTs have not been observed in TEM images, so almost all CNTs are single-walled.

3 NANO-SIZED SWNT VIAS

For growth of CNTs in holes, two methods have been devised; one method fabricates holes of silicon dioxide, and then grows CNTs in the holes [7, 8]. In contrast, another method synthesizes CNTs on patterned catalysts before formation of silicon dioxide film [9]. The second process is possible for large diameter MWNTs by plasma CVD with concentration of an electric field at the substrate.

Although our method uses plasma, an electric filed is not concentrated at the substrate because the plasma is far away from the substrate and no ions exit at the substrate. In addition, SWNTs have extremely small diameters and are very flexible. We think that although our SWNTs have a very high density, nano-sized patterned SWNTs are difficult to be free-standing with a high aspect ratio. So we used the process in which SWNTs were grown after fabrication of the silicon dioxide holes.

Figure 3 shows a schematic diagram of our process. (a) The Fe catalyst layer with the sandwich-like structure was deposited by magnetron sputtering on a Si wafer. (b) SiO_2 was formed on the catalyst by tetraethylorthosilicate (TEOS)-CVD. (c) Nano-sized resist patterns were formed by electron beam lithography. A chemically-amplified negative resist was used here. (d) A 50 nm-thick Ni layer was deposited as a metal mask for the next SiO_2 etching process. Then, the patterned resists were removed by lift-off. (e) For fabrication of the holes, SiO_2 was etched by an inductively-coupled plasma (ICP) system using fluoride gas. (f) SWNTs were grown by radical CVD at the condition outlined above.

CNTs in nano-sized holes were shown in Fig. 4. CNTs were grown in holes with various sizes and shapes. The holes are 220nm in depth. Figure 4(b)-(d) show circle holes with diameters of 250nm, 170nm, and 130nm, respectively. Dense CNTs can be also synthesized in holes with square and triangle shape as shown in (e) and (f). As expected, nano-sized patterned CNTs curved and were not vertically aligned as their length increased. Note that no CNTs were observed on the Ni mask. Thick Ni film was difficult to become small particles at the CVD condition used in this study or was affected by fluoride gas during the SiO_2 etching.

Characterization of as-grown CNTs was performed by micro-Raman spectroscopy. In Fig. 5, sharp RBM peaks can be observed, indicating existence of SWNTs. However, Raman data in high frequency region shows a higher D peak than that in Fig. 2. In the process of fabrication of the holes, it is difficult to stop the etching of SiO_2 layer at just above the sandwich-like structure of Al_2O_3 / Fe / Al_2O_3. We speculate that a part of the top Al_2O_3 and the Fe films were removed in the process of the SiO_2 etching. As mentioned above, the top Al_2O_3 layer is very important to synthesize vertically aligned SWNTs. The region without the top Al_2O_3 layer resulted in a mixture of SWNTs and MWNTs, which caused the higher D-peak.

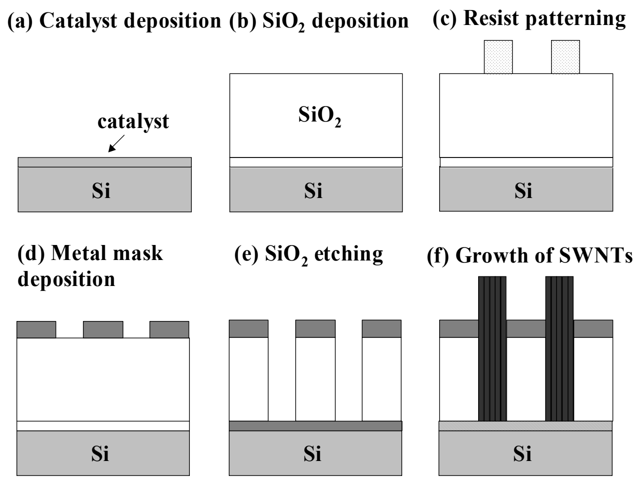

Figure 3: Schematic diagram of process for growth of SWNTs in nano-sized holes.

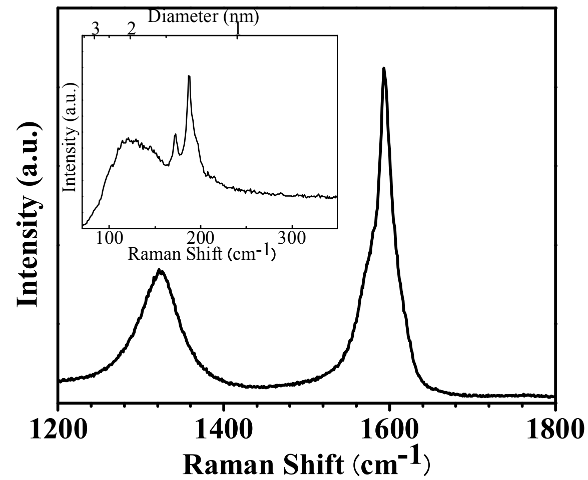

Figure 5: Raman spectroscopy of CNTs grown in nano-sized holes, measured using a 633 nm laser. An inset shows Raman data for RBM.

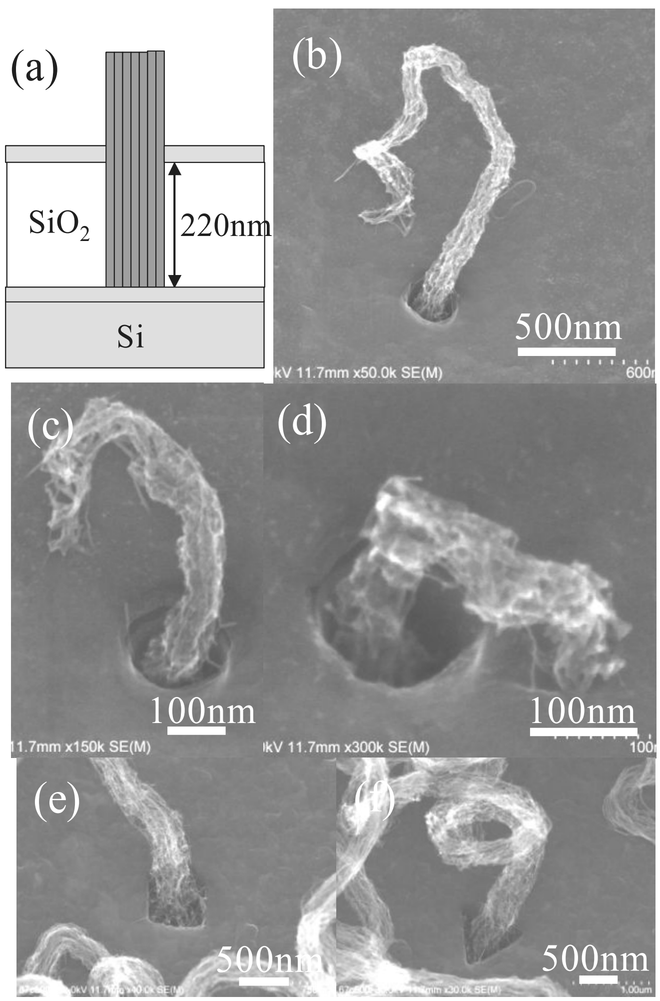

Figure 4: CNTs grown in holes with various sizes and shapes. Circle holes with diameters of (b) 250nm, (c) 170nm, (d) 130nm. (e) Square hole. (f) Triangle hole.

Fabrication of interconnects with a low resistance and a high current density and transistors with a high current is expected using this densely-packed SWNTs vias. A contact of a SWNT and an electrode is one of the most important issues for fabrication of electronic devices [11-13]. Positions of catalytic particles should be clarified because there is a possibility that they affect a SWNT-electrode contact characteristic. In our case, catalysts are anchored at the root of SWNTs, which indicates the root growth mode. The root growth mode was revealed by a marker growth method [14]. This method grows vertically aligned SWNTs intermittently. When two SWNT layers are deposited with different growth time, we can identify the two layers using a marker between the two layers. Our experimental results showed that the first grown layer was above the second one, so we could conclude the root growth mode. Characteristic of vertically aligned SWNT-electrode contact is under investigation.

4 MULTI-ANTENNA SYSTEM FOR LARGE AREA DEPOSITION

To fabricate the SWNT-via holes in the present LSI process, large area deposition of SWNTs must be achieved. We have an antenna in the CVD chamber at the present time. But we can scale up the radical CVD apparatus easily by introducing multi-antenna system as shown in Fig. 6. Although the picture shows a system with three antennas as an example, the number of antennas that can be introduced in the chamber is unlimited in principle. SWNTs with a uniform length on a large substrate can be expected by an appropriate design of multi-antenna. In addition, because we use a very low power of 60W for an antenna during growth of SWNTs, the multi-antenna system also needs a low power that is an advantage for industry.

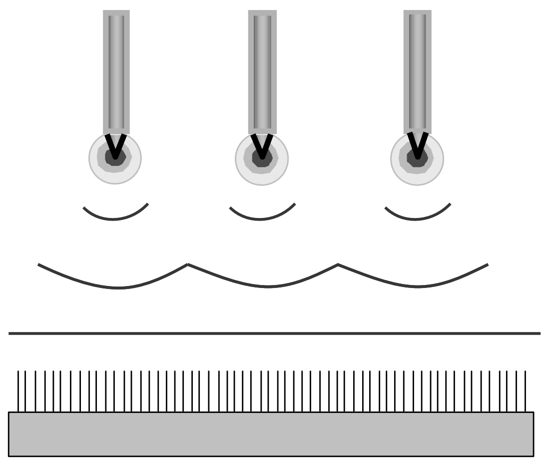

Figure 6: Concept of multi-antenna system for large area deposition of vertically aligned SWNTs.

5 CONCLUSIONS

Densely-packed vertically aligned SWNTs were synthesized at a low temperature of 600°C by radical CVD on a substrate with a sandwich-like structure of Al_2O_3 / Fe / Al_2O_3. Nano sized SWNT-vias were fabricated although some MWNTs were mixed. To prevent MWNTs from being synthesized in the holes, more precise control of SiO_2 etching technique or other processes are required. Multi-antenna system will achieve the large area deposition for integration of SWNTs.

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