High-Precision Selective Deposition of Catalyst for Facile Localized Growth of Single Walled Carbon Nanotubes

Rong Xiang[†], Tianzhun Wu[†], Erik Einarsson[†], Yuji Suzuki[†], Yoichi Murakami[†,‡], Junichiro Shiomi[†], Shigeo Maruyama*[,†]

[†]*Department of Mechanical Engineering, The University of Tokyo, Tokyo 113-8656, Japan*

[‡]*Global Edge Institute, Tokyo Institute of Technology, Tokyo 152-8550, Japan*

E-mail: maruyama@photon.t.u-tokyo.ac.jp

The excellent properties of carbon nanotubes (CNTs), particularly chirality-dependent electrical conductivity of single-walled carbon nanotubes (SWNTs), make them one of the most attractive building blocks for next-generation nano-devices.[1] Localizing the growth of CNTs, therefore, has attracted much attention because it is a critical step for the fabrication of on-substrate devices.[2] The conventional way to pattern the growth involves either selective sputtering (evaporation) of metal (e.g., using lift-off),[2a,b] or fabricating SiO_2 patterned Si wafer (e.g., using HF etching).[2c,d] These conventional MEMS techniques, although work well on the micro-scale, require multiple steps that complicate the fabrication process and limit the resolution. Higher resolution (<100 nm) may be obtained, but these advanced techniques (e.g. ultra high resolution electron beam lithography[2e] or scanning probe oxidation[2f]) are more complicated. Alternatively, deposition of dense nano-particles onto substrates using liquid-based dip-coating possesses great advantages in cost and scalability over conventional physical deposition.[3] However, no compatible method for selective coating was proposed due to the insufficient understanding in the mechanism.

In this communication, we show how surface wettability strongly affects the deposition of catalyst in dip-coating. By tailoring the termination group on the surface we succeed in achieving localized deposition of catalyst through an all-liquid-based route. This method can simplify fabrication without sacrificing the resolution in the case of using conventional UV photolithography. By utilizing an electron beam, the line width of an SWNT pattern can be easily reduced to 50 nm (About10 nm resolution may also be obtained potentially). The patterned region can be easily located and visualized under a scanning electron microscope (SEM).

Dip-coating was found to be very efficient to yield catalyst on a substrate and suitable for the growth of random and vertically aligned (VA-) SWNTs in alcohol catalytic chemical vapor deposition (ACCVD).[3,4] The substrate is typically kept in solution for 3-5 min before being slowly withdrawn. This residence time does not affect the catalyst coating because the system is expected to have reached equilibrium rapidly. The concentration of catalyst precursor solution determines whether SWNTs grow into aligned or tangled structure. (details in supporting information)

A closer look at the solid-liquid interface shows that a meniscus (as indicated in red in Fig. S1) is formed with a contact line typically located at 2-3 mm above the free surface of the ethanol pool, suggesting the substrate is hydrophilic. We examined the effect of this surface wettability on the formation of catalyst and consequently on the growth of SWNTs. Among the different methods to modulate the surface potential, forming a self-assembled monolayer (SAM) is both simple and nondestructive.[5] In addition, the theoretically perfect flatness of a SAM makes the topography-induced effect negligible. Figure 1a shows the profiles and contact angles of deionized water droplets on the surface of Si/SiO_2 after reaction with octadecyltrichlorosilane (OTS) in toluene for different time durations.[6] It is clear that when the OTS SAM coverage increases the silicon oxide surface (originally very hydrophilic, with a contact angle of almost 0°) becomes increasingly hydrophobic. After catalyst dip-coating and SWNT growth on this substrate with graduated OTS coverage, the SEM images in Figure 1b taken at different positions clearly show that the amount of SWNTs decreases with increasing hydrophobicity. AFM imaging of the SAM formation clearly indicates that the density of catalyst deposited on the surface decreases when the substrate becomes less wettable. Finally, no SWNTs were found on the substrate with 15 min of SAM formation. Raman spectra taken at corresponding positions agree well with the SEM images; the G-band gradually diminishes in intensity and finally disappears. Clear RBM peaks in all cases indicate SWNTs are obtained regardless of the wettability. (details in Fig. S2 and Fig. S3)

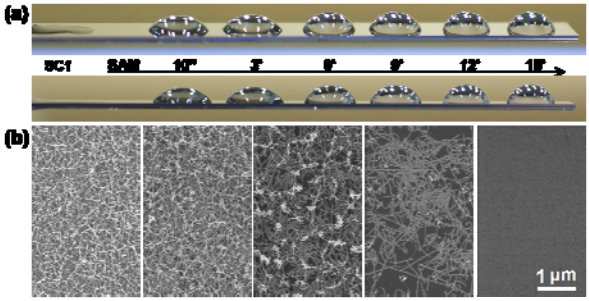

Figure 1. (a) Various contact angles of water droplets on hydrophilic surface terminated by OH after standard cleaning 1 (SC1) and hydrophobic surface functionalized by OTS monolayer with different SAM converge; (b) SEM images of SWNTs grown on substrate shown in (a) after catalyst dip-coating.

The appeal of using an SAM lies in not only the easy fabrication and drastic change of surface energy (by only one layer of molecules), but also the reversibility of the SAM process. For example, deep UV light (here 254 nm) is known to be able to remove the SAM effectively.[5] The exposed surface can retrieve its hydrophilicity (water contact angle returns to almost 0°) and SWNTs can efficiently grow on it. Therefore, by combining with a masking technique, silicon surfaces with sharp hydrophilic/hydrophobic patterns can be easily obtained. A

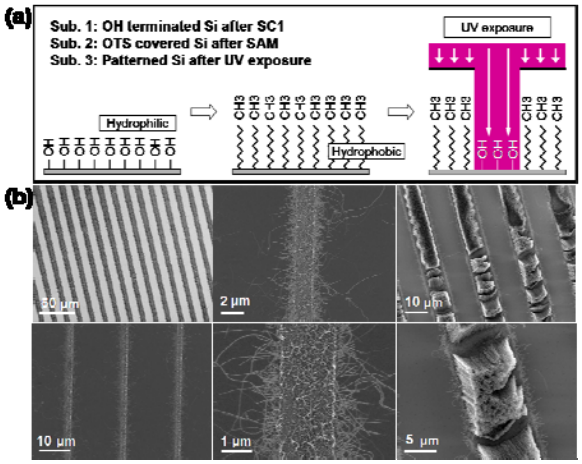

Figure 2. (a) Schematics describing the fabrication procedure of hydrophilic/hydrophobic patterns using a selective removal of OTS SAM by UV exposure; (b) SEM images of random and vertically aligned SWNT line-shape patterns.

schematic of this process is presented in Figure 2a. Line patterned SWNTs obtained after dip-coating and CVD are shown in Figure 2b. Regions exposed to UV radiation after SAM formation clearly produced SWNTs with high density. On the other hand, no SWNTs grew in the masked areas, as no catalyst was deposited due to the high hydrophobicity of the surface. Importantly, the fabrication of patterned catalyst through this all-liquid route is both simpler and more efficient than conventional photolithography, as developing and removal of photoreisit is bypassed. Compared to the post-pattern techniques,[7] which normally introduce some irreversible destruction and contamination (e.g. pre-dispersion with surfactant) to the SWNTs, these high-quality as-grown SWNTs are expected to give better performances in device applications.

The OTS SAM can also be damaged by electron beam irradiation.[8] Destruction of SAM and therefore deposition of catalyst can be controlled in a more precise manner. Preliminary results show that in a conventional SEM when an electron beam with diameter of several nanometers is used for etching the SAM, SWNT growth can be easily confined to a linear region with a width of 200 nm. As the magnification increases, the resolution can be almost linearly improved. An example of a 50 nm pattern is shown in Fig S4. Note that this 50 nm wide exposed area was scanned by many lines, the resolution could be still improved if only one line scan is applied. In theory, OTS may be manipulated at the several-molecule width level,[8] as illustrated in Figure 3a. The ultimate resolution of one line scan could be as low as 10 nm.

The ability of using a SEM also makes the localization process visible. Figure 3b shows one example of defining the growth area of SWNTs at desired positions. Arrow-shaped Si/SiO_2 patterns were first fabricated on the substrate to indicate the area where we want the SWNTs to grow. In those four gray boxes, the SAM was removed to different degree by increasing exposure to the electron beam. Enlarged images show SWNTs were obtained in these regions after CVD. In both UV and e-beam cases, the edge between regions with and without catalyst is very sharp. The density of SWNTs may also be controlled by changing the dose (e.g. scanning times and current density) to a given area. Since the damage to the SAM is negligible at low magnification and low current density, these conditions can be used to locate the desired area. This makes it possible to first look for pre-designed circuits, and then grow SWNTs at certain positions to bridge the electrodes. Finally, this simple method may be also applied to pattern other nano-particles. (An example presented in Fig. S5)

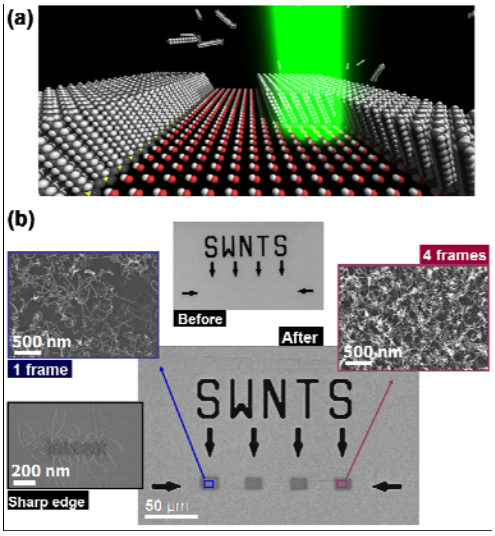

Figure 3. (a) Schematics describing the process of removing OTS by nanometer-size electron beam; (b) SEM images of SWNTs grown in the regions where OTS were selectively removed, suggesting the location and density of SWNTs can be controlled.

To summarize, we propose a surface-energy-difference driven selective deposition of catalyst for localized growth of SWNTs. The presented all-liquid-based approach is much simpler than state to the art techniques, but may provide potentially higher resolution and better scalability. We believe this can greatly advance the fabrication of nano-devices using high-quality as-grown SWNTs.

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Supporting Information Available: Experimental details, Schematics of dip-coating process, morphologies of SWNT arrays, AFM and SEM images of SAM partially covered surface, Raman spectra of SWNTs grown on a substrate with varying OTS coverage, a SWNT pattern with line width of 50 nm, SEM images of silicon quantum dots patterns obtained using current approach. This material is available free of charge via the Internet at http://pubs.acs.org.

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(6) This was done by dipping a hydrophilic silicon wafer into OTS/Tolune solution and then slowly pulling up. Since it took 15 mins for the whole chip to emerge from the liquid, surface with a continuously gradient of OTS coverage (generated from reactions for 0-15 min) was formed.

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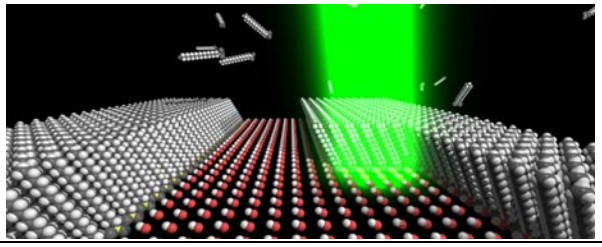

In the liquid-based dip-coating, hydrophilicity of Si/SiO_2 substrate is found to be critical for the successful deposition of catalyst and hence the growth of single-walled carbon nanotubes (SWNTs). When the surface is functionalized by self-assembly monolayer (SAM) and becomes hydrophobic, no catalyst remains and no SWNT grows. This concept can be utilized to localize the growth of SWNTs at designed regions where SAM were selectively removed by, e.g. UV or electron beam. Patterned high-quality as-grown SWNTs with potential line width ~10 nm can be obtained.