Fabrication of Directionally Aligned Carbon Nanotube Thin Films on Solid Surfaces Using Chemical Patterns

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We propose a simple fabrication process of directionally aligned single-walled carbon nanotube (SWCNT) thin films. This process consists of dropping of a highly dispersed SWCNT suspension followed by its drying. We used a substrate surface on which hydrophilic and hydrophobic patterns are formed by chemical processes. A SWCNT suspension dropped on the hydrophilic areas is transferred to the hydrophilic areas in the early stage of the drying. During the drying, the SWCNTs in the suspension are self-aligned by the surface tension. When the degree of hydrophilicity on the hydrophilic areas is too large, deposition of the SWCNTs on small hydrophilic areas is blocked by the repulsive force owing to hydration between the hydrophilic substrate and the SWCNT surfaces. We demonstrated that narrow line patterns of the SWCNT thin films can be fabricated by controlling the hydrophilicity on the hydrophilic areas on the substrate. [DOI: 10.1380/ejssnt.2010.207]

Keywords: Carbon nanotube; Self-assembly; Solid-liquid interfaces; Surface chemical reaction

I. INTRODUCTION

Carbon nanotubes (CNTs) has attracted intense interest both in scientific and applicatory points of view owing to their unique properties, such as large capability against a high electric current density [1], excellent mechanical strength [2], high thermal conductivity [3], and stable chemical properties. From the nanoscale features, CNTs are expected to be ideal materials for one-dimensional field effect transistors [4-6], interconnects in LSIs (large scale integrated circuits) [7-9], photovoltaic cells [10-12], and biosensors [13-15].

In these applications, CNTs have to be assembled as arrays or sheets in specified areas on the substrate. In addition, directionally aligned CNTs are required in the applications to electrically conducting films, such as interconnects in the electric packaging. To form well-ordered CNT thin films, several approaches have been intensively studied, such as Langmuir-Brodgett method [16-18], dropping the CNT suspension [19-21], self-assembly method [22,23], trapping by chemical combination [24,25], using liquid-liquid interface [26], and laminar flow in microfluidic channel [27].

These wet processes have advantages, such as performance at room temperature, a high throughput, and a low cost. Therefore, these techniques are compatible with any conventional process used in the electrical device fabrication. These techniques, however, are difficult to apply to directionally aligned CNT thin films deposited on specified areas.

In this paper, we propose a new fabrication technique of single-walled CNT (SWCNT) thin films that can be applied to formation of well-aligned SWCNT sheets and their patterning. This process is very simple because it includes only dropping of a SWCNT suspension and its drying, and closely-packed SWCNT thin films can be deposited on specified regions of the substrate surface.

II. EXPERIMENTAL PROCEDURE

Figure 1 shows schematics of the proposed process flow to fabricate patterned SWCNT sheets. This is a very simple process that consists only of dropping of a SWCNT suspension and its drying on a substrate surface, on which hydrophobic/hydrophilic patterns are formed in advance, as shown in Fig. 1(a). When a suspension of SWCNTs wrapped with the detergents are dropped on the patterned surface, the SWCNTs on the hydrophobic areas are transferred to the hydrophilic areas together with the solution and agglomerated during the drying process, as shown in Fig. 1(b). During the drying, the SWCNTs in the suspension are self-aligned by the surface tension, as shown in Fig. 1(c). After the solution is completely evaporated, aligned SWCNTs are selectively attached on the hydrophilic areas, as shown in Fig. 1(d).

SWCNTs used in this work were synthesized by the HiPco method [28] (purchased from Unidym, Inc.). CNTs can be suspended using many mediums, such as organic solvents [29], aqueous mediums [30,31], and polymers [32]. Although sodium dodecyl sulfate (SDS) [33] is often used as a dispersant for CNTs, we selected Brij-700 \( (H(CH_2OCH_2)_{10}OCH_2CH_3) \), a non-ionic detergent, which exhibits a solubilization capability larger than that of SDS. First, the SWCNTs (0.2-0.3 g/L) were dispersed into a Brij-700 aqueous solution (1 g/L) using sonication. Though we can easily disperse the SWCNTs using this procedure, some of the SWCNTs form bundles also after this process. We, therefore, removed the SWCNT bundles by filtering (pore diameter is 450 nm), because it is much easier than the ultracentrifugation, which is often used for the separation of CNT bundles.

Hydrophilicity on a surface can be controlled by a simple process [34] using self-assembled monolayers (SAMs). We prepared three kinds of Si surface to investigate the basic process of SWCNT rearrangement. The first one was a SiO\(_2\) surface on a Si substrate prepared by chemical oxidation using a mixture of H\(_2\)SO\(_4\) and H\(_2\)O\(_2\), the second one a hydrophobic surface prepared using an octadecyltrichlorosilane (OTS) monolayer, and the third

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FIG. 1: Schematics of the proposed process for selective deposition of directionally aligned SWCNT thin films. (a) A SWCNT suspension is dropped on a patterned surface with both hydrophobic and hydrophilic areas. (b) SWCNTs on the hydrophobic areas are transferred to the hydrophilic areas and aligned during the drying process. (c) Behavior of the SWCNTs on the hydrophilic areas. (d) Directionally aligned SWCNT thin films are selectively fabricated on the hydrophilic areas after the aqueous solution disappeared.

One a hydrophilic surface prepared using a 3-aminopropyltriethoxysilane (APTES) monolayer. The SAMs of OTS and APTES were deposited by the dipping method. The SWCNT suspension was dropped on these surfaces, and the substrates were dried at 150 °C. Formed SWNT sheets were observed by scanning electron microscopy (SEM).

To demonstrate selective deposition of SWCNTs by the proposed process, we fabricated patterned surfaces that include both hydrophobic and hydrophilic areas using the microcontact printing (μCP) technique, which is widely used in the direct patterning of biomolecules [35], cells [36], and SAMs [37] on solid surfaces. We used OTS to form the hydrophobic areas and chemically grown SiO$_2$ for the hydrophilic areas. To form OTS patterns on the SiO$_2$ surfaces, we used a polydimethylsiloxane (PDMS) stamp that was prepared using a patterned silicon wafer as a mold and cured at 60 °C for 70 min. After the curing, the PDMS stamp was separated from the mold and immersed into the OTS solution (1.0 vol.%) of dehydrated toluene in a nitrogen atmosphere. The OTS layer was deposited on the silicon oxide surface by contacting the PDMS stamp. Some SiO$_2$ surfaces were annealed before the OTS deposition to investigate the effects of the hydrophilicity of the SiO$_2$ surfaces on the formation of the SWCNT patterns. Generally, hydrophilicity on the SiO$_2$ surfaces depends on the density of OH groups, and the OH group density is reduced by thermal annealing. Since the desorption of OH groups as water molecules occurs during annealing above 400 °C [38,39], we annealed the substrates at 800 °C to obtain hydrophobic SiO$_2$ surfaces. We observed the hydrophilicity of the chemically or thermally prepared SiO$_2$ and the OTS surfaces by the water contact angles (WCA). As shown in Fig. 2, the hydrophilicity was controlled by the procedure used in this work.

After preparing the above mentioned patterned surfaces, a SWCNT suspension using Brij-700 was dropped and slowly dried at room temperature. During this drying process, SWCNTs were selectively deposited on the SiO$_2$ areas, as shown in Fig. 1. The SWCNT patterns were observed by SEM.

III. RESULTS AND DISCUSSION

Figure 3 shows SEM images of SWCNT sheets prepared by dropping a suspension of the SWCNTs modified with Brij-700 and drying it, (a) on an OTS-modified surface (hydrophobic) and (b) on an APTES-modified surface (hydrophilic). In Fig. 3(a), aligned SWCNTs are observed. On the hydrophobic OTS surface, the SWCNT suspension was concentrated on some small areas by the surface tension immediately after the dropping. During this agglomeration and the following drying processes, the CNTs were locally aligned by the capillary force. After the drying completed, aligned SWCNTs formed on the hydrophobic surface, as shown in Fig. 3(a). On the hydrophilic APTES surface, on the other hand, the SWCNTs modified with Brij-700 were deposited on the surface without any transfer after the drying. Therefore, the deposited SWCNTs were uniformly distributed over the surface. In this case, the macroscopic alignment of the SWCNTs observed on the OTS surface did not occur, as shown in Fig. 3(b). Fig. 3 suggests that the surface hydrophilicity is an important factor in the SWCNT sheet formation in solution processes. From these preliminary results, we employed substrates on which hydrophobic and hydrophilic areas were patterned. In the process

FIG. 2: Optical images of water drops on (a) the chemically prepared SiO$_2$ surface, (b) the thermally prepared SiO$_2$ surface, and (c) the OTS-deposited surface.

FIG. 3: SEM images of the SWCNT thin films deposited (a) on the hydrophobic OTS-modified surface and (b) on the hydrophilic APTES-modified surface.

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we propose, the hydrophobic areas are utilized to align the direction of the SWCNTs, and the hydrophilic areas to gather and assemble the SWCNTs that are excluded from the hydrophobic areas.

Figure 4 shows SEM images of the SWCNT sheets formed on a patterned surface that consists of chemically formed SiO$_2$ and OTS areas. We observed that the SWCNTs modified with Brij-700 were transferred from the hydrophobic areas to the hydrophilic areas. The aligned SWCNTs were deposited on the hydrophilic side near the boundary between the hydrophilic and the hydrophobic areas (Fig. 4(a)). The thickness of the SWCNT sheets is difficult to measure owing to their rough morphology, but we estimated the thickness of the sheet shown in Fig. 4 to be approximately ten and several nanometers from the SEM observation. This assembling process is specific to the surface where hydrophobic and hydrophilic areas coexist. The SWCNTs transferred from the hydrophobic areas to the hydrophilic areas without adsorption onto the substrate were aligned owing to the surface tension of the solution during the drying process. Aligned SWCNTs were finally adsorbed on the hydrophilic surfaces. This process can be used to fabricate aligned SWCNT sheets selectively on the hydrophilic areas. However, it was often observed that the SWCNTs were not deposited on small hydrophilic areas, such as narrow lines and small squares of the chemically prepared SiO$_2$, which exhibits a strong hydrophilicity, as shown in Fig. 4(b). The reason why aligned SWCNT sheets were obtained only on the large hydrophilic areas is probably that adsorption of the SWCNTs on the strongly hydrophilic surface was blocked by the hydration repulsion between the SiO$_2$ and the SWCNTs modified with Brij-700 in the early stage of the drying process. Generally, the interaction working between hydrophilic surfaces depends on the degree of their hydrophilicity. Therefore, it is reasonable that a strong repulsive force was generated between the SWCNTs wrapped with Brij-700 and the chemically prepared SiO$_2$ because both surfaces are highly hydrophilic. For these reasons, the SWCNTs were again transferred from the small hydrophilic areas to the large hydrophilic areas before deposition occurred. To deposit the SWCNTs also on the small hydrophilic patterns, we controlled the hydrophilicity of the SiO$_2$ by an annealing, as shown in Fig. 2, where the WCAs of the chemically oxidized SiO$_2$, the thermally prepared SiO$_2$, and the OTS surfaces were 4.9°, 29°, and 107°, respectively. Fig. 5(a) shows a SEM image of the SWCNT sheet on the patterned surface that consists of the OTS and the thermally annealed SiO$_2$ areas, where the used process was same as the previously described one. The SWCNTs were adsorbed also on the narrow hydrophilic areas when the hydrophilicity of the SiO$_2$ surface was controlled. Fig. 5(b) shows a magnified image around a narrow hydrophilic area, where aligned and densely-packed SWCNTs were observed. This successful deposition on the narrow or small hydrophilic areas was owing to the reduction of the repulsive force between the SWCNTs and the SiO$_2$ surfaces. During the drying process, the SWCNTs above the weakly hydrophilic areas are aligned and deposited before being transferred to large hydrophilic areas. Through these steps, gathered and aligned SWCNTs were fixed on the thermally prepared SiO$_2$ areas after the solution disappeared. In this process, aligned SWCNT sheets are assembled from the periphery of a SiO$_2$ region, and the degree of the alignment depends on the shape and size of the SiO$_2$ regions. Since the SWCNTs can be more regularly aligned around the periphery of the hydrophilic regions, the degree of alignment is poorer in the center if the hydrophilic region is wide. In the present experiments, we used only SWCNTs with an average length of about 1 μm, and, therefore, a relation between the length and the degree of orientation are not known. But, we think that a higher degree of orientation will be obtained by using shorter SWCNTs. We found that there is an optimum hydrophilicity on the SiO$_2$ regions because both the separation of the water layer into the hydrophilic regions and the deposition of the SWCNTs on their surfaces are involved in the sheet formation. But, from the present results, it was difficult to quantitatively determine the optimum hydrophilicity defined by a contact angle.

In the proposed process, there are two important factors: one is coexistence of hydrophobic and hydrophilic areas on a surface, and the other control of the hydrophilicity of the hydrophilic areas to deposit SWCNTs also on the small patterns. Concentration of the SWCNT suspension and the evaporation rate may also be important factors to form well-aligned SWCNT sheets, though they
are being progressed.

IV. CONCLUSION

We have developed a selective deposition process of directionally aligned SWCNT thin films. In this process, we used a substrate on which hydrophilic and hydrophobic areas coexist. A SWCNT suspension was dropped on the hydrophilic areas and directionally aligned by the surface tension. As a result, self-aligned SWCNT thin films were fabricated selectively on the hydrophilic areas. Since this process is very simple, it is promising for many applications, such as the interconnect process in the electrical packaging. We also found that control of hydrophilicity on the hydrophilic side is particularly important because the SWCNTs are not deposited on small areas when the hydrophilicity is too strong. This is owing to a hydration repulsive force between the SWCNT and SiO2 surfaces.

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